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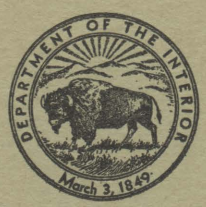
Bulletin 544
BUREAU OF MINES

BIBLIOGRAPHY OF THE FISCHER-TROPSCH SYNTHESIS AND RELATED PROCESSES

(In Two Parts)

I. REVIEW AND COMPILATION OF THE LITERATURE ON THE PRODUCTION OF SYNTHETIC LIQUID FUELS AND CHEMICALS BY THE HYDROGENATION OF CARBON MONOXIDE

By H. C. Anderson, J. L. Wiley, and A. Newell



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Foreword

The importance of the chemistry of carbon monoxide in industrial processes such as production of synthetic liquid fuels, and of chemicals (particularly alcohols) has been increasing rapidly during the past decade. Although the staff of the Bureau of Mines has produced a critical review of Fischer-Tropsch and related syntheses (J. Wiley & Son, 1951), continued development of such synthetic liquid fuel processes demanded an exhaustive bibliography containing abstracts of all relevant publications. The need for this was especially evident in work on the production of synthesis gas and hydrogen from coal and byproduct hydrocarbon gases. It is anticipated that this bibliography will serve the needs of all experimenters in the field of chemistry of carbon monoxide.

BIBLIOGRAPHY OF THE FISCHER-TROPSCH SYNTHESIS AND RELATED PROCESSES

(In Two Parts)

1. REVIEW AND COMPILATION OF THE LITERATURE ON THE PRODUCTION OF SYNTHETIC LIQUID FUELS AND CHEMICALS BY THE HYDROGENATION OF CARBON MONOXIDE [1]

By

H. C. Anderson,[2] J. L. Wiley,[3] and A. Newell [4]

Introduction

THIS REVIEW contains abstracts of the technical literature and patents dealing with the history, development, and commercial application of the Fischer-Tropsch synthesis and related processes for the hydrogenation of carbon monoxide and the production of synthetic fuels and chemicals. Attempt has been made to include abstracts of all the published information on the above subjects as well as of the captured foreign documents collected and classified as TOM and FIAT reels and CIOS, FIAT, and BIOS reports.

The material in this review is divided into two sections—literature (part I) and patents (part II)—each with a comprehensive subject index. A numerical patent list by countries will appear in part II. The abstracts in each section are arranged alphabetically by author or patentee with further chronological arrangement under each author or group of authors. Secondary authors and patentees as well as assignees are cross-indexed to the main entry. In serial articles or reports the complete series appears in the alphabetical arrangement according to the author of the first member of the series. Succeeding members as well as secondary authors are entered as cross-references. Titles of the periodicals are used as the authors in anonymous references. By following the above procedure, no author index is required.

The authors take particular pleasure in acknowledging the cordial interest and assistance rendered by Dr. H. H. Storch, Chief, Fuels-Technology Division, Dr. M. A. Elliott and Dr. R. B. Anderson, Chiefs, Synthetic Fuels Research Branch, Bureau of Mines, 4800 Forbes Street, Pittsburgh 13, Pa. They wish to thank Helen C. Douglass, Myrtle R. Lee, Harriett E. McCrea, Mary T. Palmer, Frank J. Ball, Elizabeth M. Reid, and Frances G. Stewart for their able assistance in preparing the manuscript.

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JOURNAL REFERENCES

Abbreviations	*Journal titles*
Acad. Sci. Petrograd	Petrograd academie science.
Acqua e Gas	Acqua e Gas.
Acta Cryst	Acta Crystallographica.
Acta Physicochim. U. R. S. S	Academy of Sciences of the U. S. S. R.
Advances Chem. Ser	Advances in Chemistry Series —
Akad. Verlagsgesell., Leipzig	Akademische Verlagsgesellschaft m. b. H. Verlagsbericht Leipzig.
Allgem. Oel- u. Fett-Ztg	Allgemeine Oel- und Fett-Zeitung.
Allgem. Osterr. Chem. u. Tech.-Ztg	Allgemeine Österreichische Chemiker und Techniker-Zeitung.
Am. Chem. Soc., — Meeting Abs	American Chemical Society, — Meeting Abstracts.
Am. Gas Assoc. Monthly	American Gas Association Monthly.
Am. Gas Jour	American Gas Journal.
Am. Inst. Chem. Eng	American Institute of Chemical Engineers.
Am. Inst. Min. and Met. Eng	American Institute of Mining and Metallurgical Engineers.
Metals Technol	Metals Technology.
Tech. Pub	Technical Publication.
Tech. Proc	Technical Proceedings.
Am. Paint Jour	American Paint Journal.
Am. Perfumer Essent. Oil Rev	American Perfumer and Essential Oil Review.
	American Petroleum Institute. *See* Bull. Am. Petrol. Inst.; Proc. Am. Petrol. Inst.
Am. Petrol. News	*See* National Petroleum News.
Am. Soc. Mech. Eng	American Society of Mechanical Engineers *See also* Mech. Eng.; Trans. Am. Soc. Mech. Eng.
Anal. Chem	Analytical Chemistry.
Anales asoc. quím. argentina	Anales de la asociatión quimíca argentina.
Anales soc. españ. fís. y quím	Anales de la sociedad española de fisica y química.
Angew. Chem	Angewandte Chemie.
Ann. chim	Annales de chimie (Paris).
Ann. chim. applicata	Annali di chimica applicata.
Ann. chim. phys	Annales de chimie et de physique.
Ann. combust. liquides	Annales de l'office national des combustibles liquides.
Ann. mines	Annales des mines.
Ann. mines et carburants	Annales des mines et des carburants.
Ann. Physik	Annalen der Physik.
Ann. Rept. Progress Chem., (Chem. Soc. London).	Annual Reports on the Progress of Chemistry (Chemical Society of London).
Ann. Rev. Petrol. Technol	Annual Review of Petroleum Technology (London). *See also* Rev. Petrol. Technol.
Anthracite Inst. Bull	Anthracite Institute Bulletin.
Anyagvizsgálók Közlönye	Anyagvizsgálók Közlönye.
Anz. Maschinenw	Anzeiger Maschinenwesen.
Apoth. Ztg	Apotheker Zeitung.
Apparatebau	Der Apparatebau.
Arch. Eisenhüttenw	Archiv für das Eisenhüttenwesen.
Arch. Math. Naturvidensk	Archiv for Mathematik og Naturvidenskab.
Arch. Metallkunde	Archiv für Metallkunde.
Arch. Wärmewirt	Archiv für Wärmewirtschaft.
Armed Forces Chem. Jour	Armed Forces Chemical Journal.
Asphalt Teer Strassenbautech	Asphalt und Teer Strassenbautechnik.
Assoc. franç. techn. pétrole	*See* Bull. assoc. franç. techniciens pétrole.
Assoc. Tech. Services	Associated Technical Services.
ASTM	American Society for Testing Materials.
Atti cong. intern. chim. — Cong., (City), (Year).	Atti del congresso internazionale di chimica, —th Congress, (city) (year).
Atti cong. nazl. chim. ind	Atti del congresso nazionale di chimica industriale.
Atti cong. nazl. chim. pura applicata	Atti del congresso nazionale di chimica pura ed applicata —th Congress, (city).
Australia Council Sci. Ind. Research, Bull	Australia, Commonwealth of, Council for Scientific and Industrial Research, Bulletin.
Australian Chem. Inst. Jour. and Proc	Australian Chemical Institute Journal and Proceedings.
Australian Jour. Sci	Australian Journal of Science.
Australian Jour. Sci. Research	Australian Journal of Scientific Research.
Auszüge Deutscher Patent-Anmeldungen	Auszüge Deutscher Patent-Anmeldungen.
Automobil tech. Ztschr	Automobiltechnische Zeitschrift.
Bányász. Kohász. Lapok	Bányászati és Kohászati Lapok.
Ber. deut. chem. Gesell	Berichte der deutschen chemischen Gesellschaft.

Abbreviations	*Journal titles*
Ber. Gesell. Kohlentech	Berichte der Gesellschaft für Kohlentechnik.
Ber. Inst. physik. Chem., Akad. Wiss. Ukr. S. S. R.	Berichte des Instituts für physikalische Chemie, Akademie der Wissenschaften der Ukrainischen S. S. R.
Bergbau	Bergbau.
Bergbau Arch	Bergbau Archiv.
Bergbau u. Energiewirtsch	Bergbau und Energiewirtschaft.
Bib. Sci. Ind. Repts	Bibliography of Scientific and Industrial Reports.
Biochem. Ztschr.	Biochemische Zeitschrift.
BIOS Rept	British Intelligence Objectives Subcommittee Reports.
Bitumen, Teere, Asphalte, Peche	Bitumen, Teere, Asphalte, Peche.
Blast Furnace Steel Plant	Blast Furnance and Steel Plant.
Boi. inst. sudamer. petrol (Montevideo)	Boletin del instituto sudamericano del petroleo (Montevideo).
Braunkohle	Braunkohle.
Braunkohlenarch	Braunkohlenarchiv.
Brennstoff-Chem	Brennstoff-Chemie.
Brennstoff- u. Wärmewirt	Brennstoff- und Wärmewirtschaft.
British Abs	British Abstracts.
British Chem. Abs	British Chemical Abstracts.
British Coal Utilisation Research Assoc., Monthly Bull.	British Coal Utilisation Research Association, Monthly Bulletin.
Bul. Chim. Soc. Româna Ştiinţe	Buletinul de Chimie pură şi Aplicăta Societătea Româna de Ştiinţe.
Bull. acad. roy. Belg	Bulletin de l'académie royale de Belgique.
Bull. acad. sci. U. R. S. S	Bulletin de l'académie des sciences de l'Union des Républiques Soviétiques Socialistes.
Bull. Am. Petrol. Inst	Bulletin of American Petroleum Institute.
Bull. assoc. franç. techniciens pétrole	Bulletin de l'association française des techniciens du pétrole.
Bull. assoc. tech. fonderie	Bulletin de l'association technique de fonderie.
Bull. Chem. Soc. Japan	Bulletin of the Chemical Society of Japan.
Bull. Imp. Inst	Bulletin of the Imperial Institute.
Bull. Inst. Phys. Chem. Research (Tokyo)	Bulletin of the Institute of Physical and Chemical Research (Tokyo).
Bull. Liverpool Eng. Soc	Bulletin of Liverpool Engineering Society, Inc.
Bull. mat. grasses inst. colonial Marseille	Bulletin des matières grasses de l'institut colonial de Marseille.
Bull. Math. Biophysics	Bulletin of Mathematicl Biophysics.
Bull. sci. école polytech. Timişoara	Bulletin scientifique de l'école ploytechnique de Timişoara.
Bull. soc. belge ing. ind	Bulletin de la société beige des ingénieurs et des industriels.
Bull. soc. chim	Bulletin de la société chimique de France.
Bull. soc. chim. belg	Bulletin de la sociétés chimiques belges.
Bull. soc. encour. ind. nat	Bulletin de la société d'encouragement pour l'industrie nationale.
Bureau of Mines Bull	Bureau of Mines Bulletin (United States).
Bureau of Mines Inf. Circ	Bureau of Mines Information Circular (United States).
Bureau of Mines Minerals Yearbook	Bureau of Mines Minerals Yearbook (United States).
Bureau of Mines Rept. of Investigations	Bureau of Mines Report of Investigations (United States).
Bureau of Mines Tech. Paper	Bureau of Mines Technical Paper (United States).
Bureau of Mines Transl	Bureau of Mines Translation (United States).
Bureau Standards Jour. Research	*See* Nat. Bureau of Standards Research Journal.
Bus and Coach	Bus and Coach Operators' Journal.
Business Week	Business Week.
Butterworth's Sci. Publication	Butterworth's Scientific Publication.
Cashiers phys	Cahiers de physique.
Calif. Oil World	California Oil World.
Canadian Chem. and Met	Canadian Chemistry and Metallurgy.
Canadian Chem. Process Ind	Canadian Chemistry and Process Industries.
Canadian Jour. Research	Canadian Journal of Research.
Canadian Jour. Tech	Canadian Journal of Technology.
Canadian Min. and Met. Bull	Canadian Mining and Metallurgical Bulletin.
Canadian Min. Jour	Canadian Mining Journal.
Carburants nat	Carburants nationales.
Carnegie Inst. Techno., Coal Research Lab. Contrib.	Carnegie Institute of Technology, Coal Research Laboratory Contributions.
Chaleur et Ind	Chaleur et Industrie.
Chem. Abs	Chemical Abstracts.
Chem. Age	Chemical Age (London).
Chem. and Eng. News	Chemical and Engineering News.
Chem. and Ind	Chemistry and Industry.
Chem. and Met. Eng	Chemical and Metallurgical Engineering.
Chem. en Pharm. Tech	Chemische en Pharmaceutische Techniek.
Chem. Eng	Chemical Engineering.
Chem. Eng. and Min. Rev	Chemical Engineering and Mining Review.
Chem. Eng. Cong. World Power Conf	Chemical Engineering Congress and World Power Conference.
Chem. Eng. Progress	Chemical Engineering Progress.
Chem. Fabrik	Chemische Fabrik.
Chem. Ind	Chemische Industrie.
Chem. Inds	Chemical Industries.
Chem.-Ing.-Tech	Chemie-Ingenieur-Technik.
Chem. Week	Chemical Week.

Abbreviations	*Journal titles*
Chem. Markets	Chemical Markets.
Chem. News	Chemical News.
Chem. Obzor	Chemicky Obzor.
Chem. Products	Chemical Products.
Chem. Rev	Chemical Reviews.
Chem. Rev. (Japan)	Chemical Review (Japan).
Chem. Tech	Chemical Technology.
Chem.-tech. Rundschau	Chemisch-technische Rundschau.
Chem.-tech. Ubersicht	Chemisch-technische Ubersicht.
Chem. Trade Jour	Chemical Trade Journal and Chemical Engineer.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zentralb	Chemisches Zentralblatt.
Chem.-Ztg	Chemiker-Zeitung.
Chemie, Die	Die Chemie.
Chim. et ind	Chimie et industrie.
Chim. ind. agr. biol	Chimica nell'industria, nell agricoltura, nella biologia e nelle realizzazioni corporative.
Chimica e industria	La Chimica, e L'industria.
CIOS	Combined Intelligence Objective Sub-committee Reports.
Clay Minerals Bull	Clay Minerals Bulletin.
Coal Age	Coal Age.
Coal and Colliery News	Coal and Colliery News.
Coal Carbonisation	Coal Carbonisation.
Coal-Heat	Coal-Heat.
Coal Technol., Am. Inst. Min. Eng., Tech Pub.	Coal Technology, American Institute of Mining Engineers, Technical Publications.
Coke	Coke.
Coke and Chem. (U. S. S. R.)	Koks i Khimiya, U. S. S. R. (Coke and Chemistry).
Coke and Gas	Coke and Gas.
Coke Smokeless-Fuel Age	Coke and Smokeless-Fuel Age.
Colliery Eng	Colliery Engineering.
Colliery Guard	Colliery Guardian.
Colloid Chem	Colloid Chemistry.
Combustibles (Zaragoza)	Combustibles (Zaragoza).
Combustion	Combustion.
Compt. rend	Comptes rendus hebdomadaires des séances de l'académie des sciences.
Compt. rend. acad. sci. U. R. S. S	Comptes rendus (Doklady) de l'académie des sciences de l'U. R. S. S.
Compt. rend., Cong. Chauffage ind., — Cong.	Congrès du chauffage industriel Comptes rendus du— Congrès.
Compt. rend., Cong. chim. ind., —me, Paris	Comptes rendus, Congrès de chimie industrielle, —me, (City).
Conf.-rapports sur les combustibles	Conférence–rapports sur les combustibles.
Conf. réunion soc. belg. étude pétrole, dérives et succédanes, Brussels, 1947.	Conférence réunion société belge pour l'études pétrole, dérives et succédanes, Brussels, 1947.
Cong. chim. ind., —th Cong	Congrès de chimie industrielle, —th Congress, (City).
Cong. mondial pétrole, 2me Cong., Paris — sec., Phys. Chim. Raffinage.	Congrès mondial du pétrole, —me Cong., (City) (date) (in five sections—Section 2, Phys. Chim. Raffinage). *See also* Proc. World Petrol. Cong.
Consolidated Eng. Corp. Recordings	Consolidated Engineering Corporation Recordings.
Cours conf	Cours conference.
Crucible	Crucible.
Cuerpo de Ingenieros de Minas	Cuerpo de Ingenieros de Minas.
Current Sci	Current Science (India).
Deut. Chemiker	Deutscher Chemiker.
Deut. Gesundhw	Deutsche Gesundheitswesen.
Deut. Molkerei-Ztg	Deutsche Molkerei-Zeitung.
Dingl. poly. Jour	Dinglers Polytechnisches Journal.
Disc., Faraday Soc	Discussions of the Faraday Society.
Doklady Akad. Nauk S. S. S. R	Doklady Akademii Nauk Soyuza Sovetskikh Sotsialisticheskikh Respublik. *See also* Comptes rendus (Doklady) de l'academie des sciences de l'U. R. S. S.
Echo mines et met	Echo des mines et de la métallurgie.
Elektrotech. Ztschr	Elektrotechnische Zeitschrift.
Energia termica	Energia termica.
Eng. Jour	Engineering Journal, Journal of the Engineering Institute of Canada.
Engineer	Engineer (London).
Engineering	Engineering.
Erdöl u. Kohle	Erdöl und Kohle.
Farbe u. Lack	Farbe und Lack.
Farben, Lacke, Anstrichstoffe	Farben, Lacke, Anstrichstoffe.
Federal Sci. Progress	Federal Science Progress.
Festschrift 100-jähre Bestehen Tech. Hochschule zu Karlsruhe.	Festschrift 100-jähre Bestehen Technische Hochschule zu Karlsruhe.
Fette u. Seifen	Fette und Seifen.
Feuerungstech	Feuerungstechnik.
FIAT	Field Information Agencies Technical.

Abbreviations	*Journal titles*
Finska Kemistsamfundets Medd	Finska Kemistsamfundets Meddelanden.
Food	Food.
Food Manuf	Food Manufacture.
Food Technol	Food Technology.
Foreign Petrol. Technol	Foreign Petroleum Technology.
Forschungen u. Fortschr	Forschungen und Fortschritte.
Forschungsarb. Gebiete Ingenieurw	Forschungsarbeiten auf dem Gebiete des Ingenieurwesens.
Fortschr. chem. Forsch	Forschritte der chemischen Forschung.
Fortune	Fortune.
Frankfurter Ztg	Frankfurter Zeitung.
Fuel	Fuel in Science and Practice.
Fuel Abs	Great Britain Department of Science and Industrial Research, Fuel Research Station, Fuel Abstracts.
Fuel Econ	Fuel Economist.
Fuel Econ. Rev	Fuel Economy Review.
Fueloil & Oil Heat	Fueloil & Oil Heat.
Gas	Gas.
Gas Abs	Gas Abstracts, Institute of Gas Technology.
Gas Age	Gas Age.
Gas Age-Record	Gas Age-Record.
Gas and Oil Power	Gas and Oil Power.
Gas Jour	Gas Journal.
Gas Research Board Inf. Circ	Gas Research Board Information Circular.
Gas Times	Gas Times.
Gas- u. Wasserfach	Gas- und Wasserfach.
Gas, Wasser, Wärme	Gas, Wasser, Wärme.
Gas World	Gas World.
Gaz. Cukrownicza	Gazeta Cukrownicza.
Gazz. chim. ital	Gazzetta chimica italiana.
Génie civil	Génie civil.
Geol. en Mijnbouw	Geologie en Mijnbouw.
Ges. Abhandl. Kenntnis Kohle	Gesammelte Abhandlungen zur Kenntnis der Kohle.
Gesundh.-Ing	Gesundheits-Ingenieur.
Giorn. bibliografia tecnica intern	Giornale di bibliografia tecnica internaziole.
Giorn. chim. ind. applicata	Giornale di chimica industriale ed applicata.
Glückauf	Glückauf.
Gosudarst. Nauch.-Tekh. Izdatel'stve	Gosudarstvennoyĭ Nauchno-Tekhnicheskoe Izdatel'stve.
Gulf	Gulf Research & Development Co., Patent Survey on the Synthine Process and Related Syntheses.
Gulf Research & Development Co., Chemistry Division Rept.	Gulf Research & Development Co., Chemistry Division Report.
Hamburger Tech. Nachrichten	Hamburger Technische Nauchrichten.
Handbuch der Gasindustrie	Handbuch der Gasindustrie.
Heat Engineering	Heat Engineering.
Helv. Chim. Acta	Helvetica Chimica Acta.
Het Gas	Het Gas.
Hornický Věstnik	Hornický Věstnik.
Ind. agr. aliment	Industries agricoles et alimentaires (Paris).
Ind. Chemist	Industrial Chemist and Chemical Manufacturer.
Ind. Chim	L'Industrie Chimique.
Ind. Chim. belge	Industrie chimique belge.
Ind. Eng. Chem	Industrial and Engineering Chemistry.
Ind. Eng. Chem., anal. ed	Industrial and Engineering Chemistry, analytical edition.
Ind. Eng. Chem., news ed	Industrial and Engineering Chemistry, news edition —.
Ind. Research Service	Industrial Research Service.
Industria chimica	Industria chimica.
Industria (Milan)	L'Industria (Milan).
Industria y quím	Industria y química (Buenos Aires).
Ing. Vetenskaps Akad. Handl	Ingeniörs Vetenskaps Akademien Handlingar.
Ingegnere	L'Ingegnere (Milan).
Ingenieur	Ingenieur.
Ingeniøren	Ingeniøren.
Inst. Fuel (London) Bull	Institute of Fuel (London) Bulletin.
Inst. Fuel, Wartime Bull	Institute of Fuel, Wartime Bulletin.
Inst. Gas Eng. Pub	Institution of Gas Engineers, Publication.
Inst. Ind. Chem. Fuels, Polytechinicum, Milan.	Institute of Industrial Chemical Fuels, Polytechinicum, Milan.
Inst. Min. Eng	Institution of Mining Engineers.
Inst. Petrol. Rev	Institute of Petroleum Reviews.
Internat. Chem. Eng	International Chemical Engineer.
	International Conference on Bituminous Coal. *See* Proc. Internat. Cong. Bituminous Coal.
Internat. Cong. Appl. Chem	International Congress of Applied Chemistry.
Internat. Cong. Pure Appl. Chem., — Cong., (Place) (No.).	International Congress of Pure and Applied Chemistry, — Congress.

Abbreviations	*Journal titles*
Internat. Ztschr. Metallog	Internationale Zeitschrift für Metallographie.
Ion	Ion.
Iron and Coal Trades Rev	Iron and Coal Trades Review.
Iron and Steel (London)	Iron and Steel (London).
Iron and Steel Inst. (London), Carnegie Schol. Mem.	Iron and Steel Institute (London), Carnegie Scholarship Memoirs.
Iva	Iva.
Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk.	Izvestiya Akademii Nauk Otdelenie Khimicheskikh Nauk.
Japan. Jour. Eng	Japanese Journal of Engineering.
Jour. Am. Chem. Soc	Journal of the American Chemical Society.
Jour. Appl. Chem. (U.S.S.R.)	Zhurnal Prikladnoĭ Khimii, U.S.S.R. (Journal of Applied Chemistry).
Jour. Appl. Phys	Journal of Applied Physics.
Jour. Chem. Education	Journal of Chemical Education.
Jour. Chem. Eng. (China)	Journal of Chemical Engineering (China).
Jour. Chem. Ind. (U.S.S.R.)	Zhurnal Khimicheskoĭ Promyshlennosti, U.S.S.R. (Journal of Chemical Industry).
Jour. Chem. Met. Min. Soc. South Africa	Journal of the Chemical, Metallurgical and Mining Society of South Africa.
Jour. Chem. Phys	Journal of Chemical Physics.
Jour. Chem. Soc	Journal of the Chemical Society (London).
Jour. Chem. Soc. Japan	Journal of the Chemical Society of Japan.
Jour. chim. phys	Journal de chimie physique.
Jour. Chinese Chem. Soc	Journal of the Chinese Chemical Society.
Jour. Colloid Sci	Journal Colloid Science.
Jour. four élec	Journal du four électrique et des industries électrochimiques.
Jour. Franklin Inst	Journal of the Franklin Institute.
Jour. Fuel Soc. Japan	Journal of the Fuel Society of Japan.
Jour. Gasbeleucht	Journal für Gasbeleuchtung.
Jour. Gen. Chem. (U.S.S.R.)	Zhurnal Obshcheĭ Khimii, U.S.S.R. (Journal of General Chemistry).
Jour. Imp. Coll. Chem. Eng. Soc	Journal of the Imperial College Chemical Engineering Society.
Jour. Ind. Eng. Chem	Journal of Industrial and Engineering Chemistry.
Jour. Indian Chem. Soc	Journal of the Indian Chemical Society.
Jour. Inst. Fuel	Journal of the Institute of Fuel.
Jour. Inst. Petrol	Journal of the Institute of Petroleum.
Jour. Inst. Petrol. Technol	Journal of the Institution of Petroleum Technologists.
Jour. Iron Steel Inst. (London)	Journal of the Iron and Steel Institute (London).
Jour. Junior Inst. Eng. (London)	Journal of the Junior Institution of Engineers, Inc. (London).
Jour. Math. Phys., Mass. Inst. Tech	Journal of Mathematics and Physics, Massachusetts Institute of Technology.
Jour. Metals	Journal of Metals.
Jour. Oil & Colour Chemists' Assoc	Journal of the Oil & Colour Chemists' Association.
Jour. Path. Bact	Journal of Pathology and Bacteriology.
Jour. pharm. chim	Journal de pharmacie et de chimie.
Jour. Phys. and Colloid Chem	Journal of Physical and Colloid Chemistry.
Jour. Phys. Chem	Journal of Physical Chemistry.
Jour. Phys. Chem. (U.S.S.R.)	Zhurnal Fizicheskoĭ Khimii, U.S.S.R. (Journal of Physical Chemistry).
Jour. phys. radium	Journal de physique et le radium.
Jour. prakt. Chem	Journal für praktische Chemie.
Jour. Proc. Australian Chem. Inst	Journal Proceedings of Australian Chemical Institute.
Jour. Research Inst. Catalysis	Journal of the Research Institute for Catalysis.
Jour. Roy. Tech. Coll. (Glasgow)	Journal of the Royal Technical College (Glasgow).
Jour. Ross. Phys.-Chem. Soc	Zhurnal Russkogo Fiziko-Khimicheskogo Obshchestva (Journal of the Russian Physical-Chemical Society).
Jour. Sci. Ind. Research (India)	Journal of Scientific & Industrial Research (India).
Jour. Soc. Auto. Eng	Journal of the Society of Automotive Engineers.
Jour. Soc. Chem. Ind. (Japan)	Journal of the Society of Chemical Industry (Japan).
Jour. Soc. Chem. Ind. (London)	Journal of the Society of Chemical Industry (London).
Jour. soc. ing. automobile	Journal de la société des ingénieurs de l'automobile.
Jour. South African Inst. Eng	Journal of the South African Institution of Engineers.
Jour. Tech. Phys. (U. S. S. R.)	Journal of Technical Physics (U. S. S. R.) (Zhurnal Teknicheskoĭ Fiziki (U. S. S. R.).
Jour. usines gaz	Journal des usines à gaz.
Jour. Western Soc. Eng	Journal of the Western Society of Engineers.
Kainer	Die Kohlenwasserstoff-Synthese nach Fischer-Tropsch, F. Kainer; Springer-Verlag, Berlin, 1950.
Khim. Mashinostroenie	Khimicheskoe Mashinostroenie (Chemical Machine Construction).
Khim. Prom	Khimicheskaya Promyshlennost (Chemical Industry).
Khim. Referat. Zhur	Khimicheskiĭ Referativnyĭ Zhurnal.
Kkim. Tverdogo Topliva	Khimiya Tverdogo Topliva (Chemistry of Solid Fuels).
Khimstroĭ	Khimstroĭ (Journal for Projecting and Construction of the Chemical Industry in U. S. S. R.)
Kiev Tekh. Inst. Kozhevenno-Obuvnoi Prom.	Universite d'état de Kiev Kozhevenno-Obuvnaya Promyshlennost S. S. S. R.

Abbreviations	*Journal titles*
Kislorod (Oxygen)	Kislorod (Oxygen).
Klepzig's Textil-Ztschr	Klepzig's Textil-Zeitschrift.
Klin. Wochschr	Klinische Wochenschrift.
Kohle u. Erz	Kohle und Erz.
Kolloid-Beihefte	Kolloid-Beihefte.
Kolloid-Ztschr	Kolloid-Zeitschrift.
Koppers Review	Koppers Review.
Kraftstoff	Kraftstoff.
Kunststoffe	Kunststoffe.
Labour's Pub. Dept. London	Labour's Publications Department London.
Lamp	Lamp.
Leben u. Umwelt	Leben und Umwelt.
Lesokhim. Prom	Lesokhimicheskaya Promyshlennost.
Machinery Market	Machinery Market.
Magyar Kém. Lapja	Magyar Kémikusok Lapja (Journal of the Hungarian Chemical Society).
Magyar Mérnők-Épitészegy et Közlönye	Magyar Mérnők- és Épitészegylet Közlönye (Journal of the Hungarian Society of Engineers and Architects).
Mat. grasses	Les Matières grasses.
Mech. Eng	Mechanical Engineering.
Mechanization	Mechanization.
Mededeel. Koninkl. Vlaam. Acad. Wetenschap., Belg. Klasse Wetenschap.	Mededeelingen van de Koninklijke Vlaamsche Academie voor Wetenschappen, Letteren en Schoone Kunsten, van Belgie, Klasse der Wetenschappen.
Mem. Faculty Sci. Eng., Waseda Univ. (Tokyo).	Memoirs of the Faculty of Science and Engineering, Waseda University, Tokyo, Japan.
Mem. Inst. Chem., Ukrain. Acad. Sci	Memoirs of the Institute for Chemistry, Academy of Science of the Ukrainian S. S. R.
Mém. poudres	Mémorial des poudres.
Mem. Ryojun Coll. Eng	Memoirs of the Ryojun College of Engineering.
Mém. services chim. état (Paris)	Mémorial des services chimiques de l'état (Paris).
Mém. soc. ing. civils France	Mémoires de la société des ingénieurs civils de France.
Metallbőrse	Metallbőrse.
Metallurg (U. S. S. R.)	Metallurg (U. S. S. R.) (Metallurgist).
Metallurgia	Metallurgia.
Métallurgie	Métallurgie.
Metallwirtschaft	Metallwirtschaft.
Metano	Metano (Padua).
Métaux & corrosion	Métaux & corrosion.
Métaux, corrosion, usure	Métaux, corrosion, usure.
Mfg. Perfumer	Manufacturing Perfumer.
Mfr. Record	Manufacturer's Record.
Michigan State Coll. Agr., Eng. Expt. Sta., Bull.	Michigan State College of Agriculture and Applied Science, Engineering Experiment Station Bulletin.
Min. and Met	Mining and Metallurgy.
Min. Cong. Jour	Mining Congress Journal.
Min. Eng	Mining Engineering.
Min. Jour. (London)	Mining Journal (London).
Mineral Ind	The Mineral Industry.
Mines, carrières	Mines, Carrières, grandes entreprises.
Mines Mag., Colorado	Mines Magazine, Colorado.
Mitt. Forsch.-Anstalt. Gutehoffnungshütte Oberhausen A.-G.	Mitteilungen aus den Forschungs-Anstalten von Gutehoffnungshütte Oberhausen Aktien-Gesellschaft.
Mitt. Kaiser Wilhelm-Inst. Eisenforsch. Dusseldorf.	Mitteilungen aus den Kaiser Wilhelm-Institut für Eisenforschung zu Düsseldorf.
Mitt. Kohlenforsch.-Inst. Prag	Mitteilungen des Kohlenforschungs-Instituts in Prag. (German edition of Zprávy Ústavu Vědecky Výzkum Uhli v Praze).
Modern Plastics	Modern Plastics.
Mon. produits chim	Moniteur des produits chimiques.
Montan. Rundschau	Montanistische Rundschau.
Motorwagen	Motorwagen.
Nafta (Yugoslavia)	Nafta (Yugoslavia).
Nat. Advisory Comm. Aeronau. Repts., Tech. Mem. Notes.	National Advisory Committee for Aeronautics, Reports, Technical Memorandum and Technical Notes.
Nat. Bureau of Standards, Research Jour	National Bureau of Standards, Research Jornal.
Nat. Petrol. News	National Petroleum News.
Natural Gasoline Assoc. of America	Natural Gasoline Association of America.
Nature	Nature (London).
Nature, La	La Nature.
Naturwissenschaften	Die Naturwissenschaften.
Natuur. Tijdschr	Natuurwetenschappelijk Tijdschrift (Belgium).
Neftyanoe Khoz	Neftyanoe Khozyaïstvo (Petroleum Economy).
Neue Giesserei, Tech. Wiss. Beihefte	Neue Giesserei, Technisch-Wissenschaftliche Beihefte, Metallkunde und Giessereiwesen.
New Zealand Dept. Sci. Ind	New Zealand Department of Scientific and Industrial Research.

Abbreviations	*Journal titles*
Nippon Kinzoku Gakukai-Shi	Nippon Kinzoku Gakukai-Shi.
Notiz. chim.-ind	Notiziario chimico-industriale.
Novosti Tekhniki	Novosti Tekhniki (Technical News).
Nuclear Sci. Abs	Nuclear Science Abstracts.
Nucleus	Nucleus.
Nuovo cimento	Nuovo cimento.
Oel u. Kohle	Oel und Kohle.
Oel u. Kohle Erdoel Teer	Oel und Kohle, Erdoel und Teer.
Official Gaz	Official Gazette of the United States Patent Office.
Ohio State Univ., Eng. Expt. News	Ohio State University Engineering Experiment Station News.
Oil and Soap	Oil and Soap.
Oil Gas Jour	Oil and Gas Journal.
Oil, Paint and Drug Reptr	Oil, Paint and Drug Reporter.
Oil Weekly	Oil Weekly.
Öle, Fette, Wachse, Seife, Kosmetik	Öli, Fette, Wachse, Seife, Kosmetik.
Olearia	Olearia.
Oliën, Vetten Oliezaden	Oliën, Vetten en Oliezaden.
Org. Chem. Ind. (U.S.S.R.)	Organic Chemical Industry (U.S.S.R.) (Promyshlennost Organicheskoĭ Khimii).
OSRD Rept	Office of Scientific Research & Development (United States).
Österr., Chem.-Ztg	Osterreichische Chemiker-Zeitung.
Österr. Ing.-Archiv	Osterreichisches Ingenieur-Archiv.
Paint Manuf	Paint, Varnish, Lacquer, Enamel and Colour Manufacture.
Paliva	Paliva.
Parfumerie	Parfumerie.
Peintures, pigments, vernis	Peintures, pigments, vernis.
Pennsylvania State Coll., School of Mineral Ind.	Pennsylvania State College, School of Mineral Industry.
Petrol. Eng	Petroleum Engineer.
Petrol. et Remplacement	Petroleum et Remplacement.
Petrol. Press Service	Petroleum Press Service.
Petrol. Processing	Petroleum Processing.
Petrol. Refiner	Petroleum Refiner.
Petrol. Technol	Petroleum Technology.
Petrol. Times	Petroleum Times.
Petrol. World and Oil Age	Petroleum World and Oil Age.
Petrol. Ztschr	Petroleum Zeitschrift für die gesamten Interessen der Erdöl-Industrie und des Mineralöl-Handels.
Petroleum (London)	Petroleum (London).
Pharm. Ztg	Pharmazeutische Zeitung.
Pharmazie	Die pharmazie.
Phil. Mag	Philosophical Magazine.
Phys. Rev	The Physical Review.
Phys. Ztschr	Physikalische Zeitschrift.
Physiol. Rev	Physiological Reviews.
Planovoe Khoz	Planovoe Khoziaĭstvo.
Podzemnaya Gazifikatsiya Ugleĭ	Podzemnaya Gazifikatsiya Ugleĭ (Underground Gasification of Coal).
Power Plant Eng	Power Plant Engineering.
Prirodnuie Gazui	Prirodnuie Gazui.
Proc. Am. Gas Assoc	Proceedings of the American Gas Association.
Proc. Am. Petrol. Inst	Proceedings of the American Petroleum Institute.
Proc. Ann. Coal Conf	Proceedings of the Annual Coal Conference, — Conference.
Proc. Cambridge Phil. Soc	Proceedings of the Cambridge Philosophical Society.
Proc. Chem. Soc	Proceedings of the Chemical Society (London).
Proc. Coal. Min. Inst. of America	Proceedings of the Coal Mining Institute of America.
Proc. Imper. Acad. (Tokyo)	Proceedings of the Imperial Academy (Tokyo).
Proc. Indian Acad. Sci	Proceedings of the Indian Academy of Science.
Proc. Indian Sci. Cong., — Cong	Proceedings of the Indian Science Congress, — Congress.
Proc. Internat. Conf. Bituminous Coal	Proceedings of the International Conference on Bituminous Coal, — Conference.
Proc. "Koninkl. Akad. Wetenschappen Amsterdam".	Proceedings of the "Koninklijke Akademie van Wetenschappen te Amsterdam".
Proc. Natl. Acad. Sci. U. S.	Proceedings of the National Academy of Science of the United States.
Proc. Phys. Math. Soc. Japan	Proceedings of the Physico-Mathamatical Society of Japan.
Proc. Phys. Soc. (Japan)	Proceedings of the Physical Society (Japan).
Proc. Phys. Soc. (London)	Proceedings of the Physical Society (London.)
Proc. Pure Applied Chem., — (city) —th Internat. Cong.	Proceedings Pure Applied Chemistry, — (city) —th International Congress.
Proc. Roy. Soc. (London)	Proceedings of the Royal Society (London).
Proc. Roy. Soc. (South Wales)	Proceedings of the Royal Society (South Wales).
Proc. South Wales Inst. Eng	Proceedings of the South Wales Institute of Engineers.
Proc. World Eng. Cong., — (city)	Proceedings of the World Engineering Congress, — (city).

Abbreviations	*Journal titles*
Proc. —d World Petrol. Cong	Proceedings of the —d World Petroleum Congress.
	Promyshlennost Organicheskoĭ Khimii *See* Org. Chem. Ind. (U. S. S. R.)
Przegląd Chem	Przegląd Chemiczny.
Przegląd gorniczo-hutniczy	Przegląd gorniczo-hutniczy.
Przegląd Gorniczy	Przegląd Gorniczy.
Przegląd Mechaniczny	Przegląd Mechaniczny.
Przegląd Tech	Przegląd Techniczny.
Przemysl Chem	Przemysl Chemiczny (Chemical Industry).
Przemysl Naftowy	Przemysl Naftowy (Petroleum Industry).
Przemysl Rolny i Spożywczy	Przemysl Rolny i Spożywczy (Agricultural and Food Industry).
Pubs. assoc. ing. faculte polytech. Mons	Publications de l'association des ingenieurs de la faculte polytechnique de Mons.
Quart. Jour. Indian Chem. Soc	Quarterly Journal of the Indian Chemical Society.
Quart. Revs. (London)	Quarterly Reviews (London).
Rass. min. met. chim	Rassegna mineraria, metallurgica e chimica.
Rec. trav. chim	Recueil des travaux chimiques des Pays-Bas.
Recherches et inventions	Recherches et inventions.
Refiner and Nat. Gasoline Mfr	Refiner and Natural Gasoline Manufacturer.
Reichsamt Wirtschaftsausbau	Reichsamt Wirtschaftsausbau.
Rept. to Federal Power Commission	Reports to the Federal Power Commission.
Repts. Imperial Fuel Research Inst., Japan	Reports of the Imperial Fuel Research Institute, Japan.
Research	Research (London).
Research Council Alberta (Canada) Ann. Rept.	Research Council of Alberta (Canada) Annual Reports.
Rev. carburants France	Revue carburants France.
Rev. chim. ind. (Paris)	La Revue chimie industrielle (Paris).
Rev. combust. liquides	Revue des combustibles liquides.
Rev. Gén. Gaz	Revue Générale du Gaz.
Rev. ind. minérale	Revue de l'industrie minérale.
Rev. indust	La Revue industrielle.
Rev. inst. franç. pétrole et Ann. combustibles liquides.	Revue de l'institut française du pétrole et Annales des combustibles liquides.
Rev. mét	Revue de métallurgie.
Rev. Modern Phys	Reviews of Modern Physics.
Rev. Petrol. Technol	Reviews of Petroleum Technology (London).
Rev. pétrolifère	Revue pétrolifére.
Rev. Phys. Chem. Japan	Review of Physical Chemistry of Japan.
Rev. prod. chim	Revue des produits chimiques.
Rev. quím. ind	Revista de química industrial.
Rev. sci	Revue scientifique.
Rev. univ. mines	Revue universelle des mines.
Riv. catasto servizi tecn. erar	Rivista catasto servizi tecn. erar.
Riv. combustibili	Rivista dei combustibili.
Riv. ital. petrolio	Rivista italiana del petrolio.
Riv. ital. essenze. profumi, piante offic., olii vegetali, saponi.	Rivista italiana essenze profumi, piante officinali, olii vegetali, saponi.
Rundschau deut. Tech	Rundschau deutscher Technik.
Saggiatore	Saggiatore.
Sbornik Nauch.-Issledovatel. Rabot Kiev Tekh. Inst. Kozhevenno-Obuvnoi Prom.	Sbornik Nauchno-Issledovatel'skogo Rabot Kiev Tekhnika Institut Kozhevenno-Obuvnaya Promyshlennost.
Schweiz. Aero Rev	Schweizer Aero Revue.
Schweiz. Apoth. Ztg	Schweizerische Apotheker Zeitung.
Schweiz. Arch. angew. Wiss. u. Tech	Schweizer Archiv für angewandte Wissenschaft und Technik.
Schweiz. Bauztg	Schweizerische Bauzeitung.
Schweiz. elektrotech. Ver., Bull	Schweizerischer elektrotechnischen Vereins, Bulletin.
Schweiz. Techztg	Schweizerische Technikerzeitung.
Schweiz. Ver. Gas- u. Wasserfach., Monats-Bull.	Schweizerischer Verein von Gas- und Wasserfachmännern, Monats-Bulletin.
Sci. American	Scientific American.
Sci. and Culture	Science and Culture (India).
Sci. and Ind. Research Council, Alberta, (Canada), Repts.	Scientific and Industrial Research Council, of Alberta (Canada), Reports.
Sci. et ind., Tech. ind. pétroles	Science et industrie, Technique industries pétroles.
Sci. Lubrication	Scientific Lubrication (London).
Sci. Papers Inst. Phys. Chem. Research (Tokyo).	Scientific Papers of the Institute of Physical and Chemical Research (Tokyo).
Sci. Petrol	Science of Petroleum (Oxford University Press, London).
Sci. Repts. Tôhoku Imp. Univ	Scientific Reports of the Tôhoku Imperial University.
Sci. Repts. Tokyo Imp. Univ	Scientific Reports of the Tokyo Imperial University.
Science	Science.
Science Councilor	Science Councilor.
Seifen-Öle-Fette-Wachse	Seifen-Öle-Fette-Wachse.
Seifensieder-Ztg	Seifensieder-Zeitung.

Abbreviations	*Journal titles*
Siebert Festschr	Siebert Festschrift.
Sitz. der heidelberg. Akad. Wiss	Sitzungsberichte der heidelberger Akademie der Wissenschaften.
Soap	Soap.
Soap Sanit. Chemicals	Soap and Sanitary Chemicals.
Soc. of Automotive Engineers	Society of Automotive Engineers.
South African Ind. Chem	South African Industrial Chemist.
South African Min. and Eng. Jour	South African Mining and Engineering Journal.
Southern Power and Ind	Southern Power and Industry.
Sparwirtschaft	Sparwirtschaft.
Stahl u. Eisen	Stahl und Eisen.
Stal	Stal.
Studi ric. comb	Studi e richerche sui combustible.
Süddeut. Apoth.-Ztg	Süddeutsche Apotheker-Zeitung.
Süddeut. Molkerei Ztg	Süddeutsche Molkerei Zeitung.
Suomen Kemistilehti	Suomen Kemistilehti.
Surveyor	Surveyor.
Svensk Kem. Tid	Svensk Kemisk Tidskrift.
Syn. Org. Chem	Synthetic Organic Chemicals
T. A. C. Rept	Technical Advisory Committee Report
Tech. Blätter	Technische Blätter (Dusseldorf)
Tech. Eng. News, M. I. T	Technical Engineering News, Massachusetts Institute of Technology.
Tech. ind. chim	Technique des industries chimiques.
Tech. Mitt. Krupp	Technische Mitteilungen Krupp. A. Forschungsberichte. B. Technische Berichte.
Tech. moderne	Technique moderne.
Techn.-Wetenschap. Tijdschr	Technisch-Wetenschappelijk Tijdschrift.
Technik, Die	Technik, Die.
Teer	Teer.
Teer u. Bitumen	Teer und Bitumen.
Tek. Tid	Teknisk Tidskrift Upplaga D. Mekanik, Skeppsbyggnadskonst och Flygteknik jämte Automobile-och Motorteknik.
Tek. Ukeblad	Teknisk Ukeblad.
Teknillinen Aikakauslehti	Teknillinen Aikakauslehti (Technical Review).
Teoriya i Prakt. Met	Teoriya i Praktika Metallurgii
Tetsu-to-Hagane	Tetsu-to-Hagane.
Tids. Kjemi Bergvesen	Tidsskrift for Kjemi og Bergvesen.
TIIC Rept	Technical Industrial Intelligence Committee Report.
TOM Reel	Technical Oil Mission Reel —.
Trans. Am. Inst. Chem. Eng	Transactions of the American Institute of Chemical Engineers.
Trans. Am. Inst. Min. and Met. Eng	Transactions of the American Institute of Mining and Metallurgical Engineers.
Trans. Am Soc. Mech. Eng	Transactions of the American Society of Mechanical Engineers.
Trans. Am. Soc. Metals	Transactions of the American Society for Metals.
Trans. Am. Soc. Steel Treating	Transactions of the American Society for Steel Treating.
Trans. — Ann. Anthractie Conf., Lehigh Univ	Transactions — Annual Anthracite Conference, Lehigh University.
Trans. Canadian Inst. Min. and Met	Transactions of the Canadian Institute of Mining and Metallurgy and of the Mining Society of Nova Scotia.
Trans. Electrochem. Soc	Transactions of the Electrochemical Society, Inc.
Trans. Faraday Soc	Transactions of the Faraday Society.
Trans. Indian Inst. Metals	Transactions of the Indian Institute of Metals.
Trans. Inst. Chem. Eng. (London)	Transactions of the Institution of Chemical Engineers (London).
Trans. Inst. Marine Eng	Transactions of the Institute of Marine Engineers.
Trans. Karpov Chem. Inst	Transactions of the Karpov Chemical Institue.
Trans. World Power Conf., Chem. Eng. Cong	Transactions of the World Power Conference, Chemical Engineers' Congress.
Trans. World Power Conf., Fuel Conf	Transactions of the World Power Conference, Fuel Conference.
Trudy Leningrad. Khim. Tekhnol. Inst	Trudy Leningradskogo Khimiko-Tekhnologicheskogo Instituta.
U. O. P. Co., Lib. Bull	Universal Oil Products Co., Library Bulletin.
U. O. P. Co., Survey Foreign Petrol. Literature.	Universal Oil Products Co., Survey of Foreign Petroleum Literature.
U. S. Industrial Chemical News	United States Industrial Chemical News.
U. S. Naval Tech. Mission in Europe	United States Naval Technical Mission in Europe.
U. S. Naval Tech. Mission to Japan	United States Naval Technical Mission to Japan.
Ukrain. Khem. Zhur	Ukrains'kiĭ Khemichniĭ Zhurnal (Ukrainian (Chemical Journal).
Ullmann, Enzyk. Tech. Chem	Ullmann, F., Enzyklopädie des Technischen Chemie. Urban and Schwarzenberg, Berlin, 2d ed., 10 vols., 1928–1932.
Umschau	Umschau or Umschau in Wissenschaft und Technik.
Univ. Illinois Eng. Expt. Sta. Circ	University of Illinois Engineering Experiment Station Circular.
Uppsala	Uppsala Universitets.
Usine	L'Usine.

Abbreviations	*Journal titles*
Uspekhi Khim	Uspekhi Khimii (Progress of Chemistry).
Valve World	Valve World.
Vestnik Metallopromyshlennosti	Vestnik Metallopromyshlennosti (Metal Industry World).
Vierjahresplan	Vierjahresplan.
Vom Wasser	Vom Wasser.
Vsesoyuz. Nauch.-Issledovatel. Inst. Metrol., Kratkiĭ Obzor Vazheĭshikh Nauch.-Issledovatel., Rabot Lab.	Vsesoyuznyĭ Nauchno-Issledovatel'skiĭ Institut Metrologii, Kratkiĭ Obzor Vazhneĭshikh Nauchno-Issledovatel'skiĭ, Rabot Laboratorya
Vsesoyuz. Nauch.-Issledovatel. Inst. Metrol., Sbornik Trudov.	Vsesoyuznyĭ, Nauchno-Issledovatel'skiĭ Institut Metrologii, Sbornik Trudov.
Wärme	Die Wärme.
Westinghouse Eng	Westinghouse Engineer.
Wisconsin Eng	Wisconsin Engineer.
World Oil	World Oil.
World Petrol	World Petroleum.
	Zhurnal Fizicheskoĭ Khimii U.S.S.R. *See* Jour. Phys. Chem. U.S.S.R.
	Zhurnal Khimicheskoĭ Promyshlennosti, U.S.S.R. *See* Jour. Chem. Ind. (U.S.S.R.).
	Zhurnal Obshcheĭ Khimii. *See* Jour. Gen. Chem. (U.S.S.R.).
	Zhurnal Prikladnoĭ Khimii U.S.S.R. *See* Jour. Appl. Chem. U.S.S.R.
	Zhurnal Russkogo Fiziko-Khimicheskogo Obshchestva U.S.S.R. *See* Jour. Russ. Phys.-Chem. Soc.
	Zhurnal Tekhnicheskoĭ Fiziki U.S.S.R. *See* Jour. Tech. Phys. (U.S.S.R.)
Zprávy Ústavu Vědecky Výzkum Uhli v Praze.	Zprávy Ústavu pro Vědecky Výzkum Uhli v Praze. (*See* Mitt Kohlenforsch.-Inst. Prag.).
Ztschr. angew Chem	Zeitschrift für angewandte Chemie.
Ztschr. anorg. Chem	Zeitschrift für anorganische Chemie.
Ztschr. Elektrochem	Zeitschrift für Elektrochemie und angewandte physikalische Chemie.
Ztschr. ges. exptl. Med	Zeitschrift für die gesamte experimentelle Medizin.
Ztschr. kompr. flüss. Gase	Zeitschrift für komprimierte und flüssige Gase sowie für die Pressluft-Industrie.
Ztschr. Krist	Zeitschrift für Kristallographie.
Ztschr. Lebensm.-Untersuch. Forsch	Zeitschrift für Lebensmittel-Untersuchung und-Forschung.
Ztscyr. Physik	Zeitschrift für Physik.
Ztschr. physik. Chem	Zeitschrift für physikalische Chemie.
Ztschr. physiol. Chem	Zeitschrift fur physiologische Chemie.
Ztschr. tech. Physik	Zeitschrift fur technische Physik.
Ztschr. Ver. deut. Ing	Zeitschrift des Vereines deutscher Ingenieure.

LITERATURE ABSTRACTS

A

1. ABRAMOV, I. Underground Gasification of Coal. Gas World, vol. 123, 1945, pp. 130, 132.

Gives brief account of developments in Russia and the economic possibilities. Practical use of gas from an established experimental station has shown that its cost is about 2/5 of an equal amount of coal.

ACKERMANN, P. *See* abs. **1087, 1945, 1946, 1946a, 1948, 1950, 1955.**

2. ADADUROV, I. E., AND DIDENKO, P. D. Catalysis by Fusions. Jour. Am. Chem. Soc., vol. 57, 1935, pp. 2718–2722; Chem. Abs., vol. 30, 1936, p. 1291.

Although orientation of a metal surface may be retained at the melting point, the decomposition of CH_3OH on Zn surfaces is now found to be catalyzed by ZnO; hence the constant rise in activity from solid to liquid Zn found by Steacie and Elkin (abs. **3264**), is not conclusive proof of the nonexistence of active centers. Further evidence is that catalytic oxidation of NH_3 by Sn is due to the oxide; hence the rate increases upon fusion, but the activity of Ag falls abruptly at the melting point, and the nature of the reaction changes because the oxide is not formed. Mechanisms are cited for the formation of ZnO, and experiments show Zn chips to be coated with oxide.

ADAMS, N. G. *See* abs. **3595.**

ADCOCK, W. A. *See* abs. **767.**

ADKINS, H. *See* abs. **2073.**

3. ADKINS, H., AND KRSEK, G. Preparation of Aldehydes From Alkenes by Addition of Carbon Monoxide and Hydrogen With Cobalt Carbonyls as Intermediates. Jour. Am. Chem. Soc., vol. 70, 1948, pp. 383–386; Chem. Abs., vol. 42, 1948, p. 2925.

Application of the Oxo process (U. S. Patent 2,327,066) to organic synthesis is presented. Several aldehydes have been prepared in an average yield of 50% by the addition of CO and H_2 to the alkene linkage in pentene-2, styrene, and other alkenes. The first step in the catalysis of the reaction appears to be formation of an ether-soluble Co compound, dicobalt octacarbonyl. Although the conversion of the alkene to the aldehyde may be brought about at 150° in the presence of Co on a support, it appears advantageous to use preformed dicobalt octacarbonyl in ether or other solvent for the catalysis of the synthetic reaction. The dicobalt octacarbonyl is readily made at 150° by the direct reaction of Co and CO and may be kept in ether for use as needed as a catalyst. The addition of CO and H_2 to an alkene goes very rapidly at 125° or lower in the presence of dicobalt octacarbonyl. The reactions may be carried out at 100–300 atm. pressure in the steel reaction vessels ordinarily used for hydrogenation. Warning is given as to the health hazards involved in the use of the Co carbonyls.

4. ———. Hydroformylation of Unsaturated Compounds With a Cobalt Carbonyl Catalyst. Jour. Am. Chem. Soc., vol. 71, 1949, pp. 3051–3055.

Hydroformylation of several unsaturated hydrocarbons, ethers, and esters, through the use of dicobalt octacarbonyl in benzene at 100–300 atm. of CO and H_2, has given good yields of aldehydes free of isomers (*see* Adkins and Krsek, abs. **3**). The reaction of substituted ethylenes of the types $RCH=CH_2$ and $R_2C=CH_2$ have given in 6 cases aldehydes of the type RCH_2CH_2CHO and R_2CHCH_2CHO; however, where R was phenyl, 1-naphthyl, n-butoxy, acetoxy, and ethoxymethyl, aldehydes of the type $RCH(CH_3)CHO$. Three alkenes of the type $RCH=CHR'$ have given good yields of a single aldehyde. Some limitations of the reaction, due to formation of mixtures of aldehydes or failure of the hydroformylation reaction to take place, are illustrated. The presence of a S-containing compound in the reaction mixture did not significantly poison the catalytic activity of the benzene-soluble cobalt carbonyl catalyst. This catalyst has proved to be effective for the hydrogenation of the carbon to carbon double bond in certain α–, β–unsaturated carbonyl compounds.

5. ADKINS, H., AND NISSEN, B. H. Selective Activation of Alumina. II. Reactions of Formic Acid at the Surface of Alumina. Jour. Am. Chem. Soc., vol. 45, 1923, pp. 809–815; Chem. Abs., vol. 17, 1923, p. 2104.

Effects of Al_2O_3 catalysts prepared in different ways on the decomposition of HCO_2H were studied. The amounts of H_2 and CO_2 formed agreed very closely, so that decomposition occurs almost entirely according to the reactions $HCO_2H=CO_2+H_2$ and $HCO_2H=CO+H_2O$ and to no considerable extent according to the equation $2\ HCO_2H=HCHO+CO_2+H_2O$. It is concluded that the distances separating the molecules of Al_2O_3, as determined by the method of preparation, were the important factors in defining the activity and selectivity of the catalyst.

6. ADKINS, H., AND PERKINS, P. D. Behavior of Methanol Over Aluminum and Zinc Oxides. Jour. Phys. Chem., vol. 32, 1928, pp. 221–224; Chem. Abs., vol. 22, 1928, p. 1521.

Fifty cc. of CH_3OH per hr. was passed over 1 gm. of catalyst at 300°–400°. CH_3OH was converted almost quantitatively over the Al_2O_3 catalyst into $(CH_3)_2O$ in increasing amounts at temperatures up to 350°. Further increase in temperature resulted in a rapid increase in products other than $(CH_3)_2O$ (CO_2, CO, C_2H_4, H_2, and CH_4). Formation of $(CH_3)_2O$ over the ZnO was almost negligible. Formation of gaseous decomposition products occurred, however, above 325°. Synthesis of CH_3OH by catalytic hydration of $(CH_3)_2O$ over Al_2O_3 was accomplished at 270°–430°. Optimum H_2O : $(CH_3)_2O$ ratio as constant flow varied with the amount of catalyst used.

7. ADKINS, H., BURGOYNE, E. E., AND SCHNEIDER, H. J. Copper-Chromium Catalyst for Hydrogenation. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 2626–2629; Chem. Abs., vol. 44, 1950, p. 8564.

$CuCr_2O_4$ catalyst produced by thermal decomposition of basic Cu ammonium chromate (containing also Ba from $Ba(NO_3)_2$) contains CuO and $CuCr_2O_4$, but neither alone is the effective catalyst. By increasing the ratio Cr : Cu, the activity was enhanced in the reduction of Me laurate and Me palmitate at 600 p. s. i. and 175°. It is activated by adsorption of H_2 at 200 atm.,

and 100° and, thus activated, catalyzes the hydrogenation of aldehydes and ketones at room temperature and of certain esters at 80°.

8. AGLIARDI, N., AND MARELLI, S. [Activated Adsorption of Hydrogen and of Carbon Monoxide on Cobalt.] Gazz. chim. ital., vol. 78, 1948, pp. 707–717; Chem. Abs., vol. 43, 1949, p. 3686.

Co was prepared by decomposition of Co formate at 270° in vacuo and the adsorption apparatus was that used in previous experiments. With "cleaved" Co, adsorption of CO was at first more rapid than that of H_2, but subsequently adsorption of CO became less than that of H_2. When the Co was poisoned by CO, adsorption of H_2 was smaller; nevertheless adsorption was even then more rapid than by Co not poisoned by CO. Mixtures of CO and H_2 were adsorbed more rapidly than was pure H_2. CoC_2, traces of which are formed in the surface reactions with CO, tends to stabilize the adsorbing surface, and even with successive adsorptions of H_2, the surface does not revert to its original condition. Under the conditions of the experiments, not all of the C is reduced by H_2, and solution of the Co in dilute HNO_3 showed the presence of elemental C. The apparent energy of activation of adsorption of CO is greater than that of H_2 and decreases with increase in the amount of gas adsorbed.

9. AICHER, A., MYDDLETON, W. W., AND WALKER, J. Production of Hydrocarbon Oils From Industrial Gases. I. Jour. Soc. Chem. Ind., vol. 54, 1935, pp. 313–320 T; Chem. Abs., vol. 29, 1935, p. 8289.

In the production of hydrocarbon oils from CO and H_2, the total S content of the gas is reduced to approximately 0.1 grain per 100 cu. ft. Organic S compounds are removed by hydrogenation over a CuO–$PbCrO_4$–Et orthosilicate catalyst, and H_2S is then absorbed. The purified gas is passed over a Ni–Mn–Al catalyst supported on kieselguhr and cemented together by Et orthosilicate at 450°–480°. As the 1st few inches of the catalyst bed perform much more work than the succeeding layers, there is a tendency to produce a hot spot. Adsorption of the product on the surface of the catalyst exercises a retarding action, increasing with the partial pressure of the oil in the catalyst chamber. The preferred method of operation is to use the catalyst in 2 or 3 parts and to remove the products formed after each stage. This results in a grading of oil with definite variation in content of unsaturated hydrocarbons, increased throughput of gas per unit volume of catalyst and an increased yield of oil from a given volume of gas.

10. MYDDLETON, W. W., AND WALKER, J. Production of Hydrocarbon Oils From Industrial Gases. II. Jour. Soc. Chem. Ind., vol. 55, 1936, pp. 121–124T; Chem. Abs., vol. 30, 1936, p. 5393.

Dilution of the reactants does not lower the yield but decreases the rate when the diluents comprise reaction products that are adsorbed on the catalyst. The distillation characteristics of the products are independent of the contact time and the composition of the charge. A product of high olefin content, suitable for the preparation of motor fuel and oil, is favored by a short contact time, a CO : H_2 ratio greater than 0.5, and use of Co instead of Ni catalysts.

11. AITA, A. [New Developments in the Heavy Chemical Industry.] Notiz. chim.-ind., vol. 2, 1927, pp. 78–81; Chem. Abs., vol. 21, 1927, p. 1857.

Describes advances, since World War I, in the manufacture of fertilizers and synthetic fuels and in catalysis.

12. AKAMATSU, H., AND SATO, K. [Catalytic Decomposition of Carbon Monoxide by Iron.] Bull. Chem. Soc. Japan, vol. 22, 1949, pp. 127–131; Chem. Abs., vol. 44, 1950, p. 7637.

Pure CO was passed through a quartz reaction tube containing a piece of Kahlbaum's electrolytic Fe as catalyst. Gas flowing from the reaction tube passed through $Ba(OH)_2$ solution, which becomes turbid when the reaction proceeds as $2\,CO \rightarrow C + CO_2$. 5–10 hr. are necessary for decomposition to begin at 500° reaction temperature and CO flow of 400 cc. per hr. Once started, the reaction proceeds smoothly, and free C forms on the surface of the catalyst. Electron-diffraction patterns of the catalyst were taken just as decomposition had begun, as shown by turbidity of the $Ba(OH)_2$ solution, and after 15 hr. of decomposition. In case 1 no free C was found, but the Fe had lost its metallic luster, the pattern obtained was that of cementite. The 2d pattern was made when the surface was black or gray in parts but before C appeared in powder form; this pattern was principally of C, but some cementite spacings also appeared. Prolonged decomposition yielded a C-powder layer and the surface then gave only C spacings. Patterns of amorphus C ordinarily show only spacings corresponding to (*hk0*) and (*001*), but since the C resulting from decomposition of the CO showed spacings corresponding to (*101*) and probably (*112*) this deposit proved to be graphite. Since amorphus C must be heated above 2,500° to be graphitized, it is thought that in this case the C formed is not amorphus, but rather graphite formed by decomposition of cementite. Traces of O_2 in the CO prevented decomposition if an Fe plate was used as catalyst, but not if pulverized Fe was used.

13. AKERS, W. W., AND WHITE, R. R. Kinetics of Methane Synthesis. Chem. Eng. Progress, vol. 44, No. 7, 1948, pp. 553–566; Chem. Abs., vol. 42, 1948, p. 6085.

When CO and H_2 mixtures are passed over a reduced Ni catalyst at 300°–350° and 1 atm., CH_4 is produced by the reaction $CO+3H_2=CH_4+H_2O$. CO_2 is formed by the side reaction $CO+H_2O=CO_2+H_2$. Carbon is not formed in appreciable amounts under the conditions studied. The rate of reaction between the adsorbed reactant molecules on the active centers of the catalyst is the rate-controlling step in the synthesis of CH_4. The rate of the CH_4-synthesis reaction is correlated by the equation:

$$r=\frac{p_{CO}p_{H_2}^2}{(A+Bp_{CO}+Dp_{CO_2}+Ep_{CH_4})^4}$$

The initial rate of formation of CO_2 can be expressed by the empirical equation:

$$r=A'\,(p_{CO}-B').$$

The rate remains almost constant until the rate of CH_4 formation equals the CO_2 rate. Thereafter both rates are equal, and the CH_4 rate equation can be used as the CO_2 rate equation.

14. AKHMEDLI, M. K. [Hydrogenation of Monocyclic Aromatic Hydrocarbons on a Cobalt Catalyst.] Jour. Gen. Chem. U. S. S. R., vol. 19, 1949, pp. 462–467 (in English, pp. 229–239); Chem. Abs., vol. 43, 1949, p. 6172.

Hydrogenation of C_6H_6, PhMe, and $C_6H_4Me_2$ is not catalyzed by either asbestos, Al_2O_3, or Cr_2O_3 at 220°. On pure Co, prepared by reduction of the formate, C_6H_6 is completely hydrogenated at 172°, PhMe at 208°, $C_6H_4Me_2$ at 228°. Co deposited on carriers is more active than pure Co. Thus, with Co (61.54%), reduced from the formate, on asbestos, the temperatures of complete hydrogenation were, respectively, 105°, 100°, and 92°, with Co (68.75%) on Al_2O_3, 85°, 82°, and 41°, with Co (61.54%) on Cr_2O_3, 42°, 94°, and 139°. For the hydrogenation of C_6H_6, the most active catalysts are Cr_2O_3 and Co, and Al_2O_3 and Co; for $C_6H_4Me_2$, Al_2O_3 and Co is very distinctly more active than Cr_2O_3 and Co. The rate of hydrogenation falls

in the order C_6H_6, PhMe, $C_6H_4Me_2$. Hydrogenation of all 6 atoms takes place in 1 stage, in agreement with the multiplet theory of catalysis.

AL, J. *See* abs. **3043.**

15. ALBERTS, L. [Iron Catalysts.] FIAT Reel K–29, 1938, frames 6932–6935; PB 70,218.

Special experiences with a Lurgi Fe catalyst are presented. A conclusive evaluation is not possible because the statements are contradictory. Continuation of the tests is recommended.

15a. ALBERTS, L. W., BARDIN, J. S., BEERY, D. W., JONES, H. R., AND VIDT, E. J. Production of Methane From Coal. Chem. Eng. Progress, vol. 48, 1952, pp. 486, 493; Chem. Abs., vol. 46, 1952, p. 11,636.

It has been estimated that the investment of a plant designed to produce 100 million $ft.^3$ per day of high-B. t. u. pipeline gas is approximately $52.5 million. The cost of larger plants will be proportional to their size. The cost of producing the gas has been shown to be $0.55 per 1,000 std. $ft.^3$ when the charging stock is a noncaking coal or char having a heating value of 26 million B. t. u. per ton and containing no tar-forming materials, available at $4.00 per ton. This study has shown that the cost of CH_4 from coal is closely related to the cost of coal. With fuel costing $4.00 per ton, fuel represents 45% of the cost of gas, at $8.00 per ton it is 60%. The overall thermal efficiency of this process compares favorably with other processes for converting coal into more readily available forms of energy. It has also shown that >90% of the cost of producing high-B. t. u. pipeline gas lies in the production of the purified synthesis gas. Therefore, efforts to reduce the cost must be directed toward reducing the cost of the synthesis gas. Proper selection and pretreatment of the coal to allow its introduction into the gas generator without prior removal of its tar and oil content will effectively reduce its cost, resulting in lowered gas cost.

ALBRECHT, W. H. *See* abs. **3620, 3621.**

ALBRECHT, W. H., AND WEDEKIND, E. [Distinguishing the Different Types of Ferric Oxides and Hydrated Oxides by Their Different Magnetic Properties. III. Hydrated Ferric Oxide From the Decomposition of Iron Pentacarbonyl.] *See* abs. **3622.**

———. [Distinguishing the Different Types of Ferric Oxides and Hydrated Oxides by Their Different Magnetic Properties. IV.] *See* abs. **3623.**

ALBRIGHT, R. E. *See* abs. **1460.**

16. ALDEN, R. C. Conversion of Dry Natural Gas to Liquid Fuels. World Petrol., vol. 17, No. 4, 1946, pp. 46–49; 70. Gas abs., vol. 2, No. 5, 1946, p. 118; Chem. Abs., vol. 40, 1946, p. 3248.

Reviews Fischer-Tropsch process development in Germany and its possible application in the United States. Either coal or natural gas can be utilized, but the latter is believed to be simpler and cheaper to operate. 3.5–5 gal. of gasoline are obtainable from 1,000 cu. ft. gas. One of the developments in this country is an Fe catalyst which gives a higher octane product and oxygenated materials.

17. ———. Conversion of Natural Gas to Liquid Fuels. Petrol. Refiner, vol. 25, No. 11, 1946, p. 194; Petrol. Processing, vol. 1, 1946, p. 246.

Abstract of a paper presented before the California Natural Gasoline Association. German developments in the conversion of coke and brown coal to liquid hydrocarbons, applied to natural gas, would result in a motor fuel costing about $0.19 per gal. A number of developments in the several processes, however, including cheap O_2, large bed reactors, improved catalysts, and fluidized catalytic operations will probably reduce the cost to as low as $0.05 per gal. These, with the larger scale of American operations, have already resulted in preliminary construction work on 2 commercial installations (Brownsville, Texas, and western Kansas) and several other installations, where natural-gas reserves and other conditions are favorable, are anticipated.

18. ———. Conversion of Natural Gas to Liquid Fuels. Petrol. Engineer, vol. 18, No. 4, 1947, pp. 148, 150, 152, 154, 156, 158; Oil Gas Jour., vol. 45, No. 27, 1946, pp. 79, 81, 82, 97, 98; California Oil World, vol 39, No. 20, 1946, pp. 5–16; Chem. Abs., vol. 41, 1947, p. 264.

German development of the Fischer-Tropsch process and the American refinements to use natural gas as raw material are reviewed. Natural gas is cheaper raw material and simpler to handle, and desulfurization is easier than with coal. In a conjectured commercial-scale operation at present, desulfurized natural gas and O_2 are preheated separately and passed into a combustion reactor, where synthesis gas consisting of 2 parts H_2 to 1 part CO is produced. The exit gas is cooled from about 2,100° F. to 600° F. in a waste-heat boiler, where a portion of the power requirements of the plant is produced. The gas is then passed into the synthesis reactor, where liquid hydrocarbon products are formed. A fluid, powdered Fe catalyst is employed. The temperature is controlled by water-cooled tubes extending into the reactor. By mild refining, the raw gasoline will have a 75–80 octane number and the Diesel fuel a cetane number >50. 5,000 bbl. of total refined hydrocarbon product, consisting of about 4,100 bbl. of motor fuel and 900 bbl. of Diesel fuel, are obtained from 60,000,000 cu. ft. of natural gas. In addition, there would be 360 bbl. of oxygenated products. With natural gas at $0.05 per 1,000 cu. ft., the cost per gal. of liquid fuels would be approximately $0.05.

———. *See* abs. **1399.**

19. ALDEN, R. C., AND CLARK, A. Appraisal of Gas-Synthesis Operations. Petrol. Processing, vol. 3, 1948, pp. 425–430; Nat. Petrol. News, vol. 40, No. 14, 1948, p. 23.

Paper presented before the Western Petroleum Refiners Association, 36th annual meeting. Synthesis of liquid fuels from natural gas will require investments ranging from $3,000.00 to $4,000.00 per bbl. per day and cost $0.0914 per gal. without credit for chemical products. The steel requirement is about 6 tons per bbl. per day. To make gasoline from coal would require approximately 2 times the investment and double the amount of steel, and it would cost $0.114–$0.164 per gal. To produce 650,000 bbl. per day of synthetic oil would require 10,000 cu. ft. of natural gas or 1,360 lb. of coal per gal. of motor fuel produced. Gas-synthesis plants would cost 2.6 billion dollars to build and require 3.96 million tons of steel. Coal-synthesis plants would cost 5.2 billion dollars and use 5.65 to 7.8 million tons of steel. Natural-gas reserves required for 20 yr. operation are 47.5 trillion cu. ft. and coal reserves required are 2.92 billion tons. Gas reserves are currently estimated at 165.9 trillion cu. ft. and reserves of total liquid hydrocarbons approximately 2,512 billion bbl. Since 50% of the energy in natural gas would be absorbed in the synthesis, the fuel-oil equivalent of the gas used for synthesis is 13.8 billion bbl. About 85% or 11.7 billion bbl. would be gasoline; and, at present estimated demand, our gas reserves would last about 13 yr. It is apparent that any significant long-range liquid-fuels program must be based on coal. Gas synthesis will be limited to those regions where enough gas reserves are available, 0.5 trillion cu. ft. being necessary to run one 7,000-bbl.-per-day plant for 20 yr. Future gas-synthesis, up to several hundred thousand bbl. per day, could be sustained by our natural-gas resources provided (a) the operation

can compete economically with processing of crude oil and (b) can pay a high enough price for natural gas to stimulate new discoveries. Much will depend on the engineering and economic outcome of the 2 plants being built and on interim research and development programs. As things stand, with a marginal long-term profit prospect, a very large investment requirement, and most important, gas reserves committed otherwise, it is quite likely that new gas-synthesis operations will be undertaken slowly.

20. ———. Liquid Fuels From Natural Gas. Trans. Am. Soc. Mech. Eng. Paper 48–FET–13, 1948, 13 pp.; Oil Gas Jour., vol. 47, No. 24, 1948, p. 111.

Abstract of paper presented at American Society of Mechanical Engineers meeting, Amarillo, Texas. American research and development of the Fischer-Tropsch process have resulted in great improvements, which make the gas-synthesis operation appear in a favorable light as an economic source of liquid fuels. Plant investment is about $3,000–$4,000 per bbl. per day. Steel requirement is about 6 tons per bbl. per day for a capacity of 650,000 bbl. per day. A corresponding production of synthetic liquid fuels from coal would require about 2 times as much investment and nearly 2 times as much steel. Coal required would equal 28% of the 1945 production. Natural-gas reserves have been increasing at a faster rate than the marketed production of natural gas, which has been doubling every 11 yr. A producible natural-gas reserve of 0.5 trillion cu. ft. is required to sustain a 7,000-bbl.-per-day gas-synthesis operation for 20 yr. In only 10 States are there known gas reserves of over 1 trillion cu. ft., and only about 50 out of 426 gas-producing fields have reserves greater than 0.5 trillion cu. ft. A substantial gas-synthesis development must depend on new gas discoveries.

21. ALDRICH, R. C. Manufacture and Regeneration of Fischer-Tropsch Catalyst. Nat. Petrol. News, vol. 37, 1945, pp. R922–R924; CIOS Rept. VI–22, X–18–XV–5, 1944, 25 pp.; PB 373.

Operation of the Fischer-Tropsch unit of the Carrières-Kuhlmann plant at Harnes, France. Of the operating personnel of 120 men, 40 are employed in catalyst manufacture and regeneration. Capacity of the plant is 350 bbl. per day. The % composition by weight of the finished catalyst before hydrogenation is: Co 18.0, MgO 1.8, ThO_2 0.9, kieselguhr 79.3%, 40–50 kg. HNO_3 (36° B.), and 90 kg. of Na_2CO_3 per 100 kg. of catalyst. The Co must be 99% pure, the other 1% being Cu or Ni. ThO_2 must not contain even traces of Pb or P, and the CaO must be less than 0.2% by weight. The kieselguhr must not contain Fe or lime. The SiO_2 content must exceed 92%, but the sand content must not exceed a few %. All organic matter must be removed by roasting at 800° but not greatly above, as the structure of the particles will be destroyed. Kieselguhr from Kieselguhr-Industrie-Hannover No. 120 is one of the best both as to impurities and particle size; and Johns-Manville Filtracel is satisfactory. Describes manufacture of the catalyst and its regeneration in great detail, together with the accompanying chemical reactions.

22. ———. Synthetic Lubricating-Oil Production in France. Nat. Petrol. News, vol. 37, No. 45, 1945, pp. R859–R860; CIOS Rept. XVIII–5, 1945, 9 pp.; U. S. Naval Tech. Mission in Europe Rept. 80–45; TOM Reel 196; PB 365.

Two processes are described: The Standard Kuhlmann-Lestaque near Marseille and the Kuhlmann Co.-Harnes near Lille. The first process used Fischer-Tropsch gas oil, benzol, and dichlorethane as raw materials. The gas oil should be highly paraffinic and be produced by carrying out the $CO:H_2$ synthesis at a ratio of 2:1 and holding down the temperature of the reaction to 190° to produce as few olefins and as many paraffins as possible. The gas oil is first chlorinated, then mixed with the benzol-dichlorethane mixture in presence of $AlCl_3$, reacted for about 6 hr. at 70°–110°, the benzol stripped out, and the stripped oil settled and decanted and given a conventional refining treatment. The products are roughly 20% recycle gas oil, 30% transformer oil, 30% turbine oil, and 20% steam-cylinder oil. The viscosity index for the lubricating oils is about 100. The second process treats the Fischer-Tropsch gasoline with 3% of $AlCl_3$ for 5 hr. at room temperature, and the 2 layers are separated and treated for recovery of the oils. The quality of the lubricating oils is not good; their oiliness is poor, and they oxidize readily. Analyses are tabulated for the products of both processes.

———. *See* abs. **3038.**

23. ALI, E. [Study of the Composition and Conversion Possibilities of Fischer-Tropsch Synthesis Hydrocarbons.] Thesis, Berlin, 1941, 64 pp.

24. ALLAN, D., COCKS, L. V., AND SUTCLIFFE, H. T. Production of Synthetic Fatty Acids and Their Conversion into Soaps and the Properties of the Products. Chem. Trade Jour., vol. 122, 1948, p. 89; BIOS Final Rept. 1560, 1947, 35 pp.; PB 91,672.

Soaps from the synthetic fatty acids, even when they form only 10–20% of the fat charge, have an unpleasant odor, which is imparted to the human skin when washed with the soap. The extent varies with different individuals. The odor is not found on cloth washed with the soap. Refractionation of the fatty acids and removal of the lowest molecular-weight acids give some improvement. The odor may be due in part to decomposition that takes place during heating of the anhydrous soap to 360° C., which is common to all German processes. Development of the process in England depends on finding enough raw materials.

25. ALLEN, C. F. H. The Oxo Process. Syn. Org. Chem., Eastman Kodak Co., vol. 18, No. 3, 1946; U. O. P. Co. Lib. Bull., vol. 22, No. 5, 1947, p. 20.

Oxo process developed in Germany produces straight-chain aldehydes and ketones from olefins and water gas, the former predominating. The use of hydrocarbons terminating in $=CH_2$ favors production of aldehydes. For example, if C_2H_4 is used, the products are propionaldehyde and diethyl ketone, the former being 70% of the total. The product from unsaturated hydrocarbons containing 11–17 C atoms has been the basic starting material. The reaction can be carried out in batches or continuously. Pressures used are about 150 atm. with temperatures up to 180°. After partial conversion and separation of the oxygenated fraction by distillation, the residue is made up with new gas and recirculated. The catalyst consists of Co, Th, and Mg carbonates on kieselguhr suspended in Diesel oil. The catalyst is not sensitive to S, so removal of S compounds from the water gas is not necessary. Possibilities of the process are great. The carbonyl compounds formed can be converted into other substances by known chemical processes. For example, reduction in presence of a Raney Ni catalyst gives the corresponding alcohols. These can be sulfated to produce the modern detergents. The development is only beginning, however, and many technical difficulties remain to be overcome.

ALLEN, J. G. *See* abs. **1477.**

26. ALLGEMEINE OEL- UND FETT-ZEITUNG. [Properties of Synthetic Kogasin Lubricants.] Vol. 35, 1938, pp. 124–125.

After referring to the Fischer-Tropsch process and the advantages the product has over coal and natural oils owing to its greater uniformity, reference is made to the control that can be exercised over the product.

Viscosity-temperature curve of oil boiling 125°–250° C. is as good as that of a Pennsylvania oil. Winter-grade Kogasin oil corresponds very closely, both in viscosity and viscosity-temperature curve with a winter-grade natural oil. The specific gravity is very low due to the high H content, which is also important in giving a low C formation in an internal-combustion engine. Flash point of winter oil is rather low, but higher values can be obtained for summer and aircraft oils. Other points are: Very low setting point, complete freedom from S, and unlimited stability against the effect of O_2 and light. On these accounts the oil can be used for transformers and switchgear.

ALLISON, E. *See* abs. **890.**

27. ALLNER, W. [Bunsen Flame.] Jour. Gasbeleucht., vol. 48, 1905, pp. 1035–1040; Jour. Chem. Soc., vol. 90, (2), 1906, pp. 441–442.

In the relatively cold flames formed by burning mixtures of CO_2 and H_2, or of CO and H_2, a state of equilibrium is not attained. In the flames of mixtures of CH_4 and H_2, CH_4, H_2, and CO_2, C_6H_6 and H_2, and C_6H_6, H_2, and CO_2, the equilibrium $K=[(H_2O)\ (CO)]/[(CO_2)\ (H_2)]$, corresponding with the temperature, is established. The effect of temperature on the equilibrium is discussed, and the values of the constant in the equation $\log K=-1/0.4343.R\int q/T^{2.dt}+\text{constant}$ are calculated from the different values of K and the effect of temperature on the specific heats of the gases.

28. ———. [Brown Coal Gas for City and Synthetic Purposes—The Kassel Parallel Current Chamber, Bubiag-Didier System.] Gas- u. Wasserfach, vol. 78, 1935, pp. 438–456; Tech. Blätter, vol. 25, 1935, p. 392; British Chem. Abs., 1935, B, p. 756; Chem. Abs., vol. 29, 1935, p. 6731.

Brown coal or brown-coal briquets are carbonized in vertical chambers heated externally to 1,000°–1,300°. The brown coal gradually passes down through the chamber, and the distillation products are cracked by passing down through the hot coke before being removed through outlets at various heights. The coke in the lower part of the chamber is steamed to generate water gas, which mixes with the gas produced by carbonization. Provision is made for the continuous removal of the coke, which is used to generate producer gas for heating the chambers. The yield and quality of the gas may be varied within wide limits by adjusting operating conditions, so as to produce a gas of 450 B. t. u. per cu. ft. or higher, or a gas containing less than 4% CH_4 suitable for synthetic purposes. Gas similar in composition to coal gas may be made if the excessive amount of CO_2 is washed out. This is accomplished by means of a 20%, K_2CO_3 solution, the regeneration of this solution requiring about 1 lb. of steam per 3 cu. ft. of CO_2. Possible uses for CO_2 are discussed, and costs for its removal are given. Losses of the wash solution are negligible, less than 20% per yr. The tar is similar to high-temperature tar, but the yield is much lower. The light-oil content is about 0.095–0.16 gal. per 1,000 cu. ft., but this may be increased by introducing petroleum oils or brown-coal tar into the chamber during carbonization. Gas manufactured by this process has been used successfully in ordinary gas-burning appliances both alone and mixed with the ordinary city gas and the experimental plant has been in continuous operation since October 1934, covering ⅕–⅐ of the Kassel gas requirements. Cost data are given for German conditions. A laboratory apparatus for carbonizing brown coal is described, which permits comparison of various brown coals.

29. ———. [Direct-Current Degasification Process of the Kassel Oven of the Bubiag-Didier System.] Braunkohle, vol. 34, 1935, pp. 419–428; Chem. Abs., vol. 30, 1936, p. 7310.

Detailed description of process using various forms of brown coal for the production of domestic or synthesis gas. Coal drying, low-temperature carbonization, gas cracking, tar decomposition, coke gasification, and water-gas formation are involved in the operation. Excess CO_2 is removed by scrubbing. Economic aspects discussed.

30. ———. [Production of City Gas and Gas for Synthesis From Brown Coal by the Continuous-Current Gas Process.] Ztschcr. Ver. deut. Ing., vol. 79, 1935, pp. 1487–1492; Coal Carbonisation, vol. 2, 1936, p. 18; Chem. Abs., vol. 30, 1936, p. 1542.

Kassel plant of the Braunkohlen und Brikett Industrie A.-G., Bubiag, for degasifying brown coal by parallel-flow process is described. The raw-gas yield for purposes of synthesis amounts to 1,100–1,800 $m.^3$ per ton at normal temperature and pressure. The CO : H_2 ratio can be adjusted exactly to 1 : 2 to suit the Fischer benzine-synthesis process without special preparation. An installation of 12 parallel-flow retorts 32 ft. 10 in. in height has been in continuous service in Hungary since 1932, making about 70,000 $m.^3$ of synthesis gas per day. Plants of any desired capacity can be supplied under guarantee for the manufacture of town gas or synthesis gas.

31. ———. [Brown Coal as Raw Material for City Gas and Synthesis Gas.] Braunkohle, vol. 35, 1936, pp. 495–511; Chem. Abs., vol. 31, 1937, p. 1584.

Comprehensive review of plants and processes for making water gas for synthesis purposes and a discussion of the correct conditions for producing synthesis gas are presented, with an analysis of costs.

32. ———. [Brown Coals as Raw Material for Town Gas and Synthesis Gas.] Braunkohle, vol. 35, 1936, p. 886; Chem. Eng. Cong., World Power Conf., vol. E1, 1936, 20 pp.; Chem. Abs., vol. 31, 1937, p. 8157.

An addendum is presented. The Pintsch-Hillebrand process yields a gas suitable for the Fischer synthesis in 1 stage. It contains 15% inerts (CO_2, CH_4, and N_2) and 85% of H_2 and CO in the ratio, H_2 : CO=2. After catalytically converting the CO into CO_2 and washing out the latter, the gas contains 97–98% of H_2. Data provided by J. Pintsch A.-G., are given for the cost of erecting and operating a plant yielding 80,000 $m.^3$ of synthesis gas/hr.

33. ———. [Manufacture of City Gas and Synthetic Gas From Brown Coal and Other Low-Rank Fuels.] Gas- u. Wasserfach, vol. 79, 1936, pp. 594–596; Chem. Abs., vol. 30, 1936, pp. 8572–8573.

Carbonization and gasification processes for brown coal are reviewed briefly. At Dessau a mixture of low-temperature brown-coal gas is mixed with coal gas. Successful experiments were made with brown coal in the Bube and Heinze gas producers at the Halle and Dresden gas works. Zittau has contracted for gas to be made from brown coal in the Lurgi high-pressure gas generators, with a mixture of O_2 and H_2O vapor. Several other processes have been or are now being operated on a semi-plant scale.

34. ———. Manufacture of Town Gas and Gas for Chemical Synthesis From Lignite. Trans. World Power Conf., Chem. Eng. Cong., 1936, E 6, 30 pp.; British Chem. Abs., 1936, B, p. 724.

It is emphasized that carbonization processes must be adapted to suit brown coals. Various processes are discussed from this viewpoint, and the correct conditions for producing town gas and synthesis gas are dealt with.

ALLOLIO, R. *See* abs. **337.**

ALLUM, R. E. *See* abs. **291.**

35. ALMQUIST, J. A. Catalytic Synthesis at High Pressures. Jour. Chem. Education, vol. 3, 1926, pp. 385–389; Chem. Abs., vol. 20, 1926, p. 1937.

Reviews NH_3 synthesis and reaction of CO with H_2 to form MeOH and other substances.

36. ALMQUIST, J. A., AND CRITTENDEN, E. D. Study of Pure-Iron and Promoted-Iron Catalysts for Ammonia Synthesis. Ind. Eng. Chem., vol. 18, 1926, pp. 1307–1309; Chem. Abs., vol. 21, 1927, p. 802.

Several pure and promoted Fe catalysts are compared. The activity of pure Fe depends upon the state of oxidation of the fused oxide from which it is obtained by reduction. Fe_3O_4 gives the best results. The addition of K_2O alone lowers the activity of pure Fe, but when SiO_2 is added also there is a promoting action. It is shown that K_2O has a marked promoting action in the presence of difficultly reducible oxides of an acidic nature, for example, those of Mn, W, Si, and Al. It is also shown that its addition to Fe containing oxides of metals closely related to Fe, such as those of Ni and Co, lowers the activity.

ALTMAYER, V. *See* abs. **2217, 2218, 2219.**

ALTSHULLER, S. B. *See* abs. **784, 804.**

AMERO, R. C. *See* abs. **432.**

37. ANDERS, H. [Individualities of Catalysts for the Fischer-Tropsch Synthesis as Regards the Composition and Properties of the Reaction Product.] Chem. Tech., vol. 2, 1950, pp. 27–29; Chem. Abs., vol. 44, 1950, p. 5566.

General discussion.

ANDERSON, H. C. *See* abs. **1217, 3297.**

38. ANDERSON, J. A., AND SEYFRIED, W. D. Determination of Oxygenated and Olefin Compound Types by Infrared Spectroscopy. Anal. Chem., vol. 20, No. 11, 1948, pp. 998–1006.

Laboratory investigation of relationship between molecular structure of organic compounds and their infrared-absorption spectra has resulted in development of procedures for the quantitative to semiquantitative determination of individual compound types in complex mixtures employing infrared-absorption spectroscopy in the liquid phase. At present, it is possible to make determinations for the functional groups of alcohols, aldehydes, carboxylic acids, esters, ketones, and 5 different olefin types in complex samples such as hydrocarbon-synthesis naphthas in about 4 hr. For oxygenated types, average accuracy (deviation from true composition) ranges from + or −10% to + or −20%, depending upon type and complexity of mixture. For olefin types, the average deviation is about + or − equivalent Br number units.

39. ANDERSON, R. B. Improved Adsorption Vessel. Ind. Eng. Chem., anal. ed., vol. 18, 1946, p. 156.

Description of adsorption vessel for measuring the weight loss upon reduction of metal oxide catalysts used in the Fischer-Tropsch process. The catalyst is reduced in a vessel that is small and light enough to be weighed in an analytical balance. It is also possible with this adsorption vessel to study the effects of treatment of the catalyst with gases other than H_2, such as synthesis gas or CO, on the surface area and pore structure, and to determine the weight loss of the adsorbent upon evacuation.

40. ———. Modifications of the Brunauer, Emmett, and Teller Equation. I. Jour. Am. Chem. Soc., vol. 68, 1946, pp. 686–691; Chem. Abs., vol. 40, 1946, p. 3322.

Brunauer-Emmett-Teller theory of multilayer adsorption has been applied extensively to physical-adsorption isotherms. While the simple Brunauer-Emmett-Teller equation provides an excellent method of estimating surface areas, it usually holds only for relative pressures of 0.05–0.40. In almost every case, the amount adsorbed at relative pressures higher than 0.40 is less than that predicted by the simple Brunauer-Emmett-Teller equation. This discrepancy has been explained in 3 ways: (1) By assuming the heat of adsorption in the second layer to be less than the heat of liquefaction of the adsorbate; (2) by assuming that the structure of the adsorbent is such that it will permit adsorption to only a finite number of layers; and (3) by considering the effects of capillary condensation. The author has observed that the simple Brunauer-Emmett-Teller equation can be fitted to many physical-adsorption isotherms in the range of relative pressures of 0.05–0.70 if the relative pressure is multiplied by a constant that is less than 1, usually varying between 0.6 and 0.7. This constant is interpreted to mean that the heat or free energy of adsorption in the 2d to 10th layers is less than the heat or free energy of liquefaction, or that the entropy of adsorption in these layers is more negative than the entropy of liquefaction. A similar equation containing an additional constant denoting the upper limit of the layers in which the heat, free energy, or entropy differ from those functions for the liquid has been fitted to isotherms in the range of relative pressures of 0.05–0.98. For porous solids, equations have been presented for adsorption on solids in which the area available to each succeeding layer is less than the previous one. A new-type equation has been developed for adsorptions limited to n-layers, which has better properties than the n-equation of Brunauer-Emmett-Teller.

41. ANDERSON, R. B., AND HALL, W. K. Modifications of the Brunauer, Emmett, and Teller Equation. II. Jour. Am. Chem. Soc., vol. 70, 1948, pp. 1727–1734; Chem. Abs., vol. 42, 1948, p. 6198.

Modified Brunauer, Emmett, and Teller equation similar to that previously suggested has been derived and applied to physical-adsorption isotherms of types I and IV. With type I isotherms, this reaction can be satisfactorily applied if the free energy of adsorption in the second and subsequent layers is taken to be equal to the heat of liquefaction. For isotherms of type IV, which flatten below relative pressures of 0.85, the equation satisfactorily fits the data, if the free energy of adsorption was taken as less than that of liquefaction. For this kind of type IV isotherm, the equation was used to integrate the equation of Kistler, and the resulting expression gave surface areas of the same order of magnitude as the Brunauer, Emmett, and Teller areas. The equation is believed to be a simple method of characterizing isotherms with 4 constants.

ANDERSON, R. B. *See* abs. **51, 53a, 53b, 53c, 1090, 1449a, 1987, 2073a, 2227, 2227a, 2228, 3296, 3297, 3647.**

42. ANDERSON, R. B., AND EMMETT, P. H. Surface Complexes on Charcoal. Gas Evolution as a Function of Vapor Adsorption and of High-Temperature Evacuation. Jour. Phys. and Colloid Chem., vol. 51, 1947, pp. 1308–1329; Chem. Abs., vol. 42, 1948, p. 1410.

Gases evolved, on evacuating charcoals for gas masks, to 1,200° were collected at 300° intervals and analyzed for CO, CO_2 H_2, H_2O, and CH_4. The O_2-containing gases were formed by decomposition of surface complexes and by reduction of the inorganic oxides present as ash. CO and CO_2 evolution reached a maximum at about 600° for charcoals prepared by the $ZnCl_2$ process and at 900°–1,200° for those prepared from coal. The total O_2-containing gases evolved were always equivalent to less than 50% of the charcoal surface. Extracting charcoals with HF and reexposing them to air resulted in about a 20-fold increase in the amount of CO evolved on heating the samples to 600°. H_2 evolution in the temperature

range 600°–1,200° amounted to 25–147 cc. for the various charcoals. Activation of the charcoals by steam was shown to form very little O complex. The amount of CO and CO_2 displaced from the surface complex by the adsorption of CCl_4, H_2O, or chlorobenzene was found to be equivalent to less than 0.01 cc. per gm. NH_3 at 750°–900° formed a N complex on the charcoals that was more stable than the O complexes.

ANDERSON, R. B., AND HALL, W. K. Modifications of the Brunauer, Emmett and Teller Equation. II. *See* abs. **41.**

42a. ANDERSON, R. B., FELDMAN, J., AND STORCH, H. H. Synthesis of Alcohols by Hydrogenation of Carbon Monoxide. Ind. Eng. Chem., vol. 44, 1952, pp. 2418–2424; Chem. Abs., vol. 47, 1953, p. 291.

Processes involving the catalytic syntheses of alcohols from CO and H_2 may be divided into 2 classes: Alcohol syntheses in which alcohols are usually the predominant products, and variations of the Fischer-Tropsch process with Fe catalysts in which the product contains olefinic and paraffinic hydrocarbon, alcohols, acids, esters, aldehydes, and ketones. The alcohol syntheses include the MeOH, the higher alcohol, and the isosyntheses. The MeOH and higher alcohol syntheses employ mixed catalysts of active components such as Cu and oxides of Zn, Cr, and Mn, with alkali oxides added as promoter for the higher alcohol synthesis. Th is the active component of isocatalysts. Higher alcohols from these processes have branched C chains. Under some conditions the isosynthesis produces sizable yields of hydrocarbons. Alkali oxides seem to be the only important promoter for Fe Fischer-Tropsch catalysts. The nature of the Fe phase, oxide, carbide or nitride, is important. Processes producing sizable yields of alcohol include the fluidized, synol, and nitrided catalyst syntheses. Fischer-Tropsch alcohols are chiefly primary straight-chain alcohols. Available data indicate that the mechanism of chain growth in alcohol syntheses is different from that of the Fischer-Tropsch processes.

43. ANDERSON, R. B., FRIEDEL, R. A., AND STORCH, H. H. Fischer-Tropsch Reaction Mechanism Involving Stepwise Growth of Carbon Chain. Jour. Chem. Phys., vol. 19, 1951, pp. 313–319.

Expressions are derived that predict satisfactorily the observed isomer and carbon-number distribution of products from Fe and Co catalysts in the Fischer-Tropsch synthesis. These expressions are based on 3 postulated schemes of stepwise addition of 1 C atom to the end or adjacent-to-end C atoms of the longest C chain: (A) Addition may occur at only 1 end of the growing chain on only 1 end C atom if 2 are present or on the adjacent-to-end carbon; (B) it may occur at only 1 end of the growing chain on any end or adjacent-to-end carbon; (C) it may occur at either end of the growing chain on any end or adjacent-to-end carbon. The implications of these schemes to some general aspects of the reaction mechanism are considered.

ANDERSON, R. B., HALL, W. K., AND HOFER, L. J. E. Studies of the Fischer-Tropsch Synthesis. IV. Properties of Reduced Cobalt Catalysts. *See* abs. **47.**

43a. ANDERSON, R. B., KRIEG, A., AND FRIEDEL, R. A. Fischer-Tropsch Synthesis—Differential Reaction Rate Studies With Cobalt Catalyst. Ind. Eng. Chem., vol. 41, 1949, pp. 2,189–2,197; Chem. Abs., vol. 44, 1950, p. 2,358.

Synthesis was studied on a pelletted Co : ThO_2 : kieselguhr (100 : 18 : 100) catalyst in a fixed-bed reactor (90 cm. long bed) at atmospheric pressure and 186°–207°. The reactor contained a special tube for the removal of gas samples at 9 points along the length of the bed. About 5% A was added to the feed gas as a reference component. Synthesis gases containing H_2 : CO ratios of 3.5, 2, and 0.9 were used at space velocities ranging from 25–100 cc. of gas per cc. of total catalyst bed per hr. With all gas compositions the synthesis rate was high in the first 10% of the bed and lower and essentially constant in the remainder of the bed until the reactants were nearly completely consumed. The gas compositions in the bed in the region of constant synthesis rate varied considerably. CH_4 appears to be formed by primary reactions as well as by hydrocracking of higher hydrocarbons; the latter being favored by high H_2 and hydrocarbon partial pressures. CO_2 appears to be formed by primary reactions as well as by a secondary water-gas shift which latter was favored by high CO and H_2O partial pressures. CO_2 was reduced in the synthesis gas after CO had been completely consumed. Craxford's postulate (abs. 639) that the synthesis occurs on Co_2C with secondary reactions on Co atoms does not appear adequate to explain the data reported.

ANDERSON, R. B., HALL, W. K., HEWLETT, H., and SELIGMAN, B. Studies of the Fischer-Tropsch Synthesis. II. Properties of Unreduced Cobalt Catalysts. *See* abs. **45.**

ANDERSON, R. B., HALL, W. K. KRIEG, A., and SELIGMAN, B. Studies of the Fischer-Tropsch Synthesis. V. Activities and Surface Area of Reduced and Carburized Cobalt Catalysts. *See* abs. **48.**

ANDERSON, R. B., HOFER, L. J. E., COHN, E. M., and SELIGMAN, B. Studies of the Fischer-Tropsch Synthesis. IX. Phase Changes of Iron Catalysts in the Synthesis. *See* abs. **52.**

ANDERSON, R. B., KRIEG, A., FRIEDEL, R. A., and MASON, L. S. Studies of the Fischer-Tropsch Synthesis. VI. Differential Reaction Rate Studies With Cobalt Catalyst. *See* abs. **49.**

44. ANDERSON, R. B., KRIEG, A., SELIGMAN, B., AND O'NEILL, W. E. Studies of the Fischer-Tropsch Synthesis. I. Tests of Cobalt Catalysts at Atmospheric Pressure. Ind. Eng. Chem., vol. 39, 1947, pp. 1548–1554; Chem. Abs., vol. 42, 1948, p. 1039.

Methods of preparation and testing of a precipitated Co : ThO_2 : MgO : kieselguhr (100 : 6 : 12 : 200) catalyst are described. Usually tests with the same preparation of catalyst were quite reproducible, but tests with different catalysts prepared in the same manner showed very much wider deviations. Pelleted catalysts were shown to produce more light hydrocarbons and CO_2 than the granular catalysts. Liquid hydrocarbons containing less than 6% dissolved wax comprised about 75% of the total hydrocarbons formed in these tests at atmospheric pressure. Experiments were made in which the flow of synthesis gas was varied with the temperature adjusted to give the same degree of conversion. Under these conditions the degree of unsaturation increased with increase in flow. Except for the change in unsaturation, the product distribution was not significantly different up to temperatures of 207°. Overall activation energies of 24–26 kcal. per mol. were found for the synthesis. The reaction mechanism and rate law of the synthesis are discussed briefly.

45. ANDERSON, R. B., HALL, W. K., HEWLETT, H., AND SELIGMAN, B. Studies of the Fischer-Tropsch Synthesis. II. Properties of Unreduced Cobalt Catalysts. Jour. Am. Chem. Soc., vol. 69, 1947, pp. 3114–3119; Chem. Abs., vol. 42, 1948, p. 2739.

Surface-area and pore-volume studies are reported for 2 types of unreduced Co Fischer-Tropsch catalysts and for similar preparations with promoters, kieselguhr, or both omitted. Properties of the catalysts are compared and related to properties of the kieselguhrs that they contain. Areas of unreduced precipitated Co Fischer-Tropsch catalysts were several times greater

than those of the kieselguhr used as carriers. Catalysts prepared with natural kieselguhrs had larger areas than those prepared with calcined or flux-calcined kieselguhrs. Areas of unreduced catalysts varied from 60–150 m.^{2} per gm. Average pore diameters of granular catalysts varied from 500 Å. to 770 Å. and for pelleted catalysts from 165Å. to 310Å. Surface areas of pelleted catalysts were 10–20% lower than the areas of the corresponding granules. It was shown that the Co basic carbonate-promoter complex was precipitated chiefly in the void space of the kieselguhr. Preparations without promoters, kieselguhr, or both had areas of the Co complex per gm. of complex that roughly equaled the area of the complex of the catalyst. Natural kieselguhr as a carrier considerably increased the area of the Co complex. Catalysts prepared in small batches were quite reproducible with respect to surface area, but the areas of catalysts prepared in large batches varied considerably.

46. ANDERSON, R. B., KRIEG, A., SELIGMAN, B., AND TARN, W. H. Studies of the Fischer-Tropsch Synthesis. III. Influence of Type of Kieselguhrs. Ind. Eng. Chem., vol. 40, No. 12, 1948, pp. 2347–2350; Chem. Abs., vol. 43, 1949, p. 3167.

Testing data are presented for a series, 89 in all, of Co : Th : Mg : kieselguhr (100 : 6 : 12 : 200) catalysts prepared with a number of commercially available American kieselguhrs. Catalysts containing calcined kieselguhrs had lower activity than similar catalysts with natural kieselguhrs. These results agree with those previously obtained by Craxford, who found that catalysts prepared with natural kieselguhr had surface areas and activities greater than those of a catalyst containing calcined kieselguhr. Acid-extracted natural kieselguhrs produced catalysts of the highest activity. The density of the catalyst varied directly with the density of the kieselguhr, and the distribution of products changed with density of the catalysts, the denser catalysts forming a greater % of light hydrocarbons and CO_2.

47. ANDERSON, R. B., HALL, W. K., AND HOFER, L. J. E. Studies of the Fischer-Tropsch Synthesis. IV. Properties of Reduced Cobalt Catalysts. Jour. Am. Chem. Soc., vol. 70, 1948, pp. 2465–2472; Chem. Abs., vol. 42, 1948, p. 8058.

Reduced Co: ThO_2: MgO; kieselguhr (100: 6: 12: 200) and Co: ThO_2: kieselguhr (100: 18: 100) and similar preparations with one or more of the components omitted have been studied by N surface areas and CO chemisorptions at −195°, Hg and He densities, and X-ray diffraction. The experimental data show that the surface areas of all the catalysts studied decreased on reduction. The promoters were found to prevent excessive decreases; powdered MgO appears to be the most effective and ThO_2 the least. Kieselguhr as a carrier was somewhat effective in preventing the decrease of surface area and in increasing the pore volumes on reduction of all the catalysts. With unpromoted and unsupported Co large changes occurred in both surface area and bulk volume. The most important function of the kieselguhr was to prevent the decrease in bulk volume of the catalyst on reduction and at the same time inhibit sintering of the surface. The CO chemisorption studies showed that an appreciable fraction of the catalyst surface was occupied by promoter. The X-ray diffraction data were in qualitative agreement with the surface-area determinations but in addition indicated that the Co in supported and promoted catalysts had an anomalous structure.

48. ANDERSON, R. B., HALL, W. K., KRIEG, A., AND SELIGMAN, B. Studies of the Fischer-Torpsch Synthesis. V. Activities and Surface Areas of Reduced and Carburized Cobalt Catalysts. Jour. Am. Chem. Soc., vol. 71, 1949, pp. 183–188; Chem. Abs., vol. 43, 1949, p. 3273.

This paper relates surface area and surface accessibility of the catalyst to activity and product distribution. Data reported previously on the effect of bulk carbide on the activity of Co catalysts have been extended to include surface areas and activities and distribution of products in the synthesis with catalysts carburized with CO under conditions that form carbide (Co_2C), free C, or both. The catalysts studied were Co : ThO_2 : MgO : kieselguhr (100 : 6 : 12 : 200) and Co : ThO_2 : kieselguhr (100 : 18 : 100). The surface of the catalyst was found to be heavily covered with hydrocarbon. Hydrogenation at 200° removed 90% of these adsorbed hydrocarbons, and reduction with H_2 at 400° restored the catalyst to the same condition as after the initial reduction. There was no evidence of sintering or of C deposition. Activity data for operation at 1 and 7.8 atm. are related to the adsorbed hydrocarbon film. Decrease in the accessibility of the surface of these catalysts either by deposition of excessive quantities of wax or by reduction of average pore diameter by pelleting caused an increase in the fraction of CH_4 and other light hydrocarbons and in some cases a decrease in activity. The presence of bulk-phase carbide in these catalysts caused a marked decrease in activity, but free C did not affect the activity very much. The presence of C in both forms shifted the product distribution toward light hydrocarbons. The surface area did not change appreciably when the Co was converted to carbide. Carburization at 275°, under conditions that form predominantly free C, increased the area considerably.

49. ANDERSON, R. B., KRIEG, A., FRIEDEL, R. A., AND MASON, L. S. Studies of the Fischer-Tropsch Synthesis. VI. Differential Reaction-Rate Studies With Cobalt Catalyst. Ind. Eng. Chem., vol. 41, No. 10, 1949, pp. 2189–2197; Chem. Abs., vol. 44, 1950, p. 2358.

Differential reaction-rate data are presented for the Fischer-Tropsch synthesis with Co catalysts at atmospheric pressure. The synthesis rate was high in the initial part of the bed and lower in nearly constant throughout a large portion of the catalyst bed, until the reactants were fairly completely consumed. Over the range of relatively constant rate of synthesis, the gas composition varied considerably. CH_4 and CO_2 were formed by primary reactions; CH_4 was also formed by secondary hydrocracking of higher molecular-weight hydrocarbons and CO_2 by the water-gas reaction. These reactions occurred throughout the catalyst bed, and their extent depended upon the composition of the gas in contact with the catalyst. The assumptions of Craxford involving the synthesis occurring on Co carbide and the secondary reactions on Co atoms do not appear to be an adequate explanation of the author's data.

50. ANDERSON, R. B., SHULTZ, J. F., SELIGMAN, B., HALL, W. K., AND STORCH, H. H. Studies of the Fischer-Tropsch Synthesis. VII. Nitrides of Iron as Catalysts. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 3502–3508; Chem. Abs., vol. 44, 1950, p. 10299.

Conversion of Fe in reduced synthetic ammonia-type catalysts to nitrides by ammonia treatment greatly increased their activity in the Fischer-Tropsch synthesis. All tests described in the paper were performed with a catalyst prepared by the electrical-fusion method and having the composition: Total Fe 67.4%, ferrous Fe 21.7%, MgO, 4.61%, K_2O, 0.57%, SiO_2, 0.71%, and Cr_2O_3, 0.65%. Catalysts converted to ϵ-phase nitrides yielded a product of lower average molecular weight containing greater yields of gaseous hydrocarbons and oxygenated molecules than those products from corresponding reduced catalysts. In

the synthesis, nitrided Fe catalysts appear to resist oxidation and deposition of free C and have a greater stability and longer life.

51. HALL, W. K., TARN, W. H., AND ANDERSON, R. B. Studies of the Fischer-Tropsch Synthesis. VIII. Surface-Area and Pore-Volume Studies of Iron Catalysts. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 5436–5443.

Changes are reported in surface area and pore volume during the reduction of 2 widely different Fe catalysts, a precipitated Fe_2O_3–CuO–K_2CO_3 catalyst and a fused Fe_3O_4–MgO–K_2O catalyst. Information is presented as to the nature of Fe catalysts at the start of the Fischer-Tropsch synthesis, as well as data pertinent to the mechanism of reduction. The surface areas of raw precipitated Fe gel catalysts are high, and their pore diameters are small; conversely, unreduced Fe-synthetic NH_3-type catalysts have essentially no surface area and no pore volume. After reduction at 300° and 450°–550°, respectively, both types have moderate surface areas of about 8 $m.^2$ per gm. and reasonably large pore diameters of 350–900 Å. Thermal sintering of precipitated Fe gels causes drastic changes in structure, but removal of O_2 by reduction produces an even greater effect. The surface area and pore voume of an Fe-synthetic NH_3-type catalyst increased in a linear manner with extent of reduction, whereas the average pore diameter remained constant. It is shown that only surface-area measurements and complete chemical analysis of the raw catalyst are necessary to establish the pore structure of an Fe-synthetic NH_3-type catalyst as a function of the extent of reduction. Increasing the reduction temperature of an Fe-synthetic NH_3-type catalyst from 450° to 650° produced an 8-fold increase in the pore diameter.

52. ANDERSON, R. B., HOFER, L. J. E., COHN, E. M., AND SELIGMAN, B. Studies of the Fischer-Tropsch Synthesis. IX. Phase Changes of Iron Catalysts in the Synthesis. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 944–946; Chem. Abs., vol. 45, 1951, p. 6,032.

Phase changes in a reduced fused-iron catalyst have been studied during the Fischer-Tropsch synthesis with 1 : 1=CO : H_2 gas at 7.8 atm. In the 1st few days of the synthesis, α–iron was converted to Hägg carbide Fe_2C. The iron as Hägg carbide increased to a maximum of 29% at 200 hr. of synthesis and then decreased slowly throughout the remainder of the test. Magnetite was formed at a slower rate than Hägg carbide, apparently chiefly at the expense of the α–iron phase. The magnetite phase increased through the experiment.

53. ANDERSON, R. B., SELIGMAN, B., SHULTZ, J. F., KELLY, R., AND ELLIOTT, M. A. Fischer-Tropsch Synthesis. X. Some Important Variables of the Synthesis on Iron Catalysts. Ind. Eng. Chem., vol. 44, 1952, pp. 391–397; Chem. Abs., vol. 46, 1952, p. 5,291.

Several important variables affecting the catalyst activity and selectivity in the Fischer-Tropsch synthesis include the operating temperature and pressure and the particle size and alkali content of the catalyst. Data are presented for fused, sintered, and precipitated Fe catalysts. The variation of synthesis rate with temperature may be characterized by an overall activation energy of 20 kcal. per mol. The synthesis rate increased with pressure. For a fused catalyst the rate increased linearly with pressure; however, for other catalysts the variation of rate with pressure was less than linear. The rate increased as the particle size decreased, probably indicating that only a fraction of the surface was accessible to the reactants. For precipitated catalysts, the rate increased only slightly with alkali content, whereas, for other types the rate increased sharply to a maximum at about 0.5 K_2O per 100 Fe.

53a. SHULTZ, J. F., SELIGMAN, B., SHAW, L., AND ANDERSON, R. B. Fischer-Tropsch Synthesis. XI. Effect of Nitriding on 3 Types of Iron Catalysts. Ind. Eng. Chem., vol. 44, 1952, pp. 397–401; Chem. Abs., vol. 46, 1952, p. 5,291.

Fe catalysts of the fused, sintered, and precipitated types were tested in the Fischer-Tropsch synthesis after reduction in H_2 and nitriding in NH_3 to an ε–phase nitride, and the selectivity and activity of the nitrides were compared with those of corresponding reduced or inducted catalysts. In all cases, the nitrided catalysts yielded products of lower average molecular weight than those from reduced or inducted catalysts. The activity of fused and sintered catalysts was increased by nitriding, whereas the average activity of the precipitated catalyst was relatively independent of the method of pretreatment.

53b. SHULTZ, J. F., SELIGMAN, B., LECKY, J., AND ANDERSON, R. B. Studies of the Fischer-Tropsch Synthesis. XII. Composition Changes of Nitrided Iron Catalysts During the Synthesis. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 637–640; Chem. Abs., vol. 46, 1952, p. 5,290.

Changes in the composition of nitrided Fe catalysts during use in the Fischer-Tropsch synthesis at 7.8 and 21.4 atm. operating pressure are described. The ε–nitrides are slowly converted to ε–carbonitrides, the rate of replacement of N by C being somewhat more rapid at 21.4 than at 7.8 atm. At the lower operating pressure, oxidation and deposition of elemental C proceed at a very slow rate, whereas at 21.4 atm. these reactions are considerably more rapid in some catalysts. At the higher pressure, the type of structural promoter appears to be important in determining the rates of oxidation and of deposition of free C. When used, nitrided catalysts are treated with H_2, the N is almost completely removed, whereas the C content is not greatly changed. A part of the C appears either as Hägg carbide or cementite, depending upon the temperature of hydrogenation.

53c. HALL, W. K., TARN, W. H., AND ANDERSON, R. B. Studies of the Fischer-Tropsch Synthesis. XIII. Structural Changes of a Reduced Iron Catalyst on Reoxidation and on Formation of Interstitial Phases. Jour. Phys. Chem., vol. 56, 1952, pp. 688–691; Chem. Abs., vol. 46, 1952, p. 10,582.

Upon complete reduction at 450° or 550°, a fused Fe synthetic NH_3 catalyst develops an extensive pore structure corresponding to about 45% porosity. On reoxidation, the volumes of the individual particles remain constant, while the surface areas and pore volumes decrease. Reoxidation proceeds at an initially rapid rate, which becomes very slow after a few hours. The reoxidized catalyst is reduced much more easily than the raw catalyst. Formation of the interstitial nitrides and carbides causes the catalyst particles to expand and the pore volume and average pore diameters to increase. The % porosity, however, remains about constant.

ANDERSON, R. B., KRIEG, A., SELIGMAN, B., AND TARN, W. H. Studies of the Fischer-Tropsch Synthesis. III. Influence of Type of Kieselguhrs. *See* abs. **46.**

54. ANDERSON, R. B., MCCARTNEY, J. T., HALL, W. K., AND HOFER, L. J. E. Kieselguhrs—Suitability as Carriers in Catalysts. Ind. Eng. Chem., vol. 39, 1947, pp. 1618–1628; Chem. Abs., vol. 42, 1948, p. 1031.

Properties of a number of kieselguhrs used as supports in Co Fischer-Tropsch catalysts have been studied. Data on chemical analysis, X-ray diffraction, surface areas, pore volumes, together with electron

micrographs at magnifications of 2,000 and 20,000 diam. are presented and correlated. The comparative suitabilities of various kieselguhrs as carriers for catalysts are not discussed.

ANDERSON, R. B., SELIGMAN, B., SHULTZ, J. F., KELLY, R., AND ELLIOTT, M. A. Fischer-Tropsch Synthesis. X. Some Important Variables of the Synthesis on Iron Catalysts. *See* abs. **53.**

ANDERSON, R. B., SHULTZ, J. F., SELIGMAN, B., HALL, W. K., AND STORCH, H. H. Studies of the Fischer-Tropsch Synthesis. VII. Nitrides of Iron as Catalysts. *See* abs. **50.**

ANDO, T. *See* abs. **2198, 2199, 2200, 2201, 2202, 2203, 2204.**

ANDREWS, A. *See* abs. **574.**

55. ANDREWS, G. W. Water-Gas Equilibrium in Hydrocarbon Flames. Jour. Chem. Soc., vol. 105, 1914, pp. 444–456; Jour. Soc. Chem. Ind. (London), vol. 33, 1914, p. 303; Chem. Abs., vol. 8, 1914, p. 1659.

Andrews concludes that the explosive combustion of numerous hydrocarbon–O_2 mixtures under widely differing conditions of incomplete combustion give rise to products that at least approximately conform to the requirements of the water-gas equilibrium with a value of 4 for the thermodynamic constant, and the value is not greatly altered even when large quantities of C are separated or considerable % of CH_4 is found in the ultimate products.

56. ANDREWS, R. S., AND BENNIE, R. S. High-Pressure Gasification of Brown Coal. BIOS Final Rept. 722, 1946, 13 pp.; PB 52,856.

Some discussion relating to the use of Australian brown coals in a Lurgi high-pressure generator and whether this type of plant would be suitable for gas production in Australia. The Lurgi high-pressure gasification process is the only one of the many processes developed in Germany that has been established for a gas supply. 2 plants at Bohlen and Brüx have been operating in connection with the development of processes using brown coal for liquid-fuel production that are considered economical under the economic conditions prevailing in Germany. A detailed study is needed to determine whether the process can be operated in Australia economically simply on the basis of gas production without the production of liquid fuel.

57. ANDRIEUX, J. L. [Making Metallic Powders by Electrolysis of Fused Salts.] Rev. mét., vol. 45, 1948, pp. 49–59; Jour. four élec., vol. 57, No. 3, 1948, p. 54; Chem. Abs., vol. 42, 1948, p. 8089.

Mixture of $Na_2B_2O_4+Na_2CO_3+3$ LiF+1/12 Fe_2O_3 heated to 780° and electrolyzed with 20 amp. at 2.5 v. produces Fe_3C. With electrolytic baths of slightly different composition the product is another carbide of Fe more rich in C than cementite whose Curie Point is 245° C.

58. ANGLI, J. [Composition, Origin and Synthesis of Petroleum—The Argentine Problem.] Anales asoc. quim. Argentina, vol. 14, 1926, pp. 39–61; Chem. Abs., vol. 20, 1926, p. 2906.

An address.

59. ANTHEAUME, J. [Contribution to the Study of the Iron Catalyst in the Synthesis of Hydrocarbons From Carbon Monoxide.] Thesis, Univ. Lille, I. Special No. 1934, 69 pp; Brennstoff-Chem., vol. 15, 1934, p. 436.

After a discussion of heterogeneous catalysis and the benzine synthesis of Fischer-Tropsch, a study was made of precipitated Fe-Cu catalysts (4 : 1) and their efficiency. The effect on the yield of the method of preparation, the space velocity of the synthesis gas, and the composition and regeneration of the catalyst by oxidation were determined. An increased efficiency was shown by catalysts that had all alkali electrolytically removed. A reduction in the Cu content by 9/10 resulted in a 5-fold increase in the yield. Catalysts without a carrier were more efficient than those with one. Optimal yield: 65 gm. of hydrocarbons per $m.^3$ of raw gas. Some physical-chemical investigations of the state of the Fe during the synthesis were made. X-ray as well as thermomagnetic analyses, relation between the temperature and magnetic properties, showed the complete absence of metallic Fe. In every active catalyst the Fe_2O_3 and Fe_3O_4 were present as solid solutions. By complete exclusion of alkali the solubility of both oxides and the activity of the catalyst were increased. The extraction of the gas from used catalysts on kieselguhr showed that the quantity of absorbed gases increased with the rise in activity. In catalysts without kieselguhr, the amount of adsorbed gas increased with increasing age and decreasing efficiency. By extracting used catalysts salvelike and high-melting paraffins were obtained; they were not alone answerable for the deterioration of the catalyst. Likewise, synthesis gas carbureted with hexane caused only a slight decrease in the activity.

60. ———. [Hydrogenation of Carbon Monoxide.] Ann. combust. liquides, May–June 1935; Tech. moderne, vol. 27, 1935, p. 594; Coal Carbonisation, vol. 1, 1935, p. 151.

The author has investigated the structure and function of Fe-base catalysts in the preparation, at atmospheric pressure, of liquid hydrocarbons from CO. He concludes: (1) It is not necessary to add K_2CO_3 to catalysts prepared by precipitation of a solution of Fe and Cu nitrates—the most active preparations do not contain it. (2) Cu plays a triple part in these catalysts, that is, permitting the reduction of ferric oxide by H_2 at a relatively low temperature, activating, and stabilizing. A certain minimum of Cu is essential to obtain a durable catalyst. (3) Catalytic hydrogenation of CO at atmospheric pressure yields CO_2, H_2O, gaseous hydrocarbons, and a mixture of liquid hydrocarbons more or less rich in paraffins. (4) The hydrocarbon yield with Fe-Cu catalyst washed electrolytically is lower than with Fischer's Ni or Co catalyst but higher than hitherto obtained from Fe and Cu. (5) Structural examination reveals the presence of magnetic Fe oxide rhombohedral Fe_2O_3 in the active substance, also the absence of free Fe. In the most active catalysts the magnetite is in a state of solid solution, the formation of which is facilitated by the electrolytic washing. Precipitated magnetite used alone gives no condensation of higher hydrocarbons.

61. ———. [Iron Oxide Catalysts for the Hydrogenation of Carbon Monoxide Under Atmospheric Pressure.] Ann. combust. liquides, vol. 10, 1935, pp. 472–507; Chem. Abs., vol. 29, 1935, p. 6396.

Catalysts are prepared by coprecipitating equimolar mixtures of Fe and Ca nitrates with NaOH, washing until pH=7.4, mixing with 2% K_2CO_3, granulating, drying, and reducing with H_2 at 250°. Hydrogenation is carried out at 250° under 1 atm. on the mixture CO+1.75 H_2. The weight of liquid hydrocarbons formed decreases rapidly as the rate of flow is increased. Oxidation of the catalyst, followed by H_2 reduction, does not affect its activity. A powdered catalyst, 1 precipitated by NH_3 instead of NaOH and 1 precipitated on kieselguhr, showed very poor activity. Omitting the K_2CO_3 or washing the catalyst electrolytically increases its activity materially. Catalysts containing less Cu are more active but lose their activity after a few days. Samples of catalyst are withdrawn without contact with air, and their powder X-ray diagrams and magnetic properties are determined. These indicate the absence of Fe and the presence of Fe_2O_3 and Fe_3O_4, probably in solid solution. In the abence of Cu, no Fe_3O_4 is present in catalysts

reduced at 250°. The catalysts adsorb an appreciable amount of hydrocarbons, but this does not seem to affect their activity.

———. *See* abs. **678.**

62. ANTHEAUME, J., DECARRIÈRE, E., AND RÉANT, R. [Physicochemical Study of the Iron Catalyst Used in the Synthesis of Liquid Hydrocarbons.] Chim. et ind., Special No., April 1934, pp. 421–423; Compt. rend., vol. 196, 1933, pp. 1889–1890; Brennstoff-Chem., vol. 15, 1934, p. 413; Chem. Abs., vol. 28, 1934, p. 5935.

From investigations by the thermomagnetic-analysis method of Chaudron and coworkers for the study of metallic oxides (Forestier and Chaudron, abs. **1054**), it is concluded that catalytic conversion does not take place in presence of either Fe_2O_3 alone or of Fe_3O_4 alone. In every case in which catalytic activity is manifested, Fe_3O_4 is present, and the activity increases with the fineness of the crystalline structure. The authors admit that, with their catalysts, the production of higher hydrocarbons by hydrogenation takes place in the presence of complex solid solutions.

63. ANTHRACITE INSTITUTE BULLETIN. Refuse Anthracite Source of Synthetic Fuels. No. 1513, 1948, p. 1.

It is estimated that there are 200 million tons of anthracite silt above ground and over 5 million tons are produced annually. In the plant and process now under construction by the institute at Wilkes-Barre, Pa., silt, air, and steam will be fed into a refractory-lined cylinder where combustion takes place. The fluidized-bed principle is used, and the silt is either intermittently blown with air and steam or continuously with O_2 and steam. A producer gas is made containing CO_2, CO, H_2, and N_2. This is passed through a second bed of silt where the CO_2 reacts with the C to give additional CO, which increases the heat content of the producer gas. If a gas of still higher heat value is desired, steam is introduced into the producer gas at the top of the fluidized bed to give water gas. A logical use of the process is to produce synthesis gas and to convert this into liquid fuels.

64. ANTONENA, C. M. [Synthetic Naphtha.] Rev. quim. ind. (Buenos Aires), vol. 2, No. 16, 1949, pp. 15–18, 30; British Abs., 1950, B, I, p. 35.

Short description of the Fischer-Tropsch process for producing naphtha by the hydrogenation of CO.

ANTONOV, V. K. *See* abs. **3327.**

ANTONOVA, M. F. *See* abs. **563.**

65. APIN, A., LEIPUNSKII, O., AND REINOV, N. [Decomposition of Methanol Under High Pressures.] Jour. Gen. Chem. (U. S. S. R.), vol. 10, 1940, pp. 863–865; Chem. Abs., vol. 35, 1941, p. 2469.

With the aim to investigate the influence of high pressures on simple reactions of organic compounds, the behavior of MeOH has been investigated. The decomposition of MeOH was studied at 350° under pressures of 600, 2,000, 6,000, and 8,000 atm. The reaction products were Me_2O, CH_4, CO_2, CO, and H_2. Unsaturated hydrocarbons could not be detected. The amount of Me_2O increased with increasing pressure and decreased at a given pressure with prolonged reaction time. CO and H_2 were formed in small amounts and CH_4 in large amounts when high pressures were applied. The amount of CO and H_2 decreased with prolonged reaction time while the amount of CH_4 increased. The reaction vessel used consisted of nonrusting steel containing about 8% CrO_3 which possibly acts as a catalyst. A series of reactions is given that the decomposition reaction is assumed to follow.

APPEL, E. G. *See* abs. **99.**

APPEL, H. *See* abs. **1710.**

APPEL, H., BÖHM, H., KEIL, W., AND SCHILLER, G. Fat From Fat Acids With Odd Numbers of Carbon Atoms. IV. *See* abs. **1713.**

———. Fat From Fat Acids With Odd Numbers of Carbon Atoms. VII. Preliminary Communication Concerning Properties, Stability, Physiology, and Toxicology of Synthetic Fats From Paraffin Fat Acids. *See* abs. **1717.**

APPEL, H., BERGER, G., BÖHM, H., KEIL, W., AND SCHILLER, G. Fats From Fat Acids With Uneven Numbers of Carbon Atoms. II. *See* abs. **1711.**

66. APPLEYARD, K. C. Production of Oil From Coal by the Fischer-Tropsch Process. Gas World, vol. 111, 1939, Coke Sec., pp. 79–91; Colliery Guard., vol. 158, 1939, pp. 865–868, 968–970; British Chem. Abs., 1939, B, p. 799; Chem. Age, vol. 41, 1939, pp. 64–67; Chem. Abs., vol. 33, 1939, p. 5155.

Production of the $CO+2H_2$ mixture from coke or coke-oven gas, its purification, and the types of catalysts used for the actual synthesis of hydrocarbons, which may be carried out at atmospheric or at medium (10 atm.) pressure, are outlined. The yield of liquid products is about 79% of theory. Their nature depends on the conditions: Using a Co catalyst, they contained 8% of light hydrocarbons, b. p. $<30°$; 50% of motor spirit, b. p. 30°–200°, octane no. after redistributing 55; 39% of Diesel oil, b. p. $>200°$; and 3% of soft paraffin, m. p. $>50°$. The Diesel oil has a H_2: C ratio of 2.17, which is more than that of other liquid fuels, and a low ignition temperature of about 240°, it has proved satisfactory in engine tests. The by-products are hard paraffin, m. p. $>100°$, deposited on the catalyst and C_3H_8–C_4H_{10} mixtures. Good lubricants can be produced by polymerization over $AlCl_3$ of olefin fractions or of paraffin fractions after chlorination.

67. ———. Chemistry of Fischer-Tropsch Oil Production. South African Min. and Eng. Jour., vol. 50, 1940, pp. 585–587, 615–617; Chem. Abs., vol. 34, 1940, p. 5619.

Suitable catalysts and careful control of reaction temperature are of utmost importance in the reaction for the synthesis of liquid fuels. The primary reaction on which the synthesis is based may be indicated by $CO+2H_2=(CH_2)_x+H_2O+48{,}000$ cal. where $(CH_2)_x$ designates a light hydrocarbon. The operating conditions have the following effects upon the products: (1) Increasing pressure favors formation of alcohols; (2) increase of H_2 in reaction gases favors formation of CH_4 because of increasing saturation, unless the temperature is lowered; (3) decrease of H_2 in reaction gases favors formation of olefins; (4) increasing temperature favors formation of CH_4 and C; (5) catalyst metals in the order Fe, Co, Ni favor increasing saturation therefore lower olefin content; (6) presence of CO_2 has no influence; (7) increase in age of catalyst increases the light-oil fraction yield at the expense of heavy oil. As shown above, the gas used for the production of liquid fuel by this process consists essentially of a mixture of 1 vol. of CO with 2 vol. of H_2. This gas can be produced in a number of ways from a variety of fuels. Variations in production of this synthesis gas, depending upon economic factors, availability of raw materials, and market for byproducts are discussed. The importance of complete removal of all forms of S is emphasized. Consideration is given to the most suitable catalysts—Fe, Co, and Ni—and the physical form in which they should be used. The flexibility of raw materials and wide variety of products that this process permits are pointed out.

68. ARANDA, V. G. [Artificial Fats.] Ion, Madrid, vol. 1, No. 2, 1941, pp. 18–23; Chem. Abs., vol. 36, 1942, p. 3377.

Brief discussion of German practice in the oxidation of Fischer gatsch paraffins.

69. ARBUZOV, M. [Crystal Structure and Particle Size of the Carbide Phase in Tempered Steel.] Doklady Akad. Nauk S. S. S. R., vol. 73, 1950, pp. 83–86; Chem. Abs., vol. 45, 1951, p. 3217.

X-ray line widths were measured photometrically for carbide residues from 1% C steels tempered at 50° intervals from 100° to 700°. The calculated size and shape of the carbide particles showed that in the range 200°–350° the *c* dimension of the carbide is only about 10 lattice spacings and is about ⅓ as large as the *a* or *b* dimension. Growth in all dimensions occurred above 350°, and the difference between *c* and *a* or *b* decreased. Some X-ray lines present above 400° disappeared below this temperature. No lines were present in the pattern of carbides from the steel tempered at 150°. Even in steels tempered at low temperatures the carbide phase, Fe_xC, has the lattice of Fe_3C. The difference in diffraction patterns between Fe_xC and Fe_3C is caused by the platelet form and the small dimensions of Fe_xC. The change that occurs in the range 300°–400° is partly caused by changes in the interaction of the carbide and the solid solution.

70. ARBUZOV, M., AND KURDYUMOV, G. [State of Carbon in Tempered Steel.] Jour. Tech. Phys. (U. S. S. R.), vol. 10, 1940, pp. 1093–1100; Chem. Abs., vol. 35, 1941, p. 2456.

Monocrystals of austenite (1.4% C) that, after tempering, were in the process of transformation into the regularly oriented martensite crystals were examined by X-rays. There was found in samples tempered at 130°–300°, a phase produced by the decay of martensite and the remaining austenite. This phase represents a carbide of Fe, different from Fe_3C. The lack of sharpness of the interference picture indicates the high degree of dispersion of the low-temperature carbide crystals. At 300° the low-temperature carbide is transformed very slowly into Fe_3C; this transformation is much accelerated at 350°–380°.

ARGUE, G. H. *See* abs. **302.**

71. ARIES, R. S. The Changing Industrial Alcohol Picture. Chem. and Eng. News, vol. 25, 1947, pp. 1792–1796; Petrol. Processing, vol. 2, 1947, p. 409.

Two sources are expected to satisfy the major part of the demand for industrial alcohol in the next decade, which may arise to over 200 million gal. per yr., chiefly for chemical use. The 1st and most important source is that from C_2H_4 from petroleum as the raw material, which even now is producing 70 million gal. per yr. with many new plants in prospect. The second source is that by synthesis from natural gas, and 3 plants now are planned each to produce 8–10 million gal. per yr. as a byproduct. Doubt is expressed that the industry will depend again upon molasses as the chief raw material, or that serious competition will arise from alcohol derived from waste wood or sulfite liquors or from grain alcohol because of the economic factors involved. Alcohol is now selling at a high price ($0.80 or more per gal. compared with prewar price of $0.20–$0.25), which will be maintained only until more petroleum alcohol plants can come into production. Present costs from C_2H_4 are even now below $0.15 per gal. at present economic levels.

72. ARMBRUSTER, M. H. Solubility of Hydrogen at Low Pressure in Iron, Nickel and Certain Steels at 400°–600°. Jour. Am. Chem. Soc., vol. 65, 1943, pp. 1043–1054; Chem. Abs., vol. 37, 1943, p. 4283.

The solubility (*s*, in micromoles per 100 gm.) of H_2 was measured over a range of pressure (*p*) from 0.001 to 1.5 mm. in carefully pretreated samples of α–Fe (initially carbonyl Fe), Ni, and certain steels at 400°, 500°, 600° and at pressures up to 350 mm. in the Fe at 600°. The results are reproducible and in all cases are in accord at each temperature, within the precision of the measurements, with the linear relation $s=\alpha p^{1/2}$. The measurements on Fe and Ni at all 3 temperatures are accurately reproduced by the respective equations (*T* is absolute temperature): $\log (s/p^{1/2}) = -1454/T + 1.946$ and $\log (s/p^{1/2} = -645/T + 1.732$. A similar equation holds for each of the several steels, which fall into 3 groups, according as each is (1) ferritic with low alloy content, (2) ferritic with high alloy content, (3) austenitic. The solubility in the low alloy steels differs little from that in pure Fe, but the small individual differences for different compositions are quite reproducible. A method is presented of calculating the amount of residual H, independent of any blank measurement to determine its effective volume (or effective pressure), from a suitable plot of the actual measurements; the result, so calculated, is identical with that obtained through the use of a blank with A in the presence of the sample. Comparison by extrapolation of the new results with data in the literature shows a general accord, particularly at temperatures of 600° and higher; at lower temperatures the values obtained in this investigation are, because of their consistency with the foregoing linear relations, believed to be of superior accuracy. After the pretreatments, reproducible equilibrium was obtained within a few min., except in the case of the 13%–Cr steel in which the unreducible, barely visible, oxide film slowed down the rate.

73. ARMITAGE, G. E. Chemical Conversions of Lighter Hydrocarbons. Refiner and Nat. Gasoline Mfr., vol. 20, 1941, pp. 327–336; Chem. Abs., vol. 36, 1942, p. 1472.

Detailed discussion of the commercial processes for converting light hydrocarbons into usable products. The processes include catalytic and thermal polymerization and alkylation, gas reversion, isomerization, dehydrogenation, Fischer-Tropsch synthesis, aromatization and hydroforming, and synthetic-rubber production. 47 refs.

74. ARMSTRONG, E. F., AND HILDITCH, T. P. Study of Catalytic Actions at Surfaces. I. Hydrogenation of Unsaturated Fats in the Liquid State in Presence of Nickel. Proc. Roy. Soc. (London), vol. 96–A, 1919, pp. 137–146; Chem. Abs., vol. 14, 1920, p. 142.

75. ———. Study of Catalytic Actions at Surfaces. II. Transference of Hydrogen From Saturated to Unsaturated Organic Compounds in the Liquid State in Presence of Metallic Nickel. Proc. Roy. Soc. (London), vol. 96–A, 1919, pp. 322–329; Chem. Abs., vol. 14, 1920, pp. 884–885.

76. ———. Study of Catalytic Actions at Surfaces. III. Hydrogenation of Acetaldehyde and the Dehydrogenation of Ethyl Alcohol in Presence of Finely Divided Metals. Proc. Roy. Soc. (London), vol. 97–A, 1920, pp. 259–264; Chem. Abs., vol. 14, 1920, p. 2439.

77. ———. Catalytic Actions at Solid Surfaces. IV. Interaction of Carbon Monoxide and Steam as Conditioned by Iron Oxide and by Copper. Proc. Roy. Soc. (London), vol. 97–A, 1920, pp. 265–273; Chem. Abs., vol. 14, 1920, p. 2439.

Amount of change $CO+H_2O \rightleftharpoons CO_2+H_2$ at temperatures from 200° to 500° with Cu and Fe oxide catalyst is examined. The former is much less complete in its action than the oxide at higher temperatures but predominates over the range 200°–300°, though it never effects more than 50–70% of the possible amount of chemical change. The results illustrate beautifully the specific action of 2 different types of catalyst. Cu decomposes HCOOH from 190° up, according to: (1) $CO+H_2O \rightleftharpoons HCOOH$; (2) $HCOOH \rightarrow CO_2+H_2$, in pres-

ence of Cu. On the other hand, the Fe oxide process is dependent on the temperature ranges at which oxidation of CO and decomposition of steam by Fe or FeO occur rapidly. That H_2O enters into active association with Cu is indicated, (1) by its protective action on aldehyde by preferential adsorption at Cu surfaces; and (2) by its actual part in a chemaction when associated with Cu.

78. ———. Study of Catalytic Actions at Surfaces. V. Rate of Change Conditioned by a Nickel Catalyst and its Bearing on the Law of Mass Action. Proc. Roy. Soc. (London), vol. 98–A, 1920, pp. 27–40; Chem. Abs., vol. 14, 1920, p. 3182.

79. ———. Study of Catalytic Actions at Surfaces. VI. Surface Area and Specific Nature of a Catalyst—Two Independent Factors Controlling the Resultant Activity. Proc. Roy. Soc. (London), vol. 99–A, 1921, pp. 490–495; Chem. Abs., vol. 16, 1922, pp. 188–189.

80. ———. Study of Catalytic Actions at Surfaces. VII. Influence of Pressure on the Rate of Hydrogenation of Liquids in Presence of Nickel. Proc. Roy. Soc. (London), vol. 100–A, 1921, pp. 240–252; Chem. Abs., vol. 16, 1922, p. 1348.

81. ———. Study of Catalytic Actions at Surfaces. VIII. Action of Sodium Carbonate in Promoting the Hydrogenation of Phenol. Proc. Roy. Soc. (London), vol. 102–A, 1922, pp. 21–27; Chem. Abs., vol. 17, 1923, p. 233.

82. ———. Study of Catalytic Actions at Surfaces. IX. Action of Copper in Promoting the Activity of Nickel Catalyst. Proc. Roy. Soc. (London), vol. 102–A, 1922, pp. 27–32; Chem. Abs., vol. 17, 1923, pp. 233–234.

83. ———. Study of Catalytic Actions at Solid Surfaces. X. The Interaction of Carbon Monoxide and Hydrogen as Conditioned by Nickel at Relatively Low Temperatures. A Practical Synthesis of Methane. Proc. Roy. Soc. (London), vol. 103A, 1923, pp. 25–34; Chem. Abs., vol. 17, 1923, p. 2220.

The action between CO and H_2 in the presence of Ni or a similar catalyst at temperatures below 300° is mainly $2CO+2H_2=CO_2+CH_4$. The reaction is considered to go in 2 stages; (1) $CO + H_2O = CO_2 + H_2$; (2) the H_2 so formed with that already present causes the formation of $CH_4CO+3H_2=CH_4+H_2O$. No evidence was found for the intermediate formation of CH_2O or MeOH. CO is quite active also, and the change commences at a lower temperature than with Ni. By this method the large amount of CO in municipal gas supplies may be reduced and the content of CH_4 increased. Pure CH_4 may also be prepared by passing water gas over Ni several times, removing CO_2 from the gas each time, and fractionating the product at low temperatures.

84. ———. Study of Catalytic Actions at Surfaces. XI. Action of Alumina and Other Oxides in Promoting the Activity of Ni Catalyst. Proc. Roy. Soc. (London), vol. 103–A, 1923, pp. 586–597; Chem. Abs., vol. 17, 1923, p. 3443.

85. ———. Study of Catalytic Actions at Surfaces. XII. Some Observations Relative to Those Particles of a Catalyst Which Participate in Chemical Change. Proc. Roy. Soc. (London), vol. 108–A, 1925, pp. 111–120; Chem. Abs., vol. 19, 1925, p. 2443.

86. ———. Study of Catalytic Actions at Surfaces. XIII. Some Factors Controlling Selective Hydrogenation, With Particular Reference to Certain Terpene Derivatives. Proc. Roy. Soc. (London), vol. 108–A, 1925, pp. 121–131; Chem. Abs., vol. 19, 1925, pp. 3054–3055.

87. ARMSTRONG, E. F., AND WILLIAMS, K. A. [Development of the Technical Applications of Hydrogenation.] Chim. et ind., vol. 42, 1939, pp. 234–242. Chem. and Ind., vol. 59, 1940, pp. 3–9; Chem. Age, vol. 41, 1939, pp. 271–272, 285–288.

Discusses hydrogenation of fats, the Fischer and synthetic-oil processes, and the possibility of directly hydrogenating coal under pressure with H_2 obtained by the Lurgi process.

87a. ARNOLD, J. H. Synthesis of Liquid Fuels From Natural Gas. Advances Chem. Ser. No. 5, 1951, pp. 120–137; Chem. Abs., vol. 45, 1951, p. 10,558.

In developing a commercial process to produce liquid fuels from natural gas, reliable large-scale techniques were evolved for producing O_2 and synthesis gas. To convert synthesis gas to hydrocarbons the use of Fe catalysts in a fluidized bed was required; the method of preparation of the catalyst proved to be much less important than the conditions of its environment during synthesis. The resultant integrated process (Hydrocol process) is striking in its simplicity and, from the indicated supply of gas, can contribute an appreciable fraction of American liquid-fuel requirements along with large quantities of oxygenated aliphatic chemicals. By utilizing still more recent developments, huge amounts of C_2H_2 may be obtained.

88. ARNOLD, J. O., AND READ, A. A. Conditions in Which Carbon Exists in Steel. Proc. Chem. Soc., 1894, pp. 105–106; Jour. Soc. Chem. Ind., 1894, p. 740.

Existence is confirmed of a carbide of Fe having the formula Fe_3C. The normal carbide exists in 2 different forms identical in chemical composition—a diffused carbide consisting of granules or very small plates and a crystalline carbide arranged as plates and consisting of pure Fe_3C. The % of total C obtained as carbide is greater in hard than in soft steels. This loss is due to the presence of a readily decomposed subcarbide of Fe existing to the extent of about 25% in mild steel and capable of existing to the same amount in cold, hard steel after the latter has been heated for sometime at a white heat.

89. ———. Chemical Relations of Carbon and Iron. Jour. Chem. Soc., vol. 65, 1895, p. 788.

ARNOLD, M. R. *See* abs. **99.**

90. ARWELL, J. C. AND BARSS, W. M. Comparison of the X-Ray Diffraction and Nitrogen Adsorption Surface Areas of Carbon Blacks and Charcoals. Canadian Jour. Research, vol. 26, sec. A, 1948, pp. 236–242.

Surface areas, as determined from X-ray diffraction and low-temperature N adsorption data, were compared for a number of C-blacks and activated charcoals. Comparative data were obtained also on samples of charcoal at various stages of activation and after calcination. The X-ray diffraction data indicated that all the samples examined were composed of small, graphite-like crystallites of the same order of magnitude, which had specific surfaces of about 2,500–3,000 $m.^2$ per cc. The N adsorption surface of a highly activated charcoal was found to be about equal to the X-ray surface. It is suggested that the crystallite surface represents the potential-adsorption surface of a carbonaceous material; and, providing that crystal growth does not occur during activation, the activation process makes these surfaces available to external adsorbate.

ASCHE, W. *See* abs. **1610.**

91. ASHWORTH, J. R. Simple Characteristic Relationships Among the Ferromagnetics. Nature, vol. 116, 1925, p. 397; Chem. Abs., vol. 20, 1926, p. 2781.

Ratio of the critical temperature ($\theta°$ abs.) to the maximum intensity of magnetization (I_0) for Fe, Co, Ni, and magnetite is, respectively, 0.58, 0.95, 1.19, and 1.83, or 2 x 8/27, 3 x 8/27, 4 x 8/27, and 6 x 8/27. Heusler's alloy fits this scale, the ratio θI_0 being 1.50

or 5 x 8/27. The 2 to 6 are exactly integral within the accuracy with which θ and I_0 are known. The ration of I_0 for Fe to I_0 for Ni, and that of the values for Co and magnetite, are both 3.3, the respective ratios of the critical temperatures being 1.60 and 1.67.

92. ASKEW, H. O. Report on Fischer-Tropsch Process. New Zealand Dept. Sci. Ind. Research, Bull. 6, 1928, 28 pp.

Excellent review of development work up to and including 1927. Special emphasis is placed on the work of Patart. Discussion includes the thermodynamics and the mechanism of the reactions, reduction of CO at atmospheric and high pressures with consideration of the catalysts employed, analysis of the products obtained, together with data on plant and raw-material requirements and costs. Annotated bibliography of 51 refs.

93. ATWELL, H. V. Koppers Powdered-Coal Gasification Process. FIAT Final Rept. 1303, 1947, 51 pp., 16 figs.

Experimental work on the gasification of powdered coal was conducted from 1938 to 1944. The first unit was set up at Brabag-Schwarzheide in 1938 and subsequent units at Rheinpreussen Shaft IV near Homberg. In all cases the reactor was a horizontal drum with powdered coal introduced at one or both ends, and the gasifying agent (air or O_2 mixed with steam) was introduced at spaced points along the length of the drum so as to insure turbulent flow of the dust between inlet and outlet. Preheating of the gasifying medium to about 1,200° was found to be essential, and Cowper stoves were used for this purpose. Operation was at atmospheric pressure. By this method a very rapid ignition of the coal dust took place and a temperature of more than 2,000° was obtained. This accelerated the gasification process so that the coal was gasified to the extent of about 95%. The final Rheinpreussen unit was estimated to have a capacity of 10 tons of coal per day, but it never operated successfully because of excessive cooling by the water jacket. Previous units were somewhat smaller, and no runs longer than 5 or 6 hr. had been made. No commercial units were built, but several proposals were made on the basis of about 0.5 m.^{3} O_2 consumption and 2 m.^{3} synthesis-gas production per kg. of coal. No original experimental records were available to support the claims made for the process.

94. ———. Gumz Powdered-Coal Gasification Process. FIAT Final Rept. 1304, 1947, 53 pp.; PB 85,163.

Cooperative experimental work on powdered-coal gasification was conducted by Demag, Bergbau, Verein, and Ruhrgas during 1940–43. The design of the plant was based largely on theoretical considerations developed by Dr. W. Gumz. The plant comprised 2 vertical reaction chambers, each having an inside diameter of 1.2 m. and a height of approximately 14 m. The mixture of powdered coal and gasifying agent was passed upward through the 1st chamber and down through the 2d. Most runs were made with air-steam mixtures as the gasifying agent. A few runs were made with air enriched with O_2 but none with air replaced by O_2. Only moderate preheating of the gasifying agent was used, maximum 600°, and conversion of C was relatively incomplete in all runs. A single unit with minor modifications was used throughout the program, and trouble always was experienced owing to accumulation of slag in the first reactor. The process was not regarded as ready for commercial use.

95. ———. The Schmalfeldt Process for Making Synthesis Gas From Methane. FIAT Final Rept. 1305, 1947, 23 pp.; PB 85,164.

Translation of a document by H. Schmalfeldt in 1947, describing work done in the plant of Klöcknerwerke A.-G., Castrop-Rauxel, on the production of synthesis gas from CH_4-containing gases by noncatalytic reaction with steam and O_2. In a pilot plant built in 1931, coke-oven gas was converted under a pressure of 23–24 atm. abs. with air enriched to 33% O_2. CH_4 in the exit gas was less than 1%, and formation of soot was observed. The maintenance of the refractory lining proved quite difficult. A larger plant started in 1938 could not be operated until 1941 because of difficulties in getting materials, particularly refractory brick. Results were not entirely satisfactory because of inadequate heat recovery and lack of facilities for purging unreacted gas between cycles. Fischer-Tropsch residue gas and coke-oven gas were converted at a pressure of 8–9 atm. abs., with an O_2 consumption 30–40% above theoretical and only slight formation of soot. The process can be recommended for large-scale commercial use. O_2 consumption per m.^{3} of converted CH_4 will range 0.55–0.65 m.^{3} O_2 depending on conditions and quality of the plant. At pressures of 20 atms. and above, C formation is more or less completely avoided. If the apparatus is suitably constructed conversions of 90–95% can be obtained.

———. *See* abs. **451, 452, 453.**

96. ATWELL, H. V., AND SCHROEDER, W. C. Synthetic Lubricating-Oil Plant, Rheinpreussen, Homberg. CIOS XXIV–9, 1945, 17 pp.; TOM Reel 196; PB 283.

Describes plant and process of manufacture. Lubricating-oil synthesis consists broadly in chlorinating a Fischer-Tropsch middle oil, reacting this with naphthalene in the presence of Al chloride as catalyst, separating the sludge, neutralizing, and fractionally distilling the lube-oil product. Includes photographs.

97. ———. Steinkohlen-Bergwerk Rheinpreussen, Moers-Meerbeck. British Coal Utilization and Research Assoc., Monthly Bull., vol. 10, 1946, abs. 1045; CIOS Rept. XXV–6, XXVI–80; TOM Rept. 8, TOM Reel 196; TAC Rept. SnMC–2; PB 367,412.

Detailed account of the operation of a large Fischer-Tropsch plant from 1939 until October 1944. The layout of the plant is described. Includes plans and photographs. The synthesis gas consisted of a mixture of water gas treated catalytically to increase the H_2:CO ratio, and coke-oven gas cracked in the presence of steam. It was purified by passing it over Luxmasse and a catalyst consisting largely of Fe_2O_3 and Na_2CO_3. Special attention was paid to the composition of all catalysts used at this plant, analyses being checked with information obtained from the Ruhrchemie A.-G. Extracts have been made from record books and data sheets to show plant performance at different stages of the process. The effect of catalyst regeneration is discussed, and an account is given of methods, production figures, distribution of products to associated companies, manufacture and distribution of synthetic Diesel fuel, and recovery of hard paraffin wax. An outline of the research program is pieced together from miscellaneous documents and reproduced. Gives list of abstracts of patent applications filed up to July 1939 by the various companies collaborating in the Fischer-Tropsch process.

98. ATWELL, H. V., POWELL, A. R., AND STORCH, H. H. United States Government Technical Oil Mission Fischer-Tropsch Report 1. TOM Rept. 5, July 1945, 66 pp.; TAC Rept. SnMC–1; PB Rept. 2051, 1945, 45 pp.

This is a preliminary summary report, and much of the information contained is copied directly from the preliminary CIOS reports prepared by United States and British investigators from personal interrogations of German industrial officials or from captured German documents. Issue of a supplementary report is

planned when the final CIOS reports are completed and when all pertinent German documents have been examined and studied. A list of 17 CIOS reports reviewed is attached. The report includes synthesis-gas manufacture; detailed information with flow sheets on the preparation, reduction, reworking, and regeneration of Co catalysts and the manner of conducting the synthesis operation at Hoesch Benzin, Sterkrade-Holten, Moers-Meerbeck, and Castrop-Rauxel; the gas-recycle operation of Lurgi and Ruhrchemie; the products and byproducts from Fischer-Tropsch operations; the experimental work with sintered, precipitated, and fused Fe catalysts by the I. G. Farbenindustrie A.-G., Kaiser-Wilhelm Institut, and Ruhrchemie A.-G.; the Ru catalyst; the isoparaffin synthesis; and synthesis of aromatic hydrocarbons at the Kaiser-Wilhelm Institut.

ATWOOD, K. *See* abs. **2804.**

99. ATWOOD, K., ARNOLD, M. R., AND APPEL, E. G. Water-Gas Shift Reaction. Effect of Pressure on Rate Over an Iron Oxide-Chromium Oxide Catalyst. Ind. Eng. Chem., vol. 42, 1950, pp. 1600–1602; Chem. Abs., vol. 44, 1950, p. 9137.

Influence of pressure on the rate of the water-gas shift reaction over a commercial Fe oxide-Cr oxide catalyst was studied in the pressure range 1–30 atm. at 346° and 404°. The activity of the catalyst approximately doubled as the pressure was raised to 10 atm. and increased only slightly as the pressure was increased further. Plots of catalyst activity versus pressure gave curves similar in shape to Langmuir isotherms.

100. AUDAS, F. G. Continuous Dry Process for the Removal of Hydrogen Sulfide From Industrial Gases. Coke and Gas, vol. 13, 1951, pp. 229–234; Chem. Abs., vol. 46, 1952, p. 11,638.

This is a new process in the pilot-plant stage of removal of H_2S from industrial gases. According to the following reaction: $2H_2S+SO_2 \rightleftharpoons 2H_2O+3S$, H_2S is removed by adding SO_2 in small excess of the above reaction and passing the mixture through a bed of alumina at 60°–90° at such a rate that it emerges from the chamber containing the bed completely free of H_2S. The spent alumina is continuously withdrawn from the bottom of the reaction chamber for regenerative treatment, while regenerated material is continuously added at the top. Regeneration of spent alumina consists of heating at 500° by passing hot gases through the bed of alumina in the regenerating vessel. The process can be readily adapted for simultaneous recovery of C_6H_6, which is absorbed on the alumina in the purifier and can be recovered by heating to 140° in a steam-coil-heated chamber. This C_6H_6 recovery required the introduction of a desorption vessel between the purifier and the regenerator. A detailed approximate evaluation of costs is given.

101. AUDIBERT, E. [Manufacture of Synthetic Liquid Fuels From Mixtures of Carbon and Hydrogen.] Chim. et ind., vol. 13, 1925, pp. 186–194; Brennstoff-Chem., vol. 6, 1925, p. 244; Fuel, vol. 5, 1926, pp. 170–177; Chem. Abs., vol. 19, 1925, p. 1487.

The results obtained and conclusions drawn by Fischer and Tropsch in the preparation of Synthol (*see* abs. **1014 and 1015**) have in the main been confirmed by work carried out by the Société Nationale de Recherches sur le Traitement des Combustibles, and interesting results were obtained by using suboxides as catalyzers. These are defined as oxides that cannot be isolated as such because they oxidize spontaneously in air, for example, CrO, V_2O, VO, MoO, WO, U_2O_3, Pb_2O, BiO, etc. They must be prepared directly in the catalyst chamber by reduction of a higher oxide in the presence of a secondary catalyzer consisting of a reduced metal, which must be either inert toward CO (for example Cu) or easily eliminated after reduction of the principal catalyzer (for example, Ni, removed as Ni carbonyl at 60°–80°). When a 2 : 1 mixture of H_2 and CO under a pressure of 200 atm. is passed over the catalyzer there is no reaction below 225°; between 225° and 275°–300° (the upper limit depending on the nature of the catalyzer) practically pure MeOH is formed in 8–10% yield according to $CO+2H_2=MeOH$, not over 2% CO_2 according to $CO+H_2O=CO_2+H_2$, and traces of CH_4; above 300° H_2O, CH_4, MeOH and other organic compounds are formed.

102. ———. [Methanol. Its Synthesis.] Tech. moderne, vol. 20, 1928, pp. 861–866; Chem. Abs., vol. 23, 1929, p. 1385.

The catalysts in use are CuO and ZnO. CuO is the more active but is easily affected by the formation on its surface of substances of higher molecular weight. To prevent this, H_2 is increased to $CO+5H_2$. A long exposure to high temperature decreases the activity of catalysts. The activity is also affected favorably or adversely by the presence of other metallic oxides. Yields are roughly proportional to the square of the pressure. ZnO requires higher pressures than CuO. Maximum yields are obtained when the mixture of gases is equal to $CO+2H_2$. Since MeOH is an intermediate product, greater yields of MeOH, to the exclusion of other products, are obtained when the speed of the gases through the catalyst chamber is increased. Secondary reactions are increased with higher temperature. CuO permits the use of lower temperature. Both oxides are subject to poisoning.

103. ———. [Synthesis of Methyl Alcohol.] Chim. et ind., vol. 20, 1928, pp. 1015–1022; British Chem. Abs., 1929, B, p. 162.

Résumé of the work carried out on the synthesis of MeOH from CO and H_2 under high pressure and reported at the 2d Conference on Bituminous Coal, Pittsburgh, 1928. The conditions throughout the experiment were: Pressure 150 atm., rate of circulation of gases over catalysts 5,000 cu. m. (n. t. p.) per $m.^3$ of catalyst volume, and gas mixtures containing H_2 and CO in the ratio 5 : 1 (with catalysts having Cu as the chief constituent) and 2 : 1 (with those of which ZnO is the basis); yields of MeOH are expressed in gm. per l. of catalyst vol. per hr. It was found that, in addition to the physical changes that occur in a catalyst as a result of prolonged use even with carefully purified gases, in the case of Cu catalysts a fouling of the solid took place owing to the deposition of C compounds of high molecular weight. The rapidity of fouling is a function of the partial pressure of CO in the gas, and it is reduced to an unimportant value when the proportion does not exceed ⅙. ZnO catalysts do not foul with gases containing 33% CO; such a proportion, in fact, gives the optimum yields of MeOH. When ZnO and Cu catalysts are heated in H_2 at 550° for a number of hrs., each suffers a loss of activity, that of the ZnO catalyst being the greater. The activity of a Cu catalyst is completely removed by the addition of small amounts of the oxides of Sn and Bi; those of B, Ti, and V have no immediate effect, although they accelerate the rate at which prolonged heating reduces the activity. Al and Ce oxides, on the other hand, increase the activity. The addition of Be and Cr oxides to a Zn oxide catalyst increases the activity, the presence of W oxide affects it adversely, while U oxide is without effect. The yields of MeOH obtained with each catalyst under the conditions specified above at temperatures corresponding to the optimum amounts are compared in the cases of Cu and ZnO catalysts. With Cu at temperatures not exceeding 275°, the yield was 1,100–1,150 gm. and with Zn oxide at 375°, 300–325 gm. The effect of the

pressure (p in atmosphere) on the yield, R, for a Cu catalyst is represented approximately by $R=0.050p^2$, and for ZnO by $R=0.014p^2$. When the rate of flow over a ZnO catalyst is increased 5,000–10,000, the yield rises by 55% and 10,000–20,000 by 35%. Small amounts of S present as CS_2 or thiophen in an otherwise pure gas mixture poison the Cu but are without effect on the activity of the ZnO catalysts. Beside the desired reaction, which produces MeOH, a number of side reactions occur which result in the formation of H_2O, CO_2, and CH_4. From a study of the relative rates of the main and side reactions, it is shown that the useful conversion of CO is much greater with a Cu catalyst than is the case with 1 of ZnO. In deciding the relative value of the 2 types of catalyst, the poor yields from ZnO have to be considered in conjunction with the robustness and indifference to small traces of poisons, while the extra yields from Cu catalysts have to be offset against the much greater sensitiveness to poisoning.

104. ———. Synthesis of Methyl Alcohol. Proc. Internat. Conf. Bituminous Coal, 2d Conf., vol. 2, 1928, pp. 508–522.

Fouling of catalysts (Cu and Zn oxides), action of heat on catalysts, promoters, effect of pressure, composition of the gas, and rate of flow and parasitic reactions are discussed.

105. ———. [Synthetic Manufacture of Methanol.] Conférences-rapports sur les combustibles, Sec. tchécoslovaque soc. chim. ind., vol. 24, 1930, pp. 27–41; Chem. Zentralb., 1930, II, p. 3223; Ann. combust. liquides, vol. 5, 1930, pp. 239–272; Chem. Abs., vol. 24, 1930, pp. 4505, 5718.

An address describing the work carried out on the synthesis of MeOH by the Société Nationale de Recherches sur le Traitement des Combustibles, comprising laboratory experiments, semicommercial work on the verification of the results, and their application in the design and operation of the 5-ton commercial unit now under construction.

106. ———. [Synthesis of Methanol.] Ann. combust. liquides, vol. 6, 1931, pp. 655–709; Brennstoff-Chem., vol. 13, 1932, pp. 92–93; Chem. Abs., vol. 26, 1932, p. 1235.

Commercial synthesis of MeOH, particularly with regard to the heat of reaction, the use of pressure and low temperatures and the influence of the catalyst, and the H_2: CO ratio and the temperature upon the speed of the reaction, is discussed. The economy of the process depends upon the extent of the side reactions. Beside increasing the consumption of synthesis gas they add to the difficulties of converter regulation since they give rise to excessive temperature increases. They are of 2 types: A primary, in which only the H_2 and the CO take part, and a secondary, in which the reaction products undergo further conversion. The primary reaction is exemplified in formation of CH_4 ($2CO+2H_2=CO_2+CH_4+61$kcal.). The quotient y/x (y is that portion converted into CO_2 and CH_4, x that converted into MeOH) is independent of the space velocity but depends on the chemical composition of the catalyst and the operating temperature. A rise in temperature of about 100° increases the extent of this side reaction with a Cu-Th catalyst about 60-fold and with a Zn-Cr catalyst about fourfold. Certain measures to be taken against the occurence of these side reactions are offered. Formation of high-molecular substances can be curtailed by avoiding the presence of alkali and by correctly choosing the H_2: CO ratio. The MeOH must be removed before its concentration becomes too great. Ch_4 formation and overheating must be opposed by the efficient removal of heat through a cooling system or by addition of inert constituents to the reaction gas. Catalysts prepared the wet way are very susceptible to overheating. The injury produced thereby depends upon the chemical composition. The best catalysts are Cu and Zn oxides. As promoter for ZnO, Cr_2O_3 is suitable and for Cu a large number of additives are available. The activity with Cu-containing catalysts at 300° and 100 atm. is about 8-fold greater than with Cu-free catalysts and with at least equal resistivity toward overheating. With Cu-free catalysts the temperature must be at least 400° and the pressure 400 atm. to attain the same space-time yield. The Cu-containing catalysts require a thorough purification of the raw gas from S compounds, particularly COS. Even with this, the advantage is with them since the cost of gas purification per kg. of MeOH and down to 1.25 mg. S per $m.^3$ is only 10–12 centimes. Extreme care is necessary in preparing the catalysts. The precipitation factors, such as concentration of the solutions, excess of alkali, precipitation temperature, etc., greatly influence the activity. The volume shrinkage during the operation, amounting after 600 hr. to 60%, could be reduced to 20% by means of previous compression.

107. ———. [Obtaining Liquid Organic Compounds from Technical Gases.] Ann. combust. liquides, vol. 8, 1933, pp. 757–869; Rev. ind. minérale, No. 307, 1933, pp. 447–464, 469–488, 501–508; Chem. Zentralb. 1934, I, p. 978; Chem. Abs., vol. 28, 1934, p. 462.

Thermodynamic conditions for the hydrogenation of CO to CH_4, C_2H_6, C_3H_8, and C_6H_{14} are discussed. Equilibria for 1 and 100 atm. are recorded. The formation of MeOH from CO and H_2 is exhaustively considered.

108. ———. [Principles of Thermal Decomposition and Hydrogenation of Organic Compounds.] Ann. combust. liquides, vol. 8, 1933, pp. 565–605; Chem. Abs., vol. 28, 1934, p. 463.

The article deals with primary reactions of paraffins, cyclic hydrocarbons, hydroaromatics, olefins, and aromatics, with superimposed reactions and catalytic cracking. Berthelot's hydrogenation method and Sabatier's discoveries and their applications are also discussed.

109. ———. [Mechanism of the Oxidation of Methane.] Compt. rend., vol. 216, 1943, pp. 348–350, 449–451; Chem. Abs., vol. 38, 1944, p. 2257.

Mechanism and the kinetics of the reaction taking place between CH_4 and O_2 at temperatures 300°–650° were studied by use of quartz or Pyrex tubes. Reaction products are H_2O, CO, CO_2, H_2, and HCHO (1); the amounts of (1) and H_2 formed are small, sometimes none of the latter. Even under equal conditions the results sometimes vary considerably and depend upon the diameter of the tube and the state of its inner surface. With a quartz tube of 10 mm. inside diameter, the inner surface of which is covered with a NaCl or KCl layer, the reaction isotherm remains constantly slow at 650° with a mixture of 1 molecule CH_4 and 2, O_2. With NaCl-lined quartz tubes of greater diameter the reaction may be accelerated to such an extent that the gas mixture ignites at 550° or higher. With unlined quartz tubes, the reaction may become violent at 550°, even if the diameter of the tube is 10 mm. To study the transformation isotherm further, the oxidation of CH_4 at 300°–700° was accomplished by passing the mixture at atmospheric pressure through a ring-like tube formed by inserting 1 quartz tube within another 4 mm. wider. The latter was coated on its inner surface, the former on its outer, with NaCl. With such an apparatus CH_4 and O_2 react at all temperatures between 300° and 700° with formation of H_2O, CO, CO_2, H_2, and (1). The amounts of H_2 and (1)

are very small; the amount of CO_2 increases with the duration of heating, whereas the amount of CO increases to a maximum and then decreases. The ratio of consumption of CH_4 : O_2 is about 1 : 2 as long as the heating time is short and the temperature low. Based upon the CH_4 consumption, the reaction follows the law of Arrhenius, and the heat of activation is about 40,000 cal.; based upon the O_2 consumption, it does not follow this law, and the activation heat is 40,000 cal. at 650° or higher and 50,000 cal. at 625°. The results indicate that under the conditions used, the reaction is heterogeneous and that its course is influenced by the state of the surface of the reaction tube.

110. AUDIBERT, E., AND RAINEAU, A. [Study of the Action of Iron Catalyzers on Mixtures of Carbon Monoxide and Hydrogen.] Rev. ind. min., 1928, No. 182, pp. 286–314; Ann. combust. liquides, vol. 3, 1928, pp. 367–428; Ind. Eng. Chem., vol. 21, 1929, pp. 880–885; British Chem. Abs., 1929, B, p. 840; Chem. Abs., vol. 23, 1929, pp. 2094, 3620, 5091.

Fe, Ni, and Co exert a catalytic action on mixtures of CO and H_2, and this study was to determine if these metals when in contact with gaseous mixtures would give liquid-organic products. A study was made of different mixtures with a hydrated Fe_2O_3 base consisting of 98 parts anhydrous Fe_2O_3 and 2 parts of the following: Na_2CO_3, Li_2CO_3, $CaCO_3$, $SrCO_3$, $BaCO_3$, $MgCO_3$, $ZnCO_3$, $MnCO_3$, $CuCO_3$, Ag_2CO_3, Al_2O_3, Mo_2O_3, WO_2, or SiO_2. Of these 15 mixtures, those containing an alkali carbonate (Na_2CO_3 or Li_2CO_3) formed organic liquids with gas of composition $CO+5H_2$ under 150 atm. pressure and a flow of 3,000 $m.^3$ All the others gave CH_4, CO_2, slightly acid H_2O, and finally C. Five mixtures with a ferric hydrate base were then studied consisting of 98 parts Fe_2O_3 and 2 parts of the following: K_2SO_4, K_3PO_4, KNO_3, and K_2S. No oil was formed by the K_2S catalyzer, but the other catalyzers produced 11 $cm.^3$ per $m.^3$ of gas from the sulfate, 9 $cm.^3$ per $m.^3$ of gas from the phosphate, 13 $cm.^3$ per $m.^3$ of gas from the borate, and 19 $cm.^3$ per $m.^3$ of gas from the nitrate, with gas ($CO+5H_2$) under 150 atm. pressure and a flow of 3,000 $m.^3$. Mixtures were then prepared by precipitating a mixture of Cu nitrate and Fe nitrate with an alkali, adding to the precipitant K_2CO_3 in proportion to the Fe content, and, after drying, submitting the compound to the action of H_2 under atmospheric pressure at 200° for 4 hr. and at 300° for 14 hr. in such a manner as to reduce only the CuO but not the Fe_2O_3. It was shown that the presence of Cu increased the catalytic action of the Fe_2O_3–K_2CO_3 couple; the composition of the catalyzer after reduction at 300° was Fe_2O_3, 49.5%, Cu 49.5%, K_2CO_3, 1.0%. With this compound a mixture of H_2O and different organic liquid products was extracted from the $CO+5H_2$ mixture in the following proportions: (1) Light carburetants (55°–180° fractions of oil) 28.8%, light oil from activated charcoal 5.0%, alcohol in solution 29.0%, or a total of 62.8%; and (2) clear oil, 180°–250°, 14.0%; (3) heavy oil, 250°–330°, 10.0%; (4) paraffin 7.1%; (5) tar, 2.7%; and (6) fatty acids, distilling at 110°–140° (weak acetic, propionic, and butyric), 3.1%. With the Cu–Fe_2O_3–K_2CO_3 catalyzer, it is not possible to lower the temperature and still be assured of regularity of the phenomena of transformation of the mixture of CO and H_2.

111. ———. Synthesis of Methanol. Ind. Eng. Chem., vol. 20, 1928, pp. 1105–1110; British Chem. Abs., 1928, B, p. 920; Chem. Abs., vol. 22, 1928, p. 4461.

Results of the action of various substances in catalyzing the reaction $CO+2H_2=CH_3OH+27{,}000$ gm.-cal. are given. The following oxides were inactive: Al_2O_3, SiO_2, Mo_2O_5, V_2O_3, W_2O_5,ThO_2, TiO, MgO, CuO, BaO, and SrO. Ce_2O_3, UO_2, BeO, and ZrO_2 gave less than 2% of MeOH at 150 atm. MnO, Cr_2O_3, and ZnO, prepared by precipitation from the corresponding nitrates, converted 2–17.5% of CO into MeOH, the highest conversion being for ZnO at 350°. Metallic Cu was found to be a good catalyst if prepared at a low temperature by reduction of Cu oxides obtained by precipitation of the nitrate or by the thermal decomposition of Cu salts of organic acids. Cu catalysts prepared from the fused oxide or from Cu oxide obtained by precipitation of solutions of the chloride or sulfate were inactive. Ni and Fe catalysts favored the production of CO_2. Single-component catalysts were sensitive to heat, high temperatures impairing their activity. Mixed catalysts were more effective than single-component catalysts. A mixture of Ce_2O_3 and Cu was very effective, and the activity reached a maximum at a Ce : Cu ratio of 30 : 100 with a 92% conversion of CO. A mixture of BeO and Cu with a Be : Cu ratio of 6 : 100 was almost as good and showed the greatest heat resistance of the whole series studied.

112. ———. [Chemical Equilibrium Between Methanol, Carbon Monoxide and Hydrogen.] Ann. combust. liquides, vol. 5, 1930, pp. 454–461; Chem. Abs., vol. 25, 1931, p. 635.

With enough time of contact the following reactions take place: $CO+2H_2=CH_3OH$; $2CO+2H_2=CO_2+CH_4$; and $CO+3H_2=CH_4+H_2O$. The reaction constant for the first reaction under the above conditions can be determined, and from the experiments the following relation is found:

$$\log K=-35.38+\frac{6806}{T}+7.22\log T.$$

AVERBUKH, B. D. *See* abs. **564, 566.**

113. AYRE, A. L. Report of the Hydrocarbon Oil Duties Committee. Coke Smokeless-Fuel Age., vol. 7, 1945, pp. 88–90; Chem. Trade Jour., vol. 116, 1945, pp. 423–426; Chem. Age, vol. 52, 1945, pp. 343–345; Petrol. Times, vol. 49, 1945, pp. 304–309.

This is a report with comments indicating the importance of developing chemical manufactures based on coal byproducts. The committee recommends that imported hydrocarbon oil used for chemical synthesis should be free of duty and for indigenous oil similarly used, allowances should be paid equal to the respective duties. An interesting feature of the Fischer-Tropsch process is that the products are aliphatic, not aromatic in character and, thus, resemble petroleum rather than coal oils produced by other processes. Many of the more important chemicals that can be produced from petroleum could, therefore, be derived with equal, and in some cases greater, facility from the primary products of hydrocarbon synthesis.

114. AYRES, E. Synthine Process—a Composite of Research. World Petrol., vol. 15, No. 11, 1944, pp. 56, 99.

Importance of the chemical development of the synthine process is discussed, and its economic possibilities are emphasized. The magnitude of the technical effort already expended upon the process is indicated by the 2,000 patents that have been issued.

115. ———. Comment on Synthetic Liquid Fuels Program. Petrol. Processing, vol. 2, July 1947, p. 558.

Commenting on criticism of the Bureau of Mines synthetic liquid fuels program (abs. **2641**), Ayres says that such criticism comes from a misunderstanding of the way in which the work is conducted and that the program of the Bureau has satisfied the specification as set forth by the Advisory Committee.

116. ———. The Fuel Problem. Sci. American, vol. 181, No. 6, 1949, pp. 32–39.

As our petroleum resources decline (the peak of production is expected to be reached between 1955 and 1960) the 2 most abundant solid fuels, oil shale and

coal, must be utilized. The major problem in their utilization is their conversion into the liquid state. Technological research has already developed methods to accomplish this, and it is quite possible that in a reasonably short period further development of these methods will bring these fuels into a favorable competitive position with petroleum fuels. General discussion is given of the methods for converting the solid fuels into liquid fuels: Oil-shale retorting, direct coal hydrogenation by the Bergius process, and indirect coal hydrogenation by the Fischer-Tropsch method. The cost problem is surveyed, and the economic evaluation of each method is discussed. The Fischer-Tropsch method of conversion appears to have the best possibilities as an economic producer of liquid fuel.

116a. ———. Synthetic Liquid Fuels—When and How? Petrol. Processing, vol. 7, 1952, pp. 41–44.

Production of liquid fuel from coal and oil shale is an inevitable part of the future industrial picture. From our present knowledge of synthetic fuels, oil shale shows the best immediate promise; exploitation can take place today with only nominal operating loss and by 1965 on a profit basis in direct competition with natural petroleum. But the future fuel economy depends upon coal and its wide-scale utilization by 1980 and as the main source of fuel energy by the year 2000. This position, however, will not come about by hydrogenation; unless radically new ideas are born coal hydrogenation as a whole is dead and will remain so, only parts of the process will remain applicable. If coal were to be converted to liquid fuel without regard to other aspects of the energy problem, use would probably be made of a modified Fischer-Tropsch synthesis since this appears to be cheaper and more flexible than hydrogenation. Most favorable economics should come from a highly integrated energy industry which would supply not only increasing amounts of liquid fuel but also even more rapidly increasing amounts of electric power. Coal would be mechanically mined at low cost, crushed, cleaned and transported by pipeline to locations of adequate water supplies, and there continuously distilled to yield a maximum amount of tar, some aromatic chemical intermediates, and fine char. The tar would be hydrogenated to liquid fuels, the char converted to liquid fuels and aliphatic intermediates by the Fischer-Tropsch synthesis or burned under boilers for generation of electric power. The course of production of petroleum is estimated and the general shape of the world's future annual production curve is predicted. On the basis of ultimate producible reserves of 1,000 billion bbl., it is estimated that the peak of world production is likely to come about in 1985.

117. Ayres, E., Montgomery, C. W., and Hirsch, J. H. Some Problems Associated With the Fischer-Tropsch Process. Oil Gas Jour., vol. 47, No. 25, 1948, pp. 112, 115; Petrol. Refiner, vol. 27, No. 11, 1948, pp. 583–585.

Abs. of a paper presented at a meeting of the Am. Soc. Mech. Eng. at Amarillo, Texas. Due to the fact that about 2,000 vol. of synthesis gas plus recycle gas must be processed to make 1 vol. of liquid motor-fuel product, the latter has to bear a disproportionate part of the cost of amortizing and maintaining the plant and equipment. Because of this characteristic and to obtain greater economic space-time yields, more severe operating conditions have been imposed, with the result that the catalyst has become overloaded and undesirable side reactions have been set up, which have greatly aggravated the catalyst problem. The problem of C deterioration of the catalyst is also a serious one. In the formation of carbides (which by the way are no longer regarded as essential intermediates in the synthesis of hydrocarbons) at synthesis temperatures and above, CO will deposit C on the transition metals of the catalyst far in excess of the stoichiometric amounts indicated by the formulas for the carbides M_2C or M_3C. As the rates of decomposition of the carbides increase, the C, which was uniformly distributed through the metal lattice in the carbide form, tends to diffuse and accumulate in inclusions, thus freeing lattice sites for the addition of more C. As this excess C accumulates, the lattices are forced to expand, with the result that the catalyst structure is broken down, and excessive pressure drops through the catalyst ensue. The formation of high-molecular-weight wax in the synthesis is another serious problem, particularly in fluid operation. A study of product distribution suggests that certain thermodynamic equilibria are operative and determine the relative amounts of *n*–paraffins of each molecular-weight range, the relative amounts of the different *n*–1–olefins, the degree of branching, etc. Operation of these equilibria impose certain limitations on the flexibility of the process. Generally speaking, the modern Fischer-Tropsch process yields a disproportionately large amount of gaseous hydrocarbons, while, at the other end of the product range, relatively small amounts of extremely high molecular weight wax paraffins are found. On account of the equilibria involved, it is impossible to reduce the gas yield without simultaneously increasing the wax yield. Likewise, the ratio of diesel fuel to gasoline, normally about 1:6, cannot be increased without a corresponding increase in wax. Only relatively small amounts of wax deposited on the catalyst in fluid operation are enough to cause catalyst agglomeration and incomplete fluidization with consequent localized overheating and C deposition. The Fischer-Tropsch process is peculiar not only in its abnormal volume shrinkage but also in its loss of heat value. The power requirements are also considerable. Economically, it is essential that synthesis processes be developed that do not depend upon credits for by-products that have limited markets. The oxygenated compounds offer attractive possibilities as chemicals on a relatively small scale, but while synthesis plants of 70,000 bbl./day capacity would produce less than 3% of the country's motor fuel, the byproduct EtOH would amount to almost 100 million gal./yr., or about half the estimated demand for this material.

B

118. Baccaredda, M. [Decomposition of Methanol With Catalysts Used in Its Synthesis.] Ann. chim. applicata, vol. 27, 1937, pp. 413–422; Chem. Zentralb., 1938, I, p. 866; Chem. Abs., vol. 32, 1938, p. 2083.

Decomposition of MeOH at 356° and atmospheric pressure in the presence of catalysts used in its synthesis at high pressure is investigated. All simple ZnO-base products show similar results, while catalysts consisting of ZnO with other metallic oxides affect the reaction differently. Smithsonite calcined at 400°, which is very active in the synthesis of MeOH, was also found very active in promoting the decomposition. The formation of HCO_2Me does not appear to be due to condensation of 2 moles of CH_2O but rather to a secondary reaction between MeOH and CO.

119. Bach, A. [Reduction, Electrolysis, and Photolysis of Carbonic Anhydride.] Compt. rend., vol. 126, 1898, pp. 479–481; Jour. Chem. Soc., vol. 2, 1898, p. 332.

It is found that when CO_2 in aqueous solution is reduced by means of H_2 occluded in Pd, some CH_2O is also produced.

120. BACQUEYRISSE, L. [French Fuels: Their Conservation and Replacement.] Mem. soc. ing. civils France, vol. 92, 1939, pp. 241–286; Chem. Abs., vol. 34, 1940, p. 7573.

A review of possible sources of gasoline substitutes: Hydrogenation products of coal and CO, low-temperature tar, benzene, coal gas, wood charcoal, alcohol (from beets, molasses, wine, maize).

BADAMI, G. N. *See* abs. **1187, 1188.**

121. BADISCHE ANILIN und SODA-FABRIK. [Review of the Industrial Synthesis of MeOH.] Ztschr. angew. Chem., vol. 38, 1925, pp. 546–547.

Explanation of the dispute between the company and Patart as to the priority of the process.

122. BADISCHE ANILIN UND SODA FABRIK, and PATART, G. Synthetic Methanol Controversy. Ind. Eng. Chem., vol. 17, 1925, p. 859; Chem. Ztg., vol. 59, 1925, p. 463; Chem. Trade Jour., June 5, 19, 1925.

Discussion between Badische and Patart as to the validity of patents by both parties on the pressure synthesis of MeOH from CO and H_2.

BADSTÜBNER, W. *See* abs. **3433.**

123. BAHR, —. Medium Pressure Synthesis of Paraffins. FIAT Reel L5, frames 151–155, 1939; PB 70,159.

Observations are made on various phases of the operation of medium pressure synthesis as follows: Homogeneous filling of the furnace, putting a new catalyst into operation, furnace control, behavior of the catalyst during stoppages, charging of the paraffin catalyst, behavior of the paraffin catalyst under hydrogen action, and favorable conditions for emptying the furnace.

124. ———. [Comparative Gas Conversion of Synthesis Gas and Water Gas on Cobalt and Iron Catalysts.] FIAT Reel L5, frames 148–150, 1940; PB 70,159.

Results of comparative tests at a pressure of 7 atm. are presented in a numerical table. Decisive factors for the selection of the base gas and the type of catalyst are their cost, their availability, and the kind of products desired, with special reference to their olefin contents and their composition.

125. BAHR, H. [Influence of Sulfur in the Water Gas and in the Catalyst on the Action of the Contact Material in the Synthesis of Petroleum.] Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 514–516; Chem. Abs., vol. 25, 1931, p. 3806.

In the synthesis of paraffins from water gas at 270° over an Fe-Cu catalyst, the same result was obtained whether a synthetic water gas was made from pure H_2 and CO or a normally purified water gas was used. The S content of the latter had no appreciable effect. Of 2 Cu-Co catalysts differing in S content, the one with the lower S content was the more readily deactivated.

126. ———. [Occurrence of Hydroaromatic Constituents in Synthetic Benzine.] Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 521–523; Chem. Abs., vol. 25, 1931, p. 3807.

The action of Ni-Al_2O_3 catalysts on aliphatic and hydroaromatic compounds in presence of H_2 depends on the composition of the catalyst. One containing 75% Ni was found to be without action on *n*-hexane, but decomposed the corresponding cyclo compound, thus providing a means for separating the 2. The treatment of synthetic benzine with such a catalyst gave a small condensate of a characteristic aromatic odor, indicative of the presence of cycloaromatic compounds.

127. ———. [Reutilization of the Exit Gas From Petroleum Catalysts and Its Conversion Into Methane.] Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 519–521; Chem. Abs., vol. 25, 1931, p. 3806.

Exit gas from catalysts used for petroleum syntheses was passed over Fe at 850°. H_2 and hydrocarbons reduced the CO_2 to CO. This gas could be reused for petroleum synthesis. The gas can also be converted into CH_4 by passing over Ni at 240°. The calorific value of the gas after extraction of CO_2 was 6400 kg.-cal. per m^3.

———. *See* abs. **973, 974, 975, 976.**

128. BAHR, H. A. [Behavior of Water Gas on Various Catalysts; Contribution to the Equilibrium $6CO_2+C_6H_6 \rightleftarrows 12CO+3H_2$] Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 217–219; Chem. Zentralb., 1929, II, p. 3263; Chem. Abs., vol. 24, 1930, p. 5207.

Heating a mixture of CO_2 and C_6H_6 vapor with various metallic catalysts to 550°–750° led only to the formation of traces of CO in the final gas. The gas mixture of $4CO+H_2$ heated on the same catalysts to 200°–800° did not show a reaction; only when $ZnO+0.5\%$ Fe_2O_3 was employed as a catalyst, the formation of 24% CO_2 produced by decomposition of CO on Fe was observed.

129. ———. [Reduction of Carbonic Acid.] Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 219–224; Chem. Zentralb., 1930, I, p. 185; Chem. Abs., vol. 24, 1930, p. 5207.

Reduction of CO_2 according to $CO_2+H_2=CO+H_2O$, which up to the present has been investigated only at relatively high temperatures, can be carried out also at moderate temperature if the proper catalysts are employed. With metallic Cu the reaction is noticeable at 200°. With the employment of $Cu \cdot Cr_2O_3$ $Fe \cdot Cu$, $Fe \cdot CO$, and $Co \cdot Cu \cdot Zn$ as contact materials with temperatures between 200° and 450° and with mixtures of CO_2 and H_2 in the ratio 1:1 and 1:3, respectively, the CO quantities obtained were up to 16%. With a slow current of the gas mixture, reduction of CO to CH_4 occurred, especially when contacts containing Co were employed.

130. BAHR, H. A., AND BAHR, T. [Decomposition of Carbon Monoxide on Nickel.] Ber. deut. chem. Gesell., vol. 61B, 1928, pp. 2177–2183; Chem. Abs., vol. 23, 1929, p. 756.

Metallic Ni or NiO catalyzes the reaction $2CO=C+CO_2+38.9$ cal. by first forming Ni_3C. Below 270°, the decomposition of CO continues until the Ni is completely transformed into Ni_3C; then the reaction stops. Between 270° and 380°–420°, the CO decomposition continues, the catalyst being Ni_3C, which is free from metallic Ni. This is proved by analysis, which shows that the amount of C bound chemically by the catalyst corresponds to Ni_3C, excess C being present as the free element. (To determine the ratio of bound C to free C, H_2 is passed over the catalyst. The amount of CH_4 formed indicates the quantity of bound C. Free C remains inert.) Above 380°–420°, free Ni again appears in the catalyst because Ni_3C dissociates at such temperatures. Ni_3C_2 is probably an intermediary step in the decomposition of Ni_3C. It is believed that Ni_3C formed in the catalysis process is identical with that isolated from fusions of Ni in the presence of C.

131. ———. [Synthesis of Methane From Carbon Monoxide and Hydrogen by Nickel.] Ber. deut. chem. Gesell., vol. 61B, 1928, pp. 2465–2469; Chem. Abs., vol. 23, 1929, p. 1106.

Mixture of CO–H_2 in a ratio of 1:3 is passed over a Ni_3C catalyst at 250°. This catalyst is much less sensitive than Sabatier's Ni catalyst for the same reaction. The Ni_3C catalyst is pyrophoric and, therefore, must be handled in an atmosphere of inert gas as N_2. The reactions occurring are: $2CO+2H_2=$

CH_4+CO_2; $CO+3H_2=CH_4+H_2O$; $Ni_3C+2H_2=CH_4+Ni_3$; and $2CO=C+CO_2$. After a short period of operation the initial catalyst Ni_3C is reduced to Ni but again reacts to give Ni_3C. The main reactions are (1) $Ni_3+CO=Ni_3C+O$ (2) $Ni_3C+2H_2=CH_4+Ni_3$.

132. ———. [Reactions of Nickel Carbide (Ni_3C) Prepared at Low Temperatures.] Ber. deut. chem. Gesell., vol. 63B, 1930, pp. 99–102; Chem. Abs., vol. 24, 1930, p. 1812.

Finely powdered Ni_3C, resulting from the action of CO on Ni at low temperatures, is pyrophoric. This property is destroyed by displacing the adsorbed CO with pure N_2 at 250°. The stabilized carbide may be heated to 110° without oxidation. The activity toward CO and H_2 is also decreased by the stabilization. Ni_3C absorbs moisture from the air. It has a specific gravity of 7.97 and is slightly magnetic. Its heat of formation is—9.2=0.8 kcal. It begins to decompose into its elements when heated to about 400°. With H_2 at 180°–250°, CH_4 and C_2H_6 are formed in the ratio of 10 : 1. In gaseous-hydrogenation reactions with Ni as a catalyst, the primary hydrogenation is evidently much faster than the secondary polymerization reaction. An increase in pressure increases the latter. At 300° H_2O vapor acts on the carbide with the production of H_2 and CH_4. Similarly, NH_3 at 420° gives H_2, CH_4 and some C_2H_6. H_2S yields heavy hydrocarbons as low as 240°. HCl gas acts similarly. Contrary to the action of Fe_3C, Ni_3C usually dissolves in acids without the liberation of free C and produces hydrocarbons of lower molecular weight than the former carbide. In 3 *N* HCl, 67% of the C is converted to gaseous hydrocarbons and 33% to liquid. In dilute HNO_3 nitro compounds of the hydrocarbons are formed. Some free C results from the action of dilute H_2SO_4 on the carbide.

133. Bahr, H. A., and Jessen, V. [Dissociation of Carbon Monoxide on Cobalt.] Ber. deut. chem. Gesell., vol. 63B, 1930, pp. 2226–2237; Chem. Abs., vol. 25, 1931, p. 22.

Finely divided metallic Co does not dissociate CO at 225°. The dissociation of CO takes place on the Co combined with 9.24% C as Co_2C. At temperatures above 225°, Co_2C decomposes, giving free C. No evidence of other Co carbides than Co_2C is found. Co carbide prepared from CO dissociation on finely divided Co gives up its carbide C as CH_4 on treatment with H_2 at temperatures as low as 240°–250°, while the carbide prepared from free C + finely divided Co forms CH_4 on reacting with H_2 above 400°.

134. ———. [Fission of Carbon Monoxide on Iron Oxide and Iron.] Ber. deut. chem. Gesell., vol. 66B, 1933, pp. 1238–1247; Chem. Abs., vol. 28, 1934, p. 984.

Pure Fe_2C (9.7% C) can very probably be prepared from Fe and CO at 225° or lower; at 230°–400°, a mixture of Fe_2C, Fe_3C, with free C probably results; while above 400° only Fe_3C (6.68% C) is formed. Carbonized products obtained by means of Fe oxide always contain O; detection of combined C by hydrogenation with H_2 is not quite trustworthy in this case and must be performed at 255°–260°. The products obtained with Fe up to 330° are free from O; at higher temperatures, the oxidizing action of the liberated CO_2 is observed. The hydrogenation of combined C with H_2 can take place at 280°–290°. Carbide formation occurs relatively rapidly; subsequently, the main reaction is the separation of free C.

135. Bahr, T. [Reduction of Carbon Monoxide and Carbon Dioxide on Oxide Catalysts.] Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 292–297; Chem. Zentralb., vol. II, 1937, p. 3990; Chem. Abs., vol. 32, 1938, p. 6435.

CO was reduced at 250°–495° over S-resistant catalysts. Over MoO_3–ThO_2 (1 : 1) with 10% BaO and at 1 atm. and 350°–495°, 10–17% of CH_4 was obtained. In reduction at higher temperatures the hydrocarbon showed a somewhat higher C number. The reaction occurred as follows: $2\ CO+H_2=CH_4+CO_2$. Results were similar with a catalyst of Cr_2O_3–MoO_3 (1 : 1) with 10% BaO, but with a catalyst of ThO_2–MnO (1 : 1) with K_2CO_3 precipitated on kieselguhr, the results were entirely ineffectual. In the tests at increased pressure, Al_2O_3–MoO_3 (7 : 3) was used as catalyst, and beside CO_2 some H_2O and a small amount of low boiling hydrocarbons were obtained. From CO_2 at 20–30 atm. and 450°, CO and only a small amount of hydrocarbons were obtained.

———. *See* abs. **130, 131, 132, 1030, 1031.**

136. Baikoff, A. A. [Reduction and Oxidation of Metals.] Metallurg (U. S. S. R.), No. 3, 1926; Rev. mét., vol. 25, 1928, pp. 47–54; Chem. Abs., vol. 22, 1928, p. 2129.

General discussion and review, dealing particularly with reduction of Fe oxides by H_2 and by CO and with the oxidation of Fe.

Bailey, R. W. *See* abs. **3184.**

137. Bailleul, G., Herbert, W., and Reisemann, E. Aktive Kohle und ihre Verwendung in der chemischen Industrie. Ferdinand Enke, Stuttgart, 1937. 2d Ed., 114 pp.

One chapter describes the technical use of active C with special reference to benzine recovery from natural gas and obtaining gasol and benzine by the Fischer-Tropsch-Ruhrchemie process.

138. Bain, E. C. Rates of Reactions in Solid Steel. Trans. Am. Inst. Min. and Met. Eng., vol. 100, 1932, pp. 13–46; Chem. Abs., vol. 27, 1933, p. 4509.

Basis for evaluating the contribution of any alloy addition toward the development of deep-hardening or air-hardening quality in steel is suggested, dependent on the effect of the addition to retard transformation in the 600°–500° range. This is the only fundamental property involved in securing the final quality of hardening without drastic quench. Mn, contributing greatly to this effect, is contrasted with Ni, which shows only a little retarding effect. In a series of similar steels, differing substantially only in Mn, the range in transformation velocity is 1–1,000,000. Graphite is the stable form in C in a 0.50 C–3.5 Ni steel free from significant amounts of other elements. Cementite, because of its high speed of formation, forms in large proportion, even though less stable than graphite. The relative velocities of the reaction producing carbide and that producing graphite are considered to be the cause of the presence of carbide alone in Ni steels in common use. A stable condition of ferrite, austenite, and carbide in equilibrium exists in certain Mn steels and results after long heating at a proper temperature regardless of whether the original metal is austenite or pearlite, but it is reached much more quickly when the starting material is austenite. Since white martensite is converted into coarse ferrite-carbide aggregate thousands of times faster than is austenite of the same composition, it is concluded that martensite cannot be an intermediate state in the austenite-pearlite reaction. Almost all of these reactions show a velocity pattern very nearly that of simple first-order chemical reactions. Certain reactions in steel begin at very high velocity and then slow up until it is barely possible to find any further change. The solution of carbide in austenite at temperatures above A_{cm} and the coalescence of carbide during tempering are 2 such reactions.

Bakshi, J. B. *See* abs. **1190, 1191.**

Balandin, A. A. *See* abs. **2092.**

139. BALANDIN, A. A., AND MARUSHKIN, M. N. [Formation of Olefins From Higher Paraffinic Hydrocarbons.] Compt. rend. acad. sci., U. R. S. S., vol. 40, 1943, pp. 226–228, 254–257; Chem. Abs., vol. 39, 1945, p. 271.

Solid paraffin, m. p. 50°, av. mol. wt. 554, was exposed, at 450°–550°, to the action of a dehydrogenating catalyst containing Cr (*see* Chem. Abs., vol. 37, 1943, p. 867). Tabulated analyses of the reaction products indicate that 4 different reactions occurred: (1) Dehydrogenation to form olefins without cracking; (2) formation of aromatic compounds without cracking, but with splitting off of H_2; (3) simple fission to form olefin and saturated hydrocarbons; (4) complete cracking to CH_4, C, and H_2. Extent of these reactions was as follows: At 450°, (1) 20%, (2) 2%, (3) 20%, (4) 4%; at 500°, (1) 36%, (3) 21%, (4) 5%. At 550° the total yield of olefin was larger yet, but cracking also increased as indicated by the liquid character of the condensate and by halving the latter's average molecular weight.

140. BALDESCHWIELER, E. L. Production of Synthetic Fatty Acids and Edible Fats and Deutsche Fettsäurewerke, Witten. British Coal Utilisation and Research Assoc., Monthly Bull. 10, No. 1, 1946, abs. 943; Chim. et ind., vol. 55, 1946, pp. 329–330; CIOS Rept. XXVI–50; TAC Rept. SnMC–7; TOM Rept. 21; Chem. Abs., vol. 40, 1946, p. 7662; PB 225.

Wax from various Fischer-Tropsch plants was oxidized in Al vessels, the oxidation reaction being exothermic. A certain proportion of the fatty acids produced was used in the manufacture of edible fats similar to oleomargarine.

141. BALY, E. C. C., PEPPER, W. P., AND VERNON, C. E. Adsorption of Hydrous Metallic Oxides by Kieselguhr. Trans. Faraday Soc., vol. 35, 1939, pp. 1165–1175; Chem. Abs., vol. 33, 1939, p. 9084.

Method is described for purifying kieselguhr: The clay and part of the organic matter were removed by repeated extraction with hot 4 *N* HCl, the last traces of organic matter being oxidized by heating the extracted kieselguhr at 600° in a current of air for 8 hr. The purified kieselguhr was remarkably constant in its properties. It showed a surface area of 2.869×10^6 cm.^{2} per 100 gm. It adsorbs the anhydrous oxides of Al, Th, Ni, and Co. The adsorbate in each case is activated (shown by enhancement of the ζ-potential) as the result of the formation of adsorption complexes. Al_2O_3 and ThO_2 form a single unimolecular layer; with Ni and Co oxides, 3 unimolecular layers are adsorbed together, forming 1 layer of crystal unit cells. When a mixture of Ni and Th oxides (1 ThO_2: 24 NiO) is adsorbed, 1 out of every 7 groups of 4 Ni and 4 O in each of the 3 layers of the crystal lattice is replaced by a molecule of ThO_2. This is also true when CoO is substituted for NiO. The effect of the adsorbed layer of metallic oxide was determined by measuring the surface potential by cataphoresis methods.

BANDEL, G. *See* abs. **3323.**

142. BANDTE, G. [Manufacture of Motor Fuel From Carbon Monoxide and Hydrogen.] Naturwissenschaften, vol. 14, 1926, pp. 732–735; Chem. Abs., vol. 20, 1926, p. 3225.

Review dealing with new processes for complete gasification and oleofication of coal. Synthesis of the Badische process (German Patents 293,787, 295,202, 295,203), transforms water gas by means of metal-oxide catalysts into oily and aqueous products. One example of this process is the MeOH synthesis (ZnO catalysts, temperature 200°–600°, 50–150 atm. pressure); iron carbonyl $Fe(CO)_5$, antiknock (motalin), is a byproduct. Franz Fischer prepares synthol by catalysis at 400°–450° up to 150 atm. pressure with an alkali-Fe mixture and obtains a motor fuel from the water-insoluble fraction. This synthesis is possible also (see abs. **1021**) without high pressure if a Fe–Zn oxide catalyst is used (or Co–Cr oxide) and yields higher CH_4 homologs at temperatures around 270°; metal carbides are intermediary products (at higher temperatures CH_4 is the only product formed). Yield of useful hydrocarbons is about 55%. The product gasol, is mainly C_2H_6, C_3H_8, and C_4H_{10}, little unsaturated, nonresinifying, clear, and not sensitive to light. Refining appears unnecessary for use as motor fuel, d_{15}= 0.6718, distillation 75.3% up to 100°, 96.4% up to 180°; the rest is kerosinelike, d_{20}=0.7804. Occasionally solid paraffin, melting at 61°, was formed. The importance of the absence of high-pressure installations for this synthesis is emphasized.

BANGERT, F. *See* abs. **977.**

BANGERT, W. M. *See* abs. **1729.**

143. BANGHAM, D. H., AND BENNETT, J. G. Chemistry of Gasification With Reference to Small Producers. Fuel, vol. 19, 1940, pp. 95–101; Chem. Abs., vol. 34, 1940, p. 7581.

Present knowledge of steam-C and water-gas reactions is summarized and applied to several theories of gasification. 34 refs.

BARCLAY, K. M. *See* abs. **3744.**

BARDGETT, H. *See* abs. **2731.**

BARDIN, J. S. *See* abs. **15a.**

144. BARKER, K. R., SEBASTIAN, J. J. S., SCHMIDT, L. D., AND SIMONS, H. P. Pressure Feeder for Powdered Coal or Other Finely Divided Solids. Ind. Eng. Chem., vol. 43, No. 5, 1951, pp. 1204–1209.

High cost of compression of the synthesis gas before purification and synthesis to liquid fuels favor gasification at elevated pressures of powdered coal with superheated steam and O_2. Thus, it was necessary to develop a method of continuous charging of finely powdered coal into a pressurized gas generator. Experimental work under pressures up to 150 p. s. i. proved that powdered coal can be conveyed pneumatically, in a dense phase (26 lb./cu. ft.), from a fluidized bed and discharged at constant rate. With other conditions equal, the discharge rate is solely a function of the pressure differential across a conveying line of given dimensions. The differential pressure across the fluidized coal bed is a direct function of the amount of coal fluidized and, to a lesser extent, of the fluidization rate, but it is not influenced by the operating pressure. For a given rate of fluidization, the amount of coal in the fluidized bed is conveniently gaged by the pressure drop between the bottom and the top of the column. Regardless of the operating pressure, the amount of coal conveyed per unit volume of gas, measured at the existing pressure, is virtually constant, but the weight of coal carried per unit weight of gas rapidly decreases with increasing operating pressures. Further work should be done to determine the effects of using various fluidizing gases, such as synthesis gas, air, CO_2, and steam at various pressures and temperatures up to 500° F.

144a. BARKLEY, L. W., CORRIGAN, T. E., WAINWRIGHT, H. W. AND SANDS, A. E. Catalytic Reverse Shift Reaction. A Kinetic Study. Ind. Eng. Chem., vol. 44, 1952, pp. 1,066–1,071.

It is possible to make adjustments in the H_2:CO ratio of synthesis gas using the reverse shift reaction $CO_2(g)+H_2(g)\rightleftharpoons CO(g)+H_2O(g)$ over a standard Fe–Cu shift catalyst at 1,000° F. The kinetics of the reaction were studied, a rate equation was obtained, and a probable mechanism for the reaction is postulated: (a) A molecule of CO_2 is adsorbed on a single active center; (b) the adsorbed CO_2 reacts with H_2

to form a molecule of adsorbed CO plus a molecule of H_2O in the gas phase; (c) the molecule of CO is desorbed; (d) step (b) controls the rate of the reaction. The results of the investigation show that this method of adjusting the synthesis gas composition is feasible, but that its use would depend upon the economic advantage of employing a large excess of superheated steam in the coal gasification step.

BARNES, D. K. *See* abs. **3273a.**

145. BARR, W. E. Glass-Blowing Art in Petroleum Research. Petrol. Refiner, vol. 26, No. 2, 1947, pp. 103–106.

This discussion, originating in the laboratory of the Gulf Research & Development Co., has been undertaken with the view of clarifying, in general terms, the operation of a glass-blowing shop and its relation to petroleum research. Its application to the fabrication of Fischer-Tropsch apparatus is shown.

146. BARRAL, J. [Total Gasification of Fuels by the Koppers Process.] Chim. et ind., vol. 57, 1947. pp. 441–443; Jour. Inst. Petrol., vol. 33, 1947, p. 308 A; Chem. Abs., vol. 41, 1947, p. 6385.

The Koppers process is designed to convert low-grade solid fuels into a synthesis gas suitable as feed to a Fischer-Tropsch plant. A simplified flow diagram of the process is given, as well as an analysis of the fuel and gas and of the costs involved. The process is applicable to fuels having an ash content as high as 20%. The plant and the operation at Schwarzheide are described. With this installation, it appears that Koppers prepared directly, by partial combustion and reduction of steam at high temperatures, not only gases for the synthesis of motor fuel and of MeOH but also heating gas, without using O_2 but only air mixed with steam.

147. ———. [Use of Oxygen in the Gasification of Fuels.] Génie civil, vol. 124, 1947, pp. 333–335; Chem. Abs., vol. 42, 1948, p. 9120.

Descriptions with diagrams are given of the Lurgi process utilizing O_2 and pressure for the direct gasification of lignite for city gas, and the Koppers process using O_2 and steam and atmospheric pressure to gasify a wide range of fuels. Synthesis gas is produced by the latter process by modifying the proportions of O_2 and steam.

148. BARRER, R. M. [Intercrystalline Sorption.] Jour. chim. phys., vol. 47, 1950, pp. 82–94; Chem. Abs., vol. 44, 1950, p. 6701.

Comprehensive summary is presented of work published on the sorption of gases in silicate and ionic crystals. The relative accessibilities of the interstitial adsorption sites increase in the order: beryl< silicate glasses<silica glass<harmotome<levynite< mordenite<gmelinite, chabazite, and a synthetic crystalline zeolite $BaAlSi_2O_6.2$–$3\ H_2O$. Special attention is given to a summary for analcite and for the last 6 of the zeolites listed above—of their sieve action in adsorption, their thermodynamics of adsorption, and their kinetics of adsorption.

———. *See* abs. **895.**

BARSS, W. M. *See* abs. **90.**

149. BARTHOLEMÉ, E., AND SACHSSE, H. [Catalytic Phenomena With Aerosols.] Ztschr. Elektrochem. vol. 53, 1949, pp. 326–331; Chem. Abs., vol. 44, 1950, p. 2355.

The synthesis-gas generator consists of a burner for coal gas to form $CO+H_2$ with Ni–MgO catalyst to convert residual CH_4 with steam into $CO+H_2$. Soot particles (diameters of frequency maximum about 2 microns) in the flame are nearly completely removed by reaction with steam catalyzed by Ni vapor originating from the catalyst bed or from Ni-salt solutions injected into the generator. Injection of solutions of alkali and alkaline-earth salts likewise suppresses the formation of soot. Since these catalysts are present as colloidal particles, they facilitate the reaction between soot and steam by preventing coagulation of the primary soot particles.

150. BARTLETT, E. P., HETHERINGTON, H. C., KVALNES, H. M., AND TREMEARNE, T. H. Compressibility Isotherms of Carbon Monoxide at Temperatures From 70°–200° and Pressures to 1,000 Atmospheres. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 1374–1381; Chem. Abs., vol. 24, 1930, p. 2925.

CO is shown to be similar to N_2 in physical properties at high pressure. In the low-pressure range, CO is slightly more compressible than N_2 and in the high-pressure range slightly less compressible. At about 375 atm. pressure, the deviation of CO from the law of the ideal gas is approximately constant (1.217) through 270°. At this pressure, the volume of a given mass of CO is a linear function of the absolute temperature.

BASAK, N. G. *See* abs. **1182, 1187, 1188, 1189, 1771a.**

151. BASHKIROV, A. N., AND CHERTKOV, I. B. [Oxidation of High-Molecular-Weight Synthetic Paraffin.] Bull. acad. sci. U. R. S. S., Sec. Tech. Sci., 1947, pp. 817–824.

Paraffin obtained by the Fischer-Tropsch reaction (molecular weight, about 1,000) was oxidized with air in the liquid phase to obtain fatty acids. Results of investigation of various factors are charted and tabulated. They show a maximum yield (55%) at 115°–120° with 0.2 permanganate and 8-hr. reaction time. The various acids separated and identified, ranged from CH_2O to the C_{20} acid, distribution being fairly uniform.

152. BASHKIROV, A. N., KRYUKOV, Y. B., AND KAGAN, Y. B. [Mechanism of the Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Compt. rend. acad, sci. U. R. S. S., vol. 67, 1949, pp. 1029–1031; Assoc. Tech. Services, Transl. RJ–21, March 1950; Chem. Abs., vol. 43, 1949, p. 9415.

The reaction observed on Fe catalysts, $2CO+H_2\rightarrow: CH_2+CO_2$ (I), in contrast to the reaction $CO+2H_2\rightarrow: CH_2+H_2O$ (II) occurring on Ni and Co, is interpreted as the sum of the primary reaction (II) and the subsequent secondary reaction $CO+H_2O\rightarrow CO_2+H_2$ (III). This point of view is corroborated by analyses of the gaseous products obtained, on precipitated Fe catalyst, with mixtures of $CO:H_2=1:1$ in the presence of added H_2O vapor, at 220°–250°, under atmospheric pressure, at space velocity~100 per hr. The balance, by reaction I, is expressed by $CO+mH_2\rightarrow 1/2xCH_2: +1/2xCO_2+(1-x)CO+(m-1/2x)H_2$, where x=mole fraction CO reacted, m=moles H_2 per mole CO. With reaction III occurring simultaneously with II, the balance is $CO+mH_2+pH_2O\rightarrow 1/2xCH_2: +(1/2x+z)CO_2+(p-z)H_2O+(1-x-z)CO+(m-1/2x+z)H_2$, where z=mole fraction CO reacted according to equation III, and p=moles H_2O per mole CO in the initial gas. The contraction k, in the first case, is $k=2a/(1+2a/(1+2a)$ (where $a=CO_2$ content in the product), in the second case, $k'=[2a/(1+2a)]-[3z/(1+2a)(1+m)]$. The difference $\Delta=k-k'$ is termed the contraction depression. Experimentally, Δ attains high values, up to 60–70%. H_2O added in amounts up to 20% of the reacting gas mixture is found to have reacted completely according to III, for example, with an initial mixture $CO:H_2:H_2O=44.5:44.5:11$, on an Fe–Cu–Zn–K_2CO_3–kieselguhr catalyst, at 240°, a=36.6%, Δ experimental=22.3%, calculated=21.4%. A gas mixture $CO:H_2:H_2O=33:34:33$, on an Fe–Cu–Mn–K_2CO_3–kieselguhr catalyst, at 230°, gave a negative contraction of −32.5%, a=29.7%, Δ=72.4%; the yield of hydrocarbons is depressed by H_2O but is restored when H_2O is eliminated. The ratio

of the rates of reactions III and I, on the 1st catalyst, at 240°, is 3.4, on the 2d catalyst, at 230°, it is 13.6. The primary reaction on Ni, Co, and Fe is reaction II, and CO_2 is a secondary product.

152a. ———. [Mechanism of the Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Doklady Akad. Nauk S. S. S. R., vol. 78, 1951, pp. 275–276; Chem. Abs., vol. 45, 1951, p. 7,861.

Assumption (abs. **152**) that the primary act in the Fischer-Tropsch synthesis is $CO+2H_2 \rightarrow CH_2+H_2O$, and not $2CO+H_2 \rightarrow CH_2+CO_2$, and that CO_2 is formed only as a result of the secondary reaction $CO+H_2O \rightarrow CO_2+H_2$, was confirmed directly by flow experiments in which a very short contact time prevented the secondary reaction from taking place to any appreciable extent in 1 single pass, and the H_2O formed in each pass was removed by condensation between passes in repeated recirculation. The experiments were conducted with a $CO:H_2=1:2$ mixture at 300° under 20 atm., at a gaseous space velocity of 150,000 l. per l. catalyst per hr., practically complete conversion was ensured by repeated recycling, with the fresh gas admitted at the rate of 44 l. per hr. Under these conditions, 290 l. gas gave, after several hr., liquid hydrocarbons 22.5 gm. per $m.^3$, gaseous hydrocarbons (C_3+C_4) 44.2, CH_4 100.0, H_2O 252.2 gm. per $m.^3$, and no CO_2. This result excludes the direct reaction $2CO+H_2 \rightarrow CH_2+CO_2$ and demonstrates that on Co, Ni, and Fe catalysts alike, CO_2 is formed only through a secondary reaction between CO and H_2.

153. Basore, C. A. Research and the Coal Industry. Mfrs. Record, vol. 100, No. 12, 1931, pp. 29–30.

Discusses briefly production of synthetic MeOH and homologous alcohols from CO and H_2. Possibilities are emphasized.

Batchelder, H. R. *See* abs. **1431, 2455, 3311.**

154. Batchelder, H. R., and Sternberg, J. C. Thermodynamic Study of Coal Gasification, Applicable to Suspension Gasification of Pulverized Coal. Ind. Eng. Chem., vol. 42, No. 5, 1950, pp. 877–882.

Thermodynamic studies of the continuous gasification of suspended powdered coal with superheated steam and O_2 have been undertaken. A method of calculation has been devised and will be presented in detail in a later paper. Through systematic application of the method of calculation, series of curves have been obtained for the probable ranges of operation in the gasification of a typical Rock Springs, Wyo., coal and a Union County, western Kentucky, coal with O_2 and superheated steam. These curves indicate certain trends that may be expected to hold even if the assumptions underlying the calculations are subsequently found to be not strictly valid, and at least 2 economic studies of much importance in reducing the cost of the gasification step are indicated.

155. Batchelder, H. R., Dressler, R. G., Tenney, R. F., Skinner, L. C., and Hirst, L. L. Role of Oxygen in the production of Synthetic Liquid Fuels From Coal. Bureau of Mines Rept. of Investigations 4775, 1951, 15 pp.

Steps in the production of O_2 by the liquefaction and fractionation of air are discussed. All commercial designs involve the following basic steps: (1) Supply of air into the plant apparatus; (2) refrigeration of the apparatus; (3) heat transfer between ingoing air and outgoing products; (4) removal of impurities from the air supply; (5) fractionation of liquefied air into components N_2 and O_2 and delivery of both as product gases; (6) removal of C_2H_2. Characteristics of 4 commercial-size plants in this country for the production of O_2 are presented, and the type and size of 4 other plants under construction are listed. The relationship of O_2-plant size to plant cost and to O_2 cost is discussed. Increases in O_2 cost are quite rapid as the size of the plant is reduced: \$7.00 for a 100-ton plant; \$4.80 for 300 tons; and \$3.50 for 1,000 tons. The function of O_2 in the production of synthetic liquid fuels is primarily the gasification of coal with O_2 to produce mixtures of $CO+H_2$, which then may be used directly, in the case of the Fischer-Tropsch synthesis, or as a source of H_2 for coal hydrogenation. Among the potential advantages of the substitution of O_2 for air in the coal-gasification step are the following: (1) Fuel economy; (2) increased capacity of equipment; (3) wider range of possible fuels; (4) greater adaptability to pressure operation; and (5) higher range of attainable temperatures. The amount of O_2 necessary to produce synthetic fuel by Fischer-Tropsch is about 690 lb. per bbl. of liquid fuel. This amount of O_2 at \$5.00 per ton would amount to \$1.72 per bbl. and at \$3.00 to \$1.03. Each change of \$1.00 per ton for O_2 will change the cost per bbl. of synthetic fuel from this process by about \$0.35. In the coal-hydrogenation process, a relatively large part of the required H_2 is to be recovered from the tail gases by low-temperature separation and produced by reforming the product CH_4 with steam. Thus, the O_2 requirement for coal gasification is only a fraction of that for Fischer-Tropsch. About 90 lb. of O_2 will be required to make 1 bbl. of synthetic fuel by coal hydrogenation. At \$5.00 per ton, the O_2 cost would amount to about \$0.22 per bbl. of oil and at \$3.00 to about \$0.14. Each change of \$1.00 per bbl. in O_2 cost will change the cost per bbl. by about \$0.04.

156. Batchelder, H. R., Tenney, R. F., Skinner, L. C., Dressler, R. G., and Hirst, L. L. Role of Oxygen in Production of Synthetic Liquid Fuels From Coal. Trans. Am. Soc. Mech. Eng., Process Ind. Div. Conf., Paper 50–PRI–7, 1950.

Use of O_2 in place of air or of external heating in the gasification of coal for the production of H_2 for coal hydrogenation or of $CO–H_2$ mixtures for Fischer-Tropsch synthesis may have 1 or more of the following advantages: (1) Fuel economy; (2) increased capacity of equipment; (3) wider range of possible fuels; (4) greater adaptability to pressure operation; and (5) a higher range of attainable temperature. As to the relation of O_2 cost to that of synthetic fuel, it is well established that for the Fischer-Tropsch process about 690 lb. O_2 are needed to make 1 bbl. of synthetic liquid fuel. This amount of O_2 at \$5.00 per ton would amount to \$1.72 per bbl. and at \$3.00 to \$1.03. Each change of \$1.00 per ton in the cost of O_2 will change the bbl. cost of synthetic fuel by about \$0.35. For comparison, similar calculations made on coal would show that a change of \$1.00 per ton in price would result in a change of about \$0.40 per bbl. The O_2 requirement for coal hydrogenation is only a fraction of that for the Fischer-Tropsch process due to the fact that in the former process a relatively large part of the required H_2 is to be recovered from the tail gases by low-temperature separation or by reforming the product CH_4 with steam. It is estimated that about 90 lb. O_2 will be required to make 1 bbl. of synthetic fuel by coal hydrogenation. At \$5.00 per ton the O_2 cost would be \$0.22 per bbl. of oil and at \$3.00 about \$0.14. Each change of \$1.00 per ton in the cost of O_2 will change the bbl. cost of oil by about \$0.04.

157. Bates, L. F. Curie Points. Proc. Phys. Soc. (London), vol. 43, 1931, I, pp. 87–95; Chem. Abs., vol. 25, 1931, p. 1715.

Description of the magnetic behavior of a ferromagnetic substance may require 3 temperatures, (1) the ferromagnetic critical point, at which the rate of change of the square of the intrinsic magnetic moment per unit volume with temperature is a maximum; (2) the ferromagnetic Curie point, at which the intrinsic magnetization may be considered zero; and (3) the paramagnetic Curie point, given by θ in the Curie-Weiss law

$\chi = C/(T-\theta)$. The significance of the ferromagnetic and paramagnetic Curie points is discussed in the light of the results of a number of investigators on Fe, Ni, Co, the ferrocobalts, magnetite, and manganese arsenide. The paramagnetic behavior of these substances can be accounted for by a slight extension of the idea that ferromagnetism is due to a magnetic particle consisting of a group of associated atoms.

BATUEV, M. I. *See* abs. **802, 802a, 802b.**

BATZ, W. *See* abs. **3649.**

158. BAUER, W. [Mersol.] Seifensieder-Ztg., vol. 68, 1941, pp. 524–526; Chem. Zentralb., 1942, I, p. 1571; Chem. Abs., vol. 37, 1943, p. 6370.

Mersol is a sulfonyl chloride of an alphatic hydrocarbon of the formula RSO_2Cl, which is made by the action of SO_2Cl or chlorosulfonic acid on paraffin gatsch. It smells strongly of HCl and SO_2 and contains about 17–20% of unsaponification residues of hydrocarbons. Its saponification number is approximately 390. The saponification to Mersolate is carried out by pouring Mersol into alkali that is not warmer than 60°. The concentration of the alkali plays an important role in the formation of the final product. If the Mersolate glue is thick, a large part of the salt precipitates. If it is thin, the unsaponified part can be removed as a thin oil a few days later. In practical operations a thick liquid is prepared first, and after the removal of the salt, it is diluted. Contrary to soap glue, the Mersolate glue always remains fluid. Numerical data are given for a saponification, and the processing of Mersolate to soaps and soap powders is described.

BAUGH, H. M. *See* abs. **2804.**

159. BAUKLOH, W. [Destruction of Cast Iron by Carbon Monoxide Gas Mixtures at High Temperature.] Metallwirtschaft, vol. 18, No. 3, 1939, pp. 57–59; Chem. Abs., vol. 33, 1939, p. 2864.

A cast Fe vessel was destroyed by a hot CO–gas mixture after 1½ yr. The gas penetrated along pores and graphite particles, leaving deposited C. At 550° the following reaction, catalyzed by Fe, takes place: $2CO \rightarrow C+CO_2$. Steel is not affected.

160. ———. [Destructive Action of Carbon Monoxide and of Gases Containing It.] Chem. Fabrik, vol. 13, 1940, pp. 101–104; Chem. Abs., vol. 34, 1940, p. 6559.

Decomposition of CO into C and CO_2 is accelerated by metals and by some oxides of metals. Deposition of C occurs within the structure of the metal, weakening or even destroying it. The temperature regions in which this action is appreciable are plotted for Fe, Fe_2O_3, Ni, NiO, Ni_2O_3, Cr, Mn, Co, and Co_3O_4. The effect is smallest for Cr and Mn.

161. BAUKLOH, W., AND EDWIN, B. [Effect of Temperature and Pressure on the Disintegration of CO.] Arch. Eisenhüttenw., vol. 16, 1942, pp. 197–200; Chem. Abs., vol. 37, 1943, p. 5903.

It is shown theoretically that the CO disintegration $2CO \rightleftharpoons C+CO_2$ is a special case of adsorption catalysis, which under normal conditions progresses only very slowly but assumes technical importance in the presence of suitable catalyzers such as Fe, Ni, or Co. The adsorption of CO molecules by the metallic surface is connected with an increase in their activity. The theory for the calculation of amount and concentration of disintegration and of disintegration velocity is developed, and the respective formulas are given. A maximum of disintegration exists, which depends on temperature; with increasing temperature the chemical reaction velocity increases, the adsorption possibility of Fe, and thus its capacity to influence the process catalytically, decreases. The C disintegration increases with increasing pressure (at constant temperature) to an asymptotic maximum value.

162. BAUKLOH, W., AND FOROUD, A. K. [Decarburization of Cast and Malleable Iron in Hydrogen and in Mixtures of Hydrogen and Water Vapor.] Arch. Eisenhüttenw., vol. 16, 1943, pp. 355–362; Chem. Abs., vol. 37, 1943, p. 6619.

Addition of about 2% by volume of H_2O vapor to H_2 decreases the time required for decarburization. Low contents of Mn have but little effect on H_2 decarburization; 80% ferromanganese could not be decarburized with pure H_2. The decarburization in gases with oxidizing components is determined mainly by the diffusion velocity of C in the Fe; in annealing in pure H_2 at higher temperatures, the purely chemical reaction between H_2 and C is the slower one and thus determines the decarburization velocity.

163. BAUKLOH, W., AND HELLBRÜGGE, J. [Effect of Some Substances on the Decomposition of Carbon Monoxide and Methane.] Arch. Eisenhüttenw., vol. 15, 1941, pp. 163–166; Brennstoff-Chem., vol. 23, 1942, p. 7; Chem. Abs., vol. 36, 1942, p. 7268.

In the presence of catalysts, such as metallic Fe, and at certain temperatures, CO disintegrates forming free C. The velocity of decomposition depends on the nature of the catalysts and is greatest at temperatures between 500°–600°. Fe_2O_3 mixed with SiO_2, CaO, Al_2O_3 or Cr_2O_3 caused a lowering in the catalytic decomposition of CO. Cr_2O_3 is the most effective. CH_4 has no critical-decomposition region; at higher temperatures, however, it is more unstable than CO and decomposes with greater velocity. Mixtures of Fe_2O_3 with $CdSO_4$, $HgCl_2$ or B_2O_3 are equally good.

164. BAUKLOH, W., AND HENKE, G. [Effect of Metals and Metal Oxides on the Decomposition of Carbon Monoxide and Its Technical Significance.] Metallwirtschaft, vol. 19, 1940, pp. 463–470; Chem. Abs., vol. 36, 1942, p. 317.

At 500°–600°, Fe oxides and cast Fe cause decomposition of CO accompanied by deposition of C according to $2CO=CO_2+C$, by strong loss of Fe from the oxides, and by destructive action on cast Fe. Fe-containing ceramic materials are also destroyed. The harmful effects occur only in the temperature and pressure range in which Fe, Fe oxides, C, CO, and CO_2 coexist. The maximum effect on decomposition of CO is shown at 500°. The oxides have virtually no effect on the decomposition; Fe metal itself is the catalytic agent. Decomposition occurs in the adsorption layer and is proportional to the amount of CO adsorbed. H_2O vapors retard CO decomposition by preventing formation of metallic-Fe surfaces. When CO is passed over Fe_2O_3 at 550°, the maximum rate of decomposition is reached at a streaming velocity of about 1 cm. or 2 cc./sec.; a marked maximum rate of decomposition at 1 atm. pressure occurs around 500°; below 400° and above 800°, virtually no deposition of C was observed. The maximums are eventually the same whether Fe, Fe_2O_3, FeO, or Fe_3O_4 is used; the initial activity is greater the lower the temperature at which reduction to Fe took place. Sintering is rapid above 600°. Addition of 1% $(CN)_2$, NH_3, or H_2S reduces the deposition of C by as much as 95%. Near 500° the oxides of Fe, Co, and Ni cause deposition of C; the maximum effects are at 500° for Fe_2O_3 and at 700° for NiO and CoO Mg, Ca and Ba oxides and Fe_2SiO_5 are weak catalysts; the oxides of Cu, Ag, Zn, Al, Ti, Si, V, Cr, Mo, W, U, Mn, C, SiC, and $FePO_4$ are inert. Of the free metals, only Fe, Co, and Ni are strongly active; Mg, Al, Ce alloys, and Ti, Cr, and Mn react with CO and cause deposition of C. Ag, Cu, Zn, Si, Mo, W, Pd, and Pt are inert. The destructive action of CO on various materials as firebricks can be prevented by avoiding the harmful-temperature and pressure limits, by removal of Fe, Co, and Ni, by conversion of the oxides of Fe, Co, and Ni to compounds such as the silicates or phosphates, which

are not reduced to the metal, or by protective glazes. Experiments on the destructive action show that it is due to very strong mechanical forces of crystallization of the deposited C.

165. BAUKLOH, W., AND HIEBER, G. [Influence of Various Metals and Metallic Oxides Upon Carbon Monoxide Decomposition.] Ztschr. anorg. Chem., vol. 226, 1936, pp. 321–332; Chem. Abs., vol. 30, 1936, p. 5139.

Reaction $2CO=CO_2+C$ was studied by passing CO gas over Fe_2O_3, Fe_3O_4, Fe, Co_3O_4, Co, Ni_2O_3, NiO, Ni, Cr_2O_3, Cr, Mn_3O_4, Mn, Al_2O_3, Al, ZnO, Zn, and Cu at 350° to 850°. The extent of the reaction is measured by weighing the C produced. The quantity of C separated rises to a maximum and then decreases, the maximum being at 550° for Fe and Fe oxides, at 650° for Co and Co oxides, at 450° for Ni oxides but at 750° for Ni, at 650° for Cr, and at 850° for Mn. No C separates with Mn_3O_4, Al_2O_3, Zn or ZnO, nor with CuO. It is concluded that not the oxides but metals produced from them cause the CO decomposition.

166. BAUKLOH, W., AND KNAPP, B. [Progress of the Reaction Between Hydrogen and Carbon in Iron.] Arch. Eisenhüttenw., vol. 12, 1939, pp. 405–411; Iron and Steel Inst. (London); Carnegie Schol. Mem., vol. 27, 1938, pp. 149–164; Chem. Abs., vol. 33, 1939, p. 3732.

Basic reaction $Fe_3C+2H_2\rightleftarrows 3Fe+CH_4$ is theoretically discussed. At first, independently of temperature and C content, H dissolves C present on the Fe surface in cementite or γ-solid solution. The Fe formed in this stage obstructs further direct access of H to C, so the reaction can continue only after diffusion of H. As long as diffusion is the slower process, the progress of the reaction is determined by the diffusion and, thus, depends on temperature, C content, and H_2 pressure. The CH_4 equilibrium is another factor. Beginning at 850° the migration velocity of C is higher than the reaction velocity of H and C, so the reaction becomes the slower process and is determined by the equilibrium conditions. Three types of marginal decarburization zones are distinguished: (1) Purely ferritic, up to 850°; (2) transition; and (3) hypereutectoid, above 850° within the 2-phase range of austentite + cementite. Experiments, which corroborate the theoretical deduction, are described in detail. 10 refs.

166a. BAUKLOH, W., CHATTERJEE, B., AND DAS, P. P. Decomposition of Carbon Monoxide in the Presence of Iron, Cobalt and Nickel as Catalysts. Trans. Indian Inst. Metals, vol. 4, 1950, pp. 271–278; Chem. Abs., vol. 46, 1952, p. 7415.

Maximum decomposition of CO by Fe, Co and Ni as catalysts takes place at 550°, 700°, and 350°, respectively. The speed of the decomposition reaction increases up to an hour and then decreases. The decrease in reaction speed is due to the formation of metal carbides which have a lower activity than the pure metal. Decomposition of the metal carbide by H_2 restores the activity of the metal. If the metal is heated in H_2 the metallic activity is lower, owing to a sintering process. C decreases this sintering.

167. BAUKLOH, W., SCHULTE, F., AND FRIEDERICHS, H. [Decarburizing Annealing of Plain and Alloyed Malleable Cast Iron in Carbon Monoxide–Carbon Dioxide Mixtures.] Arch. Eisenhüttenw., vol. 16, 1943, pp. 341–354; Chem. Abs., vol. 37, 1943, p. 6619.

Effects of wall thickness, duration of annealing, temperature, gas composition, and contents in the casting of Mn, Ni, Cr, V, Mo, and S on decarburization velocity were investigated on white-cast Fe in $CO–CO_2$ mixtures at 950°–1050°. The diffusion constant for C in Fe was determined. The decarburization velocity increases with increasing temperature and decreases with time approximately hyperbolically. The gasification of C takes place virtually only at the surface of the specimen. The velocity of diffusion of C from the interior to the edges determines the decarburization velocity. The quantity of C gasified in unit time does not increase proportionally with the original C content in hypoeutectoid white-cast Fe, as it does in steel. For short annealing times, the primary cementite inclusions seem to decrease the diffusion velocity and thus the decarburization velocity, but for longer annealing times this is hardly noticeable. Low contents of Mn, Ni, Cr, and V have hardly any effect on decarburization velocity. Mo at 1050° increases decarburization velocity. S seems to hinder decarburization. The highest decarburization velocity is obtained, for low-flow velocity, with a gas mixture of about 28% of CO_2 and 72% CO. CO_2 contents above 28% at 1050° cause scaling of the Fe and decrease of decarburization velocity. The results obtained with pure $CO–CO_2$ mixtures can be applied also to the tempering in N_2-containing $CO–CO_2$ mixtures.

168. BAUR, E., AND GLAESSNER, A. [Equilibrium Between Iron Oxides and Carbon Monoxide and Dioxide.] Ztschr. physik. Chem., vol. 43, 1903, pp. 354–368; Jour. Chem. Soc., vol. 84, 1903, (2) p. 423.

Equilibria, which may be established by passing CO or CO_2 over Fe, are represented by the equations: $Fe+CO=FeO+C$; $FeO+CO=Fe+CO_2$; and $C+CO_2=2CO$. The reaction $Fe_3O_4+CO=3FeO+CO_2$ is also one of equilibrium. The equilibrium relationships were determined by heating the solid in an atmosphere of CO or CO_2 in a boat contained in a porcelain tube connected with a gas burette. After equilibrium had been established the gas was drawn off and analyzed. The solids examined were ferrosoferric oxide and ferrous oxide and ferrous oxide and Fe. The equilibrium curve in the 1st case exhibits a maximum at 490°, when the gas phase contains 47% CO. This indicates the temperature at which ferrosoferric oxide is reduced most difficultly. In the 2d case, the curve shows a minimum point at 680° when 59% CO is present; this corresponds to the temperature at which ferrous oxide is most easily reduced to Fe. The results are plotted along with Boudouard's values for the equilibrium between C and CO_2, and from points where the curves cut, it is deduced that at atmospheric pressure, CO, CO_2, ferrous oxide, ferrosoferric oxide, and C can exist side by side at 647°, and the 3 solids are in equilibrium at 685°. Above 685°, C and Fe can exist together, and below 647°, C and ferrosoferric oxide. When applied to the blast furnace, the results show that the reductions of ferrosoferric oxide and ferrous oxide must take place at different zones, which are characterized by different contents of CO. Fe in contact with a gas rich in CO at temperatures below 647° is oxidized and C is deposited, but no C can be deposited from the gas at a temperature higher than 680°. The heat of formation of ferrosoferric oxide at 490° under constant pressure is calculated to be 267,380 cal., and that of ferrous oxide at 680° is 67,350 cal.

169. BAUSCHINGER, C. [Utilization in the Soap Industry of Carboxylic Acids Made from Paraffin.] Fette u. Seifen, vol. 45, 1938, pp. 629–630; Chem. Abs., vol. 33, 1939, p. 9695.

Synthetic fatty acids for use in the soap industry should contain the least possible amounts of hydroxy acids, lactones, lactides, keto acids, dicarboxylic acids, and unsaponifiable matter. The insufficient plasticity of soaps from synthetic fatty acids is ascribed to absence of unsaturated acids. Peculiar phenomena observed in the soap kettle in preparing soap from synthetic fatty acids are discussed briefly.

BAYAN, S. *See* abs. **2553.**

170. BAYER, O. [Newer Large-Scale Technical Developments in the Chemistry of the Aliphatic Com-

pounds.] Angew. Chem., vol. 54, 1941, pp. 353–356; Chem. Abs., vol. 35, 1941, p. 6923.

Technical production of aliphatic compounds is a much later development than that of aromatic compounds but has already surpassed the latter and promises to surpass the production of inorganic chemicals. Unlike the countries with large supplies of petroleum and carbohydrates, Germany is forced to use coal, CO, and H_2 as raw materials. Among several most important developments mentioned are paraffin oxidation to fatty acids and MeOH and higher alcohols.

171. BEAMER, C. M. Production of Synthetic Alcohol from Ethylene. Chem. Eng. Progress, vol. 43, 1947, pp. 92–96.

Alcohol manufacture from grain, molasses, and C_2H_4 is briefly reviewed. The properties are charted and the prewar and war uses of industrial EtOH are shown. 1 bu. of grain will yield about 2.5 gal. of alcohol. About 2.5 gal. of molasses is required to produce 1 gal. of 190 proof alcohol, and theoretically about 3.9 lb. of C_2H_4 will make 1 gal. of alcohol. The price of alcohol at present depends largely upon supply and demand and on the fluctuation in the cost of grain and molasses. Expansion in the synthesis method will tend to relieve the situation. Other possible sources of alcohol within the next few years are: Waste sulfite liquors, sawdust, and hydrocarbon synthesis. In the next 5–10 years, the production of industrial EtOH by the Fischer–Tropsch synthesis process may have to be reckoned with and will become an important producer.

BEAN, E. H. *See* abs. **1442.**

BEATI, E. *See* abs. **2401.**

172. BECK, R. A. Evaluation of Fluid Catalyst—Development of Laboratory-Scale Units. Ind. Eng. Chem., vol. 41, No. 6, 1949, pp. 1242–1243.

Two types of laboratory scale units for evaluation of fluidized catalyst have been developed. A mechanically stirred unit with helically finned rotor makes it possible to simulate fluidization independently of the gas velocity below 1 ft. per sec. A steel-stirred reactor is used in research where great flexibility in regard to reactant flow rates is desired. A baffled nonstirred unit is less subject to mechanical difficulties than the stirred type. Both types have proved to be effective laboratory units for the testing of small batches of experimental catalysts with moderate amounts of charge gases. For example, the use of a superficial linear velocity of 1 ft. per sec. in the 0.75-in. baffled reactor at 400 p. s. i. g. and 600° F., requires approximately 140 standard cu. ft. per hr. of total charge gas as contrasted with over 1,000 required for the open 2-in. reactor originally cited. With the stirred reactor the feed rate can be reduced to any desired level without decreasing the effectiveness of catalyst fluidization.

173. BECKER, M. L. Carburizing and Graphitizing Reactions Between Iron-Carbon Alloys, Carbon Monoxide and Carbon Dioxide. Jour. Iron Steel Inst. (London), Adv. Copy 3, 1930, pp. 1–25; Chem. Abs., vol. 24, 1930, p. 3203.

Description of work carried out in an investigation to determine the quantitative influence of the temperature and C content of solid solutions upon the composition of a gas consisting of CO and CO_2.

BECKETT, C. W. *See* abs. **654a.**

174. BECKLEY, J. S. Chemicals From Coal—New Developments. Coal-Heat, vol. 47, No. 1, 1945, pp. 26–27, 30; Fuel Abs., No. 2079.

Coal is utilized as a raw material for the chemical industry in 3 ways: By carbonization, yielding valuable byproducts; directly as a reactant in a chemical reaction, yielding a finished product for commerce or an intermediate product, other than water gas, which serves as a raw material for subsequent processing; using the coke to make water gas, a starting material for many important synthesis. The production of some of these chemicals is discussed, in particular the synthesis of MeOH and the production of nylon.

BEEBE, R. A. *See* abs. **1771.**

175. BEEBE, R. A., AND STEVENS, N. P. Heats of Adsorption of Gases on Iron-Synthetic Ammonia Catalysts at Low Temperatures. Jour. Am. Chem. Soc., vol. 62, 1940, pp. 2134–2140; Chem. Abs., vol. 34, 1940, p. 6515.

Data are given for the adsorption isotherms of the following gases on doubly promoted Fe catalyst containing 1.59% K_2O and 1.3% Al_2O_3, O_2, CO, N_2, A, and H_2 at −183°, CO_2 and CO at −78°, and CO at 0°. The heats of adsorption are given for these gases on this catalyst and on an unpromoted pure Fe catalyst containing 0.15% Al_2O_3 impurity. These measurements indicate that the adsorption of N and of A at −183° is exclusively of the van der Waals type; that the adsorption of H at −183° and of CO at −183°, −78° and 0° is in part chemisorption; and that CO_2 is chemisorbed on the alkali-promoted catalyst at −78°, although the adsorption of this gas on the pure catalyst is exclusively van der Waal's. These conclusions are in general agreement with those of Emmett and Brunauer (see abs. **388**) on an analysis of the low-temperature isotherms. The heat evolved in the irreversible adsorption of O at −183° approaches, in order of magnitude, that of Fe oxide formation. The form of the time-temperature curves with O at −183° indicates that the adsorption process involved is complex.

BEEBY, G. H. *See* abs. **327.**

176. BEECK, O. Catalysis—a Challenge to the Physicist. Rev. Modern Phys., vol. 17, 1945, pp. 61–71; Chem. Abs., vol. 40, 1946, p. 4593.

A review.

177. ———. Surface Catalysis. Rev. Modern Phys., vol. 20, 1948, pp. 127–130; Chem. Abs., vol. 42, 1948, p. 4435.

Review of work of Beeck and associates. The discovery of the effect of traces of H_2O and H_2S in lowering the decomposition temperature of hydrocarbons is discussed. The molecular-ray experiments also seem to indicate the decomposition of CH_4 into CH_3 and H and C_2H_6 into 2 CH radicals. There is evidence that the CH radical is formed in the decomposition of acetylene. The adsorption step is the crucial step in surface catalysis, and the reaction of ethylene and H_2 is cited as an example. Finally the tracer technique is discussed in connection with the isomerization of butane to isobutane.

177a. ———. Catalysis and the Adsorption of Hydrogen on Metal Catalysts. Advances in Catalysis, Academic Press, Inc., New York, vol. 2, 1950, pp. 151–195.

Review includes a discussion on adsorption, surface of metal catalysts, H_2 adsorption isobars and the effect of sintering, heat of adsorption of H_2 on Ni, Fe, W, metal films partially covered with other adsorbed gases, sintered films and the criterion for mobility as well as Frankenburg's experiments and the experiments of Roberts. The following conclusions are reached: The adsorption (chemisorption) of H_2 on clean metal surfaces is almost always accompanied by absorption of H_2 into the interior of the structure. This absorption is a slow activated process and has in the past been mistaken for activated adsorption of H_2 on the surface. The heat of absorption of H_2 is considerably lower than the heat of chemisorption. The heats of

chemisorption of H_2 on Ni and Fe are nearly identical and decrease from about 30,000 cal. for the sparsely covered surface to about 18,000 cal. for the completely covered surface. The heat of chemisorption on W decreases from 45,000 cal. to about 13,000 cal. as a function of surface coverage. The lower values of Frankenburg for higher surface coverage can be satisfactorily explained on the basis of surface impurities on Frankenburg's W powders. The heat of adsorption of H_2 on metals has been found to be constant over wide temperature ranges (for Ni by Beeck and coworkers from —183° to 23° C., by Frankenburg on W for temperatures up to over 500°). The activation energy for the chemisorption of H_2 on all metals studied is extremely low. Chemisorbed H_2 atoms on Ni are mobile. They are able to migrate from one crystallographic site to another site even at —183° C. On Fe, H_2 atoms are mobile at room temperature but are not mobile at —183° C. The decrease of heat of adsorption as a function of surface coverage can be explained satisfactorily by interaction of the adsorbed atoms with each other. While the surface of clean metal films appears to be homogeneous with regard to heat of adsorption and surface coverage (the latter within the limits of size of different crystallographic sites), the rate of hydrogenation of ethylene is markedly dependent on the crystal parameter. On Ni, chemisorption of H_2 is still taking place at 20° K. The true extent of metal surfaces cannot be measured by the B. E. T. method using N, since N is chemisorbed at —196° C. The H_2 adsorption at this temperature measures the surface more accurately and is in close agreement with the chemisorption of CO at both liquid N and room temperature and with the van der Waal's adsorption of krypton. 18 references are given.

———. *See* abs. **3712.**

178. BEECK, O., AND WHEELER, A. Activated Adsorption of Nitrogen on Iron at 23° and 100°, and Ammonia Synthesis. Jour. Chem. Phys., vol. 7, 1939, pp. 631–632; Chem. Abs., vol. 33, 1939, p. 8363.

178a. BEECK, O., COLE, W. A., AND WHEELER, A. Determination of Heats of Adsorption Using Metal Films. Disc., Faraday Soc., 1950, No. 8, pp. 314–321; Chem. Abs., vol. 45, 1951, p. 9990.

A calorimeter is described for heats of adsorption of H_2 as a function of fraction of surface covered for Ni and Fe films at room and liquid-air temperatures. A criterion for mobility of adsorbed layers is presented.

BEECK, O., GIVENS, J. W., AND RITCHIE, A. W. Adsorption of Hydrogen on Nickel Catalysts. II. Sorption Isobars from 20° K. to Room Temperature. *See* abs. **180.**

179. BEECK, O., RITCHIE, A. W., AND WHEELER, A. Adsorption of Hydrogen on Nickel Catalysts. I. Effect of Sintering. Jour. Colloid Sci., vol. 3, 1948, pp. 505–510; Chem. Abs., vol 43, 1949, p. 2079.

High-vacuum-evaporated Ni films prepared at 23° by the method previously described adsorb H_2 virtually instantaneously. There is little difference in the amount adsorbed at —196° and at room temperature. This is in marked contrast to the results obtained with Ni catalysts prepared from NiO by H_2 reduction, which sorb H_2 slowly at room temperature in amounts 2–4 times the amounts adsorbed at —196°. If the vacuum-evaporated films are sintered at 100°–400°, slow sorption of H_2 is observed. The ratio of slowly sorbed H_2 to rapidly adsorbed H_2 increases with increasing sintering temperature. The so-called "activated adsorption" of H_2 on Ni is not adsorption on the metal surface but is slow sorption of H_2 into the interior of the metal structure. The adsorptive capacity of Ni indicated by chemisorption of CO or physical adsorption of Kr corresponds to the capacity for rapid H_2 sorption, chemisorption, and for catalytic reactions such as C_2H_4 hydrogenation but does not correspond to the capacity for slow sorption.

180. BEECK, O., GIVENS, J. W., AND RITCHIE, A. W. Adsorption of Hydrogen on Nickel Catalysts. II. Sorption Isobars From 20° K. to Room Temperature. Jour. Colloid Sci., vol. 5, 1950, pp. 141–147; Chem. Abs., vol. 44, 1950, p. 6228.

Sorption isobars were determined for H_2 at 0.1 mm. Hg pressure on evaporated Ni films, over the temperature range —253°–25°. Slow activated sorption, interpreted as absorption of H_2 into the interior of the metal structure, was observed in agreement with previous results. The process is exothermic and, after initiation by raising the temperature to approximately —150°, will continue at much lower temperatures.

181. BEECK, O., SMITH, A. E., AND WHEELER, A. Catalytic Activity, Crystal Structure and Adsorptive Properties of Evaporated Metal Films. Proc. Roy. Soc. (London), vol. 177, 1940, A, pp. 62–90; Chem. Abs., vol. 35, 1941, p. 2061.

Metal films of high reproducible catalytic activity were obtained by condensation of their vapors on glass at any desired temperature. The catalytic activity was measured by the hydrogenation of C_2H_4. The crystal structure of these films was investigated by electron diffraction. By controlling the pressure of an inert gas, N_2, A, and others, during evaporation of the metals, unoriented and oriented films could be produced at will, and their catalytic activities were compared. Completely oriented Ni films were obtained with an inert-gas pressure of 1 mm., the (110) plane, the least dense of the planes, lying parallel to the backing and the 2 remaining axes showing random distribution. Fe films were oriented with their (111) plane parallel to the backing, again the least dense plane thus oriented. Low-pressure adsorption of H_2 at room temperature and of CO at liquid-air temperature revealed that the oriented gas-evaporated Ni films have 2 times the available surface/gm. of randomly oriented high-vacuum films, but 10 times the activity. The oriented films have therefore 5 times the activity of unoriented films. Oriented films of an available surface equal to unoriented but of 5 times the activity could also be obtained in high vacuum by evaporation onto oriented films previously produced by evaporation in an inert gas. The activity/unit weight of the films was constant; this indicates ready accessibility to the interior of the film by the reacting gases. Adsorption of H_2 was found to be immeasurably fast in all cases. Adsorption isotherms on Ni films were obtained for C_2H_4, CO, N_2, H_2, and O_2; and the effect of catalyst poisoning by CO and O_2, as well as the effect of sintering, was studied. Loss of activity, decrease of H_2 adsorption, and amount of poison were found to be proportional. The most extensive studies were made on Ni films, but films of Fe, Co, Pd, Pt, and Cu were also investigated, and with the exception of Cu similar results were obtained. The enhanced activity of oriented films appears to be associated with the larger distances in the (110) plane of Ni or the (111) plane of Fe. The bearing of the results on the definition of active centers and on the general problem of adsorption is discussed.

BEERY, D. W. *See* abs **15a.**

BÉGUI, Z. E. *See* abs. **550.**

BELETSKIĬ, M. S. *See* abs. **3371.**

182. BEL'KEVICH, P. I. [Sorption of Hydrogen by Metals of the Platinum Group. I. Character of the Sorption Isotherms of the Iridium–Hydrogen, Rhodium–Hydrogen, Osmium–Hydrogen and Ruthenium–

Hydrogen Systems.] Jour. Gen. Chem. (U. S. S. R.), vol. 9, 1939, pp. 944–954; Chem. Abs., vol. 33, 1939, p. 8468.

Sorption isotherms for 20° and 50° for the Ir–H_2, Rh–H_2, and Os–H_2 systems are analogous to that of the Pt–H_2 system. The metals were used in the finely dispersed form (Ir, Os, Rh, and Ru blacks), prepared by the reduction of their chloride salts with hydrazine–HCl in weakly alkaline solution. By strict control of thermal conditions of treatment of blacks (temperature of sorption 20° and 50° and that of desorption for Ir 120° and for Rh and Os 150°), reproducible isotherms can be obtained. An increase in temperature of sorption and desorption causes decrease in the sorptive power of the blacks. Data are tabulated and plotted. 44 references covering the period from 1866–1926.

183. Bell, E. A. Synthetic fuel and Chemical Plants in France. Petrol. Times, vol. 46, 1942, p. 180; Chem. Abs., vol. 36, 1942, p. 4312.

Review.

184. Bell, H. S. Costs of Oil From Coal and Shale. Am. Petrol. Refining, chap. 36, rev. ed.; Nat. Petrol. News, vol. 37, No. 10, 1945, pp. R 205–206; Chem. Abs., vol. 39, 1945, p. 2190.

Three methods for the production of oil as a substitute for petroleum are compared from an economic standpoint: (1) Bergius coal hydrogenation; (2) Fischer-Tropsch gas synthesis; and (3) recovery of oil from shale. (1) Yield about 100 gal. of gasoline/long ton of coal, capital cost $0.90, operating cost $0.17–$0.22/gal. (2) 36 gal. of synthetic crude/ton of coke, capital cost $1.18, operating costs are believed to be comparable. (3) average of 43 gal. of gasoline/ton of shale, with a recovery of oil from the shale varying from 75–90%, capital cost $0.39, operating cost $3.20/bbl. of crude oil, assuming 60% yield of gasoline, $0.14–$0.15/gal. It is concluded that none of the methods is commercially attractive and none, with the possible exception of extraction of rich shale, could compete with petroleum. Adaptation of the second method to natural gas probably will precede commercial hydrogenation of coal in the United States.

185. Bell, I. L. Chemistry of the Blast Furnace. Jour. Chem. Soc., vol. 22, 1869, pp. 203–254.

Catalyzing effect of Ni, Co, and Fe upon the velocity of the reaction $2CO=CO_2+C$ is investigated. Higher temperatures of 500°–800° were unfavorable for the decomposition of CO to C in the case of metallic Fe. At the temperatures investigated, the oxides were as effective as the metals themselves in determining the decomposition of CO.

186. Bellamy, L. J., and Nillson, K. T. German Chemical Industries—Synthetic Fatty Acids. Chem. and Met. Eng., vol. 52, No. 12, 1945, pp. 178, 182, 184. PB Rept. 6, 1945, 3 pp.; Chim. et ind., vol. 56, 1946, p. 18; Chem. Abs., vol. 40, 1946, p. 7662.

Synthetic fatty acids have been produced on a large scale in Germany at a number of plants. They have all used a similar method; that of oxidation of paraffins (normally from the Tief Temperatur-Hydrierung process on lignite) by air, using the same method as that worked by the Pasco Co. of America, which holds licenses from I. G. The Tief Temperatur-Hydrierung process is a new single-step hydrogenation process in which brown-coal tar is treated in the liquid phase with a catalyst of Florida clay + Cr and Mo oxides, yielding a low-quality gasoline, 50-cetane number diesel oil, and wax. The first fraction consisting of C_1–C_4 acids is recovered, fractionated, and used for various purposes. The C_5–C_{10} acids, which are insoluble in H_2O, are obtained as the first fraction of vacuum distillation and separated into the C_5–C_7, C_7–C_9 and C_9–C_{11} fractions. The first 2 are hydrogenated to the corresponding alcohols, the C_7–C_9 fraction finds application in fire extinguishers of the foamite type, and the C_9–C_{11} fraction is used in the flotation of minerals. The C_{10}–C_{18} fraction, isolated by vacuum distillation at 3 mm. pressure, is used directly for the production of soaps and edible fats, the latter of which appear to be of excellent quality. The C_{18}–C_{24} acids are used in greases as Na, Ca, and Li soaps and in combination with triethanolamine as softening agents for leather. The Zn, Mg, and Ca soaps have also been used as lubricants for plastic molding. The pitch residue is used in lacquer production and as a molding agent for foundry cores and in the manufacture of vaseline.

Beltz, J. C. *See* abs. **927.**

Bemmann, R. *See* abs. **205, 206.**

187. Bénard, J. [Role of Diffusion in Surface Oxidation of Iron.] Métaux, corrosion, usure, vol. 18, No. 2, 1943, pp. 20–29; Chem. Abs., vol. 44, 1950, p. 9781.

Rate of oxidation of pure Fe at 250°–900° was investigated. The chemical nature of the films formed and the mechanism of the diffusion of metal through the oxide film are discussed.

188. ———. [Variation of the Composition of Ferrous Oxide.] Bull. soc. chim. France, 1949, D, pp. 109–116; Chem. Abs., vol. 43, 1949, p. 6901.

Composition of FeO corresponds exactly to the theoretical for FeO (77.7% Fe) above 750°. Fe_3O_4 attains 75.9% Fe at 1,100° and does not change with increase in temperature. At 580°, an equilibrium exists between the 3 phases FeO, Fe, and Fe_3O_4 corresponding to 76.9% Fe. The apparatus is described, together with experimental technique. Reviews literature.

———. *See* abs. **478, 1279, 2275.**

189. Bénard, J., and Coquelle, O. [Oxidation of Iron at High Temperatures Determined Metallographically.] Rev. mét., vol. 43, 1946, pp. 113–124; Chem. Abs., vol. 41, 1947, p. 3418.

Sheets of Armco Fe 3 mm. thick were heated in an open electric-resistance furnace provided with a free circulation of air for 5 hr. at temperatures from 570°, at which no perceptible oxide is formed, to 1,050°, cooled, sectioned, and examined under a microscope for the nature and distribution of scale constituents. These experiments were supplemented by isothermal heating at 700°–960° for up to 20 hr. Oxidic film produced on heating Fe is a result of Fe diffusion outward and of O_2 diffusion inward into the metal. These rates of diffusion, which vary with temperature, specify the character of the scale. Structure of scale produced at or above 910°, the A_3 point of the steel, is greatly different from the scale formed under this temperature, because there is a crystallographic continuity between α–Fe and scale, that is absent in case of γ–Fe. The formation of the scale as a whole follows a parabolic function. Individual constituents of it form according to other curves, Fe_2O_3 and Fe_3O_4 following a straight line and FeO a parabolic function. The influence of temperature on total scaling up to 900° can be presented by the well-known exponential equation.

190. Bénard, J., and Moreau, J. [Kinetic Study of Reduction of Peroxide With Hydrogen.] Compt. rend., vol. 231, 1950, pp. 904–906.

At 500° the curve shows an induction period of 20 min., a period of accelerating reaction 10 min., a period of steady reaction rate 23 min., and a period of decelerating reaction. At 450° the induction period is >2.5 hr., at 550° the induction period is suppressed; at 700°

the period of accelerating reaction and period of steady reaction rate are suppressed.

191. BENDER, R. J. German Wartime Diesel Fuels Were Blends of Natural and Synthetic Products. Nat. Petrol. News, Tech. Sec., vol. 38, No. 6, 1946, pp. R–104, R–106; BIOS Miscell. Rept. 71, 30 pp.; U. S. Naval Tech. Mission in Europe, Rept. 187–45, 1945, 42 pp.; TOM Reel 200; PB 1,675 and 2,529.

Principal sources of German diesel fuel were the following: (a) Natural-petroleum distillates; (b) synthetic distillate known as Kogasin II, the high-boiling fractions distilled from Fischer-Tropsch low-pressure, low-temperature catalytic process, having a high cetane No., 90–100, but as compared with petroleum diesel fuel of 47-cetane rating, not suitable when used alone because of its higher consumption and the increase of 25% in the exhaust-gas temperature. It was, therefore, used mainly to upgrade the ignitibility of other fuels such as petroleum–gas oil or coal or lignite-tar oil, in which case the mixture is purified by selective extraction; (c) Kogasin I, the lighter fraction distilled in the Fischer–Tropsch process boiling below 430° F. with a cetane number of 35–60; (d) distillates from the low-temperature carbonization of coal and lignite; (e) distillates from the hydrogenation process containing 38–49% aromatics and unsaturates good for blending with Kogasin II; (f) shale oil.

192. BENEDICKS, C. [Dissertation.] Upsala, 1904, p. 215.

A physical and physicochemical study of carburized steel.

193. BENEDICKS, C., AND LÖFQUIST, H. [Solubility of Oxygen in Iron of Ferrous Oxide (Oxoferrite, Wüstite).] Ztschr, anorg. Chem., vol. 171, 1928, pp. 231–238; Chem. Abs., vol. 22, 1928, p. 3612.

Diagram given for the system Fe–O (abs. **3053**) contradicts the fact claimed by Schenck and Dingman (abs. **3052**) that the solubility of O is as high as 2.8% (oxoferrite). It is only 0.05%. It has been suggested that traces of Al_2O_3 picked up from the container by Fe_2O_3 would explain the discrepancies. The solubility of O in a pure Fe–O system is so low that it is difficult to admit that this solubility is increased by the presence of foreign matter, MgO for instance.

BENEDICT, W. S. *See* abs. **2321, 2322.**

194. BENESCH, F. [Stability of Complex Iron-Manganese Carbides.] Anyagvizsgálók Közlönye, vol. 19, 1941, pp. 1–30; Chem. Zentralb, 1942, I, pp. 1180–1181; Chem. Abs., vol. 37, 1943, p. 2322.

Investigates the stability of complex Fe–Mn carbides in the austenitic 12 and 20% Mn steels (1.1% C). Annealed for a long time at 650°–850°, the free Fe–Mn carbides lose their homogeneity and change their structures similar to the hypereutectoid-carbon steels at corresponding temperatures. In the cases investigated, the hardness and, therefore, the number of precipitated double carbides are a direct function of time and temperature. In the range of carbide precipitation hardness increases steadily; at 650°–850° the double carbides decompose, and in spite of water quenching, hardness decreases and ductility increases. The magnetic properties missing in austenitic steels are also absent in the pearlitelike arrangements of the Fe–Mn carbides despite the fact that pearlite of straight carbon steel is magnetic.

195. BENKE, R. [Transfer of Heat From Widely Spaced Tubes to a Transverse Current of Air.] Arch. Wärmewirt., vol. 19, 1938, pp. 287–291.

Question of whether a staggered or a line arrangement of tubes in a system gives better conditions for heat transfer has been discussed often but not definitely answered. Experimental investigations are described from which it is concluded that within the range examined the heat transfer is independent of the arrangement and spacing of the tubes in the system.

BENNETT, H. A. *See* abs. **2804.**

196. BENNETT, J. G. Coal and the Chemical Industry. Jour. Inst. Fuel Wartime Bull., vol. 17, 1944, pp. 185–192.

First J. Arthur Reavell lecture. Discusses existing processes for coal utilization—carbonization, fractionation by solvent extraction, and synthesis of hydrocarbons. The principal defect of the latter process is its wastefulness; only about 30–40% of the coal substance is recovered in the products.

———. *See* abs. **143.**

196a. BENNETT, M. T. [Industrial Significance of Natural Gas.] Metano, vol. 5, No. 2, 1951, pp. 17–28; Chem. Abs., vol. 45, 1951, p. 4,427.

Review is given describing uses of natural gas followed by a discussion of methods of production of synthesis gas from CH_4 with diagram, description and composition of the gas for production of NH_3.

BENNIE, R. S. *See* abs. **56.**

197. BENOIT, J. [Ten Years Progress in the Chemical Industries. III. Synthetic Organic Chemicals.] Ind. chim., vol. 36, No. 11, 1949, pp. 237–249.

Summary of progress in the fields of synthetic-coal chemistry as exemplified by the Fischer-Tropsch and the Bergius processes, benzene, and acetylene; petroleum chemistry—methane, ethylene, butylene, propylene; oxygenated products—methanol, ethanol, formaldehyde, acetaldehyde, acetone, acetic anhydride, ethylene oxide, and phenols.

198. BENOIT, R. [Thermomagnetic Study of Boroferrites.] Compt. rend., vol. 231, 1950, pp. 1216–1218; Chem. Abs., vol. 45, 1951, p. 2355.

Magnetic susceptibilities were determined in the range 0°–1,100° for boroferrites, $B_2O_3 \cdot Fe_2O_3 \cdot xMO$, in which M=Mg, Cu, Co, Ni, and Fe; $x=2$ in the Mg compound and 4 in the others. The Curie constants were, respectively, 8.66, 10.5, 19.8, 16.9, and 20.6. (I) decomposed above 1,100°. Cu (II) changed to Cu (I) at 890°.

BENSMANN, C. H. N. *See* abs. **3393.**

BENSON, H. E. *See* abs. **646, 647, 648.**

BENTON, A. F. *See* abs. **3681.**

199. BENTON, A. F., AND WHITE, T. A. Adsorption of Hydrogen by Nickel at Low Temperatures. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 2325–2336; Chem. Abs., vol. 24, 1930, p. 3937.

Adsorption of H_2 on Ni was studied at pressures 0–1 atm. and at 11 temperatures between —210° and 110°. At a given pressure the adsorption is relatively large at the lowest temperature, decreasing to a minimum at between —200° and —175°, then rising to a maximum in the neighborhood of —100°, and finally decreasing again at higher temperatures. At 600 mm. the adsorption is constant between —100° and 0°, presumably indicating the formation of a monomolecular layer of adsorbed gas in this region. All adsorption values are easily reversible with respect to pressure. However, on cooling to about —190° a sample previously brought to equilibrium at 0°, the adsorption does not decrease to the value obtained isothermally at —190° but reaches a new reversible equilibrium at which larger quantities of gas are adsorbed than at 0°. For some unexplained reason, at —191° and —183° the adsorption increases in a discontinuous manner with increase of pressure.

200. ———. Sorption of Gases by Iron. Jour. Am. Chem. Soc., vol. 54, 1932, pp. 1820–1830; Chem. Abs., vol. 26, 1932, p. 3712.

Sorption of N_2, CO, and H_2 was studied on reduced Fe at temperatures 195°–400°. At the low tempera-

tures sorption consists solely of physical adsorption. Activated adsorption takes place at higher temperatures. The rate of this process is greatest for CO and least for N_2. With H_2 at 110° and above, a probable solution of the gas occurs. A stepwise increase in the adsorption at low temperatures suggests the accumulation of definite layers of molecules.

BERG, A. *See* abs. **1389.**

201. BERG, C. Hypersorption Process for Separation of Light Gases. Trans. Am. Inst. Chem. Eng., vol. 42, 1946, pp. 665–680.

Hypersorption is a light hydrocarbon recovery process developed by the Union Oil Co. of California to permit processing and recovery of hydrocarbons from streams that cannot be handled economically by the conventional recovery processes. The process employs a moving bed of activated C to adsorb hydrocarbons out of lean gas streams. Its applications include the recovery of C_2H_4 from gases produced in thermal and catalytic cracking operations, the recovery of C_3H_8 and heavier components from natural gas, the separation of CH_4 from H_2 and many other separations. Essential operation involves contacting the gas stream with a moving bed of active C that has been previously stripped and cooled to the desired temperature. Separation of the components of the feed takes place in the contacting bed by controlled selective adsorption of the heavier constituents. These are subsequently stripped from the C at an elevated temperature by steam. The stripped C is returned to the top of the unit where it is dehydrated and cooled, and the cycle of operation is repeated.

202. BERG, C., FAIRFIELD, R. G., IMHOFF, D. H., AND MULTER, H. J. Hypersorption. Oil Gas Jour., vol. 47, No. 52, 1949, pp. 95, 97, 130, 132, 135; Petrol. Refiner, vol. 28, No. 11, 1949, pp. 113–120.

The hypersorption process for the separation and recovery of light gases is operating in 2 commercial units, with others under construction. A moving bed of activated carbon absorbs hydrocarbons out of lean gas streams at low pressure. The general construction of a typical plant is described and its operation outlined. It can be utilized for recovering C_2H_4 from refinery gas or coke-oven gas at an efficiency of 98%, recovering C_3H_8 and butanes from natural gas, purifying hydrogenation gases, and separating CO_2 and S compounds from synthesis gas.

203. BERGBAU. [Motor Fuel From Fischer-Tropsch Process.] 1937, pp. 2–10.

It is estimated that German production of motor fuel by the Fischer-Tropsch process is 150,000 tons per yr.

BERGER, G. *See* abs. **1710,1711.**

BERGO, G. Y. *See* abs. **2088, 2089.**

204. BERKMAN, S., MORRELL, J. C., AND EGLOFF, G. Catalysis. Reinhold Pub. Co., New York, 1940, pp. 685–689, 813–814.

Catalytic synthesis of MeOH, industrial process, and catalytic hydrogenation of CO are covered.

205. BERL, E., AND BEMMANN, R. [Catalytic Experiments With High-Pressure Circulation Apparatus.] Ztschr. angew. Chem., vol. 44, 1931, pp. 34–39; Chem. Abs., vol. 25, 1931, p. 1432.

Water gas was subjected to catalytic high-pressure synthesis in a circulation apparatus in which the liquid-reaction product is separated from the gas mixture. A sketch of the apparatus and details of the design of the high-pressure bomb, separating vessel, fittings, and device for measuring gas velocity are given. The results, in general, confirmed data reported in the literature. Alkali-free ZnO catalyst forms MeOH chiefly. In contrast, higher alcohols, acids, and aldehydes are formed by using an alkali-containing ZnO. S has an injurious effect on the catalyst. The preparation and reduction of the catalyst are very important. The gas velocity over the catalyst has considerable influence on the reaction. With increasing velocity more unstable intermediate compounds are obtained, while at low velocities the stable end products predominate.

206. ———. [Effect of Hydrogen on Charcoal and Active Carbon and the Methane Synthesis.] Ztschr. physik. Chem., vol. A162, 1932, pp 71–93; Chem. Abs., vol. 27, 1933, p. 223.

Pressure hydrogenation of charcoal and activated C gives CH_4 almost entirely. The thermodynamic equilibrium leads to certain conclusions on free energy of para-crystalline C. Natural C gives liquid hydrocarbons, but since charcoal and activated C give none of them, their structure must be fundamentally different. Presents views of the structure and reaction mechanism.

207. BERL, E., AND JÜNGLING, K. [Synthesis of Higher Hydrocarbons From Water Gas at Atmospheric Pressure.] Ztschr. angew. Chem., vol. 43, 1930, pp. 435–440; Chem. Abs., vol. 24, 1930, p. 3984.

In the Fischer and Tropsch water-gas reaction (*see* abs. **1018**), an Fe catalyst gives a different course of reaction than a Co catalyst; Fe reacts with CO, Co with H_2. In the preparation of catalysts, it is best to start with metal nitrates and convert them to oxides or metals. The presence of Cu in a catalyst is advantageous. Co catalysts are more active than Fe catalysts, the former converting O_2 to H_2O the latter O_2 to CO_2. The method of reduction is important in catalyst preparation. It must be done slowly at low temperature, preferably not above the operating temperature. The same precautions are needed in catalyst regeneration. With Co, heating in H_2 to about 330° is best. With Fe, heating in pure H_2 is not satisfactory; air regeneration at about 400° and reduction by water gas at the operating temperature is preferable. Catalysts can operate for weeks or months without regeneration.

208. BERNIER, R. [Thermomagnetic Study of Iron and Nickel Carbides. I. Nickel Carbides. II. Nickel Nitrides. III. Cementite. IV. Iron-Nickel Carbides.] Ann. chim., vol. 6, No. 12, 1951, pp. 104–161.

I. Dispersion of Ni in ThO_2 makes carburization easier. In $2:1=H_2:CO$, carburization took place at 150°–200°. No hexagonal carbide was obtained for unsupported Ni. Only with 10–30% ThO_2 was the cubic phase eliminated by carburization. In pure CO the carburization conditions differ from those for synthesis gas. Chemical analyses were inconclusive but reported in detail. X-ray diffraction pattern for hexagonal Ni_3C is given; a=2.646 Å, c=4.320 Å, c/a=1.633 Å. Thermomagnetic study showed decomposition starting at 210°, and Curie point of product at 314°. Product is face-centered cubic with a=3.529 Å (Ni, a=3.516 Å). On further and higher-temperature heating, the Curie point gradually goes up to normal, and a goes down to normal, showing that a face-centered cubic carbide had been transformed homogeneously to Ni+C. H_2 starts attack at 206° and leads to Ni with Curie point=359° and normal a. The face-centered cubic carbide is believed to be Ni_4C and is assumed to be intermediate in the Ni_3C formation. No real proof is given for the formula Ni_2C. In N_2, decomposition of Ni_3C starts at 276°; in H_2 at 171°; and in CO at 440°. In all cases the product went through a lower face-centered cubic carbide stage. 19 refs.

II. NH_3 passed over reduced Ni supported on ThO_2 at 170° leads to hexagonal close-packed Ni_3N, which is always contaminated by face-centered cubic Ni_4N. Thermomagnetic analysis seems to indicate that the hexagonal close-packed product is paramagnetic. It starts to decompose near 190° C into the face-centered cubic ferromagnetic nitride with Curie point=342°. X-ray diffraction data fit hexagonal close-packed phase with a=2.668 Å, c=5.294 Å, c/a=1.609 Å. For the face-centered cubic phase, a=3.521 Å. It is concluded that nitriding goes by way of face-centered nitride to hexagonal close-packed nitride. The latter reacts with H_2 at 155°, decomposes in N_2 near 450°. 8 refs. III. Gives discussion and bibliography on the thermal stability of Fe_3C. Fe_2O_3 and reduced Fe powder were treated with 2 H_2+CO at 560°–1,000°. Heating at 800° for 24 hr. of mixtures of carbonyl Fe with acetylenic C or C from CO produced Fe_3C. Fe_3C made with 2 H_2+O_2 at 560° had a Curie point of 210° and at 1,000°, a Curie point of 216°. This spread is believed to be due to slight differences in composition, the former being richer in C than the latter. Stepwise destruction of the former gave higher Curie points with each step and partial reduction with H_2 at 500°. At 900°, 28.3% was destroyed after 4 hr., 29.9% after 19 hr.; at 1,050°, 48% was destroyed after 2 hr., 71% after 17 hr., and 79% after 37 hr. Partial destruction at these 2 temperatures and subsequent heating at 800° showed reformation and new formation of Fe_3C in the former case but no change in the latter. The difference is attributed to differences in crystallinity of the C. Fe_3C reacts with H_2 at 590° and with N_2 at 690°. 23 refs. IV. Fe–Ni–C alloys were prepared from Fe and Ni salts (with about 20% ThO_2 added for >30% Ni) in solution, precipitated with boiling K_2CO_3 solution, washed, dried, granulated, and reduced at 450°–600°, depending on the Fe content. Ferronickels were studied. Temperature of carburization varied between 170° and 560°. From 0–40% Ni, substituted cementite was formed (I); from 40–70% Ni, a mixture of (I) and substituted hexagonal close-packed Ni_3C (II) was formed; from 70–100%, Ni only (II) was formed. The Curie point of (I) varies with composition from 210° (0% Ni) to 234.5° (23.5% Ni) to 231° (30% Ni), and the recalescence decreases from 770° and 682° (0% Ni) to 572° (30% Ni). (II) decomposes on heating to form ferromagnetic face-centered cubic carbide, starting at about 210°. In a mixture of (I) and (II) a Curie point of 150° was found for (I), showing that the Curie point drops sharply when >30% Ni is added. A graph of Curie point of (I) versus % Ni is given. (I) was stable up to 600° (II) was stable up to 480° in vacuum. (I) is less stable than pure Fe_3C. 150° is the Curie point limit of (I) for about 40% Ni. 16 refs.

———. *See* abs. **2271, 2276.**

209. BERNIER, R., AND MICHEL, A. [Hexagonal Phase Appearing in Evolution of Fischer Nickel Catalyst.] Bull. soc. chim., France, 1948, p. 1073.

Ni dispersed on ThO_2 forms a hexagonal carbide during the synthesis with 6–7% C. The hexagonal close-packed structure has a=2.64 Å, c=4.32 Å, c/a=1.63. The paramagnetic carbide is destroyed in vacuo at 210° and forms a ferromagnetic face-centered cubic phase with Curie point=314°.

210. BERR, R. [Recent Developments in Chemical Industry.] Chim. et ind., vol. 17, 1927, pp. 3–20; Brennstoff-Chem., vol. 8, 1927, pp. 205–211; Chem. Zentralb., 1927, II, p. 1497; Chem. Abs., vol. 22, 1928, p. 648.

Discussion is given of progress in the manufacture of synthetic NH_3, hydrocarbons, and MeOH, also the Bergius process, the Fischer-Tropsch process, industrial H_2, and synthesis in organic chemistry.

211. ———. [Progress of Industrial Chemistry From F. Kuhlmann to Berthelot.] Bull. soc. encour. ind. nat., vol. 138, 1939, pp. 152–174; Ind. chim., vol. 26, 1939, pp. 89–96; Génie civil, vol. 114, 1939, pp. 104–109.

Discusses ammonia and synthetic nitrates, synthetic MeOH, the hydrogenation of coal, the Fischer synthesis, the chemistry of C_2H_4 and C_2H_2, artificial rubber, the chemistry of pétroleum, and antiknock agents.

212. ———. [Progress of Industrial Chemistry With Respect to Hydrocarbon Synthesis.] Rev. pétrolifère, No. 829, 1939, pp. 370–372.

Reviews the hydrogenation of coal and the Fischer synthesis. Stresses economic and military aspect of the problem of synthetic fuels.

213. ———. [Water Gas and Commercial Synthesis.] Ind. chim. belge, vol. 32, 1945, pp. 153–170; Chaleur et ind., vol. 26, No. 244, 1946, p. 68 D; Chem. Abs., vol. 40, 1946, p. 7566.

Contents of a paper presented in May 1943 before L'École Superieure des Mines. Discusses manufacture of water gas and the thermal balance of its production, the utilization of water gas for the production of H_2 and NH_3, proportions of CO and H_2 necessary, and utilization for the synthesis of alcohols and fuels. The following systems are described: Didier with external heating; Pintsch and Koppers with circulation of hot air; Winkler with the use of O_2; and the Lurgi pressure system.

214. BERTAUT, F. [Coercive Force and Crystallite Size.] Compt. rend., vol. 229, 1949, pp. 417–419.

Coercive force of Fe powders prepared at different temperatures by H_2 reduction of the formate show marked peak (~1,000 gauss) for size, about 200 Å. This is generally in accord with Néel's views on shape anisotropy and the results suggest a critical size below which the Fe crystallites behave paramagnetically, but traces of Fe_2O_3 may complicate the interpretation.

215. BERTAUT, F., BOCHIROL, L., AND BLUM, P. [Synthesis and Space Groups of the Boroferrites.] Compt. rend., vol. 230, 1950, pp. 764–765; Chem. Abs., vol. 44, 1950, p. 5749.

Boroferrites of the composition A.4MO, where A=Fe_2O_3 or B_2O_3 and M=Ni, Co, or Cu, were prepared by dissolving the oxides in alkali borates and slowly cooling the solutions. Acidification with HNO_3 gave long, crystalline needles. The unit crystal contains 2 mol. of A.4MO; the lattice parameters are given. Boroferrites of the composition A.2MO (M=Mg, Fe, Co, or Ni) are all paramagnetic at ordinary temperature.

216. BERTHELOT, C. [Composition of Coal and Its Utilization in the Chemical Industry.] Bull. soc. encour. ind. nat., vol. 126, 1927, pp. 485–511; Chem. Abs., vol. 22, 1928, p. 152.

Address reviewing present-day knowledge of the chemical composition and constitution of coal and its possible applications in the manufacture of MeOH, EtOH, petroleum hydrocarbons, and NH_3, more particularly from the standpoint of supplying the French market with products prepared from domestic raw materials.

217. ———. [New Views on the Chemical Utilization of Coal.] Bull. soc. encour, ind. nat., vol. 127, 1928, pp. 822–854; Bull. soc. ing. civ. France, vol. 81, 1928, pp. 1105–1181; British Chem. Abs., 1929, B, p. 344; Chem. Abs., vol. 23, 1929, p. 2012.

General review of the coal question, the following being briefly considered: (a) General methods for the chemical utilization of coal including high- and low-temperature carbonization, hydrogenation, reduction of CO with Badische Anilin- und Soda-Fabrik patents

of 1913–1914, synthesis of MeOH, Patart's patent, Fischer's synthol, Fischer's and Tropsch's hydrocarbons, Kling and Florentin's process, and Bergius process; (b) N_2 question including preparation of $(NH_4)_2SO_4$ from gypsum, mixed fertilizers, $(NH_4)_2HPO_4$, and Claude's "potazote;" (c) the general organization for fuel and synthetic NH_3 manufacture, with some Norwegian, Italian, German, and French financial data.

218. ———. Chemical Utilization of Coal—Its Methods of Realization. Proc. World Eng. Cong., Tokyo, 1929, vol. 32, 1931, pp. 309–338. Chem. Abs., vol. 26, 1932, p. 578.

Review of synthetic-chemical industries that depend directly on coal: Coal-hydrogenation, synthetic-MeOH, and N-fixation industries are included.

219. ———. [Cost of Hydrogen Necessary for Manufacture of Synthetic Gasoline.] Chim. et ind., vol. 34, 1935, p. 815.

Average cost of H_2 from water gas used in the synthesis of gasoline amounts, at 30 centimes/m.^{3}, to 600 or 1,200 francs/ton of gasoline, depending upon the process used—Bergius or Fischer-Tropsch. Thus, the cost of the necessary H_2 is more than the cost of natural gasoline. By carbonizing coal at 900°–920°, 300 m.^{3} of a gas containing 72–74% H_2 can be recovered/ton treated. The cost of a 95% H_2 from this source is much less than that from water gas. Abstract of a paper presented at the XVth Congres de Chimie Industrielle.

220. ———. [Evolution of Semicarbonization and the Manufacture of Synthetic Carburants.] Génie civil, vol. 106, 1935, pp. 353–357, 384–387; Chem. Abs., vol. 29, 1935, p. 8293.

Comparison, with drawings, of modern practice in France, England, and Germany is presented. Germany will be able to make 500,000 tons of motor fuel annually by the Bergius process at Oppau, and 100,000 tons by the Fischer-Tropsch process. State experimental hydrogenation plants are to be laid down in France. The present trend in the synthetic preparation of motor fuels is outlined, the heavy capital investment required by the Bergius process is mentioned, and the need for subsidies to cover the difference between the cost of natural and synthetic fuels is emphasized. Attention is drawn to the attractive features of the Fischer process, particularly its operation at atmospheric pressure and relatively low temperatures, its moderate capital cost, and its utilization of existing coke ovens. On the other hand, the octane number of the fuel produced is from 47 to 62, requiring antiknock additions.

221. ———. [New Sources of Production of Hydrogen.] Ind. chim., vol. 22, 1935, pp. 406–407; Chem. Abs., vol. 29, 1935, p. 6370.

Attention is drawn to the possibility of producing cheap H_2, suitable for the synthesis of NH_3 or for the manufacture of gasoline by the Fischer-Tropsch process, by the carbonization of anthracite agglomerates (manufacture of artificial anthracites) and by injection of steam in coke ovens.

222. ———. [Synthetic Gasoline.] La Nature, No. 2958, 1935, pp. 121–124; Chem. Zentralb., 1936, I, p. 689; Chem. Abs., vol. 29, 1935, p. 8304.

Commercial application of various processes by I. G. Farbenindustrie, A.-G. at Leuna and at Oppau, Germany, is described. Hydrogenation is conducted at 425° under 200 atm. pressure in the presence of Sn $(OH)_2$, Ni, Co, or Fe as catalysts. Improvement in the Fischer-Tropsch synthesis is reported, especially the heat exchange, better catalysts, and a more valuable, more knock-resistant Kogasin fuel. Kogasin II lubricating oil has a constant viscosity between +25° and −25°, a pour point about 26° lower and a specific gravity about 1/6 less than the corresponding winter oil from Pennsylvania crude.

223. ———. [Large Gas Generators for the Production of Water Gas.] Génie civil, vol. 109, 1936, pp. 103–106; Chem. Abs., vol. 30, 1936, p. 7308.

Drawings and description of the Winkler and Didier systems are given. The thermal efficiency of the latter plant is about 75% and the total cost about $0.15/1,000 cu. ft. of gas using lignite briquettes at $4.00/ton.

224. ———. [Lubricants From Coal and Lignites.] Chim. et ind., vol. 36, 1936, pp. 270–280; Chem. Age, vol. 35, 1936, p. 139; British Chem. Abs., 1937, B, p. 864.

Fischer and Bergius processes are described. The former embodies non-catalytic polymerization of hydrocarbons, catalytic polymerization of olefins, dechlorination of chlorinated hydrocarbons and condensation of these with olefins, and condensation of chlorinated products with aromatic hydrocarbons. It is shown that ethylene and paraffins, byproducts of the Fischer process, constitute an important source for the production of lubricants.

225. ———. [Manufacture of Synthetic Gasoline.] La Nature, 1936, pp. 155–162; Chem. Abs., vol. 30, 1936, p. 4647.

Detailed discussion is presented with flow sheets and illustrations to show the methods used for commercial production of gasoline from charcoal in France, Germany, and England.

226. ———. [Metallurgical Problems Presented in Making Hydrogenation Tubes and Cracking Chambers.] Rev. mét., vol. 33, 1936, pp. 566–573, 619–626, 677–690, 727–746; Chem. Abs., vol. 31, 1937, p. 1738.

Phenomena taking place during working of the equipment used for hydrogenation and cracking are described and methods for meeting them suggested. The qualities required in metals for the above uses are summarized. A survey of published data is given.

227. ———. [Respective Advantages and Disadvantages of the Bergius and Fischer Processes for Production of Synthetic Liquid Fuels.] Chim. et ind., vol. 35, 1936, pp. 768–791; Coal Carbonisation, vol. 2, 1936, p. 222; Chem. Abs., vol. 30, 1936, p. 4647.

From an extensive comparison it is concluded that the 2 processes are complementary rather than competitive. The great distinction is that in one case the coal molecule is reduced from about 2,000 to the molecular weight of gasoline, about 100, by reconstitution with the addition of H_2, while in the other case it is completely destroyed and the hydrocarbon is built up synthetically from CO. The Fischer process is incomparably simpler than high-pressure hydrogenation in the choice of raw material, since any fuel is satisfactory that gasifies with a suitable yield of CO and H_2. Choice of fuels for hydrogenation is relatively narrow. Equipment required for the synthesis of gasoline is very simple and comparatively inexpensive. On the other hand, the hydrogenation process has a higher thermal efficiency, 43% of the heat content of the coal being available in the motor fuel, compared with 35% of the heat input recovered in synthetic gasoline. In the hydrogenation process, 4 ton of coal yields 1 ton of gasoline, 24% aromatics, 28% naphthenes, 7% olefins, sp. gr. 0.78, octane number 70–85. The Fischer-Tropsch process yields 195 lb. gasoline, octane number 50–60, from 1,000 lb. of coal of 12,600 B. t. u./lb. net calorific value. On the basis of stated capital costs for plant of 50,000 ton annual output, the cost/gal. of gasoline is about 7.9–8.6 d. by the Fischer-Tropsch process and 9.6–10.6 d. by hydrogenation.

228. ———. [Sources of Hydrogen for Production of Liquid Fuels.] Cong. chim. ind., 15th Cong., Brus-

sels, 1936, pp. 833–846; Brennstoff-Chem., vol. 16, 1935, p. 430; Chem. Abs., vol. 30, 1936, p. 5756.

Assuming 2,000 and 4,000 $m.^3$ of H_2 is required, respectively, for the Bergius and Fischer processes and that H_2 from water-gas costs 30 centimes/$m.^3$, it is estimated that the cost of H_2 required for 1 metric ton of gasoline would be 600 francs for the Bergius process and 1,200 francs for the Fischer process. Much cheaper H_2 could be obtained from the carbonization at 900°–920° of anthracite agglomerates, which can give 300 $m.^3$/ton of gas containing 72–74% of H_2.

229. ———. [Synthetic Motor Fuels in Belgium and France.] Génie civil, vol. 108, 1936, pp. 59–62; Mech. Eng., vol. 58, 1936, pp. 377–378.

There are enough sources of coke-oven gas in Belgium to provide 20% of the gasoline requirements in the form of MeOH. Technically and commercially the Bergius and Fischer-Tropsch processes are capable of producing fuels suitable for any admixture with natural gasoline or for replacement of natural gasoline. The choice between these 2 methods depends on the nature of the coal available and the means of producing H_2. Operating conditions in these 2 processes and some recent developments are noted.

230. ———. [Economic Problems Raised by Production of Synthetic Fuels for Internal-Combustion Engines.] Compt. rend., Cong. chim. ind., 17me, Paris, September-October 1937, pp. 424–429; Chem. Abs., vol. 32, 1938, p. 6429.

General discussion. The possibilities of existing synthetic processes and of substitutes for liquid motor fuels are discussed from the viewpoint of French national policy.

231. ———. [Extraction of Hydrogen From Coke-Oven Gas for use in the Manufacture of Synthetic Gasoline.] Génie civil, vol. 110, 1937, pp. 459–461; Chem. Abs., vol. 31, 1937, p. 7626.

Messer process is described with a drawing showing the operation. A gas containing 98–99% H_2 is obtained.

232. ———. [High-grade Fuels and Lubricants for Internal-Combustion Engines.] Chim. et ind., vol. 37, 1937, pp. 1043–1055; British Chem. Abs., 1937, B, p. 869.

Specifications for various grades of petrol are discussed. Aviation spirit for use at high altitudes should have high octane number and relatively close distillation range. Gum formation is also a greater hazard than in automobile use and this constitutes a difficulty for petrols prepared by the Fischer process or from shale oil. Lubrication requires an oil stable at 150°. Specifications for lubricants are discussed and the advantages of refining with solvents are pointed out. Satisfactory synthetic lubricants can be produced by hydrogenation or by $AlCl_3$ treatment of oils produced by the Fischer synthesis; chlorination of this material and condensation with an aromatic hydrocarbon gives Paraflow, which depresses the setting point of paraffin lubricants.

233. ———. [Production of Fuels by Catalytic Hydrogenation of Carbon Monoxide.] Génie civil, vol. 110, 1937, pp. 497–501; Chem. Abs., vol. 31, 1937, p. 7621.

Details are given of the manufacture of MeOH at the Mines de Béthune. Operating at pressures of 50–600 atm. and temperatures of 275°–600° C., according to the purity of the gas, the product is MeOH, whereas at atmospheric pressure and a temperature of 175°–200° gasoline is produced. Examples are given of the catalysts used in the respective cases and the production of MeOH and gasoline in various countries is reviewed. Process for making EtOH from the C_2H_4 in coke-oven gas is also described. Discusses also the synthesis of gasoline by the Fischer and Robinson–Bindley processes, the elimination of organic S from industrial gases, and the composition and preparation of catalysts.

234. ———. [Realizable Progress in Hydrogenation.] Génie civil, vol. 110, 1937, pp. 53–60, 86–90; Chem. Abs., vol. 31, 1937, p. 4082.

Deals mainly with researches in progress with a view to reducing the cost of gasoline made by direct hydrogenation of coal or lignite. Description is given with illustration of an intermittent conversion plant used at a Pas-de-Calais colliery to produce the gas mixture required by the Fischer process.

235. ———. [Synthetic Liquid Fuels Resulting From Reduction of Carbon Monoxide by Hydrogen: Methanol, Fischer Gasoline.] Chim. et ind., vol. 37, 1937, pp. 211–223; Chem. Abs., vol. 31, 1937, p. 4083.

General description, discussion, and comparison of the relative merits of the production of MeOH and of Fischer gasoline, respectively, by the action of H_2 on CO under various conditions. The choice between hydrogenation and these synthetic processes for the production of motor fuel depends largely on the nature and quality of the raw material available. The position in France is briefly discussed.

236. ———. [Synthetic Motor Fuels.] Mines, carrières, No. 172, 1937, pp. 5–6; Coal Carbonisation, vol. 3, 1937, p. 150.

An outline is given of papers relating to the production of MeOH and Kogasin by catalytic reduction of CO with H_2, and the hydrogenation processes of Bergius, Vallettee, Audibert, and Pott-Broche. The work of successive investigators is summarized, especially as regards the temperatures and pressures used. In October 1936, 11 plants, including those of the Béthune and Liévin mines, were using stepwise hydrogenation in liquid and gaseous phases successively. The 2d type of hydrogenation process, depending on preliminary extraction by solvents and subsequent direct hydrogenation in the gaseous phase, is being applied by the Mathias Stinnes concern in Essen. The author emphasizes the serious cost of large, high-pressure, high-temperature catalytic tubes of special steel and commends from this standpoint the Vallette and Audibert processes.

237. ———. [Economics of Synthetic Fuels Industry.] Génie civil, vol. 112, 1938, pp. 409–413.

A discussion of the reports by Lord Falmouth of Great Britain and Sir David Rivett of Australia.

238. ———. [Evolution of Processes for Production of Motor Spirit by Catalytic Reduction of Carbon Monoxide by Hydrogen.] Chim. et ind., vol. 40, 1938, pp. 434–460; Chem. Abs., vol. 33, 1939, p. 3106.

Critical review and discussion from which it is concluded that the most satisfactory economical procedures would be to combine hydrogenation of liquid products with a catalytic-reduction process of CO by H_2.

239. ———. [Conversion of Methane Into Carbon Monoxide and Hydrogen.] Rev. chim. ind. (Paris), vol. 48, 1939, pp. 194–198; Chem. Abs., vol. 33, 1939, p. 8562.

Review of various processes for the conversion of CH_4 into H_2 and C, CO, or CO_2 with special emphasis on a process involving the reaction of CH_4 with a mixture of O_2 and steam in the presence of active Ni, whereby CO (with some CO_2) and H_2 are formed. In this latter process the CH_4 reacts mainly with the O_2.

240. ———. [Conversion of Methane into Hydrogen and Carbon Monoxide. Process of the Société belge de l'azote at Renory.] Génie civil, vol. 115, 1939, pp. 461–464; Chem. Abs., vol. 34, 1940, p. 2541.

Continuous catalytic process recently developed, which works under atmospheric pressure, is reviewed with 2 diagrams.

241. ———. [Hydrogenation of Coal and Heavy Oils for Production of Airplane Fuels.] Génie civil, vol. 114, 1939, pp. 214–216, 234–237.

Recent progress is shown and statistical data are given on the production of synthetic fuels in France. The economic organization of a synthetic-fuel industry is outlined.

242. ———. [Synthetic and Substitute Fuels for Internal-Combustion Motors.] Chim. et ind., vol. 44, 1940, pp. 465–470; Chem. Zentralb., 1941, I, p. 1629; Chem. Abs., vol. 37, 1943, p. 2907.

Present-day accomplishments and trends in the production of synthetic-hydrocarbon fuels—hydrogenation, catalytic cracking, polymerization, isomerization, alkylation, Fischer process, and addition of $PbEt_4$—are outlined in a lecture.

243. ———. [The Complex Coal–Chemistry–Petroleum.] Chim. et ind., vol. 45, 1941, pp. 551–554; Chem. Abs., vol. 36, 1942, p. 3025.

At the Établissements Kuhlmann in Pas-de-Calais gases containing CH_4 are heated with O_2 and steam in the presence of active Ni on a refractory support (the catalytic activity lasts for more than 1 yr.) according to the equations $CH_4+0.5\ O_2=CO+2H_2$ and $CH_4+H_2O=CO+3H_2$. Gives other references to coal-hydrogenation processes.

244. ———. [Production of Methanol and Its Derivatives, Formaldehyde, Hexamethylenetetramine, Resins, etc.] Chim. et ind., vol. 45, Special No. 42–43, 1941; Chem. Zentralb., 1942, I, p. 418; Chem. Abs., vol. 37, 1943, p. 2715.

245. ———. Program for Synthetic and Substitute Fuels. Jour. Soc. Auto. Eng., vol. 15, 1942, p. 265.

Discusses use of peat for fuel in France. Includes some remarks concerning the production and utilization of alcohol and synthetic gasoline.

246. ———. [Some Aspects of the Fuel Industry. Conversion of Methane Into Carbon Monoxide and Hydrogen by the Action of Steam in Presence of Catalysts.] Chim. et ind., vol. 52, 1944, pp. 153–154; Chem. Abs., vol. 40, 1946, p. 2958.

Brief description of method and precautions required.

247. ———. [Synthetic and Substitute Lubricants.] Chim. et ind., vol. 53, 1945, pp. 160–166; Chem. Abs., vol. 42, 1948, p. 6096.

To replace imported petroleum products, lubricants can be obtained from anthracene oil, rosin oil, shale oil, low-temperature tar, and coal (by hydrogenation or by Fischer-Tropsch synthesis). The development of vegetable-oil production in North Africa will provide open-chain material for Friedel-Crafts syntheses on a $C_{10}H_8$ nucleus, and the chemical or electrical polymerization of C_2H_4 can also yield lubricants.

248. Berthelot, C., and Hot, M. Carburants de synthèse et de remplacement. H. Dunod, Paris, 1936, 350 pp.; Chem. Abs., vol. 31, 1937, p. 241.

249. ———. Technique et économie nouvelles des carburants de synthèse. H. Dunod, Paris, 369 pp.; Chem. Abs., vol. 32, 1938, p. 4312.

Reviewed in Bull. assoc. chim., vol. 55, 1938, p. 268; Coal Carbonization, vol. 4, 1938, p. 50.

250. Berthelot, D., and Gaudechon, H. [Photochemical Synthesis of Carbohydrates From Carbon Dioxide and Water.] Compt. rend., vol. 150, 1910, pp. 1690–1693; Jour. Soc. Chem. Ind. (London), vol. 29, 1910, p. 904.

Oxides of C and water vapor have been made to react with each other by means of the light of the Hg vapor lamp. CO and O_2 produce a small amount of CO_2, while the latter gas yields CO when exposed to the rays in the presence of P. CO_2 and H_2 give H_2O and HCHO. HCHO can be made directly from H_2 and CO.

251. Berthelot, M. [Chemical Effects of the Silent Electric Discharge.] Compt. rend., vol. 126, 1898, pp. 561–567, 567–575, 609–616, 616–627; Jour. Chem. Soc., vol. 1, 1898, pp. 393–396.

Various mixtures of CO and H_2 were subjected to the action of the silent discharge. Some carbohydrates of the general formula $(CH_2O)n$ were obtained.

252. ———. [Chemical Equilibrium Between Hydrogen and the Oxides of Carbon.] Ann. chim. phys., ser. 7, vol. 14, 1898, pp. 170–176; Jour. Chem. Soc., vol. 2, 1899, p. 286.

CO_2 when heated at high temperatures is partly dissociated into CO and O_2. In the presence of C or H_2, the O_2 thus liberated is employed in oxidizing this element, and further dissociation of CO_2 must take place to preserve the equilibrium. When a mixture of CO_2 and H_2 is raised to a high temperature, equilibrium is established, not between the binary systems (CO_2+H_2) and $(CO+H_2O)$ but between the more complicated system $[(n\text{-}a)\ CO_2+a\ (CO+O)]$ resulting from the partial dissociation of CO_2 and that produced by the partial dissociation of steam $[(m\text{-}B)\ H_2O+B\ (H_2+O)]$ and a further complication results from the dissociation of CO which reacts as follows: $[pCO=(p\text{–}2)\ CO+CO_2+C]$. This explanation is based on the observed behavior of these compounds at high temperatures, each of them dissociating in the manner indicated, independent of the presence of the others.

253. ———. [Generation of Hydrocarbons by Metallic Carbides.] Compt. rend., vol. 132, 1901, pp. 281–290; Jour. Chem. Soc., vol. 1, 1901, p. 245.

Mentions or discusses following carbides: Acetylides, Na, Li, Ca, Ag, Al, Mn, Ce, La, Y, and U.

254. ———. [Study of Chemical Reactions.] Ann. chim. phys., vol. 6, 1905, (8), p. 183; Compt. rend., vol. 140, 1905, pp. 905–914; Jour. Chem. Soc., vol. 88, 1905, (2), p. 308A.

Attempt was made to cause the direct synthesis $C+2H_2\rightleftharpoons CH_4$ by passing H_2 through quartz tubes heated to 1,300°. Results were negative although Bone and Jerdan had effected the direct synthesis at 1,200° over pure-sugar C (abs. **296**).

255. Berthelot, M. A. L'Industrie des combustibles liquides. Part 2. Les Carburants de synthèse. Gauthier-Villars & Cie, Paris, 42 pp.; Chem. Abs., vol. 30, 1936, p. 3971.

Bever, M. B. *See* abs. **2562**.

256. Bhatia, G. L. Synthetic Petroleum. 1950, XV, 92 pp.; Nature (review), vol. 166, 1950, p. 624.

Object of this booklet about synthetic gasoline is to arouse the interest of laymen, manufacturers, chemists and engineers, and the Government of India to the vital importance of building up a key industry on national lines comparable with what has already been done in America, Britain, Germany, and Japan.

256a. Bhattacharyya, S. K., and Rao, B. C. S. Oxo Process. I. Synthesis of Propionaldehyde From Ethylene, Carbon Monoxide and Hydrogen in the Gas Phase in the Presence of Cobalt Catalysts at High Pressures. Jour. Sci. Ind. Research (India), vol. 11 B, 1952, pp. 80–81; British Abs., 1952, B II, p. 794.

In preparing propionaldehyde by the Oxo process, the optimum conditions are: A gas mixture of C_2H_4, CO, and H_2 (1:1:1), 150°, 150 atm. (3 hr.), and a catalyst containing 20% of Co (prepared by precipitating from nitrate solution with K_2CO_3) on kieselguhr.

Biljcevic, P. *See* abs. **2433**.

257. Billig, R. Studies on Solid Paraffin Hydrocarbons Which Originate in Gasoline Synthesis Accord-

ing to Fischer-Tropsch, and on Conversion of Produced Cracking Process Distillates Rich in Olefins Into Lubricating Oils. FIAT Reel C268, 1939, frames 4687–4699; PB 73,606.

———. *See* abs. **1818, 1819.**

258. BINDER, G. G., AND WHITE, R. R. Synthesis of Methane From Carbon Dioxide and Hydrogen. Chem. Eng. Progress., vol. 46, No. 11, 1950, pp. 563–574.

Rate of formation of CH_4 from CO_2 and H_2 was measured by passing feed gas ranging in composition from 80% H_2 and 20% CO_2 to 30% H_2 and 70% CO_2 over a reduced Ni catalyst in a continuous apparatus. Several runs were made in which the feed gas contained CH_4. The space time was varied from 0 to 8 x 10^{-5} hr. The temperature range was 500°–750° F., and the pressure was maintained at 1 atm. in all runs. Average rates of CH_4 formation, obtained by differentiation of the data, vary from 0–5.60 lb. mols./day (lb. catalyst). Rate of reaction can be correlated by a mechanism that assumes that the major resistance to the overall process is offered by the reaction of an adsorbed CO_2 molecule with at least 2 adsorbed H_2 molecules. Presents two equations for the rate of CH_4 formation resulting from the extremes of the range of correlating mechanisms.

259. BIRCH, S. F., WITHERS, J. G., NARRACOTT, E. S., AND HABESHAW, J. Miscellaneous Information on Fuels, Detergents, and Lubricants. BIOS Final Rept. 1646, 1946, 160 pp., PB 91,685.

Gives general notes on the Michael hot-gas recycle and the foam processes, the Ruhrchemie method of olefin analysis, description with diagram of a Kaiser Wilhelm Institute capillary flowmeter for measuring gas flows at high pressures, and some discussion of Rheinpreussen Fe catalysts of composition 100% Fe, 1.7% Cu, 0.1–2% K_2CO_3, and 50–100% kieselguhr. The Oxo reaction is also discussed, and a translation of a report by Dr. Nienburg on its development is given. Also gives considerable space to lubricants and lubricating-oil additives. An appendix offers a report of 30 pp. by Dr. Sachsse on the explosive limits and flame velocities in hydrocarbon-oxygen mixtures.

260. BIRK, E. AND NITZSCHMANN, R. [High-Pressure Synthesis of Dimethyl Ether and Its Theoretical Foundations.] Metallbörse, vol. 19, 1929, p. 2807; vol. 20, 1930, pp. 1295–1296, 1351, 1407; Chem. Abs., vol. 24, 1930, pp. 2106, 5719.

Critical review of the literature and calculation of equilibrium conditions for the formation of dimethyl ether from MeOH. A tabulation of the volume relations of the reaction gases for 50% and 100% conversion to dimethyl ether. Discusses the formation of dimethyl ether along with the synthesis of MeOH from water gas. Expresses water-gas-MeOH equilibrium for pressures of 100–400 atm. and for temperatures 300°–400°. Calculates volume relation of the reaction gases for a direct formation of dimethyl ether combined with the MeOH synthesis. Tabulates calculated values, and lays basis for a MeOH output of 10–50% and a 50–100% conversion of MeOH to dimethyl ether. Another table gives, for the same relations, the amounts of water gas necessary for the production of 1 kg. of dimethyl ether.

261. ———. [Methanol Synthesis and Its Theoretical Basis.] Metallbörse, vol. 19, 1929, pp. 1350–1351, 1405–1406, 1462–1464, 1573–1575, 1629–1632, 1742–1744, 1798–1799, 1910–1912; Chem. Abs., vol. 23, 1929. p. 5157.

Outlines development of synthetic processes for the production of MeOH and explains fully fundamental equations for the gas reactions involved; 141 such equations, with deductions from them, curves involved, etc., are given.

262. BISHOP, T. Tonnage Oxygen Plant. Iron and Coal Trades Rev., vol. 156, 1948, pp. 733–739.

Description of the Oxyton plant designed by La Société Anonyme l'Air Liquide of Paris illustrates layout of equipment for producing 100 ton per day of O_2 of 92% purity, using 3 units in parallel and utilizing power at the rate of 340 kw.-hr. per ton of O_2 and 0.53 kw.-hr. per $m.^3$ of 100% O_2.

BLACKBURN, W. H. *See* abs. **691, 692, 693, 694.**

262a. BLANCHARD, A. A., AND GILMONT, P. Preparation of Cobalt Carbonyl, Cobalt Nitrosyl Carbonyl and Cobalt Carbonyl Hydride by the Cyanide Method. Jour. Am. Chem. Soc., vol. 62, 1940, pp. 1192–1193; Chem. Abs., vol. 34, 1940, p. 4,354.

An alkaline suspension of a Co salt absorbs CO almost quantitatively to form $KCo(CO)_4$, but only in the presence of a carrier such as a small amount of a cyanide. Treatment of $KCo(CO)_4$ with NO gives $Co(NO)(CO)_3$. The addition of an excess of HCl to the reaction mixture gives the volatile $HCo(CO)_4$, which condenses at —79° to a solid; it melts at —33° and decomposes above that temperature into $(Co(CO)_4)_2$ and H_2.

263. BLAND, W. F. Gasification of Coal May Foreshadow New Industry Replacing Oil Refineries. Nat. Petrol. News, vol. 39, No. 14, 1947, pp. 23–24.

An announcement of the joint plans of Standard Oil Co. of New Jersey and the Pittsburgh Consolidation Coal Co., for gasifying coal and converting it to liquid fuels, high-B. t. u. gas, and chemicals. The plans have only reached the design stage of a $300,000 demonstration-size pilot plant to continue the studies and bring the process to a commercial basis. It is expected that the pilot plant will be ready for operation by the end of 1947 and the commercial plant by 1950 or 1951. The pilot plant, as planned, will be devoted primarily to studies of the application of the fluidized-solids technique to coal gasification. About 50 tons of coal/day will be consumed, producing about 2.4 million cu. ft. of gas. Powdered coal in suspension is reacted with O_2 and steam in the generator, and the gas produced is suitable for the synthesis of hydrocarbons by the Fischer-Tropsch reaction. The flexibility of the operation may be used to obtain the maximum yield of domestic fuel gas or for the greatest possible yield of gasoline and other liquid fuels.

264. ———. Processing Coal Into Liquid Products May Be Practicable in a Few Years. Petrol. Processing, vol. 2, 1947, pp. 325–327.

Editorial comment on recent developments in coal processing as follows: The Standard Oil Co.-Pittsburgh Consolidation Coal Co. announcement; the report on the coal industry in Fortune magazine; experiments in underground gasification of coal in Alabama; and the economic picture of coal resources and utilization.

265. ———. Synthesis Gas From Solid Fuels. Petrol. Processing, vol. 2, 1947, pp. 731–733.

Brief reviews of the more important papers given at the symposium on Production of Synthesis Gas at the 112th meeting of the Am. Chem. Soc.

266. ———. Oil's Synthetic Fuels. Nat. Petrol. News, vol. 40, No. 7, 1948, pp. 22–23; Petrol. Processing, vol. 3, 1948, pp. 203–206.

Survey of research and development work done and planned by several members of the oil industry up to the present on the production of synthetic liquid fuels.

267. ———. Oil A-Plenty—But Bureaucrats Press for a Synthetic-Fuel Industry. Petrol. Processing, vol. 4, No. 6, 1949, pp. 653–654.

Editorial criticism of the attempt by the Department of the Interior and the Bureau of Mines "to force synthetic fuels upon the country." The argument, sup-

ported by the opinions of oil-industry executives, leads to the conclusion that the time is not ripe for Government intervention in the fuel program. The oil industry itself is capable of supplying all the fuel needed for any and every purpose. So extraordinarily rapid is the progress of technical development, commercial plants erected now for the production of synthetic fuels would be obsolescent before they could even be built.

268. BLAND, W. F., AND UHL, W. C. Bureau of Mines Asks Thirty Million Dollars More for Synthetic Liquid Fuels Research. Petrol. Processing, vol. 2, 1947, pp. 85–87.

Comments on the bill recently introduced in the Senate by Senator O'Mahoney extending the Bureau of Mines program of research on synthetic liquid fuels. Presents abstracts from the progress report recently made by the Secretary of the Interior and a tabulated summary of actual and estimated expenditures for the years 1945 to 1948, inclusive.

BLASCHCZYK, G. *See* abs. **1498.**

269. BLASS, K. [Influence of Raw Materials on the Synthesis of Fatty Acids.] Fette u. Seifen, vol. 51, 1944, pp. 221–223; Chem. Abs., vol. 42, 1948, p. 8773.

Discusses production of synthetic fatty acids by the paraffin-oxidation process, with refs.

270. BLATCHFORD, J. W. Oxygen Replaces Air in Water-Gas Process. Chem. Eng. News, vol. 28, 1950, p. 1922.

Abstract of paper presented at the chemical conference of the Am. Gas Assocn. Operation is described of a 360-ton/day O_2 plant built for the DuPont Co., by Linde Air Products Co., together with several mechanical blue-gas sets. The rate of O_2 feed to the generators in general was low, although in 1 test the flow averaged 2,000 cu. ft./min. for 45 hr. No loss in product quality at this high rate of gasification is reported as compared with the normal rate, which is about 25% lower. At normal operating conditions the units used about 23.7 lb. of coke, 243 cu. ft. of O_2, and 32.4 lb. of steam to make a million cu. ft. of water gas. The use of O_2 for this process appears to be decidedly advantageous because of the increase in capacity it permits, as well as from the standpoint of fuel consumption and maintenance of equipment. It seems probable that almost any kind of fuel can be used and almost any type of gas maker be modified to use O_2.

BLUM, P. *See* abs. **215.**

271. BLUMENTHAL, L. M. Activated-Carbon Production in Germany During the War. FIAT Final Rept. 1181, 1947, 21 pp.; PB 85,143.

General review of German developments in the production and uses of activated C in such fields as gas-mask C, C-depolarizer for dry cells, purification of water, deoiling of boiler condensate, industrial vapor and gas adsorption, and regenerated cellulose fiber containing active C. The production capacity of plants had increased from a total of 990 tons in 1939 to 1,377 tons per month in 1944. A list of trade names is appended. Particular attention was paid to the use of gas-adsorption carbons in the Fischer-Tropsch synthesis. A higher recovery of C_3H_8 was achieved by increasing the size of adsorbers and by the use of special gas-adsorption carbons, TS and SK identical with type G used in gas masks. SK, an improved supersorbon, 4 mm., 400 gm. per l., was found to be 50–60% more effective than supersorbon T for this application. SK carbon also was found to be very effective in the adsorption of C_2H_4 and of CH_4. Purification of gas for the Fischer-Tropsch process can be carried out as follows: H_2S is removed, then a treatment with supersorbon follows at room temperature to remove gum-forming hydrocarbons, dienes, indenes, and stable cyclic S compounds. The supersorbon is regenerated by the Bayer procedure and liquid-aromatic fuel obtained in this manner. Labile S compounds such as COS are then eliminated by purifying with alkaline Fe hydroxide at 150°–300°. Continuous use of the Fischer-Tropsch catalyst for 6–7 months is insured by this treatment of the gas, which lowers the S content to less than 0.1 gm. per 100 m.[3]

BLYUDOV, A. P. *See* abs. **2772, 2774.**

272. BÓBR, W. [Gaseous and Solid-Fuel Substitutes.] Przeglad gorniczo-hutniczy, vol. 29, 1937, pp. 383–397; Chem. Zentralb., 1937, II, p. 4142; Chem. Abs., vol. 33, 1939, p. 6020.

Review of use of motor fuels coming from sources other than petroleum.

273. ———. [Production of Synthetic Benzine From Coal.] Przeglad Tech., vol. 77, 1938, pp. 277–286; Chem. Abs., vol. 33, 1939, p. 9589.

Review.

274. ———. [Progress in the Technique of Liquefaction of Coal.] Przeglad gorniczo-hutniczy, vol. 30, 1938, pp. 67–78; Chem. Zentralb., 1938, II, p. 2873; Chem. Abs., vol. 34, 1940, p. 6041.

Review of the development of hydrogenation, low-temperature carbonization, extraction (method of Pott and Broche), the Japanese hydrogenation process, and the synthesis of hydrocarbons from CO and H_2 by the methods of Fischer-Tropsch, of Robinson-Bindley, and of the I. G. Farbenindustrie A.-G. Considers costs of individual methods.

275. ———. [Synthetic Motor Fuel in Poland and Austria.] Przemysl Naftowy, vol. 13, 1938, pp. 311–318; Chem. Zentralb., 1939, I, p. 864.

Hydrogenation and synthesis motor fuel and their use.

276. ———. [Progress in the Field of Coal Hydrogenation.] Przeglad gorniczo-hutniczy, vol. 31, 1939, pp. 112–121. Chem. Zentralb., 1940, I, p. 811.

Report on the present status of the production of liquid fuels from coal and recent improvements in the hydrogenation and synthesis processes.

BOCCAREDDA, M. *See* abs. **2390.**

BOCHAROVA, E. M. *See* abs. **725.**

277. BOCHAROVA, E. M., AND DOLGOV, B. N. [Synthesis of Formaldehyde From Water Gas.] Jour. Gen. Chem. (U. S. S. R.), vol. 4, 1934, pp. 145–152; Chem. Abs., vol. 28, 1934, p. 5211.

Best results of 0.5–1.2% Ch_2O were obtained with $4MgO.Mn_2O_3$ catalyst at 400° and 150 atm. pressure.

278. ———. [Synthesis of Higher Alcohols From Water Gas Under Pressure. I.] Compt. rend. acad. sci., U. R. S. S., vol. 3, 1934, pp. 115–118 (in English, pp. 118–120); Chem. Abs. vol. 28, 1934, p. 6698.

CO and H_2 react under pressure with alkalized MeOH catalyzers to give a condensate consisting mainly of a mixture of various alcohols (from Me to octyl). Syntheses were carried on in a circulation apparatus with 4 l. capacity at a temperature of 350°–450° and with a falling (220–150 atm.) or constant (220 atm.) pressure and a space velocity of 5,000–6,000. In every case, 300 cc. of the catalyzer in the form of shavings was used. The optimum ratio of CO : H_2 was about 1 : 1. Zn aluminates gave unsatisfactory results. The substitution of Na for K completely cuts down the yield of oil. The group of catalyzers ($4ZnO.PbO$, $4ZnO.PbO.Zn(OK)_2$, $4ZnO.PbO.O.2Zn(OK)_2$ and $4ZnO.PbO.O.2Zn(OK)_2.CdO$) gave very low yields for all attainable temperatures. Alkaline-Zn vanadates, $4ZnO.V_2O_5.KOH$ and $8ZnO.V_2O_5KOH$, gave the best results. An increase in percentage of Zn lowers the yield. A decrease in V_2O_5 content from 34.24% to 8.06% lowers the yield of oil from 41 to 17%.

279. BOCHAROVA, E. M., DOLGOV, B. N., AND PETROVA, Y. N. [Synthesis of Higher Alcohols From Water

Gas Under Pressure. II.] Jour. Chem. Ind. (U. S. S. R.), vol. 12, 1935, pp. 1249–1255; British Chem. Abs., 1936, B, p. 404; Chem. Abs., vol. 30, 1936, p. 2171.

Apparatus used is the same as that for MeOH synthesis, but the catalyst is more alkaline, and the rate of gas flow is slower, but the temperature is higher (400°–425°) than for MeOH. The pressure is 220 atm. A ratio of H_2 : CO of close to 1 : 1 is best. CO_2 tends to accumulate in recirculated gases. Zn–V catalysts are better than Zn–Al ones, but the best is $8ZnO.AL(OK)_3.0.1V_2O_5$. The total yield of alcohols is 60%, of which 35% is MeOH. The others are EtOH, PrOH, iso–PrOH, BuOH, and iso–BuOH.

280. Bochabova, E. M., Dolgov, B. N., and Prokhorova, Z. M. [Synthesis of Higher Alcohols From Water Gas Under Pressure. III.] Khim. Tverdogo Topliva, vol. 6, 1935, pp. 665–680; Chem. Zentralb., 1936, II, p. 4254; Chem. Abs., vol. 30, 1936, p. 8147.

Syntheses of higher alcohols were accomplished in the Fischer circulating apparatus of 4.5-l. capacity, at 350°–425°, 220 atm. pressure, with a volumetric velocity of the order 6,800–8,400 (time of contact, 26.5–29 sec.) and a duration of 1 hr. In all cases 300 ml. of catalyst were used. The mixture of CO and H_2 was taken in the proportion 1 : 1, as this was found to be best in previous experiments. (*See* abs. **278.**) The best catalyst was found to be $8ZnO.Al(OK)_3 \cdot O.1–V_2O_5$, which gives 47% of an oily layer with a yield of 225 ml. of oil/hr./m.^{3} of gas. The total content of alcohol higher than MeOH in the condensate was found to be 35%, along with 60% MeOH. Qualitatively the aqueous condensate consists of: MeOH, EtOH, iso–PrOH, and the oily layer of C_3H_7OH and a mixture of C_4H_9OH, mainly iso–BuOH. 22 refs.

281. Bocharova, E. M., Dolgov, B. N., Petrova, Y. N., and Yatskovskaya, N. S. [Synthesis of Alcohols of High Molecular Weight From Water Gas Under Pressure. IV. Rechecking of the Methods for Analysis of the Condensate.] Khim. Tverdogo Topliva, vol. 8, 1937, pp. 533–548; Chem. Abs., vol. 32, 1938, p. 1431.

Existing methods for the analysis of the condensate investigated and rechecked. 26 refs.

282. Bocharova, E. M., Dolgov, B. N., Kan-Kogan, K. I., and Petrova, Y. N. [Synthesis of Higher Alcohols From Carbon Dioxide and Hydrogen Under Pressure. V.] Khim. Tverdogo Topliva, vol. 8, 1937, pp. 1107–1121; Chem. Abs., vol. 32, 1938, p. 4518.

This method was described previously. The synthesis was carried out at 350°–425° at a constant pressure of 220 atm. The previously described catalysts, $8ZnO.Al(OH)_3O.1\ V_2O_5.3KOH$ and $8ZnO.Al(OH)_3.O.1\ V_2O_5.O.1\ MoO_3$. 3KOH used in the above synthesis yielded water 70%, MeOH 25%, and higher alcohol 5% by weight of the condensate. The best CO_2 : H_2 ratio for the synthesis of higher alcohols than MeOH was 1 : 2.2. The yield of alcohol fraction boiling 70°–95° for the first catalyst was 266 cm.^{3}/l. of catalyst/hr. Qualitative analysis of the condensate disclosed the presence of considerable amounts of MeOH and 5% of the azeotropic mixture of iso–PrOH, PrOH, and iso–BuOH. 17 refs.

Bocharova, E. M., Dolgov, B. N., and Petrova, Y. N. [Synthesis of Higher Alcohols From Water Gas Under Pressure. II.] *See* abs. **279.**

Bocharova, E. M., Dolgov, B. N., and Prokhorova, Z. M. [Synthesis of Higher Alcohols From Water Gas Under Pressure. III.] *See* abs. **280.**

Bocharova, E. M., Dolgov, B. N., and Kan-Kogan, K. I., and Petrova, Y. N. [Synthesis of Higher Alcohols From Carbon Dioxide and Hydrogen Under Pressure. V.] *See* abs. **282.**

Bocharova, E. M., Dolgov, B. N., Petrova, Y. N., and Yatskovskaya, N. S. [Synthesis of Alcohols of High Molecular Weight From Water Gas Under Pressure. IV. Rechecking of the Methods for Analysis of the Condensate.] *See* abs. **281.**

Bochirol, L. *See* abs. **215.**

Bode, K. *See* abs. **2921.**

283. Bodendorf, K. [Production, Application and Detection of Methanol and Isopropyl Alcohol.] Apoth. Ztg., vol. 45, 1930, pp. 1141–1144; Chem. Abs., vol. 25, 1931, p. 166.

Address dealing with both the earlier and present methods of manufacture, their various uses, and methods of detection.

Boedeker, E. R. *See* abs. **2285.**

284. Boehm, E., and Bonhoeffer, K. F. [Gaseous Reactions of Active Hydrogen.] Ztschr. physial. Chem., vol. 119, 1926, pp. 385–399; Chem. Abs., vol. 20, 1926, p. 3645.

Reactions of H_2 activated by luminous discharge have been studied semiquantitatively for the following substances: O_2, H_2O, N_2, NH_3, Cl_2, HCl, Br_2, HBr, H_2S, CH_4, CO, CO_2, and CH_3Cl. The H_2 behaves as though it consisted of free atoms; with O_2 it forms directly H_2O_2, with CO and CO_2 it forms small quantities of CH_2O. The halogens, which react very rapidly, form H halides. The active form of H is rapidly and completely destroyed by HCl, HBr, H_2S, and CH_3Cl, probably because of reactions like $H+HCl=H_2+Cl$. N_2, H_2O, NH_3, and CH_4 are indifferent. Small quantities of O_2 increased the yield of active H_2 as they also increase the intensity of the Balmer spectrum; but the other gases tried had no effect.

285. Boericke, F. S. Equilibria in the Reduction of Chromium Oxide by Carbon, and Their Relation to the Decarburization of Chromium and Ferrochrome. Bureau of Mines Rept. of Investigations 3747, 1944, 34 pp.; Chem. Abs., vol. 38, 1944, p. 3539.

Reduction of Cr_2O_3 by C involves 4 distinct reversible-reaction steps: (1) $3Cr_2O_3+13C=2Cr_3C_2+9CO$; (2) $5Cr_2O_3+27Cr_3C_2=13Cr_7C_3+15CO$; (3) $5Cr_2O_3+14Cr_7C_3=27Cr_4C+15CO$; (4) $Cr_2O_3+3Cr_4C=14Cr+3CO$. Describes apparatus and methods for measuring equilibria in these reaction steps, and thermodynamic values for each reaction are derived from equilibrium and requisite auxiliary-thermal data. The resulting thermal properties of the Cr carbides show that each carbide is stable with respect to dissociation into a lower carbide and C, into a higher carbide and Cr, or into the elements at all temperatures below the melting point of the carbide. The intermediate carbide is likewise stable with respect to dissociation into the other 2 carbides. A theoretical consideration is given of the decarburization of Cr and ferrochrome by Cr_2O_3, Fe_3O_4, H_2, and Si. Cr_2O_3 is an effective decarburizing agent at 2,000°, particularly if means are furnished for operating under low CO partial pressures. Magnetite, theoretically, is a more effective decarburizer than Cr_2O_3, but in practice the rapid exchange of Fe in the refining agent with Cr in the metallic phase results in about the same net effectiveness as for Cr_2O_3. Both H_2 and Si are unsatisfactory agents for decarburizing Cr or ferrochrome.

———. *See* abs. **1729.**

Bogoyavlenskaya, A. N. *See* abs. **1806.**

Bogrow, A. *See* abs. **2174.**

Boguslavski, I. M. *See* abs. **1671.**

Böhm, H. *See* abs. **1711, 1713, 1717.**

Bökmann, J. *See* abs. **3052, 3053.**

Bollhorn, A. *See* abs. **1504.**

Boltus-Goruneanu, M. *See* abs. **659.**

286. BOLZAU, W. [New Oils and Compounds for Metal Working.] Oel u. Kohle, vol. 39, 1943, pp. 416–418; Chem. Zentralb., 1943, II, p. 1433; Chem. Abs., vol. 38, 1942, p. 1868.

Sulfonic acid obtained from hydrocarbons of the Fischer-Tropsch synthesis, Fettsaure D and its derivatives, and Emulgator H and M, are used for the preparing of water-soluble cutting oils. Oxidation products of synthetic paraffin wax are proposed as emulsifiers for the manufacture of cutting oils and drawing compounds. Emulgierwachs PS is less highly oxidized than Emulgierwachs PHS, and Emulgierwachs PVS is a saponified product.

BONAR, F. *See* abs. **768, 3150, 3151, 3152.**

BONDY, H. F. *See* abs. **2731.**

287. BONE, W. A. Discussion on Catalytic Reactions at High Pressures. Proc. Roy. Soc., vol. 127, A, 1930, pp. 240–267; British Chem. Abs., 1930, A, p. 867.

Reviews work in the High-Pressure-Gas Research Laboratories at the Imperial College during the last 3 yr. with special reference to the formation of HCHO, MeOH, and CH_4 from CO and H_2. By selecting a suitable catalyst and temperature any one of these 3 substances may be produced to the practical exclusion of the other 2. Absence of satisfactory equilibrium data in regard to the MeOH synthesis previous to the present series of investigations is pointed out, and the extreme importance of determining the equilibrium constant by approaching the equilibrium from both sides is emphasized. Discusses errors due to the fact that at the high pressures used the equilibrium mixtures do not obey the sample gas laws.

288. ———. High-Pressure Reactions. Trans. Inst. Chem. Eng., (London) vol. 8, 1930, pp. 98–106; Chem. Abs., vol. 26, 1932, p. 1168.

Recent applications of pressure in promoting useful chemical changes are reviewed with particular emphasis on the synthesis of NH_3 and catalytic syntheses from CO and H_2 mixtures. The influence of pressure upon gaseous explosions of CO–air and H_2–air mixtures and the N_2 activation in CO–air explosions are also considered. Describes and illustrates equipment for a high-pressure research laboratory.

289. ———. Formation of Methanol by the Direct Oxidation of Methane. Nature, vol. 127, 1931, p. 481; Fuel, vol. 10, 1931, pp. 194–195; Chem. Abs., vol. 25, 1931, p. 2968.

Studies on the slow combustion of C_2H_6 showed that the initial product was not a peroxide but either EtOH or some less-oxygenated substance. It has now been found that direct oxidation of CH_4 at 360° and 100 atm. gives MeOH as the initial product. In mixtures of CH_4 and O_2 in the ratio of 9 : 1 the action was complete in a few minutes. About 17% of the CH_4 that was burned was recovered as MeOH, 0.6% as CH_2O, and the remainder as CO, CO_2, and H_2O. No H_2 was liberated, and not even a trace of peroxide was formed. The MeOH was identified by conversion into $HOC_6H_4CO_2Me$ and p–$NO_2C_6H_4CO_2Me$ and was estimated as the nitrite.

290. ———. Initial Formation of Methyl Alcohol in the Oxidation of Methane. Nature, vol. 136, 1935, p. 910; Chem. Abs., vol. 30, 1936, p. 1735.

Explosions of 5 CH_4+2 O_2 mixtures yielded among the suddenly cooled products 0.13% MeOH and 0.03% HCHO. Not the faintest trace of peroxide formation could be detected. The MeOH is formed before the HCHO.

———. *See* abs. **2315.**

291. BONE, W. A., AND ALLUM, R. E. Slow Combustion of Methane. Proc. Roy. Soc. (London), vol. A134, 1932, pp. 578–591; Chem. Abs., vol. 26, 1932, p. 2697.

Results of this investigation and of that summarized in abs. **2445,** demonstrate a case of direct hydrocarbon oxidation, entirely uncomplicated by any sign of peroxidation, in which the most reactive mixture is that corresponding with the alcohol-forming proportion; substantial quantities of MeOH have actually been isolated in circumstances favoring its stability and survival, that is, chiefly at high pressure. The results fulfil the predictions of Bone's hydroxylation theory.

292. BONE, W. A., AND COWARD, H. F. Direct Union of Carbon and Hydrogen. I. Synthesis of Methane. Jour. Chem. Soc., vol. 93, 1908, pp. 1975–1993; Proc. Chem. Soc., vol. 24, 1908, p. 221; Chem. Abs., vol. 3, 1909, p. 887.

Sugar charcoal was purified by prolonged ignition in dry Cl first at 700° and then at 1,100°. The purity of the H_2 used was carefully tested. When less than 0.1 gm. of the charcoal is heated in a stream of pure, dry H_2 at 1,100°–1,200°, in an apparatus similar to that used by Bone and Jerdan, abs. **296,** large quantities of CH_4 were formed. On 2 separate experiments the yields obtained were 73%, the remainder being lost by unavoidable oxidation or decomposition in contact with the walls of the porcelain tube. In 1 group of 4 experiments, 422 $cm.^3$ of CH_4 were obtained from 0.306 gm. of C. Results of the experiments by Bone and Jerdan showing the formation of CH_4 from its elements are fully confirmed.

293. ———. Direct Union of Carbon and Hydrogen. II. Synthesis of Methane. Jour. Chem Soc., vol. 97, 1910, pp. 1219–1225; Proc. Chem. Soc., 1910, vol. 26, p. 137; Chem. Abs., vol. 4, 1910, p. 2938.

From less than 0.03 gm. of purified sugar charcoal, containing not more than 0.06% ash and less than 0.1% H_2, not less than 95% CH_4 results by maintaining it in a stream of pure dry H_2 at 1,150° for 17–25 hr.

294. ———. Thermal Decomposition of Hydrocarbons. I. Methane, Ethane, Ethylene and Acetylene. Jour. Chem. Soc., vol. 93–94, 1908, pp. 1197–1225; Proc. Chem. Soc., vol. 24, 1908, p. 167; Chem. Abs., vol. 2, 1908, p. 3061.

Results of a systematic investigation of the modes of decomposition of the 4 hydrocarbons 500°–1,200° were described. CH_4, which is by far the most stable of the 4 hydrocarbons, and a principal product of the decomposition of the other 3, especially above 800°, decomposes for the main part into C and H_2. The decomposition is, within the range investigated, a surface effect, and the C deposited is of a peculiarly hard and lustrous type. Decomposition of the other 3 hydrocarbons takes place chiefly throughout the main body of the gas, with formation of large quantities of CH_4, which is explained on the supposition that residues such as $\equiv CH$ and $=CH_2$ (which may be considered to have momentary existence during the dissolution process), are directly hydrogenized in an atmosphere rich in H_2. Assumption of the momentary formation of such residues (or the tendency to give rise to them, which actually becomes operative at moderately high temperatures) as the result of the initial dissolution of the hydrocarbon molecule, renders it possible to formulate a rational scheme of the chief causes at work and their modes of operation in each particular case. It may be supposed that these residues are capable of (*a*) forming $H_2C{=}CH_2$ or $HC{\equiv}CH$ as the result of encounters with other like residues, (*b*) breaking down directly into C and H_2, (*c*) combining with H_2 to form CH_4, and that all 3 possibilities may be realized simultaneously in proportions dependent on the temperature and the amount of H_2 present.

295. BONE, W. A., AND GARDNER, J. B. Comparative Studies of the Slow Combustion of Methane, Methyl Alcohol, Formaldehyde, and Formic Acid. Proc. Roy. Soc. (London), vol. A154, 1936, pp. 297–328; Chem. Abs., vol. 30, 1936, p. 4461.

The induction period in the slow combustion of CH_4 at 390°–420° (1) is not influenced by preheating the reactants or exposure of the reacting medium to ultraviolet light, (2) is lengthened by increasing the surface: volume ratio of a SiO_2 reaction vessel, (3) is shortest with a $2CH_4+O_2$ medium, (4) is characterized by the successive formation of small equilibrium amounts of MeOH and CH_2O, and is greatly shortened by additions of either of them or of NO_2, and (5) is markedly lengthened by additions of I. The slow oxidation of MeOH was much faster and less influenced by the SiO_2 surface than that of CH_4 at 390°. It shows no appreciable induction period but may be speeded up by small additions of CH_2O or NO_2. $2MeOH+O_2$ is the most reactive medium, its end products being principally steam and the oxides of C, with a high $CO:CO_2$ ratio. A still higher oxidation rate was found for CH_2O, which showed no induction period even at 275°. HCO_2H as well as performic acid and formaldehyde peroxide were formed as intermediate products. The slowest oxidation rate was observed with HCO_2H, the gaseous end products being principally CO, CO_2, steam, and H_2. The results for CH_4 are explained on the basis of the hydroxylation theory. No sign of an initial peroxidation of the CH_4 was found in any of the experiments.

296. BONE, W. A., AND JERDAN, D. S. Direct Union of Carbon and Hydrogen. I. II. Jour. Chem. Soc., vol. 71, 1897, pp. 41–61; vol. 79, 1901, pp. 1042–1063.

At a temperature of about 1,200°, C unites directly with H_2 to form CH_4, no C_2H_2 or other unsaturated hydrocarbons being formed. H_2 was passed over pure sugar C in a porcelain tube.

BONHOEFFER, K. F. *See* abs. **284.**

BONIFIELD, L. W. *See* abs. **3151, 3152.**

297. BOOMER, E. H. Natural Gas. Sci. and Ind. Research Council, Alberta, Canada, 9th Ann. Rept., 1928, pp. 51–53; Chem. Abs., vol. 24, 1930, p. 4612.

Gas from the Viking field, containing CH_4, 93%, C_2H_6, 3.5%, and N_2, 3%, has been used as a raw material for thermal decomposition into C-black or low-boiling hydrocarbons. Direct oxidation processes are found to be of little value, but conversion into water gas has been achieved. Use of the gas for high-pressure synthesis is considered, and attention is being paid to the removal of S, which is present in large amount.

298. BOOMER, E. H., AND BROUGHTON, J. W. Oxidation of Methane at High Pressures. I. Preliminary Experiments. Canadian Jour. Research, vol. 15, B, 1937, pp. 375–382; Chem. Abs., vol. 31, 1937, p. 8502.

Mixtures of O_2 and CH_4 at pressures 100–180 atm. were passed at various temperatures between 300° and 350° over various catalysts with the object of discovering the optimum conditions for the production of CH_3OH. Preliminary experiments indicated that oxide catalysts were relatively inactive. Catalysts of the hopcalite variety promoted oxidation violently for a short time and then became inactive. Cu and Ag catalysts were found to be the most desirable for the formation of CH_3OH. O_2-natural gas (largely CH_4) mixture containing 7.3–7.5% O_2 were used. A maximum production of CH_3OH was found to be a function of the rate of flow of the gas mixture. Small amounts of HCOOH and HCHO were obtained, the former appearing as $HCOOCH_3$ when Ag was the catalyst.

299. BOOMER, E. H., AND THOMAS, V. Oxidation of Methane at High Pressure. II. Experiments With Various Mixtures of Viking Natural Gas and Air. Canadian Jour. Research, vol. 15, B, 1937, pp. 401–413; Chem. Abs., vol. 32, 1938, p. 751.

Mixtures of a natural gas, substantially CH_4, and air in various proportions were passed over catalysts, and the effects of the variables, composition of mixture, pressure, temperature, and space velocity were determined. Similar experiments were made with mixtures of CH_4 and air. Mixtures containing from less than 3% to more than 13% of O_2 as air were used. The temperature range was 350°–500°, and the pressure range 140–230 atm. MeOH was the principal product, and yields as high as 74% on the basis of C oxidized were obtained. Cu was the principal catalyst used. Traces of S poisoned the catalyst very effectively. The yield of useful products was found to depend primarily on the catalyst, the O_2 concentration, and the temperature. The influence of the time of reaction and the pressure was found to be slight. Low yields of HCHO and HCOOH and high yields of MeOH, when the oxidation was carried out under pressure and with a deficiency of O_2, are explicable on the basis of the hydroxylation theory. Formation of peroxides was not observed.

300. ———. Oxidation of Methane at High Pressure. III. Experiments Using Pure Methane and Principally Copper as Catalyst. Canadian Jour. Research, vol. 15, B, 1937, pp. 414–437; Chem. Abs., vol. 32, 1938, p. 751.

Mixtures of CH_4 containing some N_2 and O_2 were passed over Cu and Ag catalysts. The effects of the variables, composition of mixture, pressure, and temperature were determined. From 3–7% of O_2 was used in various experiments at pressures from 140–220 atm. at a temperature of 475°. The effect on yields of additions of CO_2 to the mixture was determined. Yields of MeOH up to 75% on the basis of C oxidized were obtained, but this is too low to be of commercial import since the yield of MeOH calculated on the basis of total C is less than 5%. O_2 loss in the conversion ranged from 50–10%. All the O_2 entering the system did not appear in the products, and nearly all experiments had O_2 in the off gases. Reactions are offered for the products observed based on Bone's hydroxylation theory and Norrish's chain reaction theory.

301. BOOMER, E. H., AND MORRIS, H. E. Hydrogen–Carbon Dioxide Reaction. Jour. Am. Chem. Soc., vol. 54, 1932, p. 407; Chem. Abs., vol. 26, 1932, p. 1180.

With an unsupported Zn–Cu–Al catalyst, a gas mixture of 27% CO_2, 71% H_2, and 2% N_2 at 325° and 1,700 lb. pressure gave an effluent gas containing 4% CO. This suggests that the primary step in the synthesis of MeOH from CO_2–H_2 involves the reduction of CO_2 and the nature of the catalyst determines the extent to which the resultant CO is hydrogenated. As the activity of the catalyst decreases the MeOH reaction is most affected; experiments with this same catalyst and water gas gave appreciable amounts of CO_2. This suggests a new mechanism for the synthesis of MeOH, which will be discussed later.

BOOMER, E. H., and THOMAS, V. Oxidation of Methane at High Pressure. II. Experiments With Various Mixtures of Viking Natural Gas and Air. *See* abs. **299.**

———. Oxidation of Methane at High Pressure. III. Experiments Using Pure Methane and Principally Copper as Catalyst. *See* abs. **300.**

302. BOOMER, E. H., MORRIS, H. E., AND ARGUE, G. H. Apparent Formation of Copper Carbonyl. Nature, vol. 129, 1932, p. 438; Chem. Abs., vol. 26, 1932, p. 2932.

Apparent formation of Cu carbonyl was noted in the synthesis of MeOH with a catalyst containing Cu.

This fact offers a new view on the mechanism of the synthesis of MeOH, which is to be be presented later.

303. Booth, N. Chemicals From Carbonization Gases. I. Separation of Methane and Ethylene. II. Treatment of Methane and Ethylene. Coke Smokeless-Fuel Age, 1945, pp. 85–87, 112–114.

CH_4 may be decomposed by the action of heat with or without catalysts. Natural gas and steam passed over Fe, Ni, and Co oxides at 5,000 lb. and 560°–600° C. gave liquid hydrocarbon products. This process is not economically satisfactory unless the raw material is very cheaply obtained. The yield of products is only moderate under the best conditions so far found. CH_4 can be oxidized. For example, the reaction $CH_4+H_2O \rightarrow CO+3H_2$ has been used to produce the gas for the Fischer-Tropsch synthesis; $CH_4+O_2 \rightarrow CH_3OH$ and $CH_4+O_2 \rightarrow CO+2H_2$, the last reaction occurring over a Ni catalyst at temperatures of about 850°–1,200° C., the product again being useful for hydrocarbon syntheses.

———. *See* abs. **1628.**

304. Booth, N., Wilkins, E. T., Jolley, L. J., and Terboth, J. A. Catalytic Synthesis of Methane—Experimental Work of the Fuel Research Station. Gas Research Board, Copyright Pub. 21/11, 1948, 44 pp.; Chem. Abs., vol. 43, 1949, p. 3169.

Ni catalysts supported on kieselguhr and promoted with ThO_2 and MgO have been used with water gas–H_2 mixtures of varied compositions. In a laboratory-scale apparatus with a throughput of 1 cu. ft. of gas per hr. at atmospheric pressure, the catalysts enabled the conversion of over 99% of the CO in the process gas to be maintained for long periods with space velocities of 3,700 volumes of gas per volume catalyst space per hr. and at reaction temps. of 250°–350°. The performance of the catalysts was limited by a slow loss of activity, owing to poisoning by S compounds in the process gas and to deposition of C on the catalyst. The effect of the S compounds can be minimized by use of process gases containing less than 0.004 grain S/100 cu. ft. The deposition of C on the catalyst can be controlled by suitable conditions in the preparation of the catalyst, by the choice of suitable promoters and supports, by the use of $3H_2:1CO$ ratio in the process gas, by additions of moderate proportions of water vapor to the process gas, and by effective removal of the exothermic heat of reaction so that high temperatures in the catalyst bed are avoided. Little, if any, advantage appeared to accrue from the use of 50 atm. pressure. Results in a unit processing 200 cu. ft. of gas per hr. were in substantial agreement with those in the laboratory unit. The best performance of the catalysts was equivalent to about 2,200 ton CH_4 per ton of catalyst used in experiments in which the catalyst was extended as a thin layer.

305. Boreskov, G. K., and Slin'ko, M. G. Basis for Calculation of Catalyst Apparatus for Reversible Exothermic Processes. Jour. Appl. Chem. (U. S. S. R.), vol. 16, No. 9/10, 1943, pp. 377–396 (English summary); Chem. Abs., vol. 38, 1944, p. 6135.

Mathematical theoretical-design data. It is shown that for calculation of optimum temperature it is enough to know the apparent activation energy of the forward reaction. Graphical and analytical methods of determination of optimum temperature are presented. Shows graphic calculation method by determination of the catalyst mass necessary for changing the degree of contact under different heat-flow conditions.

Borisenko, A. I. *See* abs. **3413, 3414.**

306. Borisov, P. B., and Eventova, M. S. [Production of Gasoline from Paraffin Residues from Synthine in the Presence of Aluminum Chloride.] Neftyanoe Khoz., vol. 20, No. 12, 1939, pp. 43–45; Khim. Referat. Zhur., No. 6, 1940, p. 110; Chem. Abs., vol. 36, 1942, p. 4994.

Liquid fraction, boiling, 240°–300°, of synthine residue and the solid fraction requires 20% of $AlCl_3$ for cracking. The solid-fraction boiling above 300° is cracked with only 10% of $AlCl_3$. Maximum yields of gasoline, up to 48%, are obtained on cracking with 15% $AlCl_3$. The gasoline obtained, boiling 22°–150°, consists nearly exclusively of isoparaffins. The octane number of the 22°–50° fraction containing pentanes and hexanes is 88, of the 50°–100° fraction it is 73, and of the whole 22°–150° fraction it is 79.

Borisova, G. P. *See* abs. **2169.**

Bormann, W. *See* abs. **2929, 2930, 2931, 2934.**

307. Bosch, C. [Problems of Commercial Hydrogenation Processes.] Chem. Fabrik, vol. 7, 1934, pp. 1–10; Chem. Abs., vol. 28, 1934, p. 1424; British Chem. Abs., 1934, B, p. 256.

Hydrogenation of N_2 to NH_3, CO to alcohols, and coal, petroleum, and tar to benzine as developed by the I. G. Farbenindustrie A.–G. presented in an address.

308. ———. Where There's a Will, There's a Way. Ind. Chemist, vol. 10, 1934, pp. 90–94, 113.

Abridged version of a lecture before the Norwegian Academy of Science in which the author discusses the problems arising during the development from the laboratory to the technical scale of the processes carried out in the works of I. G. Farbenindustrie A.–G., namely hydrogenation of N_2 to NH_3, of CO to MeOH, and of coal or tar to gasoline. The principal items dealt with are the production and purification of H_2, the development of suitable catalysts, and the selection of constructional materials of high chemical resistance.

309. Bosworth, R. C. L. Synthetic Fuels From Carbon Monoxide and Hydrogen. Australian Jour. Sci., vol. 5, 1942, pp. 28–33; Chem. Abs., vol. 37, 1943, p. 741.

Production of synthetic fuels by catalytic reduction of CO with H_2.

310. Botolfsen, E. [Studies of Catalysts.] Arch. Math. Naturvidensk., vol. B41, pt. 2, No. 7, 1938, p. 29.

1. Water-gas reaction. The effect of $MgCO_3$ and MgO, alone and as carriers for other catalysts, on the course of the water-gas reaction is studied at temperatures 300°–800°. 2. CH_4 formation in CO-steam mixtures. A catalyst obtained by precipitation from Ni nitrate solution forms CH_4 from CO–H_2O mixtures at temperatures at which formation of H_2 does not yet occur. 3. Decomposition of CO in CO-steam mixtures. The catalyst described yields from this mixture a gas containing no CO. The reaction, separating out C, begins at 150° and is complete at 190°–195°. 4. Formic-acid formation in CO–steam mixtures. HCOOH formation can be regarded as an intermediate stage of the water-gas reaction. 5. Ni carbonyl as catalyst.

———. *See* abs. **2583.**

311. Boudouard, O. [Decomposition of Carbonic Anhyride in Presence of Carbon.] Compt. rend., vol. 128, 1899, pp. 824–825; Jour. Chem. Soc., vol. 2, 1899, p. 417.

When CO_2 is heated at 650° with charcoal and with C from the decomposition of CO, the proportion of CO in the gas gradually increases, the reaction being more rapid with the charcoal than with the C. The limit of the reaction with charcoal was reached after 12 hr., and the composition of the gaseous mixture (CO_2 61 vol., CO 39 vol.), is identical with the composition of the gas at the limit of the reaction between CO and Co oxide at the same temperature.

312. ———. [Decomposition of Carbonic Anhydride in Presence of Carbon.] Compt, rend., vol. 128, 1899, pp. 1524–1525; Jour. Chem. Soc., vol. 2, 1899, p. 596.

Reaction between CO_2 and C at 800° and 925° has been studied. Different forms of C were used. The speed of reaction was greatest with wood charcoal and least with bone black. As is the case at 650°, at 800° the decomposition ceases when the composition of the gaseous mixture is the same as that obtained by the action of CO on Ni or Co oxide at the same temperature, in this case, 7% of CO_2 and 93% of CO. At 925° the proportion of CO_2 is 4%.

313. ———. [Decomposition of Carbonic Oxide by Metallic Oxides.] Compt. rend., vol. 128, 1899, pp. 1522–1523; Bull. soc. chim., vol. 21, 1899, pp. 463–465, 712–713; Jour. Chem. Soc., vol. 2, 1899, p. 595.

When CO is decomposed at 800° in presence of oxide of Ni or Co or of FE_2O_3, the amount of decomposition depends on the time of reaction. The speed of reaction at 800° is greater than at 650°, equilibrium being attained in 2 hr. at the higher temperature and only after 6 hr. at the lower. In the presence of Ni or Co oxide at 800°, no further change occurs after the gaseous mixture contains 7% of CO_2 and 93% of CO.

314. ———. [Decomposition of Carbonic Oxide in Presence of Ferric Oxide.] Compt. rend., vol. 128, 1899, pp. 98–101; Jour. Chem. Soc., vol. 2, 1899, p. 287.

When finely divided ferric oxide is heated at 445° in sealed tubes with pure and dried CO, the decomposition of the latter is a function of the time and of the quantity of ferric oxide present. The quantity of CO_2 formed increases regularly and eventually the decomposition is complete. Similar experiments are being made with Co and Ni oxides at 445° and with all 3 oxides at higher temperatures.

315. ———. [Decomposition of Carbonic Oxide in Presence of Metallic Oxides.] Compt. rend., vol. 128, 1899, pp. 307–309; Jour. Chem. Soc., vol. 2, 1899, p. 365.

When CO is passed over heated Ni and Co oxides at 445°, the rate of oxidation is much more rapid than with ferric oxides, as in the latter case the amount of decomposition increases with the quantity of oxide used and with the time. In all these cases the amount of C deposited is of the same order of magnitude as the oxide employed. When a large excess of purified C is mixed with the oxide, the results are the same but the action appears to take place more slowly.

316. ———. [Decomposition of Carbonic Oxide in Presence of Metallic Oxides.] Compt. rend., vol. 128, 1899, pp. 822–824; Jour. Chem. Soc., vol. 2, 1899, p. 417.

Decomposition of CO at 650° in presence of Fe_2O_3, Ni_3O_4, and Co_3O_4 is a function of the time and within certain limits depends on the quantity of metallic oxide present. Whereas at 445° the decomposition is complete, at 650° it is limited, and in presence of Co_3O_4 decomposition ceases when the gaseous mixture contains 61% CO_2 and 39% CO.

317. ———. [Influence of Pressure in Phenomena of Chemical Equilibrium.] Compt. rend., vol. 131, 1900, pp. 1204–1206; Jour. Chem. Soc., vol. 2, 1901, p. 151.

It has been shown that the reaction $CO_2+C \rightleftharpoons 2CO$ proceeds as a reversible reaction in accordance with dynamical deductions (*see* abs. **318**). Experiments previously conducted at atmospheric pressure are now supplemented by determinations at lower pressure, which are wholly in accord with the previous results and again verify the formula given there.

318. ———. [Numerical Laws of Chemical Equilibrium.] Compt. rend., vol. 130, 1900, pp. 132–134; Jour. Chem. Soc., vol. 2, 1900, p. 199.

In a gaseous system in equilibrium at all temperatures and pressures a relation exists between the concentrate of the various gaseous phases In the case of the system $2CO \rightleftharpoons CO_2+C$ the final equilibrium does not depend on the initial state between 650° and 800°. From an equation set up, the ratios of the concentrate of CO and CO_2 at various temperatures may be calculated and agreement with experimental determinations may be seen:

Temperature	CO_2 found	Calculated	CO found	Calculated
650°	0.61	0.61	0.39	0.39
800°	.07	.10	.93	.90
925°	.04	.03	.96	.97

319. ———. [Chemical Equilibria.] Ann. chim. phys., ser. 7, vol. 24, 1901, pp. 5–85; Jour Chem. Soc., vol. 2, 1901, p. 646.

Résumé of earlier papers containing a full discussion of the reversible reaction $2CO \rightleftharpoons CO_2+C$. In the presence of finely divided metallic substances such as Fe heated at 445°, the velocity of the direct reaction is increased without modifying the proportions of the gaseous reagents in the final system when equilibrium is attained. The experiments prove that the equilibrium ratio $CO : CO_2$ in contact with C is a function of the temperature, and the results are in general agreement with the laws respecting equilibria in gaseous systems.

320. ———. [Reducing Action of Carbon on Metallic Compounds.] Bull. soc. chim., ser. 3, vol. 25, 1901, pp. 282–287; Jour. Chem. Soc., vol. 2, 1901, p. 314.

Reduction of metallic compounds by heating with pure C at temperatures of 445°–1,150° is not due directly to C but to CO, a trace of which is always present to start the reaction. The CO_2 formed is then decomposed by C with the regeneration of CO and so on indefinitely. The results are in accord with the reaction $2CO \rightleftharpoons CO_2+C$.

321. ———. Reversible Reaction $CO_2+H_2 \rightleftharpoons CO+H_2O$. Bull. soc. chim., vol. 25, 1901, pp. 484–489; Jour. Chem. Soc., vol. 2, 1901, p. 383.

Mixture of equal volumes of dry CO_2 and H_2 was heated in a porcelain vessel at 850° and 1,100°, and an analysis was made of the mixture of CO_2, CO, H_2, and aqueous vapor produced. The results agree fairly well with Le Chatelier's formula (*see* abs. **318**) for the equilibrium of gaseous mixtures. Pressure has no influence on the equilibrium since the numbers of reacting and produced molecules are equal. The reaction is of interest in connection with the manufacture of water gas.

BOUNDY, R. H. *See* abs. **1363.**

BOWEN, A. R. *See* abs. **2368.**

BOWMAN, N. J. *See* abs. **420b, 3642b.**

BOYD, C. A. *See* abs. **1428.**

322. BOYD, J. Petroleum Industry Has Definite Role in Synthetics Development. Petrol. Refiner, vol. 29, No. 12, 1950, pp. 77–85.

Barring unexpected developments in atomic or solar energy, an anticipated gap between domestic oil demand and supply will have to be met by synthetic liquid fuels and imports. Although the amounts of oil ultimately recovered from domestic oil fields will be far greater than present proved reserves, it is obvious that the security of the Nation's liquid-fuels position will be greatly enhanced when the supply is based in part on solid fuels, such as coal and oil shale, which compose more than 95% of our proved fuel reserves. Synthetic fuel processes also can play an important part in meeting requirements for strategic chemicals. Current

shortages and increasing requirements for benzene, phenol, toluene, and certain other chemicals could accelerate the schedule for constructing the initial coal-hydrogenation plants, in view of the fact that these chemicals would be produced from such plants in important quantities.

323. ———. Synthetic Fuels Future. Oil Gas Jour., vol. 49, No. 28, 1950, p. 184; Petrol. Refiner, vol. 29, Dec. 1950, pp. 77–85.

Research on synthetic fuels has progressed to the point where it has set a ceiling on the prices of petroleum products, and the time may not be far distant when economic considerations will bring about a substantial synthetic-fuels industry. The oil industry is the logical one to handle this business, particularly after the coal or oil shale is brought above ground and a gradual shift of some parts of the liquid-fuels market to synthetics is predicted. Domestic and foreign supplies of crude petroleum are briefly analyzed and figures on costs and capital investment for synthetic fuels are cited.

324. ———. Changing Patterns of Fuel Supply. Mech. Eng., vol. 73, 1951, pp. 189–190; Chem. Abs., vol. 45, 1951, p. 3143.

The actual quantity of coal produced has remained relatively unchanged for some time, but the % of our fuel requirements supplied by coal has declined from over 78% in 1920 to less than 40% in 1949, while that of petroleum has increased from 15% to almost 37% and natural gas from 4% to almost 19% in the same period. Petroleum production and reserves of gas and oil have increased and further reserves will be found, but the gap between production and consumption will be narrowed so that there must be recourse to synthetic fuels, especially gasoline from coal. High yields of aromatic hydrocarbons can be secured both in the hydrogenation of coal and by suitable treatment of oil shale.

325. BOYER, J. [Industrial Syntheses of Methanol.] La Nature, No. 3137, 1947, pp. 177–180.

Synthesis gas for the production of MeOH is produced by the gasification of wood in the presence of O_2 and steam, yielding a synthesis gas with a H_2: CO ratio of 2:2 and 7% of inerts. The gas is converted by means of the Grande Paroisse process using a mixture of ZnO and Cr_2O_3 as the catalyst at 425° and 650 kgm. per cm.^{2} pressure. After rectification the MeOH obtained is 99.9% pure. The yield per ton of dry wood is 3 hl.

BRADFORD, B. W. *See* abs. **341.**

BRADLEY, T. F. *See* abs. **2241, 2442.**

BRAMLEY, A., AND BEEBY, G. H. Gaseous Cementation of Iron and Steel. II. Cementation With the Nitrogenous Vapors of Pyridine and Methyl Cyanide. *See* abs. **327.**

326. BRAMLEY, A., AND JINKINGS, A. J. Gaseous Cementation of Iron and Steel. I. Cementation by Carbon Monoxide. Iron and Steel Inst., Carnegie Schol. Mem., vol. 15, 1926, pp. 17–69; Chem. Abs., vol. 21, 1927, p. 1622.

Carburizing action of CO is studied by placing test bars in a SiO_2 tube, glazed inside and out and heated with Nichrome wire, the gas being generated by the action of concentrated H_2SO_4 on HCOOH. Preliminary experiments showed that it was necessary periodically to reverse the direction of flow of the gas and support the bars centrally in the furnace tube to obtain uniform carburization. Thoroughly dry gas was essential. A detailed study was made of the amount and distribution of C introduced during the process of cementation, as affected by (*a*) the rate of flow of the gas through the furnace, (*b*) the period of carburization, (*c*) the temperature of carburization, (*d*) the concentration of C in the original steel. Curves and photomicrographs are shown. No evidence of the liquation described by Giolitti was found. In the low-C steels the increases in diameter are in the same order as the weight of C introduced. In the bars carburized below 900° and those originally containing considerable amounts of C, the changes in dimensions were small.

327. BRAMLEY, A., AND BEEBY, G. H. Gaseous Cementation of Iron and Steel. II. Cementation With the Nitrogenous Vapor of Pyridine and Methyl Cyanide. Iron and Steel Inst. Carnegie Schol. Mem., vol. 15, 1926, pp. 71–125; Chem. Abs., vol. 21, 1927, p. 1622.

Object is to ascertain the amount and distribution of both C and N introduced when the bars were heated in an atmosphere of CO saturated at 18° with the vapors of either pyridine or MeCN. The CO is passed up a column down which the liquid containing the vapor with which the gas is to be saturated is kept dripping through Cu gauze. Otherwise the equipment is the same as in Part I. The following factors were studied for CO saturated with C_5H_5N: (*a*) Rate of flow of gas stream; (*b*) period of cementation; (*c*) temperature of cementation. MeCN is a more efficient cementing agent than C_5H_5N. The condition of the bars after cementation was similar to that obtained with C_5H_5N. The effect of increasing initial concentration of C was studied both for CO+C_5H_5N and CO+MeCN. In the presence of N compounds, the importance of reversing the direction of gas flow is greater than with CO alone, as even in this case the cementation was at times more intense at the ends than in the middle of the bars. Photomicrographs show that a characteristic feature of a case produced by a nitrogenous cement is the presence of a narrow zone near the inner edge of the case in which fairly deep etching shows needles. The presence of N also reduces the amount of C in the steel of eutectoid composition and tends to preserve the Fe in the γ state.

328. BRAMLEY, A., AND LAWTON, G. Gaseous Cementation of Iron and Steel. III. Influence of Hydrocarbons on the Carburization of Iron and Steel. Iron and Steel Inst. Carnegie Schol. Mem., vol. 16, 1927, pp. 35–100; Chem. Abs., vol. 22, 1928, p. 207.

From a study of photomicrographs, it is concluded that the cementation produced when a carburetted gas (such as CO saturated with toluene at 18°) is passed over a specimen of Fe or steel in 1 direction only is much more uneven than when CO is used alone. Obstructions to the free circulation of carburizing gas cause uneven cementation. Alternate passing of the gas, first in 1 direction and then in the opposite, favors even cementation. The fact that the carburizing gas is often of such a nature as to be decomposed by the heat of the furnace must be taken into account if even cementation is desired. Variations from this source will depend upon the temperature and size of the various parts of the furnace and upon the decomposition. When a tubelike furnace is used and gas is passed in from both ends the cementation is often considerably weaker in the center of the bars than at the ends. This is because the carburizing agent becomes exhausted too quickly and indicates either too slow a flow of gas or excessive decomposition of the latter. Under certain conditions the decomposing gas deposits a sheath of C over the ends of the bars. This sheath prevents contact of gas and metal and further carburization at these points is difficult. Such bars show a greater cementation along their centers. The authors prove that the liquation theory of cementation as put forth by Giolitti is unsound. They find that the amount of redistribution of the C in steel, while the latter is cooling down, is inappreciable. The depth of carburization is greater

the longer the period of cementation and the higher the temperature. The depth increases with the temperature according to a linear law. As the period of cementation is increased in geometrical progression, the depth of penetration increases in the same way but with a different common ratio. The diffusivity constants for C diffusing into steel are calculated for the several carburizing mixtures and temperatures employed.

329. BRAMLEY, A., AND TURNER, G. Gaseous Cementation of Iron and Steel. IV. Action of Mixtures of Carbon Monoxide and Ammonia on Iron and Steel and Its Bearing on the Process of Cementation. Iron and Steel Inst. Carnegie Schol. Mem., vol. 17, 1928, pp. 23–66; Chem. Abs., vol. 22, 1928, p. 4437.

Cementations of Armco Fe were made at various temperatures with mixtures of CO and NH_3 and with mixtures of CO and H_2. The cementations were conducted at various temperatures ranging 700°–1,050° at intervals of 50°, and the process was continued in each case for 10 hr. The test results prove that the carbonizing action of mixtures of CO and NH_3 is much greater than that of CO alone. The carburizing properties of mixtures of CO and H_2 were stronger than CO alone but not so intense as corresponding mixtures containing NH_3. Micrographs show that the microstructure of the Fe–C alloys is entirely altered by the presence of N; this is the case especially when the cementations are made at temperatures below 800°; above 800° very marked segregation of cementite takes place.

BRAMLEY, A., AND LAWTON, G. Gaseous Cementation of Iron and Steel. III. Influence of Hydrocarbons on the Carburization of Iron and Steel. *See* abs. **328.**

330. BRAMLEY, A., AND LORD, H. D. Equilibria Between Mixtures of Carbon Monoxide and Carbon Dioxide at Various Pressures in Contact With Steels of Different Carbon Concentrations at 750°–1,150°. Jour. Chem. Soc., 1932, pp. 1641–1669; Chem. Abs., vol. 26, 1932, p. 5529.

Equilibria between CO, CO_2, and steels of C contents varying from 0.1 to 2.0% have been measured at temperatures of 750°–1,150° by means of a static method. Results indicate that C in austenite is in the form of an equilibrium mixture of monatomic C and Fe_3C. The concentration of C in the gaseous mixture follows Henry's law if the C vapor is considered monatomic. At the 700°–1,100°, graphite is the stable form of C and not Fe_3C. In the presence of graphite, further carburization will occur if the $CO : CO_2$ ratio is less than 1; if it is greater than 1, decarburization will occur. In the equilibrium diagram, the graphite-solubility line is approximately parallel to the Fe_3C-solubility line and to the left of that of amorphous C. Heats of formation were determined as follows: Dissolved Fe_3C from 3Fe+2CO 29,950 cal.; precipitated Fe_3C from 3Fe+2CO 36,950 cal.; Fe_3C from γ-iron and graphite —4,750 cal.; and Fe_3C from α-iron and graphite —6,950 cal.

BRAMLEY, A., AND TURNER, G. Gaseous Cementation of Iron and Steel. IV. Action of Mixtures of Carbon Monoxide and Ammonia on Iron and Steel and Its Bearing on the Process of Cementation. *See* abs. **329.**

BRANTING, B. F. *See* abs. **3209.**

331. BRATZLER, K. [Sorption Methods for the Analytical and Preparative Separation of Gases.] Oel u. Kohle, vol. 39, 1943, pp. 953–960; Chem. Abs., vol. 38, 1944, p. 6154.

Briefly discusses theory of the separation of gases by adsorption and desorption. Because of the lowered vapor pressure of the adsorbed gases the difference in the relative volatility of various adsorbed gases becomes great enough for purposes of separation at temperatures that would be too high for effective separation by fractional distillation. Pure C_3H_8 is obtained from the commercial gas containing C_2H_6 and C_4H_{10} by passing it slowly at 0° or room temperature over activated charcoal that had been degassed at 200° and 0.1 mm. Hg. After atmospheric pressure has been reached, which may require 20–30 min., an electric oven is placed over part of the adsorption tube and some of the gas is desorbed; the desorbed gas comes in contact with the adsorbed gas in the cold part of the tube and exchange of the heavier and lighter components of the gas takes place. In this way the light impurities are driven off first followed by pure C_3H_8, and the heavy impurities remain adsorbed. The same principle is applied to analytical methods that give satisfactory results if allowance is made for the material that remains adsorbed. This difficulty is avoided by carrying out the desorption under vacuum. The latter method is particularly suited to the determination of small concentrations of a volatile component in a less volatile gas (C_2 hydrocarbons in commercial C_3H_8). For the determination of C_3 and C_4 hydrocarbons in coke-oven gas or residual gas from the adsorption plant connected with a Fischer-Tropsch synthesis plant, it is best to concentrate these compounds by adsorption on activated charcoal and desorb them by steaming (Carbotox process). If the hydrocarbon mixture to be adsorbed contains olefins, the breakthrough of olefins, and thereby of the other hydrocarbons through the adsorbent, can be controlled automatically by bromination of the olefins with Br made in an electrolytic cell and measuring the amount of current used in the preparation of Br.

331a. ———. [Technical Production of Low-Boiling Hydrocarbons.] Erdöl u. Kohle, vol. 4, 1951, pp. 478–486; Fuel Abs., vol. 10, No. 6, 1951, abs. 5,143.

Processes for large-scale hydrocarbon production over past 30 yr. are chronologically briefly reviewed (decomposition of coke-oven gas, natural gas processes, high-pressure hydrogenation, Fischer-Tropsch synthesis, and various petroleum cracking processes). Details and flow sheets are given of processes for conversion of high-pressure hydrogenation waste gases to C_4H_{10}, C_3H_8, C_2H_6, and production of C_2H_4 from coke-oven gas. Descriptions and flow sheets are also given of batch production of gas oil and gasoline from Fischer-Tropsch waste gases and of continuous hypersorption and rectisorption processes. Disadvantages and operational difficulties of the various methods are discussed.

BRAUDE, G., AND BRUNS, B. [Kinetics and Mechanism of the Catalytic Hydrogenation of Carbon Monoxide. II. Formation of Iron Carbide During Hydrogenation of Carbon Monoxide on an Iron Catalyst.] *See* abs. **333.**

332. BRAUDE, G., SHURMOVSKAYA, N., AND BRUNS, B. [Kinetics and Mechanism of the Catalytic Hydrogenation of Carbon Monoxide. I. Method of Preparation of Metal Catalysts From Oxides and Handling the Catalysts Without Contact With the Air.] Jour. Phys. Chem. (U. S. S. R.), vol. 22, 1948, pp. 483–486; Chem. Abs., vol. 42, 1948, p 7147.

Reduced metal is kept in H_2. Samples are withdrawn in H_2 also.

333. BRAUDE, G., AND BRUNS, B. [Kinetics and Mechanism of the Catalytic Hydrogenation of Carbon Monoxide. II. Formation of Iron Carbide During Hydrogenation of Carbon Monoxide on an Iron Catalyst.] Jour. Phys. Chem. (U. S. S. R.), vol. 22, 1948, pp. 487–494; Chem. Abs., vol. 42, 1948, pp. 7147–7148.

Mixtures of CO and H_2 in the ratios 1 : 3 to 1 : 5 were circulated at 225°–350° over an Fe catalyst prepared

by H_2 reduction of Fe_3O_4. The main reaction occurring was $nFe+CO+H_2 \rightarrow Fe_nC+H_2O$ (I). This was proved by the following observations: (*a*) The gas pressure dropped first (for example, for 5 min.) rapidly and then very slowly. The rapid drop (after cooling the reaction product) corresponded to twice the original amount of CO. (*b*) The reaction product was mainly H_2O, and the amount of CH_4 and CO_2 formed was too small to account for the CO consumed. (*c*) The missing C was found in the catalyst. When the catalyst was used for longer time, the concentration of C in it increased and its efficiency decreased; the catalytic activity almost disappeared when 0.24 atom C was deposited/atom Fe. The slow drop of pressure was due to the reaction between this carbide and the excess of H_2. The rate of reaction I increased 2.5 times when the initial pressure of CO was raised from 20 to 241 mm. dibutyl phthalate and was about proportional to the square root of the H_2 pressure (46–1,103 mm. dibutyl phthalate). The energy of activation (from the temperature coefficient) of reaction I was 15,500 cal./mol. The formation of CH_4 is due to the reaction $nFe+2CO \rightarrow Fe_nC+CO_2$. This reaction was studied in the absence of H_2. It follows the equation of the first order, is slower than I, and has an apparent energy of activation (264°–350°) of 6,900 cal./mol. The mechanism of the hydrogenation of CO is discussed.

BRAUDE, G. E. *See* abs. **1591, 1592.**

334. BRAUNHOLTZ, W. T. K. Rational Utilization of Coal. Fuels Obtained by the Treatment of Coal. Colliery Guard., vol. 138, 1929, pp. 341–343; Chem. Abs., vol. 23, 1929, p. 1736.

General discussion of carbonization and hydrogenation of solid fuels and synthesis of liquid fuels from water gas as a means of obtaining more suitable fuels from coal.

335. BRAUNKOHLE-BENZIN, A.-G. [Improving the Effect of Cobalt Catalyst in Hydrocarbon Synthesis.] German Patent Abridgments, vol. 64, 1943, p. 726; British Coal Utilisation and Research Assoc., Monthly Bull., vol. 8, 1944, abs. 8305.

Addition of a relatively large amount of steam to the synthesis gas when starting up for the first time is claimed to have a beneficial effect upon the Co catalyst.

336. BRAYBROOK, F. H. Development of Synthetic Detergents and Future Trends. Chem. and Ind., 1948, pp. 404–407, 409–410.

Growth of the synthetic-detergent industry is traced and statistics are quoted. In the United States alone for 1947, it is believed that 150,000 tons (35–40% active content), or 7.5% of the American soap market, were sold. Assuming that 1 ton of synthetic soap (20% active content) replaces 1 ton of fatty-acid soap (60% fatty acid content), there is already a replacement of 15% of the United States soap market by synthetic detergents. The trend in Germany during the war years was away from the use of natural fatty acids in soap manufacture to the use of synthetic detergents based on nonfatty raw materials. The chief raw materials, therefore, were the oxidation products of Fischer-Tropsch paraffin wax or gatsch or the wax obtained by the hydrogenation of brown coal. The main concentration of effort was toward the production of the alkyl sulfonates, commonly known as Mersolates, prepared by the sulfochlorination of the Fischer-Tropsch paraffins. The total output reached 85,000 tons per annum (calculated as 100% active matter) from both I. G. Farbenindustrie factories at Leuna and Wolfen, the equivalent of probably 170,000 tons of the prewar marketed soap. The future trend is evident: an increasing consumer demand for edible fats, with a decreasing utilization of natural fats for the manufacture of soap and an increasing demand for synthetic detergents from nonfatty oil raw materials for which petroleum and synthesis products are the obvious sources.

337. BREDIG, G., AND ALLOLIO, R. [X-Ray Studies of Catalytically Active Metals.] Ztschr. physik. Chem., vol. 126, 1927, pp. 41–71; Chem. Abs., vol. 21, 1927, p. 2204.

Pt and Pd surfaces obtained by the glow discharge in H_2 at low pressures have been shown to be of very slight or negligible activity as catalysts for the hydrogenation of C_2H_4 or for the combination of H_2 and O_2. These metal preparations contain considerable amounts of H_2 as evidenced by X-ray photographs, the presence of which in the metal lattice is responsible for lack of activity. Ni, similarly prepared, is inactive at 350° in the hydrogenation of C_2H_4. When Pt and Pd are prepared as above but in O_2 at low pressures, very active surfaces are obtained. X-ray studies of these active Pt, Pd, and Ni surfaces have shown that except for differences in particle size, there is no difference between the finely divided, highly active, and the compact, slightly active metals.

338. BREDIG, G., AND CARTER, S. R. [Catalytic Synthesis of Formic Acid Under Pressure.] Ber. deut. chem. Gesell., vol. 47, 1914, pp. 541–545; Chem. Abs., vol. 8, 1914, p. 1584.

Object of this work was to determine: (1) Whether the equilibrium in the formation of HCO_2H from ordinary H_2 and CO_2 could be materially shifted in favor of the HCO_2H formation by sufficiently decreasing its partial pressure, and (2) whether the reaction velocity could be increased enough by the use of a suitable catalyzer and of high pressures. Below are given, respectively, the weight of substance used in 200 cm.^{3} H_2O, the gas pressure, the time, and the yield of formate in % of the theoretical amount that would have been formed if all of the carbonate, or borax had been converted into formate. In all cases but (1), where no catalyzer was used, 1.5 gm. Pd sponge was employed, and the temperature was 70° except in (3) where it was 95°. (1) 10 gm. $KHCO_3$, 60 atm. H_2, 24 hr., 0.6%. (2) 10 gm. $KHCO_3$, 60 atm. H_2, 23 hr., 74.7%. (3) 10 gm. $KHCO_3$, 30 atm. H_2, 26 hr., 66.3%. (4) 0.4 gm. $CaCO_3$, 50 atm. H_2+20 atm. CO_2, 4.5 hr., 100%. (5) 9.5 gm. $Na_2B_4O_{7.10}H_2O$, 30 atm. H_2+30 atm. CO_2, 16 hr., 21.7%. (6) 10.6 gm. Na_2CO_3, 60 atm. H_2, 7 hr., 0.4%. The negligible yield with Na_2CO_3, in spite of its stronger alkalinity, as compared with that obtained with $KHCO_3$, would indicate that the velocity and free energy of the HCO_2H formation rises and falls not only with the partial pressure of the H_2 but also with that of the CO_2. The small yield with $KHCO_3$ but without Pd shows that the method is really catalytic.

339. ———. [Equilibrium of the Reduction of Carbonic Acid to Formic Acid.] Chem. Ztg., vol. 39, 1915, pp. 72–73; Chem. Abs., vol. 10, 1916, p. 1036.

Considerable amounts of free HCOOH are obtained by the action of H_2 and Pd black under pressure on CO_2 in the presence of H_2O; the HCOOH is decomposed catalytically into CO_2 and H_2. The determination of the equilibrium between these reactions between 30°–90° gave no indication of the formation of HCHO as an intermediate product, so that it is unlikely that the formation of the latter is a stage in the assimilation of CO_2 in nature.

340. BREDIG, G., AND SCHWARZ VON BERGKAMPF, E. [Hexagonal Nickel.] Ztsch. physik. Chem., Bodenstein-Festband, 1931, pp. 172–176; Chem. Abs., vol. 26, 1932, p. 14.

Hexagonal Ni was prepared by the glow-discharge method of Bredig and Allolio in H_2. With the Laue powder camera, a was found to equal 2.66 A. U., $c=4.29$ and $c/a=1.61$. The theoretical value of c/a

for hexagonal close packing is 1.63. In N_2 a material was obtained in which a=2.60 A. U., c=4.15 and c/a=1.60. The hexagonal Ni is nonmagnetic, but on heating to 300° it is transformed to magnetic Ni with a cubic lattice, in which a=3.52 sq. A. U.

341. BREMNER, J. G. M., AND BRADFORD, B. W. Oxo Synthesis. Interrogation of Dr. Roelen. BIOS Interrogation Rept. 737, January 1945, 5 pp.; Bib. Sci. Ind. Rept., vol. 10, No. 2, 1948, p. 2; PB 81,965.

1. Bradford, B, W. 2. Dr. Roelen. 3. Oxo process. 4. Aldehydes production, Germany. 5. Alcohols production, Germany. 6. Detergents production, Germany. 7. I. G. Farbenindustrie A.-G., Leuna, Germany. 8. Fischer-Tropsch Plant, Courrières-Kuhlmann Oil, Harnes, France.

342. BRENDLEIN, —. Medium-Pressure Synthesis of Methanol. FIAT Reel M-38, frames 8061–8074, 1942; frames 8130–8132, 1943; PB 70,309.

Medium-pressure synthesis of MeOH takes place by way of methyl formate, which is isolated as such and then hydrogenated to MeOH. MeOH is converted into methyl formate with CO in the presence of sodium methylate at a pressure of 30 atm. The methyl formate is reduced to MeOH on a catalyst of reduced Cu oxides. Higher alcohols can also be used as starting materials since their formates can be prepared and hydrogenated in the same way. Describes apparatus.

343. ———. Synthesis of Methanol in Two Stages. FIAT Reel M-38, frames 8130–8132, Mar. 22, 1943; PB 70,309.

Proposes process that makes it unnecessary to split the synthesis gas into CO and H_2. After the synthesis gas is freed from CO_2 it is compressed at 30 atm., and the CO is rinsed out with a MeOH solution of sodium methylate, which results in the formation of methyl formate. The residual gas, which still contains certain quantities of CO, is converted by steam and supplies enough H_2 for the reduction cleavage of the methyl formate.

344. ———. Two-Stage Synthesis of Methanol. FIAT Reel CC-140, frames 1–51, September 1946; PB A70,207.

The 2 stages are: $CH_3OH+CO \rightarrow CH_3COOH$ and $CH_3COOH+2H_2=2CH_3OH$. Catalyst for step 1 is sodium methylate and for step 2 copper chromite. The process uses lower temperatures and pressures than the conventional method and eliminates side reactions. Drawings and flow sheets.

345. BRENNSTOFF-CHEMIE. [Japanese Seven-Year Plan.] Wirtschaftsteil, vol. 18, 1937, p. 39; Coal Carbonisation, vol. 3, 1937, p. 115.

Gives particulars of program under which motor-fuel requirements of Japan are to be met, mainly from domestic sources, by 1943. It is estimated that the requirements of light fuels, mainly gasoline, will then amount to about 545 million gal. per yr., 335 million gal. of which is to be supplied by home production. About 630 million gal. of heavy oils will be needed, and about half of this amount is to be produced from domestic materials. Plan is based on producing 132 million gal. of light fuels and 93 million gal. of heavy oil from coal and 86 million gal. of light oils and 46 million gal. of heavy oils by synthesis. A German firm has been entrusted with the planning of a plant for the synthesis of 33,000 tons of gasoline per yr. by the Fischer-Tropsch process. Low-temperature carbonization of coal is to yield about 9 million gal. of light motor fuels and 112 million gal. of heavy oils, requiring about 9 million tons of coal. The remainder of the liquid-fuel output is to be in the form of potato spirit and the refined products of domestic oils. It is estimated that the capital investment will be about 750 million yen apart from 127 million yen to be spent on increasing the coal output.

346. ———. [Dismantling of the Fischer-Tropsch and Gelsenberg Synthetic Fuel Plants.] Wirtschaftsteil, vol. 30, No. 11–12, 1949, pp. 29–31.

Gives German viewpoint concerning the dismantling of the synthetic-fuel plants in western Germany. Preservation and operation of the plants are economically of great significance, in that several thousand men would be employed in producing domestic-fuel and primary-chemical products. The 6 Fischer-Tropsch plants have a capacity for producing 370,000 tons of primary products annually, and the Gelsenberg coal-hydrogenation plant has a capacity for processing about 1,000,000 tons of crude oil or 540,000 tons of heavy-residual oils.

347. ———. [Status of Krupp Treibstoffwerk G. m. b. H. Operation.] Wirtschaftsteil, vol. 31, 1950, p. 41.

It is known that at the end of last year permission had been withdrawn by the Allied High Commission from the Krupp Treibstoffwerk to produce hydrocarbons by the Fischer-Tropsch process. Since that time permission has been granted to operate the Oxyl process, which has been developed by the Ruhrchemie A.-G. According to this new process valuable products, designated higher alcohols, can be produced. These products will be processed into a number of other products, which will not only be of considerable importance domestically but will also be valuable for export. Among the products are mentioned solvents for the paint and dye industries and softeners for plastics and detergents. It is the intention of both Krupp and Ruhrchemie A.-G. to work together in putting out these Oxyl products. Ruhrchemie A.-G. will make the necessary catalysts in its own catalyst factory.

348. BRETEAU. Hydrogenations in Gaseous System. Catalysis in Organic Chemistry, P. Sabatier, D. Van Nostrand Co., New York, 1922, p. 186.

CO can be reduced in the cold, or better at 400°, to CH_4 in the presence of Pd sponge.

BREWER, R. E. *See* abs. **920, 929.**

349. BREYWISCH, —. [Synol Synthesis.] Scientific Contribution No. 10 from the Laboratory of the Merseberg Ammonia Plant, April 1943, 2 pp.; PB 869.

It was discovered at Leuna that the medium-pressure synthesis for the production of hydrocarbons by the reduction of CO could be directed so that up to 60% of the product would consist of unbranched aliphatic alcohols. A catalyst similar to the Leuna NH_3 catalyst, in which the K content was 0.1–0.7% and which had been reduced in an excess of H_2 (1 : 1000) at 400°–500°, was used. The conversion of CO and H_2 amounted to 1 : 150 or 25% more than in technical benzine synthesis at 190°–200°. The pressure should be above 20 atm., preferably 25 atm. The yield of primary product was 0.4–0.5 ton/m.^{3} of catalyst/day. The CO and H_2 were in the ratio of 1 : 1, and the synthesis was performed in 3–4 successive steps. Both H_2O and CO_2 were obtained as byproducts instead of only H_2O as with Co catalyst. With the Fe catalyst, a gas ratio of nearly $2H_2$: CO could be maintained by recycling the gas so rapidly over the catalyst that the partial pressure of the water vapor, which underwent conversion with the CO, remained low. The synthesis products must be removed quickly from contact with the catalyst in order to avoid secondary reactions such as dehydration and hydrogenation. The primary products with small amounts of acids, aldehydes, 15% of gasol, and 5–10% of CH_4 were as follows:

	Percent	Alcohol	Olefins	Esters
Up to 200°	50	50	20	2
200°–230°	3	60	22	5
230°–350°	17	65	25	8
350°–400°	3	50	30	10
Above 400°	12			

Increase in pressure, CO content, and K content of the catalyst increased the yield of paraffins, whereas decrease in pressure, CO content, and K content as well as an increase in conversion increased the formation of gasol. Some directions are given for recovering and working up the products, and some possible uses for the various factions are mentioned.

350. BRIDGEWATER, R. M. British Research on Petroleum Substitutes. VI. Fischer-Tropsch Synthesis. Petroleum (London), vol. 8, 1945, pp. 109–111; Jour. Inst. Petrol., vol. 31, 1945, p. 320 A.

Although 7 million gal. of MeOH were produced in Britain in 1 yr. before the war by the interaction of CO and H_2 and about 600,000 tons of oil/yr. by Fischer-Tropsch process in Germany by 9 plants, little experimental work appears to have been carried out in Britain. British work concerned the development of robust catalysts and techniques for large-scale operation. Synthetic Oils, Ltd., worked on a process yielding a product rich in olefins, using specially prepared catalysts. A plant was built to process about 200,000 cu. ft. of gas/day, yieling 136–180 gal/day, and said to substantiate the results obtained in the pilot plant using blue water gas. With Co and Th carbonates supported on kieselguhr, the Fuel Research Station produced lubricating oils from blue water gas and H_2 in a small plant. Little has been reported on the quality of motor spirit or Diesel oils produced, but a fraction boiling 210°–300° C. has a cetene number of 93. The 7–10% wax contained in liquid products from Fischer-Tropsch process can be treated to yield marketable commodities. Studies have been made of the mechanism of the process, it being concluded that Co carbide is first formed.

351. ———. British Research on Petroleum Substitutes. VII. Synthetic Lubricating Oils. Petroleum (London), vol. 8, 1945, pp. 136, 152–153.

First gives some consideration to the existing knowledge concerning the composition and the chemical and physical properties of lubricating oils derived from petroleum. The absence of real knowledge as to the physical and chemical properties required in a lubricating oil has been a major difficulty in researches on synthetic lubricating oils. The various raw materials available for the manufacture of synthetic lubricating oils are: Coal-carbonization products, including tar fractions and C_2H_4; products of the pressure hydrogenation of coal or tar; and the primary products of the Fischer-Tropsch process. The principal methods for producing lubricating oils from these products are: Isolation of suitable fractions by distillation or solvent extraction; stabilization of such fractions by hydrogenation; polymerization of hydrocarbons, especially olefins, with or without catalysts; chlorination of hydrocarbons, especially high-boiling paraffins, followed by dechlorination; condensation of chlorinated hydrocarbons or olefins with aromatic hydrocarbons. Lubricating oils from the neutral-oil fractions of low-temperature tar were unsatisfactory, even after hydrogenation over a Mo catalyst. The viscosity was too low at the higher temperatures, and there was too great a tendency toward oxidation and carbonization. Better results might be attained by using the superior hydrogenation catalysts subsequently discovered.

352. BRIDGMAN, P. W. Recent Work in the Field of High Pressures. Rev. Modern Phys., vol. 18, 1946, p. 1–93; Jour. Inst. Petrol., vol. 32, 1946, p. 254 A.

Summarizes work on high pressures from 1930, the date of publication of Bridgman's book, The Physics of High Pressure, to June 1945, with 674 literature references. The high-pressure range now open to study extends to 100,000 atm. The effects of high pressures on chemical reactions in liquid and vapor phases, both catalyzed and uncatalyzed, are reviewed. Reactions listed include the pyrolysis, hydrogenation, oxidation, and polymerization of hydrocarbons. The majority of the chemical studies discussed are of direct industrial interest.

353. BRILL, —. Behavior of Calcium in the Ammonia Catalyst Toward Poisoning. FIAT Reel R–19, frames 7088–7104, 1941.

Test results on Fe catalysts containing Ca for the NH_3 synthesis proved that an addition of Ca in combination with the usual addition of Al has several advantages. Above all, the resistance of the catalyst to poisoning by CH_4 and H_2S is increased. Tabular data present further details. A number of catalysts with and without Ca are arranged according to the degree of their sensitivity to H_2S, H_3P, CH_4, and O_2.

354. BRILL, R. [X-Ray Investigation of the Iron Carbonyl, $Fe_2(CO)_9$.] Ztschr. Krist., vol. 65, 1927, pp. 85–93; Chem. Abs., vol. 21, 1927, p. 3775.

$Fe_2(CO)_9$ is hexagonal with a unit cell of the dimensions $a=6.45$ and $c=15.8$ Å. U., which contains 4 mol. The space group may be C_6^6, C_{v6}^4, C_{h6}^2, D_6^6, or D_{h6}^4. The 9 CO groups are at the corners of 2 octahedrons with a common face. The Fe atoms are on the trigonal axis perpendicular to this common face.

355. BRILL, R., AND MARK, H. [Röntgenographic Studies on the Structure of Complex Iron Cyanides.] Ztschr. physik. Chem., vol. 133, 1928, pp. 443–445; Chem. Abs., vol. 22, 1928, p. 3073.

$(NH_4)_4[Fe(CN)_6]$ and 8 of the substances resulting from its stepwise reduction at 400° with time were subjected to diffraction analysis. 3 crystalline phases were found, and in some cases many more. Besides the initial compound and the final α-Fe, another compound certainly was $(Fe(CN_2))_n$, cubic, $d_{100}=15.9$ Å. U., molecular formula $(Fe(CN)_2)_3=Fe_2[Fe(CN)_6]$. Hence the reduction mechanism must be: $(NH_4)_4[Fe(CN)_6]$ $\rightarrow(Fe(CN)_2)_3\rightarrow$Intermediate carbides, nitrides, etc., $\rightarrow\alpha$-Fe. The supposition is made that the appearance of certain extra lines in the diffraction pattern of the product obtained when H_2 and N_2 act on ammonium ferrocyanide at 400° is due to a carbide of unknown structure.

355a. BRIMM, E. O. AND LYNCH, M. A. Estimated Bond Order in Metal Carbonyls. Am. Chem. Soc., 121st Meeting Abs., March–April, 1952, p. 38–N.

The presence of partial double bond character of the metal–C bond in metal carbonyls has been postulated to account for the shortness of the observed bond lengths. The % double bond character of the metal–C bonds in metal carbonyls, substituted metal carbonyls, and hydrocarbonyls is estimated by means of Pauling's principle of electroneutrality. A decrease in the order of the C–O bond would result from this partial double bond formation. Changes in the characteristic infrared absorption of the C–O bond are correlated with the estimated bond orders. Evidence is presented for the presence of bridging CO in dicobalt octacarbonyl and tetracobalt dodecacarbonyl and their absence in dimanganese decacarbonyl and dirhenium decacarbonyl.

356. BRINER, E., AND SENGLET, R. [Experiments on the Carbides of Aluminum, Nickel, and Copper.] Jour. chim. phys., vol. 13, 1915, pp. 351–375; Chem. Abs., vol. 10, 1916, p. 3041.

On being heated Al_4C_3 dissociates into its elements, which in the presence of air are immediately oxidized. The reaction was studied at 540°, but the decomposition is appreciable at lower temperatures. In the synthesis of the substance, powdered Al was heated with sugar C for 2-hr. periods and the residue tested for presence of carbide by the addition of HCl to produce CH_4. At 550° no appreciable quantity was formed, but at 750° and 900°, respectively, small yields were obtained, proving the reaction of $Al_4C_3 = 4Al + 3C$ to be reversible. Attempts to measure the speed of the reaction were unsuccessful. Ni_3C is formed according to the equation $3Ni + C \rightleftharpoons Ni_3C$ at temperatures about 2,100°; at lower temperatures it dissociates into its constituents, rapidly at 1,600° and relatively slowly at 900°. At the relatively low temperatures, while the interacting substances are in the solid state, the reaction is endothermic; at the higher temperatures, when the Ni and C are gaseous and in the atomic state, it becomes exothermic. Studies of the formation of carbides of Cu indicate that an endothermic carbide is formed at high temperatures that decomposes at 1,600°, but further confirmatory work is needed.

357. BRINKLEY, S. R. Calculation of Catalyst and Gas Temperatures in Adiabatic Contact Catalytic Reactions. Am. Chem. Soc. 110th Meeting Abs., Div. Ind. Eng. Chem., 1946, p. 42 I.

Temperatures of catalyst and gas in contact-catalytic reactions is computed on the assumptions that all but a negligible amount of the heat of reaction is removed by means of the sensible heat of the gas stream and that the overall conversion of reactants to products is limited by means of small contact time to a few % of the total gas. At constant velocity, the temperatures of catalyst and gas are found to increase exponentially with increase in depth of catalyst bed. The yield is proportional to the overall temperature rise of the gas stream. The effect of change in velocity on the temperature of the catalyst is investigated by the assumption that the coefficient of heat transfer from catalyst to gas is proportional to the 0.7 power of the velocity. The temperature of catalyst and gas are estimated for a typical German operation of the Michael hot-gas recycle process for the middle-pressure synthesis of hydrocarbons from CO and H_2 on an Fe catalyst. On the basis of approximate data, it is estimated that the catalyst temperature is between 7° and 9° higher than the gas temperature for a half-meter catalyst bed, flow rate 1 m./sec., and overall gas temperature rise of 10°.

358. ———. Heat Transfer Between a Fluid and a Porous Solid Generating Heat. Jour. Appl. Phys., vol. 18, 1947, pp. 582–585; Chem. Abs., vol. 41, 1947, p. 5007.

The theory, due to Anzelius, of the transfer of heat between a fluid flowing with constant velocity through a porous solid is extended to include the case where the solid generates heat. Expressions are obtained for the temperatures of solids and fluid as functions of position and time, it being assumed that the heat source function is a linear function of the temperature of the solid with coefficients independent of position and time. The application of the theory to the calculation of catalyst and gas temperatures in a typical operation of the Michael process for the synthesis of hydrocarbons from CO and H_2 is indicated.

359. ———. Contact Times of Continuous-Flow Reacting Systems With Volume Change. Ind. Eng. Chem., vol. 40, 1948, pp. 303–307; Chem. Abs., vol 42, 1948, p. 2849.

General relation between contact time and space velocity is obtained by comparing the solutions of the Euler and Lagrange forms of the hydrodynamical steady-state equations for the composition of a flowing system that undergoes chemical reaction with accompanying volume change. It is assumed that the reactor is isothermal and isobaric and that the flow is 1-dimensional. This relation is applied to the calculation of contact times for particular rate laws. An approximate formula is developed for estimation of contact times when the rate law is unknown, and the resulting error is obtained for several cases by a direct numerical comparison with the correct expressions. These considerations apply to catalytic reactions on granular catalysts if apparent contact time is calculated from a space velocity defined as the volume of gas at the temperature and pressure of the feed gas/free vol. of the catalyst bed/unit of time.

360. BRISKINA, A. I., AND MOGILEVSKAYA, A. M. [Gasification of the Donets Anthracites to Produce Water Gas and Mixed Gas.] Khim. Tverdogo Topliva, vol. 8, 1937, pp. 1165–1181; Chem. Abs., vol. 32, 1938, p. 4309.

Under optimal conditions (the intensity of air blowing about 26,350 $m.^3$/hr., that of steam blowing 5,896 kgm./hr., the air pressure under the grating 1,264 mm., and the height of the fuel layer 1,900 mm.) the water gas contained CO_2, 6.74%, H_2S, 0.42%, O_2, 0.20%, CO 39.23%, H_2, 47.03%, CH_4, 0.51%, and N_2, 5.87% by volume and had a calorific value of 2,700–2,455 cal./$m.^3$ The air gas contained CO_2, 14.29%, H_2S, 0.08%, O_2, 0.17%, CO, 9.51%, H_2, 2.45%, CH_4, 0.15%, and N_2, 73.65%; its calorific value was 382–369 cal./$m.^3$ Gasification for production of a mixed gas yielded CO_2, 7.42%, H_2S, 0.19%, O_2, 0.17%, CO, 24.99%, H_2, 15.19%, and N_2, 0.30%, of calorific value 1,262–1,185 cal./$m.^3$

361. BRISTOW, W. A. Oil From Coal. Engineer, vol. 168, 1939, pp. 469–470; Gas Jour., vol. 228, 1939, pp. 288–290; Colliery Guard., vol. 159, 1939, pp. 625–626; Engineering, vol. 148, 1939, pp. 561–562.

Not only, as at present, can the Fischer synthesis be used to produce liquid fuels, certain fractions of which are rich in olefins useful for the manufacture of lubricating oils and paraffins subject to oxidation into fatty acids, but also it will be only a question of time and research until gases will be produced that are rich enough in mono-olefins to be polymerized into high-octane gasolines. Another revolution will be accomplished if conversion of CH_4 and its homologs into olefins can be carried out commercially. This is important to both the oil and the coal industries—to the former because of the immense quantities of CH_4 contained in natural gas and to the latter because of the high % of CH_4 in coke-oven gases.

362. ———. Fuel and Allied Industries. Gas and Oil Power, vol. 35, 1940, pp. 236–237; Chem. Abs., vol. 35, 1941, p. 875.

Lecture with emphasis on synthesis of hydrocarbons.

363. ———. Coal and Oil—Survey of New Facts and Future Possibilities. Gas World, vol. 118, No. 3065, coking sec., 1943, pp. 60–63; Chem. Abs., vol. 37, 1943, p. 3904.

An address. The blending of synthetic diesel fuel produced by the Fischer-Tropsch process with an equal quantity of the diesel fractions of the oils from high-temperature carbonization to give a suitable diesel fuel is suggested.

364. BROCHE, H. [Liquid Fuels From Coal in Relation to German Power Economics.] Glückauf, vol. 70, 1934, pp. 1137–1149; Chem. Abs., vol. 29, 1935, p. 4151.

Lacking petroleum, Germany must procure liquid fuels for future transport development largely from coal. Liquid fuels by carbonization can be increased by (*a*) mild refining of coke-oven light oils; (*b*) use of the roof-canal and the Still process for protecting coke-oven light oils from decomposition; (*c*) further development of low-temperature carbonization. Hydrogenation and synthesis from water gas will become

important sources of liquid fuels. Some progress has been made in the adaptation of the diesel motor to tar oils by use of a special fuel injector.

365. BRODIE, B. C. Synthesis of Methane and Formic Acid. Proc. Roy. Soc., vol. 21, 1872, pp. 245–247; Jour. Chem. Soc., 1873, p. 744; Chem. News., vol. 27, 1872, p. 187; Chem. Zentralb., 1873, p. 451.

On passing an electric current through a mixture of CO and H_2, after 5 hr. about 6% of CH_4 was detected in accordance with the reaction

$$CO+3H_2=CH_4+H_2O.$$

In a corresponding test with a mixture of CO_2 and H_2, the resultant gas was found to contain, besides H_2 and unchanged CO_2, some CO and CH_4 and an oily liquid identified as HCOOH.

366. ———. Formaldehyde Synthesis. Proc. Roy. Soc., vol. 22, 1873, p. 172.

CH_2O is produced when the silent electric discharge is passed through a mixture of CO_2 and H_2.

367. ———. Formaldehyde Synthesis. Angew. Chem., vol. 174, 1874, p. 284.

On passing an electric current through a mixture of CO_2 and H_2 about 5.2% of HCHO was detected in the end gas, and with CO and H_2, only CH_4 and CO_2 were obtained.

368. BRODIE, G. H., JENNINGS, W. H., AND HAYES, A. Heat of Formation of Cementite as Electrolyzed From a Pure Iron-Carbon Alloy of Eutectoid Structure and Composition. Trans. Am. Soc. Steel Treating, vol. 10, 1926, pp. 615–629; Chem. Abs., vol. 21, 1927, p. 3878.

Value of −13,580 cal. per gm. mol. was obtained at 86° F. by calorimetric determination of the heat of formation of Fe_3C.

BRODKORB, F. *See* abs. **1786, 1787.**

369. BROETZ, W. [Systematics of the Fischer-Tropsch Catalysis.] Ztschr. Elektrochem., vol. 53, 1949, pp. 301–306; Chem. Zentralb., 1950, I, p. 1432; Chem. Abs., vol. 44, 1950, p. 2358.

Fundamental Fischer-Tropsch reaction: $CO+2H_2 > CH_2+H_2O$ at atmospheric and at 5–20 atm. gage pressure between 160° and 186° is discussed. On technical catalysts at pressures up to 10 atm. gage pressure the reaction rate is given by: $d[CO]:dt=k\ [H_2]^2:[CO]$ where k at 7 atm. gage pressure varies from 7.8×10^{-3} at 173° to 18.8×10^{-3} at 186°, yielding an activation energy of 31 kcol. per mol. At atmospheric pressure an activation energy of 28 kcol. per mol. is found. At high pressures the reaction rate is: $d\ [CO]:dt= k_3\ \{H_2]:[CO]\}\{k_1[H_2]:(1+k_2[H_2])\}$. The presence of CH_4 in the reaction mixture does not affect the rate or the nature of the products. The catalysts gradually lose activity, which may be recovered by heating in H_2 at 400°. The reaction takes place directly in 1 step at the catalyst surface without formation of an intermediate carbide. The CH_2 radicals are combined at the catalyst surface under formation of double bonds at the chains ends, which are subsequently shifted by H exchange toward the center of the chains.

370. BROETZ, W., AND SPENGLER, H. [Physicochemical Behavior of Fischer-Tropsch Catalysts.] Brennstoff-Chem., vol. 31, 1950, pp. 97–102.; Chem. Abs., vol. 44, 1950, p. 6249.

Conversion behavior of a porous catalyst depends not only on its special chemical properties but also on the structure of its pore system, which makes up its inner surface and provides the path for the transport of the reactants. The following determinations were made for the purpose of clarifying the pore structure of Fischer-Tropsch catalysts: (1) Determination of the grain and lattice volumes of unreduced catalysts. From the data thus obtained the pore volumes and the porosity as well as the change in volume through reduction of the catalyst are determined. (2) Plotting a structure curve in order to find out how the micropore space is divided among the various pore radii. (3) Determination of the average pore radius of the macropores by means of a perfusion method. By this means there results for CO and H_2 an excess flow, which is designated as surface diffusion and explains the otherwise determined complete utilization of the catalyst grain. (4) Determination of the inner surface by plotting an adsorption isotherm. In connection with surface determination, absorption measurements of CO and H_2 show that the temperature region of Fischer-Tropsch synthesis corresponds to the beginning chemisorption of this gas. The heat of adsorption of CO and H_2 is calculated from the adsorption isotherms. (*See* abs. **3243.**)

371. BRONI, N. [The Motor-Fuel Crisis and Remedies for Surmounting Ia.] Giorn. bibliografia tecnica intern., 1925, No. 2, pp. 1–8, Nos. 3–4, pp. 3–13, No. 5, pp. 1–8, No. 6, pp. 1–9; 1926, No. 1, pp. 3–9; Chem. Abs., vol. 20, 1926, p. 1898.

Extended review and discussion dealing with different types of motor fuels, general methods available for increasing their supply, methods of increasing the yield of benzine from crude oils, the recovery of benzine from solid, liquid, and gaseous substances, the liquefaction of natural gas, distillation of coals, lignites, and peat, production of artificial petroleum by direct synthesis and from vegetable and animal oils, and the direct use of vegetable oils, alcohol, gas-producer gas, and colloidal mixtures as fuels. Includes economic as well as chemical and engineering data.

BROOKS, A. P. *See* abs. **2064.**

BROUGHTON, J. W. *See* abs. **298.**

372. BROWN, B. K., AND GUNNESS, R. C. Future Fuels—Liquid and Gaseous. Mech. Eng., vol. 70, No. 5, 1948, pp. 421–424; Chem. Eng. News, vol. 26, 1947, pp. 2123–2127, 2171; Chem. Abs., vol. 42, 1948, p. 4323 (Brown and Gunness), p. 6509 (Gunness).

Demand for petroleum products has quadrupled during the last 25 yr., and it may be expected to increase another 30% by 1970, at which time the total demand will exceed 7 million bbl. per day. This demand will be met by domestic crude-oil production, some foreign imports, and by synthesis from natural gas and coal. Oil from shale and tar sands seems to be more remote than from synthesis. The economics of the industry will result in a gradually diminishing supply of residual fuel oil for industrial purposes, and coal will handle an increasing share of the expanding industrial-fuel load. This means a very large future development in coal mining to take care of the increasing demand for coal. To produce even 1 million bbl. of oil per day from coal will require the mining and processing of 650,000 tons of coal per day or 236 million tons per yr., or nearly one-half of our present production.

BROWN, E. A. *See* abs. **3551.**

BROWN, G. G. *See* abs. **1121.**

BROWN, R. L. *See* abs. **921, 922, 928.**

373. BROWN, R. L., AND GALLOWAY, A. E. Methanol From Hydrogen and Carbon Monoxide. I. Ind. Eng. Chem., vol. 20, 1928, pp. 960–966; Fuel, vol. 7, 1928, pp. 518–525; Chem. Abs., vol. 22, 1928, p. 4104.

Experimental production of MeOH from H_2 and CO has been studied, with ZnO, basic $ZnCrO_4$ and normal $ZnCrO_4$ as catalysts. The last 2 are more active than ZnO, and under high temperatures and pressures the normal $ZnCrO_4$ is the most active. With the theoretical mixture of CO and H_2 at 400° and 180 atm., a 20% conversion of CO to MeOH has been obtained.

374. ———. Methanol From Hydrogen and Carbon Monoxide. II. Dimethyl Ether. Ind. Eng. Chem., vol. 21, 1929, pp. 310–313; Chem. Abs., vol. 23, 1929, p. 2150.

Production of Me_2O (I) as a side reaction of the synthesis of MeOH (II) over $ZnCrO_4$ at 300°–400° and 180 atm. has been studied. The formation of I is slow and increases with temperature to 5.2% at 397° while II reaches a maximum of about 30% at 375° and then falls off. High space velocity favors formation of II.

375. ———. Methanol From Hydrogen and Carbon Monoxide. III. Further Work on Dimethyl Ether. Ind. Eng. Chem., vol. 22, 1930, pp. 175–176; Chem. Abs., vol 24, 1930, p. 1840.

Catalyst prepared by precipitating the nitrates with NaOH to give an atomic ratio of 3 Cu : 1 Cr in contact with a 2 : 1=H_2 : CO mixture at 180 atm. yielded MeOH and Me_2O in the following molecular % ratios: 265°, 7 : 4; 285°, 14 : 6; 305°, 24 : 22; 340°, 17 : 20; 355°, 11.5 : 13.5 The region of maximum conversion was 315°–320°, and conversions were on the order of 30 mol. %, that to Me_2O being the larger.

BROWNE, R. Y. *See* abs. **576.**

BROWNING, L. C. *See* abs. **2008.**

376. BROWNING, L. C., AND EMMETT, P. H. Equilibrium Measurements in the System C–CH_4–H_2. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 581–583; Chem. Abs., vol. 45, 1951, p. 4534.

In the course of experiments relative to the Fe–Fe_3C–CH_4–H_2 equilibria, it was found that the C formed by the decomposition of Fe_3C reacted readily with H_2 at temperatures as low as 400°, the Fe catalyzing the reaction. A study was made of the CH_4=C+2 H_2 equilibrium constants in the temperature range 380°–838°, using the C formed as above. The values obtained are close to those for the reaction in which the C form is β-graphite.

377. BROWNING, L. C., DEWITT, T. W., AND EMMETT, P. H. Equilibria in the Systems Fe_2C–Fe–CH_4–H_2 and Fe_3C–Fe–CH_4–H_2. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 4211–4217; Chem. Abs., vol. 45, 1951, p. 1861.

Equilibrium constants for the reaction (I) $CH_4+2Fe(\alpha)=Fe_2C+2H_2$ were reported in the temperature range 295°–350° and for the reaction (II) $CH_4+3Fe(\alpha)=Fe_3C(\beta)+2H_2$ in the temperature range 320°–468°. Free energies of formation of Fe_2C and Fe_3C, calculated from the data for reactions (I) and (II), led to the conclusion that the formation of all mono-olefins and of saturated hydrocarbons containing more than 6 C atoms by the direct reduction of Fe_2C and Fe_3C in the temperature range 450°–650° K. is thermodynamically unfavorable. The results obtained for reaction (II) agree well with those obtained at higher temperatures by Watase (abs. **3616**).

378. BROWNLIE, D. Australian Viewpoint on Oil Production From Coal. Iron and Coal Trades Rev., vol. 136, 1938, pp. 653–654.

Summary of a report prepared for the Minister in Charge of Australian Commonwealth Council for Scientific and Industrial Research by Sir D. Rivett. The conclusion is against recommending that any public money be provided at the present time for so costly a project. The study covered low-temperature distillation, hydrogenation of coal, and synthesis of hydrocarbons from CO and H_2.

379. ———. Oil-From-Coal Developments. Coal and Colliery News. No. 2408, May 4, 1939, pp. 420–421.

Fischer-Tropsch process has not developed in Great Britain. Synthesis-gas products are known to have inferior antiknock qualities, and it is necessary to blend with benzol or add tetraethyl lead. Reports from the Robinson-Bindley synthetic-oil plant show Ni catalysts on carriers employing silicic acid to be highly resistant to S poisoning.

380. BRÜCHANOV, A. [Effect of Compressive Stress on Disintegration of Cementite.] Ztschr. anorg. Chem., vol. 218, 1934, pp. 146–150; Metallurgia, vol. 9, No. 5, 1934, pp. 37–40; Chem. Abs., vol. 28, 1934, p. 5792.

Experiments with cast bars consisting of pearlite and cementite showed that cementite was stable up to temperatures of about 500°, but under pressure it begins to disintegrate at that temperature and disintegrates more with higher pressures. As the stability of cementite decreases with increasing temperature, the effect of pressure becomes less appreciable at higher temperatures and cannot be observed above 750°.

381. BRÜCKNER, H. [Coke-Oven Gas as a Chemical Raw Material.] Ztschr. Ver. deut. Ing., vol. 75, 1931, pp. 93–97; Chem. Abs., vol. 25, 1931, p. 3806.

Availability, generation, and utilization of coke-oven gas are considered from an economic viewpoint. Separation of 10^9 cu. m. of gas of average composition into its components should furnish 49,000 tons CO_2, 23 tons C_2H_4 and homologs, 14 tons C_6H_6, 70 tons CO, 47 tons H_2 and 178 tons CH_4. Coal hydrogenation, synthesis of fuel oils, of NH_3, MeOH, and of well-known C_2H_4 derivatives are now technically perfected, and offer promising outlets, but only for very large scale operation.

382. ———. [Brown Coal and Peat-Gas Syntheses.] Handbuch der Gasindustrie, vol. 2, pt. 2, 1940, 88 pp.; TOM Reel 241.

383. ———. [Formation of Methane From Carbon Monoxide-Hydrogen Mixtures in Contact With Low-Temperature Coke at Increased Pressures.] Brennestoff-Chem., vol. 20, 1939, pp. 346–348; Chem. Abs., vol. 34, 1940, p. 7582.

Conversion of H_2 into CH_4 in presence of low-temperature coke (5 gm. of coke, 1 liter of H_2, standard conditions per hr., 50 atm.) rose from 7% at 500° to 23% at 700°. Correspondingly lower values were obtained at lower pressures. CH_4 was also formed when a water gas was similarly treated; the reaction in this case, however, was principally $2CO+2H_2=CH_4+CO_2$. The maximum yield of CH_4, 40% in the outlet gas, was obtained at 40 atm. and 700°; the yield fell with rising pressures.

———. *See* abs. **408.**

385. BRÜCKNER, H., AND CHOULAT, G. [Utility of Residual Gas From the Fischer-Tropsch-Ruhrchemie Process as City Gas.] Gas- u. Wasserfach, vol. 83, 1940, pp. 497–499; Chem. Abs., vol. 35, 1941, p. 300.

Analyses of the residual gas from the gasoline plant showed the following variations and average values over a period of 18 days: CO_2 13.5–19.8% ave. 17.0%; unsaturated 0.3–1.1%, ave. 0.7%: O_2, 0.0–0.2%, ave. 0.1%; CO, 2.9–11.9%, ave. 9.0%; H_2, 11.3–23.6%, ave. 20.0%; CH_4 27.6–40.9%, ave. 33.0%; N_2, 16.5–35.1%, ave. 20.2%. The average gross heating value was 4,170 kg.-cal. per $m.^3$ (0°, 760 mm. Hg, and dry) and average density 0.755. The maximum rate of flame propagation was 29 cm. per sec. as compared with 70–95 cm. per sec. for manufactured gas. The highest specific-flame intensity (combustion density) was approximately 740×10^{-4} kg.-cal. per $cm.^2$ per sec. as compared with about 1,200 for manufactured gas. These last two characteristics make the gas unsuitable for use alone as city gas, but a maximum of 25–30% can be mixed with coke-oven gas.

385. BRÜCKNER, H., AND JACOBUS, G. [Activity of Nickel Catalysts for the Synthesis of Methane.] Brennstoff-Chem., vol. 14, 1933, pp. 265–268; British

Chem. Abs., B, 1933, p. 772; Chem. Abs., vol. 27, 1933, p. 5154.

Addition of SiO_2 gel, Al_2O_3, ThO_2, or the oxides of Ba, Sr, and Ca activates or increases, in the order named, the life of Ni catalysts. The weekly alkaline catalysts of pure Ni, Ni-alkaline earths, and Ni-ThO_2, prepared by reducing the hydroxides, are almost completely inactive. The Ni–Al_2O_3 catalyst, however, is highly active, yet when prepared by calcining the nitrate it is inactive. On the other hand, nitrate-prepared Ni, Ni–alkaline earths, and Ni–ThO_2 are active. The best catalysts are mixtures of 90% Ni and 10% Al_2O_3 or ThO_2. Additions of alkaline earths, particularly of BaO, increase many times the activity of the catalysts prepared from the nitrate. Addition of Co greatly decreases the activity of Ni, while Cu makes it completely inactive. Reviews literature briefly.

BRUDE, G. *See* abs. **900, 901.**

BRUNAUER, S. *See* abs. **822, 823, 824, 825, 826, 827, 836, 2215, 2216.**

386. BRUNAUER, S., AND EMMETT, P. H. Use of van der Waals' Adsorption Isotherms in Determining the Surface Area of Iron–Synthetic-Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 57, 1935, pp. 1754–1755; Chem. Abs., vol. 29, 1935, p. 7168.

The determination of van der Waals' adsorption isotherms of gases close to their boiling points affords a convenient method of measuring the extent of surface of Fe–synthetic–NH_3 catalysts; low-temperature isotherms are given for N_2 at −195.8° and −183°, for O_2, CO, and A at −183°, for CO_2 at −78.5°, and for C_4H_{10} at 0°.

387. ———. Use of Low-Temperature van der Waals' Adsorption Isotherms in Determining the Surface Areas of Various Adsorbents. Jour. Am. Chem. Soc., vol. 59, 1937, pp. 2682–2689; Chem. Abs., vol. 32, 1938, p. 1159.

Van der Waals' adsorption isotherms of some or all of the following gases were determined on a variety of adsorbents at the temperatures indicated: A and N_2 at −195.8°; A, N_2, CO, and O_2 at −183°; CO_2 at −78°; normal C_4H_{10} and SO_2 at 0°. The following adsorbents were used: 2 Cu catalysts, glaucosil, pumice, NiO supported on pumice, Ni on pumice, dry powdered bacteria, Cr_2O_3 gel, "glowed" Cr_2O_3, KCl, $CuSO_4 \cdot 5H_2O$, $CuSO_4$, 2 SiO_2 gel samples, activated charcoal, and 2 Darco samples (activated carbons). All adsorbents except charcoal given sigmoid isotherms, and the values for the surface area evaluated from the different isotherms for the same adsorbent were consistent with one another.

388. ———. Chemisorptions of Gases on Iron–Synthetic-Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 62, 1940, pp. 1732–1746; Chem. Abs., vol. 34, 1940, p. 6156.

Chemisorption experiments were performed on the following Fe–synthetic-NH_3 catalysts; unpromoted catalyst containing 0.15% Al_2O_3, singly promoted catalyst containing 10.2% Al_2O_3, doubly promoted catalyst containing 1.59% K_2O and 1.3 Al_2O_3, catalyst containing 1.07% K_2O, singly promoted catalyst containing 1.03% Al_2O_3 and 0.19 ZrO_2, and doubly promoted catalyst containinng 0.35% Al_2O_3 and 0.08 K_2O. The weights and reduction schedule (time and temperature) are given for the preparation of these catalysts. The chemisorptions of O_2 and CO at −183° and −78°, CO_2 at −78 and 0°, N_2 at 400°–450°, H_2 at −78° (type A), and H_2 at 100° (type B) were studied on these catalysts. From the investigation of these adsorptions individually and from their mutual inhibitory effects the following conclusions are drawn: The CO_2 chemisorption is located on the surface alkali molecules, and the 5 other chemisorptions on the surface of Fe atoms. CO and CO_2 are chemisorbed as molecules, N and H as atoms, O probably as ions. Both the Al_2O_3 and K_2O promoters are strongly concentrated on the surfaces of singly and doubly promoted catalysts. The alkali promoter is very intimately mixed with Fe atoms on the surface. The Fe surface is heterogenous; the heterogeneity probably is due to differently developed crystal faces. The molecular CO and CO_2 chemisorptions are purely surface adsorptions; O ions penetrate several layers below the surface; N and H atoms probably do not penetrate below the surface but migrate to Fe atoms located under surface promoter molecules. Both the K_2O and Al_2O_3 promoters give evidences of specific chemical effects.

389. BRUNAUER, S., EMMETT, P. H., AND TELLER, E. Adsorption of Gases in Multimolecular Layers. Jour. Am. Chem. Soc., vol. 60, 1938, pp. 309–319; Chem. Abs., vol. 32, 1938, p. 4037.

Polarization theory of multimolecular adsorption discussed critically. The adsorption energy, owing to attraction of dipoles induced into a nonpolar gas such as A, is insufficient to constitute a major portion of the binding energy between adsorbed layers. Adsorption-isotherm equations for multimolecular adsorption are derived on the assumption that the same forces that produce condensation are responsible also for multimolecular adsorption. Numerous applications of the equations are given to experimental adsorption isotherms.

390. BRUNAUER, S., JEFFERSON, M. E., EMMETT, P. H., AND HENDRICKS, S. B. Equilibria in the Iron–Nitrogen System. Jour. Am. Chem. Soc. vol. 52, 1931, pp. 1778–1786; Chem. Abs., vol. 25, 1931, p. 3550.

At atmospheric pressure the % NH_3 in a gaseous H_2–NH_3 mixture in equilibrium with an Fe–Fe_4N mixture is 37±2 at 400° and 14.5±1 at 575°. The % NH_3 in a similar equilibrium with Fe_4N–Fe_3N is 77±2 at 400°, 70±2 at 444°, and 57±1.5 at 500°. The composition and lattice dimensions of the phases with an Fe : N ratio of 2 : 2.7 in equilibrium with various H_2–NH_3 mixtures is determined at 400° and 444°. The dissociation pressure of Fe_3N is calculated as 3×10^5 atm. at 450°.

391. BRUNER, F. H. Quality of Synthetic Gasoline From Natural Gas. Ind. Eng. Chem., vol. 41, No. 11, 1949, pp. 2511–2515.

Gasoline produced in this country by the fluidized iron-catalyzed hydrogenation of CO is of much higher quality than that produced commercially in Europe by the Fischer-Tropsch, fixed-bed, Co-catalyzed process. In contrast to the high-boiling, paraffinic material produced over Co, the hydrocarbons produced by the American process are relatively low-boiling and highly olefinic. The olefin characteristic permits the conversion of the gasoline to a high-octane fuel or blending stock by a simple catalytic treatment. A 7-lb. Reid vapor pressure, 400° F. end-point naphtha has a C. F. R. M. clear octane of 82 and a C. F. R. R. octane of 92. The synthetic fuel blends normally in straight-run and cracked products.

BRUNS, B. *See* abs. **332, 333.**

392. BRUNSCHWEIG, R. [Synthetic Liquid Fuels: Problems of the Rational Utilization of Mineral Fuels.] Chaleur et ind., vol. 9, 1928, pp. 143–151; Chem. Abs., vol. 22, 1928, p. 2256.

Address including some information on Fischer's process for hydrogenating at 700° and atmospheric pressure with a catalyst producing aromatics and paraffins.

393. ———. [Economic Aspects of the Synthesis of Liquid Fuels.] Conferences-rapports sur les combustibles, Sec. tchecoslov. soc. chim. ind., vol. 24, 1930, pp. 51–58; Chem. Abs., vol. 24, 1930, p. 4610.

Address.

394. ———. [French Problem of Substitute Fuels.] Rev. ind. minérale, No. 421, 1938, pp. 313–328.

General consideration of synthetic fuels and methods of synthesis in other countries with an explanation of the position in France with respect to alcohol fuels, coal-carbonization products, and hydrogenation.

395. BRUTZKUS, M. [Processes for the Production of Light Oils for Internal-Combustion Engines.] Chim. et ind., vol. 14, 1925, pp. 171–185, 358–362; Chem. Abs., vol. 20, 1926, p. 102.

Van't Hoff's equation, $dlnK/dT=Q/TR^2$, is expressed as follows: Any chemical reaction can be directed and accelerated in a certain direction by continuous and simultaneous external variations in pressure, temperature, and concentration, acting in a direction contrary to that of the corresponding variations caused by the desired reaction. Brutzkus suggests that the desired variations in pressure, temperature, and concentration can easily be obtained by operating in a compressor constructed and operated substantially as a diesel engine. Application of such a method for cracking or hydrogenation under various conditions (exothermic and endothermic reactions), for the treatment of petroleum, tar oils, turpentine, fats, sugars and molasses, cellulose compounds, and coal, and for the synthesis of light oil from CO, CO_2, and H_2, is discussed and compared with corresponding processes at present in use or proposed. Very high temperatures and pressure could be used, and catalyzers could be eliminated.

396. BRYANT, W. M. D. Calculations on Water-Gas Equilibrium. Choice of Suitable Molecular-Heat Equations. Heat of Reaction and Free Energy as a Function of the Temperature. Ind. Eng. Chem., vol. 23, 1931, pp. 1019–1024, 1309; Chem. Abs., vol. 25, 1931, p. 5612.

Thermal and equilibrium data for the water-gas reaction are assembled and discussed. $\Delta H_{298.1}$ for the reaction $CO_2(g)+H_2(g)=CO(g)+H_2O(g)$ is calculated to be 9,751 cal. This value is combined with molecular-heat equations from several sources to yield expressions for ΔH as a function of the temperature. These equations, in turn, are used to show the order of agreement existing between molecular-heat of different sources. For this reaction, specific-heat equations of Lewis and Randall, of Eucken, and of Eastman give similar results. Partington and Shilling's equations do not agree with these results. Expressions for the free-energy change, $\Delta F°$, and its temperature coefficient is derived, as well as for the corresponding reaction isochores. The equilibrium value of Neumann and Köhler at 1,259.1°K. is used to determine the integration constants. The molecular-heat equations of Lewis and Randall, of Eucken, and of Eastman satisfactorily reproduce the experimental equilibrium constants in the water-gas reaction. Partington and Shilling's molecular-heat equations fail to reproduce these values. $\Delta F°_{298.1}$ for the water-gas reaction is calculated. Numerical results ranging 6,828–6,750 cal. are obtained, depending on the specific heats used. These values constitute the first step in a recalculation of the free energy of formation of CO and CO_2.

397. BUECHNER, —. Oxidizability of Cobalt Catalyst. FIAT Reel K29, 1938, frames 7,095–7,108; PB 70,218; TOM Reel 296.

Operating instruction for the determination of trivalent Co is worked out as a result of tests on the determination of the content of trivalent Co in Co catalysts. 1 drawing, 2 tables, 8 graphs.

398. ———. [Recovery of Thorium From the Thorium Catalyst Suspensions.] FIAT Reel K–29, 1938, frames 6,995–7,004, 7,032–7,036, 7,091–7,094, 7,129–7,133; PB 70,218; TOM Reel 296.

Describes improved sulfate process for the recovery of Th from the preliminary precipitation suspension. Gives experiences in 2 large regeneration installations.

399. ———. [Catalysts for an Increased Preparation of Paraffin.] FIAT Reel K29, 1939, frame 6,958; PB 70,218; TOM Reel 296.

Supplement to FIAT Reel K29, frames 6,941–6,944, in which Co catalyst containing Mn is described. Separation of the obtained quantity of paraffin into 1 portion (Gatsch) with a solidification point under 50° and into another portion with a solidification point over 50° is given.

400. ———. Examination of the Reaction Water of the Iron-Catalyst Synthesis. FIAT Reel K 29, 1941, frames 7,242–7,249; PB 70,218; TOM Reel 296.

Analysis of products dissolved in the reaction water in the Fe-catalyst synthesis and description of the analytical method. Since the reaction water contains only about 4 gm. EtOH/l. a technical extraction scarcely seems possible. 5 tables.

401. ———. Alcohol-Forming Catalysts. FIAT Reel K 29, 1945, frames 7,214–7,215; PB 70,218; TOM Reel 296.

Constituents and operating data of 3 alcohol-forming Fe catalysts. 1 of them is proposed as a standard catalyst.

402. BUECHNER, —. HECHEL, H., *and* ROELEN, O. Behavior of Inorganic Impurities in Kieselguhr. FIAT Reel K–20, frames 99–102, 1939; PB 70,211; TOM Reel 287, frames 99–102.

Seasonal variations in the quality of kieselguhr 12 o. were observed. Investigation led to the opinion that these variations are due to storage in the open. When kieselguhr lies in heaps, the Fe oxidizes and the S is transformed into H_2SO_4. These processes are termed "cold combustion" and are said not to occur when kieselguhr is stored flat. When heated to 400°–500°, Fe and S form ferrous sulfate. When the kieselguhr is heated to 1,000° the ferrous sulfate is transformed into ferric silicate. The proportion of Fe, which with the O_2 of the air has already been transformed to the ferrous form, remains unchanged. Ca, S, and Al cause no changes by storage.

BUELOW, H. *See* abs. **3137.**

BUFFLEB, H. *See* abs. **2679, 2680, 2681, 2682.**

BUFORD, C. B. *See* abs. **1268.**

403. BUGGE, G. [Coal Transformation.] Ullmann, Enzyk. Tech. Chem., vol. 6, 2d ed., 1930, pp. 643–670.

Patent and literature listing and summary of the Fischer-Tropsch and the Bergius processes.

404. BUGGE, P. E., AND KERLOGUE, R. H. Determination of the Surface Area of Powders by Means of Low-Temperature Adsorption Isotherms. Jour. Soc. Chem. Ind., vol. 66, 1947, pp. 377–381.

Simple routine procedure for the determination of the surface area of powders by means of low-temperature adsorption isotherms is described with full experimental and mathematical detail. Method of interpretation has been formulated permitting the elimination of the "deadspace" determination for routine procedure where the substance is known to give an S-shaped isotherm. Apparatus and the method are based on previous work of Brunauer and Emmett.

BULANOVA, T. F. *See* abs. **1705.**

405. BULLARD, R. H. Société belge l'azote, Liége; CIOS Report II–11, 1945, 6 pp.; PB 170; TOM Reel 196; Fuel Abs., vol. 3, abs. 454.

During the war this plant produced compressed CH_4 gas from coke-oven gas for use as an auto fuel. MeOH is made now by catalytically cracking coke-oven gas to CO and H_2 and reducing it to MeOH. The catalyst used and the conditions of operation were not discussed but have been patented. The resulting gas consists of 10% N_2, 30% CO, and 60% H_2. Production of MeOH is

20,000 liters/day. A new water-gas plant has been installed with a capacity of 80,000 m.³/day. Nearly all the MeOH produced is converted to CH_2O. Before the war the company had a pilot plant for the hydrogenation of coal-tar oils producing 85–90 octane gasoline, but in 1940 it was dismantled, although in 1939 it produced 600 tons of gasoline for the Belgian army.

406. BUNTE, K. [Residual Gas From Fischer-Tropsch Synthesis as Town's Gas.] Gas-u. Wasserfach, vol. 83, 1940, pp. 497–499; British Abs., 1948, B I, p. 64.

Composition of the gas varies rather widely, mean values being: CO_2, 17%; CO, 9%; CH_4, 33%; H_2, 20%; N_2 and C_nH_m, 0.7 vol. %. The calorific value is within the town's gas range but the high density and low flame speed renders its behavior unsatisfactory unless it is mixed with 2.5 vol. of normal town's gas.

407. BUNTE, K., AND GIESSEN, A. [Influence of Coke Reactivity on Water-Gas Formation.] Gas-u. Wasserfach, vol. 73, 1930, pp. 241–247; Chem. Abs., vol. 24, 1930, p. 2862.

Experimental results indicate that the reactivity of various cokes with respect to water vapor decreases in the following order: Wet-quenched, low-temperature lignite coke; wood charcoal; dry-quenched, low-temperature lignite coke; semicoke; wet-quenched gas coke; dry-quenched gas coke and oven coke. This is in the same order as determined for O_2 alone and O_2 in CO_2 (bibliography given). Some relationship can be noted between water-vapor decomposition and ignition temperature of the coke, but this is obscured by the effect of undecomposed steam passing through the fuel bed on the water-gas equilibrium in the gaseous phase. This effect is difficult to evaluate as it is practically impossible to draw gas samples directly from the fuel surface, and, in addition, equilibrium is not reached in the water-gas reaction, even at the higher temperatures.

408. BUNTE, K., BRÜCKNER, H., AND SCHENK, P. [Synthesis of Benzine Hydrocarbons From Methane.] Gas-u. Wasserfach, vol. 84, 1941, pp. 377–381, 391–396; Chem. Abs., vol. 36, 1942, p. 3158.

Only 12 wt. % (maximum yield) of CH_4 could be converted into liquid products by passing it at a rate of 100 l./hr. through a Pythagoras tube heated at 1,200° in an electric furnace. The exit gases had the composition: C_2H_2, 1.8%; C_6H_6, 2.0%; C_mH_n, 3.8%; H_2, 45.9%; CH_4, 50.3%. The yield of liquid products was: Light oil 39.5 gm/m.³ and tar 86.0 gm./m.³ The effect of size of reaction tube (13, 10, 6, and 4 mm. diam.) was studied. Behavior of catalysts of groups I–III supported on porcelain was investigated, with the same apparatus. Most metals and metallic oxides, especially those of the Fe group, promote direct decomposition of CH_2 into C and H_2; the decomposition rate is accelerated and the reaction temperature lowered by such catalysts. The small increase in the yield of liquid hydrocarbons effected by U, W, and Mo apparently is not due to catalytic action. Ag has a slight catalytic action, 13.1 wt. % of CH_4 being converted into liquid products. At 1,150° and at a rate of 40 l./hr. the exit gases consisted of: C_2H_2, 2.7%; C_6H_6, 2.3%; C_mH_n, 5.0%; H_2, 47.4%; and CH_4, 47.6%. The yield of liquid products was: Light oil 38.1 gm./m.³ and tar 53.6 gm./m.³ Liquid hydrocarbons formed by the thermal decomposition of CH_4 are almost entirely aromatic in character, the main constituents being C_6H_6, toluene, $C_{10}H_8$, and anthracene (typical analyses given). The constitution of the oil depends chiefly on the reaction temperature and reaction time and not to any marked extent on the type of catalyst used.

409. BUNTING, R., AND HUNTER, W. Synthesis-Gas Production in the Fischer-Tropsch Process. Interrogation of Dr. Koelbel. Bib. Sci. Ind. Repts., vol. 10, No. 2, 1948, p. 184; PB 92,120.

1. Gas manufacture, Germany. 2. Fischer-Tropsch process. 3. Gas synthesis, Germany. 4. Catalysts Fe, Germany. 5. Fischer-Tropsch Plant, Courrières-Kuhlmann Oil, Harnes, France.

410. BURGART, P., AND GRAETZ, A. [Synthesis of Liquid Fuel.] Tech. moderne, vol. 19, 1927, pp. 705–713, 743–749; Chem. Abs., vol. 22, 1928, p. 676.

Review showing status of investigations in this field.

BURGOYNE, E. E. *See* abs. **7.**

411. BURKE, S. P. Use of Oxygen in the Manufacture of Gas—Gas Production Subcommittee Report. Am. Gas Assoc. Monthly, vol. 26, September 1944, p. 374; U. O. P. Co. Lib. Bull., abs. 39, 1944.

It appears probable that, if the air is replaced by 98% pure O_2 in the manufacture of blue gas, a gas of approximately 300 B. t. u. can be produced continuously without increasing the clinkering difficulties. Approximately 220 cu. ft. of O_2 is necessary to produce 1,000 cu. ft. of blue gas. The use of O_2 means a large increase in the gas-making capacity of the gas producer. A conservative estimate for the cost of 98% O_2 places it at $0.14 per M cu. ft. Electrolytic production of H_2 and O_2 under pressures up to 300 atm. has been reported as successful from sources in Germany and Sweden. At such a pressure there is a depolarizing effect and a reduction of solution resistance such that the electrical efficiency is improved enough to offset the energy of compression; the electrical requirement is no greater than that necessary at atmospheric pressure. The size and cost of such electrolytic plants are far less than for a plant for making O_2 from the air.

BURNS, J. *See* abs. **2534.**

BURNS, R. M. *See* abs. **3335.**

412. BURRELL, G. A. Hydrogenation of Coal Processes. Oil Gas Jour., vol. 27, October 18, 1928, p. 56.

Motor fuels may be prepared from coal by hydrogenation of coal (Bergius process) or of CO. Water gas (CO and H_2) is made to combine in the presence of various catalysts with or without pressure. Processes in active stages of development in Germany are the Bergius process (pressure hydrogenation of coal), the I. G. Farbenindustrie process (pressure hydrogenation of coal with a catalyst), and the Fischer-Tropsch process ($CO+H_2$+a catalyst with or without pressure); in France the Patart process (CO_2+H_2+a catalyst+high pressure) and the Audibert process ($CO+H_2$+a catalyst+pressure); and in England the Nash process ($CO+H_2$+a catalyst).

413. BURSTIN, H. [Synthesis of Fuels for Airplane Motors.] Przeglad Chem., vol. 2, 1938, pp. 250–264; Chem. Zentralb., 1939, II, p. 1423; Chem. Abs., vol. 35, 1941, p. 4178.

Topics considered include properties of fuels, composition and properties of the more important hydrocarbons, gases, and cracked benzines, processes of selective extraction and polymerization of the products of cracking, benzine substitutes and partial substitutes (ethers, alcohols), antiknock agents (alcohol, benzene, $PbEt_4$), liquefaction of coal and syntheses for benzine and Diesel fuels, production and synthesis of airplane lubricants, and the lubricating efficiency and resistance to oxidation of these oils.

414. BURWELL, R. L., JR., AND TAYLOR, H. S. Activated Adsorption of Hydrogen and Carbon Monoxide on Zinc Oxide—Effect of Water Vapor. Jour. Am. Chem. Soc., vol. 58, 1936, pp. 1753–1755; Chem. Abs., vol. 30, 1936, p. 7954.

H_2O vapor minimizes surface reduction of ZnO catalysts at lower temperatures. It is strongly adsorbed from gas mixtures by those fractions of the ZnO sur-

face to which the gas mixture has access. Saturation of ZnO surfaces by H_2O markedly inhibits the activated adsorption of H_2 and CO.

415. ———. Adsorption and Decomposition of Carbon Monoxide on Zinc Oxide Catalysts. Jour. Am. Chem. Soc., vol. 59, 1937, pp. 697–699; Chem. Abs., vol. 31, 1937, p. 4882.

Study of the activated adsorption of CO on ZnO at temperatures of 184° and higher shows that concurrently with the activated adsorption some decomposition into CO_2 and C occurs. C deposited on the catalyst is removed by H_2 at 184° and above, presumably as CH_4.

BUSCHOW, H. F. *See* abs. **1625.**

BUSI, M. *See* abs. **2106.**

416. BUSINESS WEEK. Petroleum Substitutes. July 21, 1945, p. 74; Nat. Petrol. News, vol. 37, No. 36, R744, Sept. 5, 1945.

Hydrocarbon Research, Inc., announces that it will construct a commercial Synthine (Fischer-Tropsch) plant in East Texas. The plant will have a capacity of 7,000 bbl./day of finished products, 80–85% of which will be high-octane motor gasoline. Production will be at the rate of 1 bbl. of oil/10,000 cu. ft. of gas. The process, developed in the past 20 months, has been sponsored by 3 oil producers: The Magnolia Petroleum Co., the LaGloria Corp., and the J. S. Abercrombie Co. The process is based on German laboratory research applied to American oil-industry techniques concerning plant design and construction and the use of cheaper catalysts. The plant, it is said, will be constructed at a fraction of the cost of similar German plants and will produce a higher quality gasoline.

417. ———. Fuel Research in Canada. No. 890, 1946, p. 112.

It is reported that the Canadian Government is abandoning its active participation in synthetic-liquid-fuels research and, instead, plans to appoint a fuel-research board representing both the Government and private industry and assign to it the responsibility of following current research in the United States and of drawing up a new liquid-fuel program for the Dominion. Plans approved by Parliament for a $750,000 coal-hydrogenation pilot plant will be postponed, since the Canadian Government sees no economic future for a synthetic-fuels industry in eastern Canada based on high-cost Nova Scotia coal. The same applies to the Pacific coast region. Attention will, however, continue to be given to the Mid-Continent region and research on natural gas, coal, and natural bitumen from Alberta tar sands will be continued.

418. BÜTEFISCH, —. Synthetic-Oil Production in Germany. BIOS Final Rept. 1697 (Interrogation Rept. 667), 1946, 26 pp.; PB 92,191.

A questionnaire directed to Dr. Bütefisch with his replies, which bring out several points of comparison between the Fischer-Tropsch and coal-hydrogenation processes. Data on plants, plant capacity, products, production costs, and uses of and properties of the products are reviewed. It is concluded that the Fischer-Tropsch process should be regarded as a purely chemical process yielding hydrocarbons, where as the hydrogenation process was mainly suitable for making fuel oils but not chemicals.

419. BUYLLA, B. A., AND PERTIERRA, J. M. [Synthesis of High Hydrocarbons From Water Gas.] Anales soc. espan, fis. quim., vol. 27, 1929, pp. 23–38; Chem. Zentralb., 1929, I, p. 2846; Chem. Abs., vol. 23, 1929, p. 2810.

In the catalytic reduction of CO contained in water gas by CuO, Co_2O_3, and MnO_2, a test was made at 254°, which was lower than any previous temperature used. Here the contraction was less than at higher temperature, but the yield of liquid and solid hydrocarbons was higher. The necessity of extreme purification of water gas to maintain activity of a catalyst activated by successive oxidations and reductions is shown.

BYRNE, B. J. *See* abs. **2448.**

BYSTRÖM, H. *See* abs. **1388.**

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420. CADMAN, W. H. Fuels Produced by Hydrogenation and Synthetic Processes. Ann. Rev. Petrol. Technol., vol. 6, 1941, pp. 155–165.

Review of the commercial developments in Great Britain and abroad in 1940.

CADY, W. E. *See* abs. **3642b.**

420a. CADY, W. E., LAUNER, P. J. AND WEITKAMP, A. W. Products of the Hydrogenation of Carbon Monoxide Over an Iron Catalyst. Aromatic Hydrocarbons. Am. Chem. Soc., 121st Meeting Abs., March–April, 1952, p. 10–M.

Aromatics constitute about 6 wt. % of the hydrocarbons obtained in the hydrocarbon-synthesis process. They were separated by adsorption on silica gel and by distillation and were analyzed by ultraviolet and infrared spectroscopy. Benzene is present in traces, but successive C-number fractions contain increasing concentrations of aromatics. Monocyclic, dicyclic, and tricyclic aromatics occur in proportions that decrease with the number of aromatic rings. Some of the aromatic hydrocarbons contain a nonaromatic ring fused with the nucleus. Olefinic unsaturation is an important feature of the high–molecular–weight aromatics. Some unsaturation may be in the rings of compounds of the indene or the dihydronaphthalene series; the remainder is side-chain unsaturation. Aromatic rings occur to a small extent in the structures of the oxygenated compounds. In the benzene series, monoalkyl and o–dialkyl isomers predominate. A regular pattern of alkylbenzeneisomer distribution suggests a way in which the rings may have been formed.

420b. CAIN, D. G., WEITKAMP, A. W. AND BOWMAN, N. J. Products of the Hydrogenation of Carbon Monoxide Over an Iron Catalyst. Oil-Soluble Oxygenated Compounds. Am. Chem. Soc., 121st Meeting Abs., March–April, 1952, p. 11–M.

The oxygenated compounds in the oil stream produced by hydrogenation of CO over an Fe catalyst are higher homologs of those in the H_2O stream. The main components are acids, alcohols, and carbonyl compounds of the aliphatic series. Yields of these classes decrease with increasing C number$>$5. At a given C number, the ratio of the molar quantities of each of the main components to the total molar quantity of oxygenated compounds and hydrocarbons is approximately constant. The alcohols appear to be more closely related structurally to the aliphatic hydrocarbons than are the acids. Branched isomers are more prevalent in the acids. Olefinic unsaturation and aromatic rings are present in some oxygenated molecules, but molecules containing 2 oxygenated groups have not been detected.

421. CALCOTT, W. S. Activities of I. G. Farbenindustrie A.-G., Leuna. Soap Substitute. CIOS Rept. XXII–19; TOM Reel 196; PB Rept. 187, 1945, 8 pp.

One of the important products made at Leuna was a soap substitute called Mersol, made from the Kogasin fraction of Fischer-Tropsch oil. As received, the Kogasin contained both oxygen derivatives and un-

saturated compounds, which were eliminated by catalytic hydrogenation over a Ni tungstate catalyst at 200 atm. and 300°–350°. A mixture of straight-chain hydrocarbons was obtained containing the compounds from $C_{12}H_{26}$ to $C_{18}H_{38}$, but chiefly $C_{16}H_{32}$. This mixture was treated with SO_2 and Cl while being irradiated with ultraviolet light at 30°–40°. The reaction is carried to only 70% completion to avoid formation of excessive amounts of disulfonyl chloride, which is useless for soap production. The sulfonyl chloride is used for soap making, being saponified with other soapmaking materials. A cresol ester is prepared from sulfonyl chloride and used as a plasticizer for polyvinyl chloride. The Na salt, called Mersolat, is made by saponifying the Mersol at 70° with a 10% NaOH solution. The oil is separated from the sodium alkyl sulfonate by decantation, chlorinated, and used as a solvent. At the peak of operation about 4,500 tons per month of Mersol were being produced. Equipment and process are described.

422. CALDWELL, J. M., AND SMITH, G. H. Mersol and Hostapon Processes. I. G. Farbenindustrie A.-G., Höchst. BIOS Final Rept. 1222, 1946, 9 pp.; PB 79,310.

Further information than is given in BIOS Final Rept. 478 on the manufacture of Mersol-type detergent products from a hydrogenated Fischer-Tropsch cut of boiling range 220°–320°, Mepasin. Mersol H_2 is produced by the action of SO_2 and Cl on Mepasin. Mersol H_2 can be converted to Mersolat by reacting with caustic soda in 10% solution. Hostapon is produced by the direct action of SO_2 and O_2 on Mepasin, using light or acetic anhydride as catalyst. The detergent properties of Hostapon are essentially the same as Mersolat. Gives details of methods.

423. CALVERT, G. C. Synthetic Alcohols and Liquid Fuels. Chem. Age, vol. 5, 1921, p. 153; Chem. Abs., vol. 15, 1921, p. 3735.

Calvert has developed a method of converting C into water gas and mixing this with other gases, according to the product desired. Utilization of wood waste, charcoal, or carbonizable tropical matter should yield fuel MeOH at $19/ton. Details of the process are withheld. The ratio of efficiency of MeOH to gasoline for use in internal-combustion engines is 5 : 4.

424. CAMPBELL, E. D., FINK, W. L., AND ROSS, J. F. Iron–Iron Carbide Equilibrium in Dry Hydrogen at 950°. Jour. Iron Steel Inst. (London), No. 108, II, 1923, pp. 173–178; Chem. Abs., vol. 18, 1924, p. 612.

Results of several experiments to determine the amount of C transferred from a solution of carbides in Fe to one of lower concentration. The loss in weight of the samples indicates formation of a solution of Fe carbides, which then react with H_2 to form gaseous hydrocarbons. It is suggested, from the small amount of greasy substance found in the reaction tubes, that the gaseous C compounds are not entirely CH_4 but that a part at least were hydrocarbons of higher molecular weight.

424a. CAMPBELL, W. M. AND JOHNSTONE, H. F. Reactions of Hydrogen and Carbon Monoxide in a Tubular Reactor With Iron-Copper Catalyst. Ind. Eng. Chem., vol. 44, 1952, pp. 1,570–1,575; Chem. Abs., vol. 46, 1952, p. 8,349.

Some of the factors affecting the Fischer-Tropsch synthesis were studied in order to learn more about the reaction mechanism. The reactor consisted of a porous alundum tube, impregnated with the catalyst, through which the gases flowed longitudinally. Stable and reproducible Fe–Cu catalysts which produce CO_2 and hydrocarbons from synthesis gas at atmospheric pressure were developed. When treated with steam and CO at 250° the activity of these catalysts increases. At 280° the activity drops rapidly and eventually reaches a period of constant activity where the only products are CH_4, C_2H_4, C and CO_2. The loss in activity due to H_2S poisoning is a linear function of the amount of S absorbed, and when about 0.5 atom of S/atom of metal is taken up the activity is 0. Catalysts producing CO_2 are active for the water gas shift reaction. Heating at 310° in the presence of H_2 and CO destroys the synthesis reaction activity, but does not change the shift reaction activity. H_2S destroys the activity for both reactions. The shift reaction activity of a H_2O producing catalyst can be increased by increasing the H_2 concentration in the feed gas. These results are definite proof of the existence of 2 types of active centers, 1 for the shift reaction and the other for the synthesis reaction. A dual reaction mechanism is proposed, by which paraffins are formed by Craxford's mechanism, and olefins are formed by simply splitting the $(CH_2)_n$ chain off the surface. In a CO_2-producing catalyst, the metal active centers must be present in clusters principally.

425. CANDEA, C., AND KÜHN, J. [Decomposition of Methane and Petroleum Hydrocarbons With Steam.] Bull. sci. école polytech. Timisoara, vol 5, 1934, pp. 225–232; Chem. Abs., vol. 29, 1935, p. 8302.

Reaction of steam upon CH_4 and various petroleum fractions, including a distillation residue, was studied in quartz and steel tubes with various catalysts and a wide range of temperatures. Natural gas containing 96.4% CH_4 was almost completely transformed into H_2 (70%) and CO (20%) at 1,000° with an Fe–Ni–Mn catalyst, a ratio of steam to natural gas of 1 : 3, and time of contact 20 sec. Kerosine produced 30% H_2 and 70% CO under similar conditions, except that the time of contact was less. A very good illuminating gas was obtained from the petroleum residue at 800°–900°. This gas would also be suitable as fuel for gas engines.

426. CANTELO, R. C. Thermal Decomposition of Methane. I. Jour. Phys. Chem., vol. 28, 1924, pp. 1036–1048; Chem. Abs., vol. 19, 1925, p. 204.

Calculation of the equilibrium constant for the decomposition of CH_4 into C and H_2 shows this reaction to be almost complete at 700°. Various contact catalysts were, therefore, tried to hasten the formation of C black at this temperature. Asbestos impregnated with Ni–Ni oxide was most effective.

427. ———. Thermal Decomposition of Methane. II. Jour. Phys. Chem., vol. 30, 1926, pp. 899–901; Chem. Abs., vol. 20, 1926, p. 2934.

Equations for velocity of decomposition of CH_4 to C and 2 H_2 were derived and applied to experimental results at 985°. The reaction was only 36% complete after 1 hr. The velocity was abnormally high for 5 min. until the walls were covered with C. The velocity constant is of the order of 0.15.

428. ———. Methane Equilibrium. I. Jour. Phys. Chem., vol. 30, 1926, pp. 1641–1645; Chem. Abs., vol. 21, 1927, p. 522.

Equilibrium constants for the reaction $C+2\ H_2 \rightleftharpoons CH_4+21{,}730$ cal., were calculated by Saunders' equation $\log K_p=(4583/T)-1.75\ \log T+0.000630\ T-0.7$ over the temperature range 500°–1,100°. With these values of K_p the equilibrium concentrations of CH_4 and H_2 are calculated to be: Temperature 500°, % CH_4, 63.9; % H_2, 36.1: 600°, 37.9; 62.1: 700°, 16.3; 83.7: 750°, 13.0; 87.0: 800°, 7.5; 92.5: 850°,4.5; 95.5: 900°, 3.6; 96.4: 1,000°, 2.0; 98.0: 1,100°, 0.8; 99.2. These values reconcile the results of earlier investigators. The equilibrium concentrations of CH_4 and H_2 obtained from the catalytic decomposition of pure CH_4 were measured at 565°, 670°, and 770°. The cata-

lyst was prepared by ignition of pure $NiNO_3$ deposited on asbestos fibers. This material was then reduced in H_2. The gas mixture was circulated over the heated catalyst until no further increase in volume was observed. The equilibrium composition of the gas was found by analysis to be: Temperature 565°, % CH_4, 32.7; % H, 58.9; % N_2, 6.5; % CO, 1.4: 670°, 24.4, 68.8, 5.3, 1.9; 770°, 9.2, 85.9, 3.7, 1.2. The values of K_p corresponding to these results are: 565°, 0.95; 670°, 0.47; 770°, 0.12.

429. ———. Methane Equilibrium. II. Jour. Phys. Chem., vol. 31, 1927, pp. 124–130; Chem. Abs., vol. 21, 1927, p. 849.

Equilibrium constants for the reactions that might conceivably occur along with the thermal decomposition of C_2H_4 are calculated by means of the Nernst approximation formula. The calculations are tabulated for 200°, 400°, 600°, and 800°. The reactions with their increase in heat content are:

$C_2H_4 \rightleftharpoons 2C+2H_2-14{,}600$ cal.; $C_2H_4 \rightleftharpoons C_2H_2+H_2+43{,}500$ cal.; $3C_2H_4 \rightleftharpoons C_6H_6+3H_2-32{,}500$ cal.; $C_2H_6 \rightleftharpoons 2C+3H_2+23{,}300$ cal.; $C_2H_6 \rightleftharpoons C_2H_4+H_2+37{,}900$ cal.; $C_2H_6 \rightleftharpoons C_2H_2+2H_2+81{,}400$ cal.; $3C_2H_2 \rightleftharpoons C_6H_6-163{,}000$ cal.; $CH_4 \rightleftharpoons C+2H_2+18{,}900$ cal.; $2CH_4 \rightleftharpoons C_2H_4+2H_2+52{,}400$ cal.; $2CH_4 \rightleftharpoons C_2H_2+3H_2+95{,}900$ cal. From a consideration of the equilibrium constants it appears that whether the initial system be CH_4, C_2H_4, or C_2H_6, the final equilibrium system will be CH_4, C, and H_2 in the proportions to satisfy this equilibrium. A brief review of the experimental work upon C_2H_4 and C_2H_6 decomposition shows that the above conclusion is supported by the experimental evidence.

430. ———. Methane Equilibrium. III. Jour. Phys. Chem., vol. 31, 1927, pp. 246–250; Chem. Abs., vol. 21, 1927, p. 1583.

In the catalytic decomposition of C_2H_4 the catalyst most effective is a specially prepared Ni–Ni oxide; at 300° and higher, CH_4 is present in the products, the % of CH_4 increasing with the temperature. C_2H_6 is stable up to 360° in the presence of a Ni catalyst. Equilibrium constants for the CH_4 equilibrium at 500°–770° were obtained by repeatedly circulating the products of the catalytic decomposition of C_2H_4 over the Ni catalyst, which are in general agreement with those obtained by other investigators.

431. ———. Methane Equilibrium. IV. Jour. Phys. Chem., vol. 31, 1927, pp. 417–418; Chem. Abs., vol. 21, 1927, p. 2213.

Free energy of formation of CH_4 from H_2 and amorphous C is calculated as $\Delta F=-19{,}280+10.67\ T\ln T-0.00786T^2-0.0{,}67T^3-42.2T$, from which $\Delta F=-14{,}500$.

432. Capell, R. G., Amero, R. C., and Wood, W. H. Fuller's Earth as a Binder for Catalysts and Adsorbents. Petrol. Refiner, vol. 25, No. 2, 1946, pp. 69–71.

Florigel is a grade of Florida-Georgia fuller's earth that develops its maximum adsorptive or decolorizing capacity when heated to 1,200° F. and its maximum dehydrating capacity at 600° F. Plastic properties are destroyed at 700° F., and a hard granule is formed resistant to the action of H_2O or steam. Above 1,200° F. its adsorptive and catalytic properties decline. In investigating the use of Florigel as a binding agent in catalyst manufacture, experimental samples were prepared by mixing a finely ground catalytic base material and a binding agent, kneading in the desired amount of H_2O and extruding the mixture, drying at 1,200° F., cooling, and testing for crushing strength. A pellet strength of 20 lb., the minimum usually considered acceptable, was obtained with about 8.5% of Florigel, whereas approximately 19% of ball clay was needed for good extrusion. Fine grinding and thorough mixing are essential in increasing pellet strength and use of enough H_2O to give it the consistency of a stiff mud. Florigel requires 150% more H_2O than does ball clay to obtain the same consistency. Additives, such as tannic acid, Na_2CO_3, and NaOH, dissolved in the H_2O improve extrusion characteristics. Florigel was tested as a bonding agent for a synthetic Mg silicate, an excellent decolorizing agent; at about 35% of Florigel, a maximum decoloring capacity was attained and a hardness for commercial use. The following characteristics make Florigel suitable as a binder: Mixed with H_2O and catalytic or adsorptive materials it is readily pelleted, pressed or extruded; it increases mechanical strength of soft nonplastic materials; it is irreversible with respect to H_2O; it is porous and insoluble, hence does not detract from the surface area of the material being bound; it is an adsorbent and a catalyst in its own right; it is stable at high temperature.

Capp, J. P. *See* abs. **740.**

Carlile, J. H. G. *See* abs. **450.**

433. Carlin, G. T. German Meat-Packing and Fat and Oil Operations During the War Period. Food Technol., vol. 1, 1947, pp. 404–414; Chem. Abs., vol. 41, 1947, p. 7556.

Synthetic butter was made by means of the Fischer-Tropsch synthesis for the production of fat. Both Co and Fe catalysts were used. The yields of various fatty acid fractions are listed, and the conversion of the fatty acids in triglycerides by esterification of glycerol is discussed. The synthetic butter exhibited the following values: M.p. 35°; I number 10; saponification 235; nonsaponifiable matter 0.2%; hydroxyl value 8–10; and free fatty acids 0.5%. Feeding tests indicated that fatty acid chains of odd number were just as valuable in human nutrition as the natural, even-numbered fatty acids. It was claimed that odd-numbered synthetic fats were of value in the feeding of diabetics because acetone bodies are not formed from the odd-numbered C chains. Soaps and lubricating greases were made from fatty acid fractions unsuitable for the manufacture of synthetic butter.

434. Carlsmith, L. E. Large-Scale Production of Oxygen. FIAT Final Rept. 1120, 1947, 45 pp.; PB 88,840.

This report is a compilation of miscellaneous information on oxygen production not previously recorded. The activities of the Messer Company are discussed and the larger plants built by them are listed. The Kapitza process (Russian) is reported. This is also a process in which low-pressure air is employed. The outstanding feature appears to be the use of a very efficient, compact, radial-flow, expansion turbine. Efficiencies of 81–83% are claimed for it. An energy consumption of 0.28 kw.-hr./m.^{3} of O_2 has been reported compared with 0.445 claimed by Linde and 0.35 suggested for projected large-scale units in the United States.

———. *See* abs. **1625.**

Carlson, C. S. *See* abs. **2325a.**

435. Carnegie Institute of Technology, Coal Research Laboratory Staff. Coal—An Abundant Raw Material for New Chemicals. Chem. Ind., vol. 52, 1943, pp. 202–204.

Mention is made in the discussion of chemicals derived from coal of the possibilities of the Fischer-Tropsch process.

436. Caron, M. H. [Industrial Uses of Oxygen.] Ingenieur, vol. 44, 1947, pp. M51–56; Jour. Inst. Petrol., vol. 34, 1948, p. 28A.

Review of various manufacturing processes of O_2, together with costs. Various processes in which O_2 can be used are described, including the use of O_2 in the Fischer-Tropsch, Lurgi, and Bergius processes and in underground gasification of coal.

437. CARPENTER, H. C. H., AND SMITH, C. C. Some Experiments on the Reaction Between Pure Carbon Monoxide and Pure Electrolytic Iron Below the A Inversion. Jour. Iron Steel Inst., vol. 98, 1918, pp. 139–197; Chem Abs., vol. 12, 1918, p. 2523.

Experiments with electrolytic Fe were all conducted in a quartz tube. The reaction temperature was 650° in all except the 1st few experiments. The tube was heated by enclosing it in another quartz tube, which was wound with Ni–Cr wire and suitably packed in a heat-insulating medium. The total impurities in the Fe amounted to only 0.033%. The CO was prepared by dropping pure HCOOH on concentrated H_2SO_4. Special precautions were taken with regard to all the other reagents used. The data obtained from the experiments indicate that the reaction between CO and Fe at 650° is of a complex nature and it was not possible to reach a conclusion as to the precise change or changes. It was demonstrated, however, that a substance is formed that appears to be Fe_3C. The presence of enough CO_2 in the gas prevents the formation of this substance. The addition of H_2 to CO favors the production of the carbide. In most cases, carbonaceous products are formed containing Fe, C, and O.

438. CARR, T. P. Coke Oven Managers' Association, Midland Section. Inaugural Address. Gas World, vol. 109, No. 2835, Coking Section 12–14, 1938; Chem. Abs., vol. 33, 1939, p. 1124.

Review of developments in the coking industry during the past few years. Process depends for its action on conversion of coke into water gas. The water gas is divided into 2 portions: 1 portion is specially treated in a gas-cracking apparatus, and the cracked gas is then reblended with the remaining portion of the water gas. The net result of this mixture is to give a gas consisting of approximately 30 parts by volume of CO and 60 parts by volume of H_2 The synthesis gas so produced is then passed over a catalyst consisting of a Co–Th preparation deposited on kieselguhr at atmospheric pressure and at a temperature of approximately 220° C. a mixture of oils is produced, which can be fractionated into gasol, petrol, diesel oil, and paraffin wax. The gasol consists mainly of propane and butane, which can be sold for country-house lighting and heating and is very similar to the Calor gas marketed in England. The diesel oil is of particularly high quality, having a cetane value of 100, while the petrol is of rather low octane value as compared with the spirit obtained from the hydrogenation process. This petrol can, however, be improved by cracking, and further improvements can be obtained by cracking the diesel oil and paraffin wax produced and blending these cracked products with the petrol. At present the motor-fuel production from this process in Germany is at the rate of approximately 600,000 tons per yr., while there is 1 unit in operation in France producing motor fuel at the rate of 13,000 tons per yr. It is impossible to give a detailed list of the various plants operating on the continent, but the above figures of output can be taken as being substantially correct. The actual proportion of coal or coke used for producing 1 ton of motor spirit naturally varies according to the process adopted, since the Fischer-Tropsch process can operate in a number of different ways. For example; coking coal may be converted into coke, which, in turn, is converted into water gas, as already indicated. Lignites or brown coals may be gasified in special producers to give synthesis gas direct without any intermediate coking, materials of the nature of cannel or oil shale may be carbonized, the gas being used for the conversion into synthesis gas and the coke being used for providing the necessary heat for the generation of steam and power for the process, and the large yield of tar from such carbonization being cracked to give high-octane-value spirit. With the conversion of coal into coke, the amount of coal required to produce 1 ton of primary products may be approximately 5 tons, whereas, with the use of cannels or similar materials, the quantity of coal used may only amount to 2½ tons per ton of spirit produced.

439. CARTER, D. V. Gas Conservation in West Texas. Oil Gas Jour., vol. 45, No. 36, 1947, pp. 74, 76, 77, 86.

Paper presented before the American Institute of Mining Engineers in Texas. It is shown how natural-gas resources can be conserved by way of natural gasoline, gas processing, and pressure maintenance. Tabulated statistics are shown covering the production and disposition of gas in West Texas for 1944–45. Another bright feature of utilization is the large-scale production of O_2, reducing the present cost of $70 per ton to about $3 per ton, and its combination with the Fischer-Tropsch or the Hydrocol processes in manufacturing gasoline from natural gas. Current estimates are that it can be produced for $0.05 per gal. compared with the present cost in the Texas Gulf coast of $0.07¼. Greatly improved yields from these processes, it is estimated, could extract 17 billion bbl. of gasoline from the 175 trillion cu. ft. of present gas reserve in the United States as compared to 10 billion bbl. of gasoline from our presently known oil reserves of 20 billion bbl. Increased utilization of West Texas gas should result in a higher price for the gas in competition with the manufacture of carbon black.

CARTER, S. R. *See* abs. **338, 339.**

440. CASAUS, P. L. [The Fischer-Tropsch Synthesis—a Bibliographic Study.] Combustibles (Zaragoza), vol. 6, 1946, pp. 62–75, 120–134.

Cites 184 refs.

CASAZZA, E. *See* abs. **2386.**

441. CASSAN, H. [Gas-Forming Reaction in a Gas Generator Not Under Equilibrium Conditions.] Chaleur et ind., vol. 19, 1938, pp. 441–444; Chem. Abs., vol. 32, 1938, p. 7246.

In actual operation of a water-gas generator, equilibrium is not attained, but is approached to an extent depending on the reactivity of the coke, the contact time, etc. The thermal yield, P, is defined as the ratio of the heat of combustion of the gas produced to that of the gas resulting from complete reduction of CO_2 and H_2O to CO and H_2. P is empirically determined to be a function of the volume content and degree of reduction of the CO_2 and H_2O separately, in the inlet gas. Values of this function are tabulated and plotted.

442. ———. [Water-Gas Reaction.] Compt. rend., vol. 206, 1938, pp. 1296–1299; Chem. Abs., vol. 32, 1938, p. 5187.

Actual yield (P) of a water-gas installation is defined as the ratio $R : R_o$, where R is the ratio of the amount of heat obtainable from the gas produced to that produced by burning the C used, R_o is the theoretical maximum ratio, and P is calculated on various semiempirical assumptions for varying relative amounts of CO_2, H_2O and N_2.

443. CAWLEY, C. M. Oil From Coal. Min. Jour. (London), vol. 204, 1939, pp. 179–180; Chem. Zentralb., 1939, I, p. 4415.

Review of carbonization, hydrogenation, and synthesis, their practical significance, and a summary of the results of economic and technical investigation of hydrogenation and hydrocarbon synthesis.

444. ———. Wax Industry in Germany. BIOS Final Rept., 1831, 1946, 315 pp.

A survey of the production, refining, and utilization of hydrocarbon, natural, montan, and synthetic waxes was made by contacting 65 production and utilization sources, each of which is discussed. The crude-wax

products form a substantial part of the products of the Fischer-Tropsch process employed in nine plants having a combined output of about 500,000 tons per yr. The crude wax products were of 2 kinds: A soft wax (gatsch) boiling mainly below 450° and a hard wax boiling mainly above 450°. The medium-pressure process gave a higher yield of both soft and hard waxes than the normal-pressure process. In the peak year 1943 the total production of soft wax was 46,170 tons and of hard wax 25,830 tons. The properties, treatment, and utilization of these waxes are dealt with fully. Two of the most important uses of hydrocarbon waxes were as the raw materials for the synthesis of lubricating oil and fatty acids. Because Fischer-Tropsch waxes are richer in n-paraffins than petroleum waxes, they are more suitable for these syntheses. Information is given about various methods for determining the amount of oil in wax products. All methods were based on the crystallization of wax from chilled solvents and the washing and purification of the wax. Considerable work had been carried out in the use of chlorinated solvents for the selective separation of waxes. A summary of information on Fischer-Tropsch waxes is made in an appendix by C. C. Hall, pp. 284–303.

445. ———. Coal, Shale, Peat, and Their Products in 1947. I. Fuels Produced by Hydrogenation and Synthetic Processes. Rev. Petrol. Technol., vol. 9, 1947, pp. 243–262.

Review of developments, with 126 refs.

———. *See* abs. **1770.**

446. CAWLEY, C. M., AND HALL, C. C. Fuels Produced by Hydrogenation and Synthetic Processes. Ann. Rev. Petrol. Technol., vol. 5, 1940, pp. 361–383. Chem. Abs., vol. 34, 1940, p. 8228.

Review covering 1939. Krupp-Treibstoffwerk, G. m. b. H., at Essen obtains its raw material from coal by low temperature. Carbonization by the Krupp-Lurgi process. Production of primary product was begun at the end of 1938. A plant at Deschowitz has been recently completed for the Gräflich schaffgottische Benzin G. m. b. H. of the Selesian coal industry.

447. ———. Synthetic Fuels: The Fischer-Tropsch Process. Rev. Petrol. Technol., 1941–45, vol. 7, 1947, pp. 292–306.

General review covering commercial development of the Fischer-Tropsch process, processes and plant, catalysts, reaction mechanism, properties, and uses of products.

448. CAWLEY, C. M., AND WOODWARD, L. A. Hydrogenation and Synthetic Fuels. Ann. Rev. Petrol. Technol., vol. 3, 1938, pp. 393–409.

Annual review for 1937 of hydrogenation and Fischer-Tropsch processes. 136 literature and patent refs.

449. ———. Fuels Produced by Hydrogenation and Synthetic Processes. Ann. Rev. Petrol. Technol., vol. 4, 1939, pp. 393–409; Chem. Abs., vol. 34, 1940, p. 2161.

Review of developments in 1938.

450. CAWLEY, C. M., CARLILE, J. H. G., NEWALL, H. E., AND KINGMAN, F. E. T. Experiments on the Production of Toluene From Coal-Tar Products and Other Sources. Jour. Inst. Petrol., vol. 32, 1946, pp. 660–683; Chem. Abs., vol. 41, 1947, p. 3601.

To supply the toluene requirements of Great Britain during the war, 5 sources of processes were investigated on a laboratory scale. One process was the cyclization of *n*-heptane obtained from Fischer-Tropsch oil. With the aid of CrO_3 catalyst supported on active Al_2O_3, about 57% of toluene was obtained at first, later diminishing to 51%.

CHAFFEE, C. C. *See* abs. **873, 874, 875, 876, 877, 878, 3549.**

451. CHAFFEE, C. C., THOMPSON, O. F., KING, J. G., ATWELL, H. V., AND JONES, I. H. Metallgesellschaft-Lurgi, Frankfurt am Main, Germany. CIOS Rept. XXXI–23, 1945, 54 pp. TOM Reel 196; PB Rept. 12,624.

The following subjects of interest are discussed: III. Japanese-German relationships with brief data on 9 plants; V. Fischer-Tropsch developments, 7 figures; VI. Carbonization. A. Spuelgas or direct heating process, and B. low-temperature carbonization by indirect heating; VII. High-pressure gasification with synthesis gas and O_2 production, 1 figure; VIII. Synthetic lubricating oil Rheinpreussen plant Homberg, 1 fig.

452. ———. Metallgesellschaft-Lurgi, Frankfurt am Main, Germany. V. Fischer-Tropsch. CIOS Rept. XXXI–23, 1945, pp. 6–18; TOM Reel 196; PB Rept. 12,624.

Research by the Lurgi organization has been concentrated on the development of a middle-pressure recycle operation, particularly with Fe catalysts. This type of operation is claimed to have the following advantages: use of a synthesis gas of $CO:H_2$ ratio 1:1; easier temperature control owing to high gas velocity through catalyst bed; increased olefin product; less C and CH_4 formed on the catalyst. No commercial synthesis plants using an Fe catalyst have been built in Germany, but designs had been completed for erection of a plant in Italy. Particular interest had been directed toward recycle operation of the Fischer-Tropsch process using the standard externally cooled middle-pressure reactor and a relatively low recycle ratio. A pilot-plant unit, operating for 2 yr. with a Co catalyst and a single pass, gave a yield of 155–162 gm. of liquid plus gasol/m.^{3}; increasing the recycle ratio to 3:1 increased the throughput by 30% without loss of yield or obtained a yield of 170 gm./m.^{3} at the same throughput. With the active Fe catalyst (100 Fe, 25 Cu, 9 Al_2O_3, $2K_2O$, 30 SiO_2) the yield was 170 gm./m.^{3} at the normal recycle ratio. The Fe catalyst was made by dissolving Cu and Al nitrates in 10% solution of ferric nitrate in amounts that would give the specified ratio of metals, heating nearly to boiling, adding enough 10% solution of Na_2CO_3 to precipitate the metals as hydroxides, adding kieselguhr, and washing with hot water to a *p*H of 8.0 and then with K_2CO_3 solution. The nitrates must be removed completely in order to make reduction temperature control easy and positive. After complete drying, the catalyst is reduced with H_2 at 250°–350° for 1–4 hr., the flow rate of H_2 being 1 m.^{3}/kg. of catalyst/hr. Reduction with synthesis gas is possible. It is believed that the life of the catalyst would be about 1 yr. The capital cost of a new plant is stated to be 800–900 RM./ton of liquid product/yr., although recently a quotation of 600 RM. was cited. The operating cost is given as 24 pf./kg. of product, while the most favorable income is obtained by operating for the maximum yield of hard wax at 45 pf./kg. Lurgi has built the charcoal-absorption units for nearly all of the Fischer-Tropsch plants in Germany. Charcoal absorption is believed definitely more economical than oil absorption up to 10 atm. pressure, and the latter is preferable above 15 atm. with the choice between 10 and 15 atm., depending on local conditions. A recent advance in charcoal absorption technique is the design of a plant to work at —50°, the objective being the separation of CH_4. The costs are said to be slightly less than those for refrigeration.

453. ———. Metallgesellschaft-Lurgi, Frankfurt-am-Main, Germany. VII. High-Pressure Gasification. CIOS Rept. XXXI–23, 1945, pp. 29–42; TOM Reel 196; PB Rept. 12,624.

In the high-pressure gasification process developed by Lurgi, solid fuel, preferably weakly coking or non-coking bituminous and brown coals, is continuously

gasified at from 20–30 atm. pressure with O_2 and steam. The coal need not be dry, but the water content should not exceed 25%. Four plants had been built by Lurgi: At Hirschfelde, 5 million m.³ gas/year; 2 at Böhlen, 150 million m.³; and at Brüx, 100 million m.³ The generator and its operation are described, operating results are presented, and directions are given for recovery of the liquid products. Results are given for 3 kinds of fuel—2 brown and 1 lean bituminous coal. Composition of a typical purified city gas—CO_2, 3.0; C_nH_m, 0.5; O_2, 0.1; CO, 22.8; H_2, 48.7; CH_4, 22.6; N_2, 2.3%; gas yield 760 m.³/ton; O_2 requirement 0.15 m.³/m.³ gas (about one-half that required by Winkler generator); efficiency of fuel conversion, about 85.2%; cost 2.4 pf./m.³ with brown coal at 6.5 RM./ton. In the making of synthesis gas a different procedure is followed. It has been found that the actual pressure existing in the pressure generator influences the nature of the produced gas; at lower pressures less CH_4 is formed in the presence of C, pressure displaces the CO : CO_2 equilibrium in favor of CO_2. At low temperature also the equilibrium is further displaced in favor of a reduced formation of CO. Since the required reduction of CO formation is not great, it is adequate to reduce the pressure from the usual 20 atm. to about 5–10 atm. Practical tests have shown that a CO–H_2 gas mixture suitable for the Fischer-Tropsch synthesis with Co–ThO_2 catalyst can be prepared by the gasification of low-temperature bituminous coke when employing a pressure of about 8.5 atm. with both O_2 and steam. Under such conditions a crude gas of composition (CO_2, 29.3; CO, 21.9; H_2, 44.0; CH_4, 3.3; N_2, 1.5%) is obtained, which, after the CO_2 is scrubbed out, yields a synthesis gas of composition: CO_2, 1.0; CO, 30.7; H_2, 61.6; CH_4, 4.6; N_2, 2.1%. Furthermore, by increasing the addition of steam in the pressure gasification, the formation of CO may be so reduced that a scrubbed gas containing 70–75% H_2 and only 15% CO is produced suitable for NH_3 synthesis or for hydrogenation. In preparing synthesis gas of 1.2 H_2 : CO ratio to be used with the Fe catalyst, the procedure again is different. An analysis of the various possibilities available for the solution of the problem has led to the conclusion that economically the most advantageous method for preparing the gas from brown coal is to employ O_2 at a pressure of about 23.5 atm., and after scrubbing the gas to remove about ⅓ of the CO_2 and some of the H_2S. The gas is heated to 145°, saturated with H_2O, again preheated to 500°, and by partial combustion with O_2 heated to 1,300°, in the absence of a catalyst to convert the CH_4 content to CO and H_2. After scrubbing to remove CO_2 the synthesis gas has the composition: CO_2, 2.0; C_nH_m, 0.2; CO, 42.2; H_2, 50.7; CH_4, 2.4; N_2, 2.5%. In this method of synthesis-gas production, 0.317 m.³ of O_2 is consumed per m.³ A flow sheet with diagram of apparatus is appended. O_2 for the process is produced by the Linde-Fränkl method at a cost of 2.2–2.5 pf./N m.³ in units of 1,000–2,000 N m.³/hr. capacity and power consumption of 0.65–0.68 kw.-hr./N m.³

CHAKRAVARTY, J. N. *See* abs. **1183.**

454. CHAKRAVARTY, K. M. [Equilibrium Constants of the Reactions $CO+3\ H_2 \rightleftharpoons CH_4+H_2O$; $CO_2+4\ H_2 \rightleftharpoons CH_4+2\ H_2O$; and $2\ CO+2\ H_2 \rightleftharpoons CH_4+CO_2$.] Ztschr. Elektrochem., vol. 34, 1928, pp. 22–25; Chem. Abs., vol. 22, 1928, p. 4040.

Constants for the above equilibria at temperatures 800°–1,300° have been calculated: (*a*) From the variation with temperature of the equilibrium constants for $C+2\ H_2 \rightleftharpoons CH_4$; $2\ CO \rightleftharpoons C+CO_2$; and $CO_2+H_2 \rightleftharpoons CO+H_2O$: and (*b*) from the heats of reaction and the specific heats and chemical constants of reactants and products. The figures obtained are compared and discussed.

455. ———. Catalytic Reduction of Carbon Monoxide. Sci. and Culture, vol. 4, 1938, pp. 300–301; Chem. Zentralb., 1939, I, p. 3996.

CO can be reduced at 248° by means of a Ni–Cu catalyst activated and reduced at 275° to a gas mixture, which contains more olefins (3.7%) than CH_4 (1.7%).

456. ———. Hydrogenation of Nickel Carbonyl. Ind. Eng. Chem., vol. 31, 1939, pp. 1059–1060; Chem. Abs., vol. 33, 1939, p. 7498.

Evidence is given to show that the principal reactions in the process of Litkenhous and Mann (*see* abs. **2122**) are $CO+H_2=C+O_2$ and $2\ CO+2H_2=CO_2+CH_4$. (*See* abs. **2121.**)

457. ———. Synthetic-Fuel Industry in India. Sci. and Culture, vol. 4, 1939, pp. 573–581; Chem. Abs., vol. 33, 1939, p. 5153.

Bergius, Fischer-Tropsch processes for hydrogenating coal, the preparation and use of alcohol motor fuels, compressed-fuel gases, and sewage-disposal gas, and their applications to motors are discussed with particular reference to Indian conditions. Of 103,000,000 gal. of gasoline consumed in 1937, about 15.4 million gal. was produced in India and 38.1 million gal. imported from Burma. The erection of a plant like that at Billingham, England, is recommended as a means for protecting the motor-fuel supply both in peace and war.

458. ———. Conversion of Coal Into Oil. The Fischer-Tropsch Process. Jour. Indian Chem. Soc., Ind. and News Ed., vol. 3, 1940, pp. 185–192; Chem. Abs., vol. 37, 1943, p. 4878.

Ni can replace Co in the Co-ThO_2 catalyst. At 1 atm. the yield of solid paraffins reaches a maximum at about 170°; that of liquefiable hydrocarbons, at 180°. Pressures greater than 15 atm. are not advantageous. Briefly reviews large-scale operation in the Ruhr.

———. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. IV. Specific Nature of Promoter Effect on a Nickel Catalyst Using as Reactants Water Vapor and Equal Volumes of Carbon Monoxide and Hydrogen. *See* abs. **463.**

———. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. V. Study of the Promoter Effect on Nickel Catalyst. *See* abs. **464.**

———. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. VI. Poisoning by Carbon Deposition. *See* abs. **465.**

———. *See* abs. **1184, 1190, 1191.**

459. CHAKRAVARTY, K. M., AND CHAKRAVARTY, P. B. Effect of Potassium Carbonate on Nickel Catalysts for the Fischer-Tropsch Synthesis. Sci. and Culture, vol. 12, 1946, pp. 110–111; Chem. Abs., vol. 41, 1947, p. 1989.

Catalysts containing traces of K_2CO_3 were found to lose their activity after passage of small volumes of H_2-CO mixture. The deactivated catalyst, after being washed with distilled water and reduced at 200°, was negligibly active at first but rose in activity to a steady value somewhat below that found with the original preparation. The catalyst composition was: Kieselguhr, 46%; Ni, 45.77%; ThO_2, 8.3%; and K_2CO_3, traces. A similar preparation containing 0.0823% CeO_2 behaved in the same manner; the reactivated catalyst was not very active at 178°–180° but was steadily active at 219°–220°. The presence of K_2CO_3 causes the formation of C, CO_2, and H_2O rather than hydrocarbons.

460. CHAKRAVARTY, K. M., AND GHOSH, J. C. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. I. Quart. Jour. Indian Chem. Soc., vol. 2, 1925, pp. 150–156; Chem. Abs., vol. 20, 1926, pp. 860–861.

Sugar charcoal-Ni catalyst for the reaction $CO+3H_2 \rightarrow CH_4+H_2O$ retained its activity undiminished for months when the ratio H_2 : CO was 3 : 1. The critical space velocity (cm.^{3} gas mixture per cc. catalyst per minute) below which CO disappeared was fairly great (1.3 at 300°, 1.7 at 335°, 3.6 at 358°, >4.3 at 400°). This catalyst entirely suppressed the reaction $2\,CO \rightarrow C+CO_2$ and prevented deposition of C on the Ni surface. CeO_2 acted as a promoter for this catalyst increasing the critical space velocity at 355° from 3.5 to 4.4. Some CO_2, about 9 volume % of exit gas, was produced, owing mainly to the reaction $2\,CO+2\,H_2 \rightarrow CO_2+CH_4$ and partly to the reaction $C+2\,H_2O \rightarrow CO_2+2\,H_2$.

461. ———. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. II. Production of Fuel Gases Rich in Methane. Quart. Jour. Indian Chem. Soc., vol. 2, 1925, pp. 157–164; Chem. Abs., vol. 20, 1926, p. 861.

Use of sugar charcoal–pumice–Ni catalyst for the formation of CH_4 was studied with equimolal mixtures of H_2 and CO, with view to its use in enriching blue water gas (H_2 49%, CO 42%). This catalyst was not as efficient as a sugar charcoal–Ni catalyst for promoting the reaction $2\,CO+2\,H_2 > CH_4+CO_2$ (I) and was little improved by addition of CeO_2. Pumice-V_2O_5–Ni (A) was at first very effective but rapidly lost its activity; as reaction (I) was retarded, the undesirable reaction $CO+3\,H_2 > CH_4+H_2O$ (II) was favored, though with a smaller total conversion. A sugar charcoal–pumice–V_2O_5–Ni catalyst (B) at 400°–450° retained for months the initial activity of (A). Increasing space velocity favored reactions (II), but even with a space velocity of over 25 cc. gas per cm.^{3} catalyst per min. only 20% of the CH_4 was formed by reaction (II). If sugar charcoal was replaced by coconut charcoal the catalyst deteriorated rapidly; Fe_2O_3 in place of V_2O_5 made (II) the chief reaction. The gas obtained by use of catalyst (B) was comparable in calorific value to carbureted water gas, though much less poisonous; removal of CO_2, present in amounts as great as 33%, would give a gas of very high calorific value.

462. ———. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. III. Study of Various Catalysts. Quart. Jour. Indian Chem. Soc., vol. 4, 1927, pp. 431–436; Chem. Abs., vol. 22, 1928, p. 1085.

Catalysts as follows were investigated at 300° on asbestos: $Ni(OH)_2$, $Ni(OH)_2$ and $Mn(OH)_2$, $Ni(OH)_2$ on $Mn(OH)_2$, MnO_2 on $Ni(OH)_2$, $Ni(OH)_2$ and $Mg(OH)_2$, $Ni(OH)_2$ on $Mg(OH)_2$, $Mg(OH)_2$ on $Ni(OH)_2$, $Ni(OH)_2$ and $Zn(OH)_2$, $Ni(OH)_2$ on $Zn(OH)_2$, $Ni(OH)_2$ and $Pb(OH)_2$, NH_4VO_3 on $Ni(OH)_2$, $Cr(OAc)_3$ on $Ni(OH)_2$, $(NH_4)_2MoO_4$ on $Ni(OH)_2$, $Ni(OH)_2$ and $Al(OH)_3$, $Ni(OH)_2$ on $Al(OH)_3$, $Al(OH)_3$ on $Ni(OH)_2$, $Ni(NO_3)_2$ on $Al(OH)_3$. Those with Al were most promising. A rapid fall of activity occurred in all cases. The pumice–sugar carbon–Ni catalyst at 400° did not show marked increase of activity with Ni about 10 : 2 : 0.65. Loss of activity was slow, but C always deposited on the catalyst.

463. CHAKRAVARTY, K. M. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. IV. Specific Nature of Promotor Effect on a Nickel Catalyst Using as Reactants Water Vapor and Equal Volumes of Carbon Monoxide and Hydrogen. Science and Culture, vol. 3, 1938, p. 396; Ztschr. anorg. Chem., vol. 237, 1938, pp. 381–387; Chem. Abs., vol. 32, 1938, pp. 2818, 6535.

Apart from CH_4 formation a C–Ni catalyst containing thoria and ceria accelerates the formation of CO, CO_2, and H_2 from H_2O and C, but with K_2CO_3 the formation of C and CO_2 from CO is promoted. The addition of a small quantity of a mixture of Ce nitrate and NH_4 vanadate or of Ce nitrate and $Cr(OAc)_3$ to the $Ni(OAc)_2$ used in preparing the catalyst brings about a more complete reduction of the Ni at 300°. The formation of CO_2 and CH_4 is indirectly helped by them. The thoria–ceria mixture increases the uniformity of the Ni particles, prevents granule formation on the surface and clogging of the pores of the pumice used, and prevents sintering. At 400°–450° the Ni catalysts adsorb much CO_2.

464. ———. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. V. Study of the Promotor Effect on Nickel Catalyst. Jour. Indian Chem. Soc., vol. 15, 1938, pp. 245–248; Chem. Abs., vol. 32, 1938, p. 8742.

Reduction of Ni catalyst at a temperature of 300° is incomplete when it is prepared from pure Ni acetate. Addition of a small quantity of a mixture of Ce nitrate and NH_4 vanadate or of Ce nitrate and Cr acetate helps in bringing about a more thorough reduction. Thus catalysis of a reaction $2CO+2H_2 = CO_2+CH_4$ is accelerated by these promoters through their influence on the preparation of the Ni. Whether the promoters have a direct effect on the reaction has not been settled.

465. ———. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. VI. Poisoning by Carbon Deposition. Jour. Indian Chem. Soc., vol. 16, 1939, pp. 663–670; Chem. Zentralb., 1940, II, p. 723; Chem. Abs., vol. 34, 1940, p. 4723.

Deposited C may be adsorbed on Ni particles or may form a simple layer on the surface. Moreover, Ni may undergo carbide formation and Ni_3C may have catalytic activity. It has been shown that the reaction $2CO = C+CO_2$ is catalyzed by Ni and also by Ni_3C. The reaction $CO+3H_2 = CH_4+H_2O$ is 2.50, Cu 0–1.50, Mg 0.70–1.30, Si 0.10–0.35, and Fe 0.10–0.50%. Al is the remainder, but so that if Cu is near its maximum, the total of the Ni, Sb, and Si is near the lower limit and vice versa. The alloy may also contain Mn up to 0.25%.

466. CHAKRAVARTY, K. M., AND SARKER, J. M. Catalytic Formation of CH_4 From CO and H_2—a Study of Ni and Ni- Alumina Catalysts Prepared From the Hydroxide, Using KOH, NaOH and NH_4OH as Precipitants. Current Sci., vol. 13, 1944, p. 127; Chem. Abs., vol. 38, 1944, p. 6178.

In a mixture of CO, H_2, and H_2O, roughly 1 : 1 : 1, 2 reactions occur in the presence of Ni catalysts: (1) $2CO+2H_2 \rightarrow CH_4+CO_2$, (2) $CO+H_2O \rightarrow CO_2+H_2$. The influence of KOH, NaOH, and NH_4OH, used to precipitate Ni, was small. Alumina promotes reaction (1); its maximum activity occurs at a concentration below 0.16%. Addition of K_2CO_3 to the catalyst promotes reaction (2). Results of 11 runs are tabulated, with analyses of reactants and resultants, weight and volume of catalyst, rate of flow and total volume of gases, and reaction temperatures.

467. CHAKRAVARTY, K. M., AND SEN, R. X-Ray Diffraction Studies of a Nickel–Thoria–Kieselguhr Catalyst for Fischer-Tropsch Synthesis. Nature, vol. 160, 1947, pp. 907–908; British Abs., 1948, A I, p. 155.

The presence of a few diffraction lines of kieselguhr on the X-ray diffraction diagram shows that, in the process of depositing Ni on kieselguhr, the structure has undergone a change. The 2 lines of the kieselguhr shown in the photograph are identified as the strong lines of ferric oxide present in the kieselguhr. The lines of silica of the kieselguhr are absent in that of the catalyst. It is concluded from this that during deposition of metallic Ni and Th on the kieselguhr the crystalline portion of silica becomes amorphous, while the structure and the crystallinity of the ferric oxide remain unchanged. The broadness of the lines indicates,

however, that the crystal particles of ferric oxide have disintegrated, yielding crystallites of smaller size. The change in structure was brought about, not by the heating of the kieselguhr in H_2 during the deposition of Ni and Th, but by the disintegration caused by the decomposition of the carbonates of Ni and Th deposited as an initial step in the preparation of the catalyst. Ni is present as is Th in crystalline form in these samples.

CHAKRAVARTY, P. B. *See* abs. **459.**

468. CHAO, T. Y., HSU, W. W., AND WEN, C. [Study of Iron Catalysts for the Synthesis of Liquid Fuels From Carbon Monoxide and Hydrogen.] Jour. Chinese Chem. Soc., vol. 12, 1945, pp. 1–14; Chem. Abs., vol. 40, 1946, p. 3865.

Because of the limited supply of Co and Ni in China, increased use must be made of Fe catalysts in industrial processes. In preparing the catalyst, Fe plus varying amounts of Cu as promoter are dissolved in HNO_3, mixed with starch, kieselguhr, and K_2CO_3, and ignited. Water gas is passed through the reactor at a rate of 2 l. per hr. and the yield measured in terms of ml. per $m.^3$ of gas. Each run was continued for 20 days or more, and the products were examined at 24-hr. intervals. Maximum results are obtained when about 0.5% of K_2CO_3 is present and when the Fe : Cu ratio is 5 : 1. Satisfactory yields are obtained at a reaction temperature of 240°. The activity of the Fe catalysts was long lived. The kogasins produced gave on distillation good yields of light oil as well as paraffin.

469. CHAPMAN, O. L. Synthetic Liquid Fuels. 1949 Annual Report of the Secretary of the Interior. I. Oil From Coal. II. Oil From Oil Shale. III. Liquid Fuels From Agricultural Residues. IV. Oil From Secondary Recovery and Refining. Bureau of Mines Repts. of Investigations 4651, 4652, 4653, 4654, February 1950, pp. i-xxii, 1–62, 1–70, 1–13, and 1–26.

Many technical problems are yet to be solved in placing liquid fuels from oil shale and coal on a competitive basis with petroleum fuels. Developments are now centered on operation rather than on design and construction of laboratories and demonstration plants, and process improvements should effect a reduction in operating costs and thus the establishment of a synthetic liquid fuels industry from domestic resources at reasonable rates. The estimated capital investment for a crude shale-oil plant (10,000 bbl. per day) is $4,138 per bbl. and for a coal-hydrogenation plant (30,000 bbl. per day) $8,227 per bbl. Actual production costs per gal. of gasoline are estimated at $0.073 and $0.108, respectively, or allowing for a 6% profit on average unamortized capital investment, $0.09 and $0.145. It would thus appear that oil-shale processing is not far from the point of commercial utilization. The cost of shale mining has recently been reduced to $0.29 per ton. It is conceded, however, that it is doubtful at present that a coal-hydrogenation plant producing motor gasoline would be an attractive commercial investment in view of the above costs. It is reasonable to expect that these costs can be reduced by the new developments in catalysts and operating methods under investigation, perhaps by 15–20%. Cost calculations for commercial gas-synthesis operations using coal will be based on the demonstration tests as carried out at the plant being erected at Louisiana, Mo. It will be about a year before these estimates can be made. Several gasification processes for the production of synthesis gas from coal are in the pilot-plant stage. These investigations are of prime importance, since the cost of synthesis gas will always be a large fraction (50–70%) of the cost of liquid fuels from the gas-synthesis process. (Lengthy abstract appears in Chem. Eng. News, vol. 28, pp. 914, 916.)

470. ———. Synthetic Liquid Fuels. 1950 Annual Report of the Secretary of the Interior. I. Oil From Coal. II. Oil From Oil Shale. III. Liquid Fuels From Agricultural Residues. IV. Oil From Secondary Recovery and Refining. Bureau of Mines Repts. of Investigations 4770, 4771, 4772, 4773, February 1951, pp. i–xiv, 1–74, 1–88, 1–12, 1–16.

Review of operations during 1950 of the synthetic liquid fuels laboratories and demonstration plants. Progress in the oil-shale development program reveals the commercial feasibility of these operations, and it is believed that gasoline and oil can be produced from shale at costs that compete favorably with those for petroleum products. The estimated cost of delivering raw shale to the retorting plant, exclusive of depletion, interest, and profits, is $0.426/ton or $0.015/gal. of shale oil. The retorting process has been improved as to both method and cost by the development of the gas-combustion retort. New experience has been gained in the operation of the coal-hydrogenation demonstration plant. Costs are being reestimated and will be reported on completion. It appears that the cost of producing gasoline from coal is somewhat greater than it is from shale. The potentialities of the production of aromatic chemicals, such as benzene and phenols, are being investigated. The great flexibility in the operation of coal-hydrogenation plants to produce different grades and types of fuels is of great strategic advantage. The construction of one or more commercial plants is also recommended. The gas-synthesis process for the production of synthetic liquid fuels from coal by way of synthesis gas ($CO+H_2$) is to be placed in operation at the demonstration plant at Louisiana, Mo. Studies of this process are not as far advanced as those for coal hydrogenation or oil shale. The greatest attention is being given to the completion of a method for the production of synthesis gas by gasifying pulverized coal in the presence of steam and O_2 under pressure of 450 p. s. i. The process is highly promising and preliminary cost studies have indicated that it should reduce considerably the cost of synthesis gas. Commercialization of the gas-synthesis process awaits completion of the present studies and results of the demonstration work. Other projects under investigation are: Vortex reactor for coal gasification, underground gasification, purification of synthesis gas, and the Oxo process.

471. CHAPMAN, D. L., AND HOLT, A. Synthesis of Formaldehyde. Jour. Chem. Soc., vol. 87, 1905, pp. 916–920.

By passing CO and H_2 over Ni wool heated to 480°–500°, amounts of CH_2O were obtained that could be detected only by the most careful tests with Schiff's reagent. With CO_2 and H_2 and with CO, H_2, and steam appreciable quantities of CH_2O were obtained.

472. CHARPY, G., AND PINGAULT, P. [Conditions Required for Formation of Cementite.] Compt. rend., vol. 187, 1928, pp. 554–556; Chem. Abs., vol. 23, 1929, p. 79.

Review of previous experiments, showing that Fe could be carburized at 600°–650° with the formation of a layer of cementite separated from the original metal by a narrow transition zone and that cementite could decompose at 700°. Pure electrolytic Fe filings, free from H, were carburized by cyanide or hydrocarbons, and the physical properties were studied. The density, decreased gradually with absorption of C to a limit of 7.40 at 0°. The magnetic attraction of 1 gm. of Fe filings decreased, on carburizing, from 7 gm. to a constant value of about 4 gm. The filings carburized to constant density and magnetic attraction contained 6.75% C and left no trace of insoluble C when dissolved in HNO_3. This product did not suffer

any change in properties after gradual heating to 1,000°during 10 hr. Slight separation of graphite in previous experiments of this nature may be attributed to oxidation. Fine Fe wire was transformed entirely into cementite, with no trace of graphite, after heating to 850° in cyanide. Pyrometer protection tubes of Fe 1 mm. thick from cementation furnaces were also found to be completely transformed into cementite. Carburation of solid Fe below 1,000° tends therefore to form cementite, and the distribution of the C beneath the surface is determined only by the rate of solution and diffusion of cementite in solid Fe.

473. CHARRIN, V. [Synthetic Fuels.] Chaleur et ind., vol. 10, 1929, p. 380; Chem. Abs., vol. 24, 1930, p. 1197.

Brief mention is made of some French workers, Marcelin Berthelot, Sabatier and Senderens, Prudhomme and Houdry. The Pieters furnace at Millau and the Tauzer furnace at Laluque, France, have not given the expected results. An attempt is being made to use the Prudhomme-Houdry process in the catalytic hydrogenation of the water gas from St. Julien lignite to produce a motor spirit.

474. CHASHNIK, L. M. [Synthesis of Methanol.] Jour. Chem. Ind. (U. S. S. R.), vol. 12, 1935, pp. 366–369; Chem. Abs., vol. 29, 1935, p. 7939.

Mathematical equations are derived for the calculation in general form of the equilibrium concentration of MeOH, for the maximum productivity of the apparatus, and for connecting the ratio H_2 : CO in the freshly introduced gas with that in the circulating gas. The presence of inert gas strongly affects the yield of MeOH, while a change in the ratio H_2 : CO has relatively little effect.

CHATTERJEE, B. *See* abs. **166a.**

475. CHAUDRON, G. [Reversible Reactions of Carbon Monoxide on the Oxides of Iron.] Compt. rend., vol. 172, 1921, pp. 152–155; Jour. Chem. Soc., 1921, II, p. 178.

Starting with Fe_2O_3 and CO, the equilibrium is studied over a temperature range of 300°–1,000°. The Fe_2O_3 is reduced to the magnetic oxide, and beyond this stage 2 reactions may occur. Below 580° there is a single system corresponding with $Fe_3O_4+4CO\rightleftharpoons 4CO_2+3Fe$. Above 580° there are 2 equilibria before arriving at Fe, namely, $Fe_3O_4+CO\rightleftharpoons 3FeO+CO_2$ and $FeO+CO\rightleftharpoons Fe+CO_2$. The 3 solid phases coexist in equilibrium at 580°. Below 580°, FeO is unstable and is transformed into a mixture of Fe and the magnetic oxide, $4FeO\rightleftharpoons Fe_3O_4+Fe$.

476. ———. [Reversible Reactions of Hydrogen and Carbon Monoxide on Metallic Oxides.] Ann. chim., vol. 16, 1921, pp. 221–281; Chem. Abs., vol. 16, 1922, pp. 212–213.

Apparatus combined features previously used with modifications designed to effect continuous slow circulation of the gas phase over the solid phases and to require a single thermostat well removed from the furnace. The composition of the gas phase was determined at intervals, *p*H O-*p*H by tension measurements C_{CO}–C_{CO_2} by refraction with an interferential method shown to be capable of detecting a variation of 0.5% in composition. Equilibrium was determined by both oxidation and reduction experiments. The triple point at which Fe, FeO, and Fe_3O_4 coexist was found to be 570°, the data being concordant for both gas phases. Above 570° the equilibrium curve has 2 branches corresponding to $Fe+H_2O\rightleftharpoons FeO+H_2$ (and $Fe+CO_2\rightleftharpoons FeO+CO$) and $3FeO+H_2O(CO_2)\rightleftharpoons Fe_3O_4+H_2(CO)$. Below 570° 1 system only exists: $3Fe+4H_2O(CO_2)\rightleftharpoons Fe_3O_4+4H_2(CO)$. The triple point corresponds to the invariant system $4FeO\rightleftharpoons Fe_3O_4+Fe$. This transformation was directly observed by maintaining below 570° FeO prepared at high temperature, 900°, and using metallographic methods and appearance of ferromagnetic properties. The diagram, temperature-gas composition, fixes the conditions for preparing Fe, FeO, and Fe_3O_4. The following equilibria were also studied: $Co+H_2O\rightleftharpoons CoO+H_2$; $Mo+2H_2O\rightleftharpoons MoO_2+2H_2$; $W+2H_2O\rightleftharpoons WO_2+2H_2$; $2WO_2+H_2O\rightleftharpoons W_2O_5+H_2$. The last confirm the existence of the oxides WO_2 and W_2O_5 and the diagram fixes the conditions for preparing WO_2. Ni, MnO, and UO_2 are not oxidized by water vapor. From the measurements of the systems $Fe+H_2O(CO_2)\rightleftharpoons FeO+H_2(CO)$ values of the water-gas equilibrium $K=(C_{CO}C_{H_2O}-C_{CO_2}C_{H_2})$, are calculated for 686°, 786°, 886°, and 986° in excellent agreement with Haber's values. For $K=1$ was found 810°; Haber, 825°.

477. ———. [Reduction of Metallic Oxides by Means of Hydrogen and Carbon Monoxide.] Chim. et ind., vol. 8, 1922, pp. 959–964; Chem. Abs., vol. 17, 1923, p. 521.

Review of the mechanics of the reversible reactions $Fe+H_2O=FeO+H_2$ and $Fe+CO_2=FeO+CO$ and their relation to the dissociation of FeO, H_2O, and CO_2, and application of these results to the measurement of the equilibrium of a mixture of CO and CO_2.

———. *See* abs. **1053, 1054, 1514, 2272, 2275.**

478. CHAUDRON, G., AND BÉNARD, J. [Process of Decomposition of Ferrous Oxide.] Bull. soc. chim. France, 1949, D, pp. 117–119; Chem. Abs., vol. 43, 1949, p, 6901.

Decomposition of FeO at 300°–570° is exclusively a solid-phase reaction. The reaction was followed by thermomagnetic analysis. A phase diagram is given for the system FeO–Fe_3O_4–Fe. The rate of decomposition was determined to be a function of the temperature of preparation, the concentration of O_2 during preparation, and the presence of particles of Fe or Fe_3O_4.

479. CHAUDRON, G., AND FORESTIER, H. [Decomposition of Ferrous Oxide. Anomalies of Dilatation Correlative to Its Instability.] Compt. rend., vol. 178, 1924, pp. 2173–2176; Chem. Abs., vol. 18, 1924, p. 3306.

Object was to study the velocities of 2 reactions involved in the equilibrium $4\,FEO=Fe_3O_4+Fe$. FeO was prepared at 800°–900° and cooled rapidly to avoid decomposition. It was then heated in a vacuum for 24 hr. at constant temperature and analyzed by treating with dilute $CuSO_4$ for 12 hr. Titration with $KMnO_4$ gave the weight of Fe that entered the solution. The fraction of the FeO transformed in 24 hr. was plotted against the temperature. At 300° free Fe could be determined. The fraction transformed then increased to 80% at 480°, passing through a maximum there and falling to 0% at 570°. At 592°, 24% of FeO and at 600°, 51% of FeO were formed in 24 hr. from a sample originally containing 20% of FeO. At 445° the velocity of the reaction is expressed by $dx/dt=k(100-x)^4$. When change in volume is plotted against temperature, anomalies are observed corresponding to the chemical changes.

CHAUKAVIN, M K. *See* abs. **2754.**

480. CHAUX, R. [Combustible Liquids From Coal—a Lecture Delivered at the College of France.] Bull. soc. chim., vol. 43, 1928, pp. 385–411; Chem. Abs., vol. 22, 1928, p. 2826.

Review of production of combustible liquids from coal by hydrogenation and by utilizing hydrocarbon constituents of coke-oven gas for producing alcohols and using coal tars for producing C_6H_6, its homologs, and other aromatic compounds. The syntheses of MeOH, synthol and liquid hydrocarbons from CO pro-

duced by the gasification of coal are discussed. Bibliography of 160 refs.

481. CHEMICAL AGE. Latest German Developments in Coal Liquefaction. Vol. 13, 1925, pp. 268–269.

Information on processes for coal liquefaction, the Bergius process, and a brief discussion of the possibilities of synthol.

482. ———. Fischer Process. Vol. 35, 1936, p. 367. Editorial comments on Melchett address by F. Fischer to the Institute of Fuel.

483. ———. Gasoline From Water Gas, Germany. Vol. 36, 1937, p. 152.

Loan of RM 55,000,000 for Gelsenberg Benzin A.-G. was oversubscribed on February 4, first application day. The loan is guaranteed by a mortgage over the Gelsenberg's future plant, while the debt-service security is reinforced by a guarantee of Vereingte Stahlwerke. When production starts, Gelsenberg will, with Leunawerke, another subsidiary of Vereingte Stahlwerke, be the largest hydrogenation works in Germany. But where Leunawerke uses lignite as raw material and proceeds by the costly Bergius process, depending on high-temperature pressures, involving rapid wear and tear of plant, Gelsenberg will start from coal by using the Fischer-Tropsch process, which deteriorates the plant far less and produces higher petroleum yield with very little waste.

484. ———. Hope Long Deferred. Vol. 37, 1937, p. 267.

Editorial calling attention to possible misleading statements that have been published in the official report of the committee appointed in 1937 by the Australian Government to advise upon the economics of establishing a hydrogenation plant in Australia. The committee has announced the conclusion that if interest on capital is charged at 3½% and 15 yrs. is allowed for amortization, the total cost of hydrogenated gasoline from bituminous coal will be 13.8 d. per imperial gal. If, following the Imperial Chemical Industries practice, the interest is charged at 6% and amortization is effected in 10 yrs. the cost of the gasoline is as high as 17.3 d. per gal. The operating costs, inclusive of coal at 14s.6d. per ton, are estimated as 8.4d. per gal. Admittedly, Australian costs are higher than English costs, but the committee has calculated that under English conditions the figures for total costs would be respectively 10.5 d. per gal. and 12.75 d. per gal. These figures appear high. It has been stated in certain interested quarters that the committee's report establishes the fact that the capital cost of a Fischer-Tropsch plant is not lower than that of a hydrogenation plant for the same output. The committee found that the cost of building a Fischer-Tropsch plant would be about £100 per ton of output per yr., while that for hydrogenation would be only £73 per ton per yr. The estimates we have ourselves had the privilege of examining would show a very different picture for the Fischer-Tropsch plant. We should much like to know upon what basis the Australian figure was determined. The investigators state that they were last in Europe in 1936, when only a small experimental Fischer-Tropsch plant was in operation, and the investigators admit that it was not possible for them to obtain any costs of operation or, presumably, of erection. It would be very unfortunate if the opinions expressed in this report were allowed to influence those who are considering the inception of a chemical industry in this country based on the production of hydrocarbons by the Fischer-Tropsch process. This process can be operated in much smaller units than the hydrogenation process and with a much less highly trained staff. It would be possible to situate these plants throughout the country at collieries possessing coking coal and thus bring into being another and widespread chemical industry.

485. ———. Oil From Coal in South Africa. Vol. 36, 1937, p. 215.

A Fischer-Tropsch plant is to be erected in South Africa by the Anglo-Transvaal Consolidated Investment Co., Ltd., which has acquired the rights. This will be the first Fischer-Tropsch gasoline plant in the British Empire.

486. ———. Catalysts for the Fischer-Tropsch Process. Vol. 39, 1938, p. 391.

Fischer-Tropsch process of synthesizing petrol from CO and H_2 is finding its way into large-scale industry in the Far East. The Mitsui Mining Co., which has acquired the rights for the system in the Far East, is building a plant capable of producing 30,000 kl. of petrol per yr. and the South Manchurian Oil Liquefaction Engineering Co., which was founded jointly by the Mitsui Co. and the Government of Manchukuo, is also to utilize the same process in a factory to be built at Fushin. The latter, when fully equipped, will produce 100,000 kl. per yr.

Success of these enterprises naturally depends in a large measure upon the efficiency and economy of the catalyst employed. The two firms are not likely to use the catalyst discovered and recommended by Fischer himself, which is Ni containing oxides of Mn and Al as promoters and kieselguhr as carrier; but they will probably use one of those developed in this country, such as those discovered by Dr. Genitsu Kita, Professor in the Kyoto Imperial University, and the Fuel Research Institute of the Ministry of Commerce and Industry.

Dr. Kita prepared a large range of Co catalysts containing Cu and the oxides of Th, U, and Mn as promoters and kaolin or kieselguhr as carrier, and discovered that the oxides of U and Th were the most efficient promoters and kieselguhr the best carrier. A grade, which was made of 80% Co, 10% Cu, 2.5% ThO_2, 0.5% UO_2, and the balance kieselguhr gave the highest yield, 144 cc. of petrol from 1 $m.^3$ of synthesis gas. His experiment with Ni, however, was not wholly successful. He concluded that the petrol yield could not be raised, at least to such an extent that it might be compared with the yields of other catalysts unless the metal was treated by complicated methods, which would make its commercial application difficult.

Catalysts of Ni, Co, Al, and Si had their own advantages, yet all failed to yield a large enough quantity of petrol. Finally, Dr. Kita discovered that a Ni–Co catalyst prepared by precipitation methods was the most efficient and economical agent for the petrol synthesis. This catalyst of 50 parts by weight of Co, 50 of Ni, 15 of Mn, 3 of ThO_2, 5 of UO_2, and 125 of kieselguhr was reduced with H_2 for 4 hours at 400° C. When the synthesis was conducted at 190° C., it produced 166 cc. of petrol from 1 $m.^3$ of gas treated. A further study is to be made of the means of producing this catalyst at as low a cost as possible.

The Fuel Research Institute of the Ministry of Commerce and Industry has experimented with virtually all the catalysts made of Ni, Co, and other metals suggested by Japanese and foreign chemists. As a result Tsutsumi reported that a Ni catalyst containing 20% Mn, 8% UO_2 and 4% ThO_2 is the best material, yielding 168.8 cc. of petrol per $m.^3$ synthesis gas. The reaction is carried out at 200° C. and a gas flow of 6 l. per hr.

487. ———. Oil From Coal. Vol. 39, 1938, pp. 51–52; Bull. Imp. Inst., vol. 36, No. 2, 1938.

Summary of the development of the Fischer-Tropsch process.

488. ———. Butter From Coal. Vol. 54, 1946, pp. 602–603.

The Imhausen plant at Witten, Germany, has stepped up the operation of making butter from paraf-

fin to 350 tons per mo. The paraffin is first oxidized and then heated to extract the fatty acids, which are used to make butter or soap. For butter, the fatty acid is redistilled and glycerin and carotin are added. From 100 tons of paraffin, 80 tons of fatty acids are produced, enough to make 40 tons of butter or soap. For soap, the fatty acids are not redistilled, but soda is added. The butter produced by the Imhausen method, which contains no acetone, is the only butter that can be eaten safely by diabetics.

489. ———. Coal-Chemical Transformation. Vol. 55, 1946, pp. 725–726; Coke Smokeless-Fuel Age, vol. 8, 1946, pp. 258–260.

Now that investigation of the German chemical industry has been completed, a clearer analysis of German scientific progress and development can be made. As regards the Fischer-Tropsch process, around which almost fabulous hopes and expectations had been built, the sober truth is that the vaunted German scientific ability has produced almost nothing that was not known before the war and the impression now created upon our minds is that the commercial position of the Fischer-Tropsch synthesis is much the same after the war as it was when the war started. The possibilities and the methods for making most of the transformations from coal and gas into fuels and chemicals were known before the war, and the interim research developments do not appear to have contributed greatly to improvement in the efficiency of the Fischer-Tropsch plants or to reduction in the cost of production. To make the future of the process commercially and economically practical, the process must first be cheapened, and then a study must be made to discover in what direction it should be developed. As a method for producing fuels from coal, the process is hopelessly expensive under British conditions, since the production cost, it is calculated, would be about 2s. or 2s.6d./gal. of gasoline, a condition that cannot improve because of the rising trend in the price of coal. Further research, which would enable a high proportion of the products to be utilized as high-priced chemical products, would materially improve the economic prospects of the process. For real economic improvement, however, a reduction in the cost of the synthesis gas is needed, and it must be produced from products that would otherwise be wasted, such as natural gas or refinery cracking gas. The discovery of a catalyst not susceptible to poisoning by S would also be a useful improvement.

490. ———. Synthetic Soap and Edible Fats. Vol. 54, 1946, p. 308.

Naturally occurring animal and vegetable oils and fats, which form the normal source of soap and edible fats, are glycerides of straight-chain carboxylic acids containing an even number of C atoms in the molecule. The Fischer-Tropsch process provides a means of preparing hydrocarbons with such characteristics predominating, and these products, obtained under suitable temperatures and pressure, are a source of a wide range of aliphatic chemicals, including fatty acids of the type required for soap and edible fat preparation. The maximum production of such acids from the Fischer-Tropsch soft wax by catalytic oxidation was about 40,000 tons/yr. in Germany. About 1,800 tons/yr., of edible fat were produced by reaction of the acids with glycerin, synthesized from propylene. There was a total plant capacity for synthetic margarine production of about 7,000 tons/yr. The synthetic soap had excellent lathering properties but left an unpleasant odor on the skin. The synthetic edible fat was quite satisfactory in respect to taste and odor and was assimilated and utilized by the body in the normal manner, although the long-term effect is not yet known. It had better keeping qualities than the natural product and was utilized particularly in the food supply in submarines. Its production, however, is not economical since, under the best conditions, the production of 1 ton of synthetic soap or fat required consumption of 60–70 tons of coal.

491. ———. German Fatty Acids. Production From Lignite. Vol. 57, 1947, p. 542.

The production of fatty acids by I. G. at Oppau was, in general, similar to that by the Deutsche Fettsäure Werke at Witten-Ruhr, except that the latter worked with the Fischer Gatsch paraffins, while Riebeck paraffins were used at Oppau. The latter were obtained from lignite pitch and TTH-paraffin, resulting from high-temperature hydrogenation of lignite, as well as from synthetic paraffins obtained by the Fischer-Tropsch synthesis. Output of synthetic fatty acids since 1937 amounted to 20,000 tons annually at Oppau, while Witten-Ruhr turned out double the amount. The end products were mainly used in the manufacture of soap; only a few tons were used in experiments on the manufacture of margarine. The price depended chiefly on that of the paraffins used. During the war, Oppau produced fatty acids at 2 RM per kg. or twice that of fatty acids derived from natural fats. After oxidation with air in presence of potassium permanganate, the fatty acids were distilled into 4 fractions and a residue, the latter being used for the manufacture of stove enamels, synthetic vaseline, etc.

492. ———. Utilization of Coal. Vol. 57, 1947, pp. 69–70.

Editorial comments on the economic possibility in Britain of using coal as the raw material for production of gasoline. The opinion is expressed that such utilization cannot be economical under British conditions; rather, encouragement should be given only to the use of coal for the manufacture of those products that have an export value and at the same time consume comparatively little coal in manufacture. It appears, therefore, to be more profitable from the British viewpoint to continue to import gasoline and to use the coal supplies to build up a valuable export trade and leave the production of synthetic gasoline by the Fischer-Tropsch and hydrogenation reactions to the United States where more favorable conditions exist because of the extensive supplies of natural gas and the development of the fluid catalyst.

493. ———. Fischer-Tropsch Research—Tracer Investigation. Vol. 58, 1948, pp. 680–681.

The research project, conducted by the Gulf Oil Corp., of Pittsburgh, Pa., at Mellon Research Institute using radioactive isotopes, has possibilities of improving and perhaps greatly altering the future commercial development of the gas synthesis process by further improving the conversion methods. The research method is the so-called "tracer" system which involves, in this case, the use of radioactive atoms (C_{14}), which are chemically identical with C but which emit electrons that can be detected by the Geiger counter at any point in the reaction and thus indicate the exact course that the reaction is taking. It is hoped to prove whether the gasoline produced by the Fischer-Tropsch synthesis comes from the reaction of H_2 with the metal carbides formed from CO and the metal catalyst or from some other source not involving carbide formation. In the method employed radioactive C is supplied as $BaCO_3$. Acid treatment releases radioactive CO_2 and from this is produced the desired radioactive CO by exposing a mixture of the CO_2 with ordinary CO to an incandescent tungsten filament. This radioactive CO is then reacted with an Fe catalyst to form carbide-containing radiocarbon. The hydrocarbon products derived from passage of ordinary synthesis gas ($CO+2H_2$) over this catalyst will show no radioactivity if they are derived entirely from ordinary CO gas rather than from reduction of the Fe carbide.

If they are derived from reduction of the Fe carbide, they will show a radioactivity comparable to that of the surface of the Fe carbide catalyst. The C_{14} experiments at about 250° F. show that the hydrocarbon gas formed has less than 10% of the radioactivity it would have if the entire surface of the catalyst reacted entirely through the mechanism of alternate carbide reduction formation.

494. ———. Dismantling of German Plants Canceled. Vol. 61, 1949, p. 799.

Synthetic fuel and rubber plants removed from the dismantling list are those of Bayer at Leverkusen; Chemische Werke Huels; Gelsenberg Benzine A.-G.; Hydrierwerke Scholven A.-G., Gelsenkirchen-Buer; Ruhroel A.-G., Bottrop; Ruhrchemie A.-G., Oberhausen-Holten; Gewerkschaft Viktor, Castrop-Rauxel; Krupp-Treibstoff-Werke, Wanne-Eickel; Steinkohlenbergwerk Rheinpreussen, Moers; Dortmunder Paraffin-Werke Dortmund; and Chemische Werke, Essener Steinkohle, Bergkamen. The synthetic fuel plants of Gewerkschaft Viktor and Krupp Treibstoff-Werke, which were to close down by the end of the year, are still in operation. The German interests expect that it is only a matter of time before the synthetic and hydrogenation plants will be permitted to resume production.

495. ———. Economics of Coal Gasification. Vol. 61, 1949, p. 111.

Some operating results on the new continuous coal gasifier at Louisiana are presented. A 4-hr. full-scale test was made with gasifier temperatures averaging about 2,200° F. The feed rates were coal 2,300 lb. per hr., O_2 17,000 std. cu. ft. per hr., and steam 2,000 lb. per hr. Approximately 70,000 std. cu. ft. of gas per hr. was made. The gas was 42% H_2, 37% CO, 16% CO_2, 4% N_2, and 1% miscellaneous. It is expected that, with continuous operation, the CO_2 content will be reduced and a better synthesis gas obtained.

496. ———. Reshaping German Industry. Vol. 61, 1949, pp. 377–378.

Editorial presenting some arguments for and against the dismantling of the German Fischer-Tropsch and Bergius plants and the effect that it will have on German economic prospects.

497. ———. United States Coal Gasification. Vol. 60, 1949, pp. 924–925.

The production of synthetic liquid fuel occurs in 4 distinct phases: Coal gasification; gas purification; hydrocarbon synthesis; and refining of products. Each of these receives brief description, the first by aid of a sectional diagram of the Koppers O_2 steam gasifier. Hydrocarbons are synthesized from synthesis gas either in a unit known as an internally cooled converter, through which cooling oil is circulated, or in a slurry type reactor, the Lamo process, in which the fluidized catalyst is kept suspended in the cooling oil by internal circulation. All 4 phases represent a very advanced stage in instrumentation and automatic control.

498. ———. British and German Chemists Conference. Vol. 62, 1950, pp. 895–896.

Allied High Commission has approved the German proposals for the conversion of the Krupp-Treibstoffwerk plant at Wanne-Eickel to the production of higher alcohols by the Oxyl synthesis process of Ruhrchemie A.-G. The required catalysts will be made by Ruhrchemie A.-G. Krupp-Treibstoffwerk plans to produce a number of products, such as solvents, plasticizers, and auxiliary products for the detergent industry. The German proposals also provided for conversion of the Chemischewerk Bergkamen, the Fischer-Tropsch plant of Essener Steinkohle A.-G. It had been suggested that operations for the purification of coke-oven gases and removal of poisonous substances could be carried out there, but this suggestion has not been sanctioned. The cases of Gewerkschaft Victor, Castrop-Rauxel, which was converted to the production of nitrogenous fertilizers, and of Krupp-Treibstoffwerk were given priority. Nothing further has been heard about another conversion project for the use of Fischer-Tropsch plants exempted from dismantling for paraffin synthesis.

499. ———. Sensitive Pressure Controller in Hydrocarbon Synthesis. Vol. 63, 1950, pp. 59–60.

Very efficient sensitive pressure controller is described. The basic principle of the device is the well-known use of a ball valve held on its seating by a tension spring. It is at present operating on a fluid bed, Fischer-Tropsch process, and maintains a constant 20 atm. pressure at gas-flow rates of 2 to 60 cu. ft. per hr. It is capable of maintaining a preselected pressure for indefinite periods without supervision. The control limits can be broadened by changing the tension of the spring.

500. ———. Fluid-Bed and Liquid-Phase Slurry Process. Vol. 64, 1951, pp. 773–775.

Compares 2 processes. The British Fuel Research Station is making an investigation for the purpose of improving the conventional Fischer-Tropsch process. A large-scale pilot plant is being erected.

500a. ———. Fuel Research Since the War. Vol. 65, 1951, pp. 721–726.

Fuel Research Board of Great Britain reports on a study made during the 3 yr. ending March 31, 1949, on the enrichment of water gas by the conversion of the CO and H_2 to CH_4. A reactor to treat 100–200 $ft.^3$ of water gas was constructed, in which the granular catalyst was placed in a vertical perforated tube 6 ft. by 1.25 in. enclosed in a water-jacketed steel tube 1.80-in. inside diameter. The water gas entered this tube at the bottom, flowed up the annular space, and reached the catalyst by free diffusion, the products of the reaction then diffusing back into the main gas stream. This arrangement permitted of obtaining a uniform temperature distribution along the length of the tube without deposition of C and a preferential consumption of H_2 so that gases of low H_2 : CO ratio, such as blue water gas, could be used without addition of H_2. From time to time as the catalyst deteriorated, a part of the charge was discharged at the bottom and a fresh amount added at the top by gravity feed. With the circulating H_2O at 200°, the catalyst temperature was at 350°–375°. Using a Ni–kieselguhr 1 : 1 catalyst, the plant performance, when producing enriched gas of 456 B. t. u. per $ft.^3$ was equivalent to a yield of 2,100 lb. of CH_4 per lb. of Ni in the catalyst, which had a useful life of 168 days. Kieselguhr was found to be an essential promoting constituent of the catalyst. Reduced $NiCO_3$ preparations made without the addition of kieselguhr showed no activity for CH_4 synthesis $<300°$, whereas reduced $NiCO_3$–kieselguhr catalysts were active at temperature as low as 150°. Synthesis with a fluidized bed of sintered Fe catalyst was investigated at 300°–340° at 20 atm. pressure with the synthesis-gas rate 750–2,050 vol. per vol. catalyst per hr. and with recirculation of residual gas at a velocity of 0.4–0.7 ft. per sec. to maintain the bed in a fluidized state. Yields of hydrocarbons higher than CH_4 per unit vol. of catalyst per hr. were obtained up to 30 times those obtainable by the conventional synthesis with Co catalyst. Difficulty was experienced with expansion and disintegration of the catalyst granules by deposition of nonvolatile products in the pores. Suspension of a powdered Co catalyst in molten wax (synthesis product) by recirculation of residual gas at the proper velocity was also tried. To obtain results equal to those with the conventional fixed bed of catalyst, temperatures 10°–15° higher were required. Maintenance of space velocities higher than 200 per hr. caused a rapid reduction in catalyst activity. The products obtained by liquid-phase synthesis were

found to be more volatile than those obtained by normal operation at the same temperatures. In studying the Co catalyst, it was found that a freshly reduced one did not give the X-ray diffraction pattern of Co. That the catalyst does not contain bulk metallic Co is confirmed by measurement of the surface areas of the catalysts and their components. It is considered that the reaction takes place on isolated Co atoms and not on bulk metallic Co or by way of bulk Co carbide. It is suggested that under certain conditions CH_4 present in the synthesis gas can take part in the reaction. Also, wax formed on the catalyst during synthesis reacts with H_2 to yield higher hydrocarbons distributed among the different molecular sizes in a way similar to the distribution of the synthesis products. These 2 facts, taken together, suggest that the final stages of synthesis involve a polymerization-depolymerization equilibrium. When synthesis is carried out at abnormally low temperatures and low times of contact, appreciable quantities of alcohols are present in the products produced by Co catalysts. These results, together with observations on the decomposition of alcohols under synthesis conditions are consistent with the view that the alcohols are the true primary products of the synthesis reaction.

501. ———. Sulfur Recovery in Germany. Vol. 64, 1951, pp. 375–376.

Review of various methods adopted in Germany to combat the shortage of S is given. They are divided into (a) dry-recovery processes; (b) wet-recovery processes, such as the Thylox, Dutch Mines, and Katasulf processes; and (c) scrubbing with an organic liquid, such as the Alkazid and the Girbotol processes. References are made to technical documents on British FD microfilms.

501a. ———. Expanding Horizons for Oxo Petrochemicals. Vol. 67, 1952, pp. 95–96.

Importance is stressed of the Oxo process to the petroleum refiner in upgrading byproduct olefins to aldehydes, alcohols and other petrochemicals.

502. CHEMICAL AND ENGINEERING NEWS. Catalysts Investigated for Synthesis of Methane. Vol. 22, 1944, pp. 19, 1710.

Work on the synthesis of CH_4 has been carried on both at the Gas Research Board (British) and at the Fuel Research Station (British). A preliminary exploration has indicated that a Ni catalyst is likely to give a satisfactory rate of conversion at a high space velocity. At the Fuel Research Station most of the work has been carried out using water gas. With water gas of a high H_2 : CO ratio, the most suitable catalyst for work at a relatively low temperature has proved to be a Ni catalyst promoted by ThO_2 and supported by kieselguhr. For the removal of S from water-gas mixture, a Cu–Cr catalyst supported on active C was developed at as low a temperature as 250° C. A hydrogenating catalyst of the MoS_2 type is required to protect the poisoning of the Cu–Cr catalyst when coal gas is used. A method for complete decomposition of thiophen was developed with a MoS_2 catalyst at 300° C.

503. ———. Fischer Summarizes Wartime Progress in Synthetic Oil Research. Vol. 22, 1944, p. 391.

Digest of a review of the various processes using C oxides and H_2 for the production of synthetic oils. Normal-pressure synthesis, medium-pressure synthesis, and the use of Ni, Co, Ru, and Fe catalysts are briefly touched upon.

504. ———. Ketones From Fischer-Tropsch Process. Vol. 22, 1944, p. 2114. Petrol. Times, vol. 48, No. 1234, 1944, p. 747.

Extensive experiments have been carried out in Germany with fatty acids from the Fischer-Tropsch process with a view to the production of ketones. The fatty acids were saponified with lime and the resulting calcium salt subjected to dry distillation. A mixture of ketones of great variety was obtained. Experiments were carried out with fractionated fatty acids, and these showed that the ketones obtained corresponded closely in boiling and solidification range to the theoretical figures. Various types of ketones were obtained. Some were liquids with a pleasant odor, others were white solids of waxlike appearance. They can be used in the cosmetics industry or as plasticizers.

505. ———. Lignite-Gasification Plant at Grand Forks, N. Dak. Vol. 23, 1945, pp. 1242–1244.

Federal Bureau of Mines commercial-size pilot plant for the gasification of lignite is described, and a flow sheet of the operation is shown. The process as used is a combination of the Reyerson low-temperature, continuous, isothermal system with the Parry vertical, annular, externally heated retort but over a wider range of temperature. Part of the water gas produced is formed by the reaction between the fresh lignite and its contained moisture in the upper zone, while the balance comes from the lower zone in which the lignite char reacts with steam passed countercurrently from the bottom of the retort. The 2 streams of water gas combine and pass out at the top through the center. The system is designed for an output of 75–80 cu. ft. of water gas per hr. per sq. ft. of heated retort surface. The unit produces 33,000 cu ft. of a 300-B. t. u. gas per ton of lignite containing 70–72% of H. The H_2 : CO ratio can be varied from 1.8 to 12, with changes in temperature and concentration of steam. The highest ratios giving maximum H_2 production are obtained at low temperatures, while at higher temperatures a synthesis gas, which is high in CO and suitable for use in Fischer-Tropsch reactions is obtained.

506. ———. New Sources of Fats Sought in Germany. Vol. 23, 1945, p. 1884.

The rapidly developing synthesis of hydrocarbons with fatty acids in the last 10 yr. (directly from CO_2 and H_2, or from hydrocarbons) suggested that the synthesis of fats (through esterifying fatty acids with glycerol) could soon be attempted on a large scale. In practice, however, it became apparent that the road from the fatty acid to an edible fat is extremely complicated and expensive. This is the reason why direct synthesis has not been taken up on a large technical scale. Synthetic fat is used in U-boats, however, because it never gets rancid. Actually Imhausen synthesis furnished a high-quality edible fat. Because of the above-mentioned unsatisfactory aspects of a total fat synthesis from CO_2 and H_2 by ester formation, recourse was made to biochemical methods. In this field fundamental progress was made. Some researchers succeeded in growing fat-producing fungi (yeasts, fusaria), on entirely synthetic mediums. The source of C for this synthesis is sugar (also pentose). With this method it is easy to obtain fats from timber by way of sugar. After approximately 48 hr. these fungi contain 15% of the original sugar supply in form of fat, which is suitable for human consumption. In addition, approximately 15% protein is formed. The necessary N_2 is derived from ammonium salts, nitrates, urea, amides, or easily synthesized amino acids.

507. ———. Oxo-Process Chemicals. Vol. 27, No. 4, 1949, p. 245.

Rohm & Haas Co. has announced the availability of 6 new chemicals derived from the Oxo process. A pilot plant has been constructed for preparing aldehydes catalytically from olefins, CO and H_2. The olefin first chosen for the process is diisobutylene, which reacts by the Oxo process to give only 1 isomer. The carbonyl group becomes attached to the terminal C to

produce 3,5,5-trimethylhexaldehyde. The 6 chemicals now available are derived from this nonyl aldehyde: Nonanoic acid, nonylamine, nonyl aldehyde cyanohydrin, α-hydroxydecanoic acid, octadecenyl aldehyde, and octadecyl alcohol. Some potential uses for these products are enumerated.

508. ———. Blaw-Knox Fuel Synthesis. Vol. 28, No. 5, 1950, p. 331.

Blaw-Knox Co. has announced the formation of a chemicals- and fuels-synthesis department. The new activity will deal with the conversion of fuels into chemicals and will be based initially on the Fischer-Tropsch synthetic fuels process and on related processes for making synthesis gas. An agreement has been made with Ruhrchemie and Lurgi for licenses and access to all process information developed by these German firms. The new department will adapt processes, develop pilot plants, design equipment, provide engineering, and built plants for converting plentiful fuels into more valuable chemical materials and upgraded forms of hydrocarbons.

509. ———. Cost of Synthetic Fuels. Vol. 28, No. 15, 1950, pp. 1187–1189.

Analytical summary of the economic features of the annual report of the Secretary of the Interior on the synthetic liquid fuels program.

510. ———. Synthetic Fuels Plant for India. Vol. 29, 1951, p. 1136.

Announcement has been made of plans for construction of a plant for the Kalaga Synthetic Oil Corp., Ltd., of Cuttack, Orissa, by Cie. Pan-Européenne d'Installations et d'Equipment Industriels of Paris and Ruhrchemie A.–G. of Germany. The plant will have an initial capacity of 10,000 tons, expandible later to 100,000 tons. Synthesis gas will be made from powdered coal by total gasification. The Indian Government has agreed to buy the entire output of gasoline. 5 Indian students, who have been studying in Paris for 2 yrs., will operate the plant. Production is expected to begin in 1952.

511. CHEMICAL AND METALLURGICAL ENGINEERING. Germans Investigate Methods for Processing Lignite. Vol. 41, 1934, p. 666.

Among competing projects must be mentioned the method by Prof. Franz Fischer, the leader of the Kaiser Wilhelm Institute for Coal Research in Mülheim. Petroleum products, from gasoline to high-melting paraffins, may be produced synthetically from water gas, mixtures of CO and H_2. The process has been developed to the point where 160 gm. gasoline is obtained per $m.^3$ gas at atmospheric pressure and a temperature below 200° C. with aid of highly active catalysts (alloy skeletons, *see* abs. **512**). By an oil-circulation system the temperature of the catalyst may be kept at the optimum. The first industrial pilot plant will be started in the near future by Ruhrchemie A.–G. Coal, coke, lignite, peat coke, and charcoal may all be used as raw materials. With a coke price of RM. 18 gasoline may be produced at a cost of RM. 0.22 per kg. or RM. 0.165 per l. It is hoped that an increased yield may permit a reduction in this cost.

512. ———. Synthesis of Liquid Hydrocarbons. Vol. 41, 1934, p. 215.

It is possible with highly active Co or Ni catalysts, which reach maximum capacity at 200° C., to treat a gas $CO : H_2 :: 1 : 2$ with almost complete conversion of CO in 1 pass, with up to 70% liquid hydrocarbons. Fischer has lately succeeded in replacing the precipitation catalyst formerly used with skeletons of alloys, which take up only $\frac{1}{10}$ of the volume occupied by the precipitated catalysts with almost the same capacity. Ni–Al alloy, as well as Ni–Si, Co–Si, and Ni–Co–Si were used, from which the Al and Si were dissolved by caustic potash leaving a skeleton of the heavier metals. $Ni : Co : Si :: 1 : 1 : 2$ proved most effective. Almost 100 $cm.^3$ liquid hydrocarbons was produced from 1 $m.^3$ of gas mixture in 1 pass.

513. CHEMICAL ENGINEERING. Oxygen, Past, Present, and Prospects. Vol. 54, No. 1, 1947, pp. 123–131.

The search for cheap O_2 (that containing from 88–98% O_2) has received considerable impetus recently, and it appears likely that such a low-purity O_2 can be produced for a small fraction (about 4% or less) of the present cost of high-purity gas, provided it is made in large units, operated at substantially constant rate, and installed at the point of use. Estimates of costs range from $0.048 for 1,000 cu. ft. of 95% O_2 in a plant of 48,000,000 cu. ft. per day capacity to an average of $0.12 including all the factors in power cost. In Germany the Linde-Fränkl, low-cost low-purity O_2 process was able to produce 98% O_2 in a large plant for 1.53 pf. per $m.^3$ ($0.10 per 1,000 cu. ft.). Of the total costs, power cost amounted to 58.8%, depreciation 31.4%, wages 4.9%, and water, lubricating oil, and chemicals 4.9%. Much research has been done in the United States and developments by several companies are commented upon, and a number of applications for cheap O_2 are presented. The principal uses include hydrocarbon-synthesis, steel-industry, and gas-industry applications, the technical feasability and the economic justification of which still require further proof.

514. ———. Recent Developments in Fuel Technology. Vol. 54, No. 4, 1947, pp. 127–132.

Review, particularly of the progress in Fischer-Tropsch practice in the United States.

515. ———. Liquid Fuels From Lignite in Australia. Vol. 55, No. 9, 1948, p. 236.

After several months of research and study by German scientists, one of them familiar with the development of the Lurgi process for gasification and liquefaction of coal, it has been decided that the brown coal of Victoria is suitable for gasification and as raw material for synthetic-gasoline plants. The expectation is that American pilot plants will be purchased and installed.

516. ———. South Africa Plant to Get Oil From Coal. Vol. 55, No. 1, 1948, pp. 207–208.

The Anglo-Transvaal Consolidated Investment Co. will erect an oil-from-coal plant at Vereeniging, South Africa. According to A. S. Hersov, chairman, the plant will be a replica of the Standard Oil of Indiana plant at Hugoton, with incorporation of improvements in the plant at Brownsville. Hydrocarbon Research, Inc., will act as technical consultant. The plant will cost about £14,000,000.

517. ———. Synthetic Fuels. Vol. 55, No. 6, 1948, pp. 131–138.

Review of developments and the future possibilities in synthetic liquid fuels production.

518. ———. Synthetic Fuels Program for India. Vol. 55, No. 9, 1948, p. 225.

Study is being made by the Koppers Co. looking toward establishment of a state-owned synthetic-petroleum industry based on gasification of low-grade coal. Costs are being calculated for plants of various capacity from 100,000 tons to 1,000,000 tons annually of gasoline and byproducts. Preliminary estimates for a 1,000,000-ton plant place the cost at $150,000,000 plus the outlay for a 200,000-kw. power plant.

519. ———. New Way to Make Heavy Water. Vol. 57, No. 3, 1950, p. 69.

Atomic Energy Commission plans construction of a plant to produce heavy water by a new and much cheaper process at only about one-fifth of the old cost. The process to be employed is low-temperature distil-

lation of extremely large volumes of H_2, such as are obtained in the off gas from large synthetic fuels or synthetic NH_3 plants. Total estimated cost of a plant at existing synthetic plants is $5,000,000. Surveys are under way to determine the selection of a plant site. There are about 20 synthetic NH_3 plants in the United States.

520. ———. Methanol Today. Vol. 58, No. 6, 1951, pp. 285–287.

Two major processes are being used to produce synthetic MeOH: Reaction of CO and H_2 and oxidation of selected fractions of natural or C_3H_8 and C_4H_{10}. Synthetic MeOH producers are listed. Estimated production costs are $0.138 per gal., net profit about $0.095 per gal. The major % uses of MeOH are shown. Synthetic production in 1951 should be about 160 million gal. and will probably reach 200 million gal. by 1953.

520a. ———. Fischer-Tropsch Makes Progress. Vol. 59, No. 2, 1952, p. 250.

Progress made in the operation of the improved Bureau of Mines reactor at Louisiana, Missouri. The new reactor converts 75–85% of the synthesis gas to oil. If conversion can be raised to 90%, the process can be operated in 1 stage instead of 2. Overall costs are being reduced.

521. CHEMICAL INDUSTRIES. Alcohols Above C_3 Produced From Olefins, Carbon Monoxide, and Hydrogen. Vol. 60, 1947, pp. 232–233.

Description of the Oxo process for the synthesis of primary alcohols by the interaction of olefins, CO, and H_2 over a Fischer-Tropsch catalyst. Information is taken from Bureau of Mines Information Circular 7370.

522. ———. New CO–H_2 Converter Provides Better Temperature Control. Vol. 60, 1947, p. 793.

Close control of the reaction temperature in the newest Bureau of Mines Fischer-Tropsch converter is achieved internally by vaporizing a hydrocarbon oil from the catalyst surface, instead of by means of heat exchangers alone, as in German practice, or by a fluidized fixed catalyst bed with a heat exchanger, as is proposed in the commercial installations under construction in the United States. In operation, a fraction of the liquid reaction product (boiling 110°–125°) is passed in parallel flow, along with the synthesis gas, through the column of pelleted Co catalyst at 100–150 p. s. i. and at a space velocity of about 1,000 lb. per $m.^3$ of catalyst per day. As heat is liberated by the reaction, vaporization of the injected liquid holds the temperature of the catalyst at the desired point, about 200°. In one continuous run of over 600 hr., no appreciable loss in catalyst activity was experienced. The method has another advantage in the removal of the high-melting waxes that have always blinded the surface of the Co catalysts after a short period of operation. It is estimated that an internally cooled unit should cost about the same as the fluid catalyst unit per bbl. of hydrocarbon product per day. Furthermore, it provides a more flexible operation.

523. ———. Production of Fatty Acids by Air Oxidation of Paraffin Wax. Vol. 60, No. 1, 1947, p. 64.

Reviews German method as practiced at Oppau. (*See* Bureau of Mines Information Circular 7376, abs. **1494** and **1495**). The paraffin wax used may be produced by the hydrogenation of brown coal, from petroleum or from the Fischer-Tropsch synthesis. In any case, it should consist of straight-chain hydrocarbons, with only small amounts of branched-chain or cyclic hydrocarbons. The preferred chain length is C_{16}–C_{30} and S compounds, and phenols should not be present as they inhibit the oxidation.

524. ———. Separation by Adsorption. Vol. 61, 1947, pp. 625–631; Fuel Abs., No. 3506, June 1948.

Summary of the development of adsorption as a method of separation is given with reference to the production of activated C from bituminous coal, methods for the activation of C, and hydrocarbon fractionation by means of fixed beds of C attached to Fischer-Tropsch converters and operated in a manner similar to the chromatographic separation of various components of solutions and by the hypersorption process. The adsorbent C falls through a tower countercurrently to hydrocarbon vapors. As the C falls, it adsorbs the lighter constituents. Lower down the C meets with a greater concentration of heavier constituents, which displace the lighter material. Thus, throughout the length of the column, an effect is produced comparable to refluxing in distillation. The bottom section consists of a steaming section in which adsorbed material is stripped from the C. In a C_2H_4 recovery unit now in operation, 76,900 cu. ft. of gases containing 5.7% of C_2H_4 are fed into the tower per hr., and approximately 7,000 lb. of a product containing 92% of C_2H_4 is obtained per day. Activated C has been employed to recover antibiotics.

525. ———. Oxoated Olefins. Vol. 63, No. 2, 1948, pp. 211–212.

First commercial application of the Oxo synthesis is now under way by the Esso Standard Oil Co. at Baton Rouge in the high-pressure petroleum hydrogenation unit. Iso-octyl alcohol is being produced. The price is expected to be somewhat under $0.30 per lb. It is to be used in making plasticizers. Other organizations are making plans also: Standard Oil Co. of Indiana will produce nonyl alcohol at its Whiting plant; the Oronite Chemical Co., Texas Co., and duPont are also interested in the production of high-molecular-weight alcohols, as is the Shell group in its petrochemical plant in England.

526. ———. Fischer-Tropsch Fats. Vol. 64, No. 6, 1949, pp. 914–915.

Food and Agriculture Organization of the United Nations has made a study of synthetic fats and presents the conclusion that more information on all phases of the problem is necessary before large-scale fat synthesis is advocated. It is not yet clear whether synthetic fats are suitable as human food. The production of artificial fats for industrial use in the making of soaps, detergents, greases, etc., is practical and would release a like amount of natural fats for food in countries such as Germany, where fats are in short supply. German capacity for synthetic fats production is 11,700 tons/yr. at present.

527. ———. From Wood Distillation to Oxo. Vol. 66, No. 6, 1950, p. 826.

Tennessee Eastman Corp. has been producing a small amount of isobutyraldehyde as a byproduct from its Oxo pilot plant. A petrochemical plant is being constructed at Longview, Tex. The major product is to be n-butyric acid for the production of Tenite II, a cellulose acetate-butyrate plastic. The process to be used is a modification of the Oxo synthesis. Propylene (presumably produced by propane cracking) will be reacted with a mixture of CO and H_2 to form a mixture of n-butyraldehyde and isobutyraldehyde. These will be fractionated, and oxidation of the latter compound will give *n*–butyric acid.

527a. CHEMICAL TRADE JOURNAL. Synthetic Fuels in South Africa. Vol. 129, 1951, p. 337.

Some of the technical features of the Coalbrook project are presented. Production of about 200,000 tons of liquid fuels annually will be based on a combination of improved German and American versions of the Fischer-Tropsch process, the former being a develop-

ment of the Ruhrchemie and Lurgi companies, the latter of M. W. Kellogg Co. The principal difference between the 2 methods lies in the actual synthesis stage, especially in the types of reactor vessels, catalysts, and process techniques. The coal with 26–29% ash content will be gasified in a Lurgi pressure plant thus enabling the gas to be generated under the actual pressure used for the subsequent synthesis, 300–450 p. s. i. The Ruhrchemie-Lurgi's "Rectisol" process will be used for the gas purification. The combined process is considered the most advantageous economically because of the greater flexibility of operations. Whereas Kellogg's powdered-catalyst method yields essentially fuels, the Ruhrchemie-Lurgi process may be directed either to fuels production or to a larger output of paraffin wax and base stocks for chemical manufacture. Improvements in the fixed-bed technique of the German process permits an increase in the daily output capacity from an average of 2 to about 50 tons/day. It is expected that 50,000 tons/year of primary products will be obtained from the Ruhrchemie-Lurgi plant, and 150,000 tons from the Kellogg plant, which will use the tail gas from the German plant in the synthesis operation.

528. Chemical Trade Journal and Chemical Engineer. Hydrocarbon Synthesis From Water. Vol. 99, 1936, p. 50.

Wintershall A.-G. of Berlin and Kassel is to manufacture synthetic fuel by a modification of the Fischer-Tropsch process and for this purpose has founded a subsidiary styled the "Mittel Deutsche Treibstoff und Oelwerks A.-G.", with headquarters in Kassel and an initial capital of RM 500,000. The new plant, which is being financed entirely by the Wintershall Co., is expected to start in the middle of 1937. The process employed has been established on the experimental scale at a plant at the Rauxel Nitrogen Works, which the Wintershall Co. erected in cooperation with the Klockner Co.

529. ———. Fischer-Tropsch Process in France. Vol. 100, 1937, p. 212; Gas Times, vol. 13, No. 158, 1937, p. 38.

A plant for the production of motor spirit from coke has recently been put into operation at Harnes in the Pas de Calais district of France. This plant, which is based on the Fischer process, has been designed for an annual production of 20,000 tons of spirit.

530. ———. New Fischer-Tropsch Plant. Vol. 101, 1937, p. 346.

A new company, the Kator-Fabrik Lutzkendorf G. m. b. H., has been formed in Mücheln, Geiserthal, with a capital of 1.5 million RM for the sole purpose of manufacturing catalyst for use in the Fischer-Tropsch process.

531. ———. Production of Motor Fuel in Germany. Vol. 101, 1937, p. 592.

Total capacity of all Fischer-Tropsch plants in operation or under construction in Germany is 700,000 tons per yr. as against 1,900,000 tons by the hydrogenation process. It will be several years before these ultimate capacities can be attained, the anticipated production for 1938 being 250,000 tons and 900,000 tons, respectively.

532. ———. Synthetic Fats. Vol. 105, 1939, pp. 235–236.

It is reported that Germany is to embark on large-scale production of synthetic edible fats made from glycerin and the acids obtained from Fischer-Tropsch wax. It is assumed that the glycerin would be synthesized from propylene. The synthetic product would differ from the natural fats primarily in that the component synthetic acids have both odd and even numbers of C atoms. These synthetic fats appear to be assimilated without any physiological disturbance to the human system.

533. ———. Edible Fats From Fischer-Tropsch Wax. Vol. 105, 1940, p. 235.

References to large-scale experiments on the production of "ersatz" fats by the interaction of glycerin with the fatty acids made by the catalytic oxidation of the paraffin wax from the Fischer-Tropsch process have been frequent in the continental press over the past year or so. Production of glycerin by fermentation of sugar solubles, a process used by Germany in 1914–18, may be revived, but it is more likely that the all-synthetic route to glycerin from propylene will be the one chosen.

534. ———. Iron Catalyst. Vol. 108, March 1, 1941, p. 8.

New Fe catalyst that has been developed recently in the laboratory of Dr. Kita of the Kyoto Imperial University is claimed to be quite as efficient as the German Co catalyst in the production of synthetic petrol by the Fischer-Tropsch and allied processes. A pilot plant for its utilization is to be erected. (*See* British Patent 529,390, abs. **1861.**)

535. ———. Fatty Acids From Paraffins. German Experience With Wartime Process. Vol. 116, 1945, pp. 309–311; Die Chemie, vol. 57, No. 1–2, 1944, pp. 6–11.

Review of the article by L. Mannes (abs. **2170**). In the development of a fatty acid industry in Germany for the manufacture of soap and the production of substitutes for the natural edible fats, it was found that the principal suitable material available in Germany was the waxy, paraffinic byproduct produced in the synthesis of gasoline by the Fischer-Tropsch process. This product at ordinary temperatures is virtually wholly hydrocarbons, partly liquid and partly solid, with iso- and branched-chain compounds, these latter increasing rapidly as the number of C atoms in the Fischer-Tropsch byproduct increases. In practice it was found that, even with the closest control of the oxidation and refining stages and the use of the choicest hydrocarbon raw material, numerous undesirable and overoxidized byproducts were produced, which lowered the yield and detracted from the qualities of the fatty acids of 10–20 C atom range. By the introduction of improved catalysts, accurate temperature control, and the avoidance of overoxidation there has been some improvement in the quality of the desired product. Figures quoted from laboratory investigations on the catalyst oxidation of Fischer-Tropsch paraffin wax residues show that out of a total fatty-acid yield of 55–60%, 20–25% consists of fatty acids with C atoms ranging from 1–9, and of this latter amount ½ consists of fatty acids ranging from formic to butyric. Further, about 10% of the paraffin is oxidized to CO_2 with a little CO. From the results reported it would not appear that the production of fatty acids by paraffin oxidation is a process that holds much inducement to any country having reasonable supplies of natural fatty acids.

536. ———. South African Synthetic Fuel Plans. Vol. 121, 1947, p. 484.

Anglo-Transvaal Consolidated Investment has plans to erect a new oil-from-coal plant on Vaal River near Vereeniging. Hydrocol Corp. will act as consultants. The plant will have a capacity of 60,000,000 gal. of high-octane gasoline and 9,000,000 gal. of Diesel oil yearly. South Africa will start with low-grade coal to make synthesis gas, but the subsequent processes are identical with the American modification of the Fischer-Tropsch process.

537. ———. Coal Oils in South Africa. Vol. 123, 1948, p. 503.

Union Government has published a copy of the draft license it proposes to grant to Anglo-Vaal Consolidated

Investment Co. for producing liquid fuels from coal. The following stipulations are given: Production shall be started within a period of 4 years. Production is to be 76,000–100,000 gal. per yr. The process to be used is the generation of gases from C material and the catalytic conversion of the gases to petrol and petroleum-like hydrocarbons. The coal used shall be from the deposits in Vredefort in the Orange Free State. All of the coal in each seam is to be used, and no coal containing less than 30% ash is to be rejected, unless it can be proved that the properties of such coal, other than its ash content, render it unsuitable for this purpose. The Government will not grant a similar license to any other concern for a period of 4 yr.

538. ———. South African Synthetic Petrol Plans. Vol. 122, 1948, p. 44.

In his statement for the general meeting of Anglo-Transvaal Consolidated Investment Co., Ltd., at Johannesburg, Dec. 19, 1947, A. S. Hersov reported that rights to the synthetic petrol process developed by Hydrocarbon Research, Inc., had been obtained. Application has been made for license to produce 60,000,000 gal, of petrol and 10,000,000 gal. diesel oil per yr. The factory will cost £12,000,000–£12,500,000 and take 2–3 yr to erect.

539. ———. Synthetic Fatty Acids. Vol. 122, 1948, p. 70.

Production of synthetic fatty acids, on a limited scale, has been resumed by Deutsche Fettsäurewerke at Witten since small amounts of Fischer-Tropsch Gatsch have been received with the restarting of the Fischer-Tropsch plants at Castrop-Rauxel and Wanne-Eickel. These Witten works were idle from the end of the war until September 1947.

540. ———. German Fischer-Tropsch Plants. Vol. 125, 1949, p. 410.

According to information in the German press, the Fischer-Tropsch plants that were operating in Bizonia during the first half of 1949 produced 28,146 tons primary products compared with 24,838 tons, January–June 1948. The yield in finished products was: Benzine, 10,319 tons: kogasin I, 2,453 tons, kogasin II, 4,453 tons, paraffin Gatsch, 2,949 tons; and hard paraffin, 970 tons.

541. ———. Germany's Synthetic Oil Plants. Vol. 124, 1949, p. 336.

Production of synthetic petrol and oil in Germany is still prohibited. At present 2 plants using the Fischer-Tropsch process are producing primary materials for the manufacture of fatty acids and synthetic detergents for the soap and washing-powder industry. Permission has been given for 2 plants, originally built for hydrogenation of coal by the Bergius process, to be used to a limited extent for the hydrogenation of residues from the initial refining of imported crude oils and also for the production of synthetic ammonia.

542. ———. Hydrocol's New Hydrocarbon Synthesis Plant Approaching Completion. Vol. 124, 1949, p. 689.

Initial production is expected before the end of the year. Coproducts of the new plant, in excess of 300,000 lb. of water-soluble oxygenated compounds, are to be separated and refined by Stanolind Oil & Gas Co. to yield methyl, ethyl, *n*-propyl, *n*-butyl, and *n*-amyl alcohols; acetaldehyde, propionaldehyde, and butyraldehyde; acetone, methyl-ethyl ketone, methyl-propyl ketone, and methyl-butyl ketone; and acetic, propionic, and butyric acids. These products will be distributed by United States Industrial Chemicals, Inc.

543. ———. Leuna Works Production. Vol. 125, 1949, p. 410.

Leuna Works near Merseburg (Russian zone) produced 150,000 metric tons of nitrogenous fertilizers in 1948–49, according to "Aufbau". The plant is again producing Buna synthetic rubber. Oil hydrogenation is 25% of prewar rate.

544. ———. Synthetic Fatty Acids in Germany. Vol. 125, 1949, p. 410.

According to Die chemische Industrie, Düsseldorf, the Hydrierwerk of Rodleben near Rosslau (formerly Deutsche Hydrierwerke) is building a plant for production of fatty acids by oxidation of paraffin. The material is to be used in the manufacture of soap. The new plant will have an annual capacity of 6,400 tons per year. The first section, 185 tons per mo., is expected to be ready soon.

545. ———. Fischer-Tropsch Plants. Vol. 126, 1950, p. 616.

Both the Government and private pressure groups in western Germany are doing their utmost to keep some of the Fischer-Tropsch plants intact and in operation. As the manufacture of synthetic-oil products is now a prohibited industry and as the need for running the plants for the production of Gatsch is no longer urgent, the Federal Ministry of Economics has submitted to the Allied experts a memorandum suggesting conversion of the remaining plants to the synthesis of alcohols. The Germans now maintain that, by suitable modification, the process can be operated without production of any hydrocarbon fractions. The conversion can be completed in 6–8 months. The views of the Allies are not known. In another direction the Federal German Government has already been successful in negotiations with the Allies. They have agreed that Gelsenberg-Benzin A.–G. will resume refining this month, though not by the Bergius high-pressure hydrogenation process. The main charging stock will be crude oil from the Emsland fields, of which large supplies exist, supplemented by imported oil from the German-American Oil Co., Ltd. The monthly output is expected to be 15,000–20,000 tons petrol, 5,000–10,000 tons diesel oil and about 1,000 tons gas oil.

546. ———. Germany's Oil Industry—Fischer-Tropsch Plants Not To Be Restarted. Vol. 126, 1950, p. 984.

Regarding rumors that Fischer-Tropsch plants in the Ruhr were still producing despite the Allied ban, a high official of the American High Commission's fuel and power branch reported that the last 2 plants working on the method had closed down Dec. 31, 1949, when a temporary allied production permit expired. The North Rhine-Westphalian Economics Ministry has shown a cold shoulder to German industrialists' hopes for reviving the industry. While prices of basic materials, especially coke, had risen by up to 150%, sales prices for products had risen no more than 50%. The price of catalysts was 3 times the prewar level, since the only West German plant producing the catalysts, at Oberhausen-Holten, was working at considerably reduced capacity. Gelsenberg Benzin A.–G. at Gelsenkirchen and Union Rheinische Braunkohlen-Kraftstoff A.–G. at Wesseling are making petroleum from crude oil by the high-pressure Bergius hydrogenation process from German and imported crude oil. Together they are expected to process 1,000,000 tons of crude oil this year and 2,000,000 tons by 1952. No new plants operating on the Bergius process will be built in West Germany. More cracking plants are planned.

547. ———. Indian Coal-Oil Plans. Vol. 126, 1950, p. 1435.

Indian Government has granted a license to B. Patnaik as sponsor for erection of a Fischer-Tropsch plant at Talcher in Orissa on the eastern seaboard. Production is expected to begin some time in 1951. The

plant, coming from the French zone of Germany, will have an output of 10,000 metric tons/yr. The Government has also contracted with Koppers Co., United States, to prepare plant designs for utilizing lower-grade Indian coals for synthetic-oil manufacture by hydrogenation. The plant will have an output of 100,000 metric tons of products/yr. and will require a capital investment of 220,000,000 rupees (£16.5 million).

548. ———. German Oil Processing. Vol. 128, 1951, p. 36.

Ruhrchemie A.-G. and the Omnipetrol Oil Processing Co. of Karlsruhe (representing the West German interests of the Omnium Français Pétroles) have concluded a contract providing for close cooperation in oil processing. The contract provides for the repair of Fischer-Tropsch installations of the Ruhrchemie A.-G. and the construction of a refinery at Oberhausen. The crude oil supplied by Omnipetrol from the Middle East will be finished by Ruhrchemie A.-G. A processing capacity of 200,000 tons is planned. The oil will be topped in a distillation plant and the residues processed in a cracking plant. Diesel oil, heating oil, and refinery gas will be produced in addition to gasoline. Gasoline output is estimated at 100,000 tons/yr. The cost is estimated at about 10,000,000 RM,

548a. CHEMIKER-ZEITUNG. [Synthetic Fuels Production.] June 15, 1951; Chem. Trade Jour., vol. 128, 1951, p. 1502.

Chemische Werke Bergkamen, the Krupp Treibstoff A.-G. of Wanne-Eickel and the Gewerkschaft Viktor of Castrop-Rauxel, have decided that the present price of coal renders resumption of liquid fuels production by the Fischer-Tropsch process uneconomic. The 3 companies are to operate their plants only for the production of hard paraffins, propyl alcohol and materials which can be processed into synthetic detergents.

549. CHEREPENNIKOV, A. A. [Chemical Application for Methane From Natural Gas.] Neftyanoe Khoz., vol. 18, 1930, pp. 796–799; Chem. Abs., vol. 25, 1931, p. 397.

Review of the literature comprising chlorination, oxidation, water-gas reaction, reaction with CO and CO_2, decomposition into C and H_2 and preparation of higher hydrocarbons, carbides, and HCN.

CHERTKOV, I. B. *See* abs. **151.**

CHESEBRO, P. R. *See* abs. **2600.**

CHESSICK, J. J. *See* abs. **1372.**

550. CHEVALIER, R., AND BÉGUI, Z. E. [Thermomagnetic Properties of Ferric Oxide.] Bull. soc. chim., vol. 4, No. 5, 1937, pp. 1735–1742; Chem. Abs., vol. 32, 1938, p. 3219.

Coefficients of magnetization, χ at 20° and 720°, were measured by Curie's method, for some 20 Fe_2O_3 samples differing in preparation. For these the Curie point is remarkably constant between 690° and 700°. Above this temperature, χ is constant, with a mean value of 19×10^{-6} at 720°, even when the oxides contain traces of impurities. This value appears to be a lower limit for the susceptibility of Fe_2O_3 and characterizes α–Fe_2O_3. It is the value for very fine, artificial oxide at ordinary temperature, for very finely pulverized hematite, for hematite along the crystal axis, as well as for all the oxides above the Curie point. The different preparations at 20° gave widely differing values of χ.

551. CHEVALIER, R., AND MATHIEU, S. [Variation in Magnetic Susceptibility of Hematite Powder With Size of Grains.] Compt. rend., vol. 204, 1937, pp. 854–856; Chem. Abs., vol. 31, 1937, p. 3352.

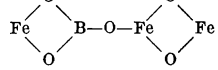
Three samples of hematite were separated, by powdering, sifting, and levigation in EtOH, into 9 samples of different average diameters, 500–10μ, and the magnetic susceptibility χ of each was determined in a field of 700 gausses. χ diminishes by about 10% as d decreases from 500 to 100μ, then more rapidly to only about 25% of the initial value for $d=10\mu$. Extrapolated to $d=0$, $\chi=20\text{–}30\times10^{-6}$, or approximately that of powdered artificial rhombohedral Fe_2O_3.

552. ———. [Adsorption in Precipitation of the Hydroxide From Ferric Sulfate.] Compt. rend., vol. 206, 1938, pp. 1249–1251, 1469–1471, 1955–1958; and vol. 207, 1938, pp. 58–61; Chem. Abs., vol. 32, 1938, pp. 4854, 5269, 6516.

In precipitating ferric oxide from a solution of ferric sulfate with KOH, the magnetic susceptibility of the precipitant is a strong function of the concentration and excess of base employed. The higher the concentration and excess of base, the higher the magnetic susceptibility of the precipitant. Studies conducted at the Bureau of Mines have shown that precipitated oxides prepared from ferric nitrate behave very similarly to the oxides studied above.

553. CHEVALIER, R., MATHIEU, S., AND GIRARD, J. [Monograph of Ferrous Boroferrite.] Bull. soc. chim., vol. 15, 1948, pp. 611–615; Chem. Abs., vol. 42, 1948, p. 7649.

Mixture of 2 gm. Fe_2O_3 and 3 gm. $Na_2B_4O_7$, heated in a Pt boat at 1,000°, is reduced with either H_2 or CO; the cooled mass is treated with 3 *N* HNO_3, and the residue is dried after being washed with hot H_2O. Likewise the oxidation of a mixture of 2 gm. fine Fe and 4 gm. $Na_2B_4O_7$, heated in N_2 at 1,000° and oxidized with air, yields crystals of the boroferrite $B_2O_3.Fe_2O_3.4$ FeO. The product appears as fine black, opaque, orthorhombic crystalline needles. The boroferrite is readily attacked by dilute HCl, but less readily by H_2SO_4 and HNO_3; the resulting solution shows properties of B_2O_3, Fe^{2+} and Fe^{3+}. The constitution is believed to be



554. CHEVENARD, P. [Metallographic Interpretation of the Instability of Reversible Ferronickels.] Compt. rend., vol. 223, 1946, pp. 1074–1076; Chem. Abs., vol. 41, 1947, p. 3031.

Quenched ferro-Ni alloys show 2 stages of recovery. The 2d, starting about 300°, is accompanied by graphite precipitation and severe contraction. The 1st stage is, in general, an expansion effect from room temperature to 175°, but elongation-time curves show a contraction preceding the expansion. This is attributed to precipitation of cementite, favored by the Mn in the alloys, which subtracts Fe from the ferro-Ni and diminishes density. To suppress this instability C should be held below 0.05%, remaining C should be stabilized with Ti or V, and the pieces should be treated before use to provoke all precipitation that can occur.

555. CHILTON, L. V., AND TOPP, N. E. Production of Mersol Products at I. G. Farbenfabrik, Wolfen. BIOS Final Rept. 1305, 1946, 7 pp.; PB 79,230.

Mersol is made by sulfochlorination of the hydrocarbon Mepasin (obtained by hydrogenation of Fischer-Tropsch Kogasin) using ultra-violet activation. Gives details of method. Petroleum hydrocarbons were not considered economically usable.

556. CHIWALA, A. [Formation of Mineral Oil by Chemical Interaction of Mineral Oil Hydrocarbons and the Synthetic Production of Derivatives.] Oesterr. Chem.-Ztg., vol. 48, 1947, pp. 2–6; British Abs., 1949, B, I, p. 238.

Review of interconversion of hydrocarbons by cracking and condensation, the formation of derivatives

from hydrocarbons by oxidation, chlorination, sulfochlorination and nitration, and the reaction of olefins with compounds containing hydroxyl, with HOCl, CO, and H_2 (catalytically), and with formaldehyde. The importance of these processes in the Austrian oil industry is considered.

557. CHLOSTA, J. [Wash-Oil Problem.] Oel u. Kohle, vol. 37, 1941, pp. 961–962; Chem. Abs., vol. 37, 1943, p. 6110.

Paraffin oils from brown-coal tar and low-viscous oils from the Fischer-Tropsch hydrocarbons synthesis process are both being successfully used for benzene scrubbing.

558. CHOULAT, G. [Residual Gas From Fischer-Tropsch Synthesis as Town's Gas.] Gas u. Wasserfach, vol. 83, 1940, pp. 497–499; British Abs., 1948, B, I, p. 64.

Composition of the gas varies rather widely, mean values being: CO_2, 17; CO, 9; CH_4, 33; H_2, 20; N_2, 20; C_nH_m 0.7 volume %. The calorific value is within the town's gas range, but the high density and low flame speed render its behavior unsatisfactory unless it is mixed with not less than 2.5 volumes of normal town's gas.

———. *See* abs. **384.**

CHOVIN, P. *See* abs. **2329.**

559. CHRISTESCO, J. [Procedure for Obtaining Synthetic Alcohols From Gas Mixtures.] Chaleur et ind., vol. 15, No. 167, 1934, pp. 456–458; Compt. rend. Cong. chauffage ind., 3d Cong., Paris, 1933; Fuel, vol. 14, 1935, pp. 23–25; British Chem. Abs., 1935, B, p. 259; Chem. Abs., vol. 28, 1934, p. 6423.

Method consists of bubbling a gas mixture through H_2O at ordinary pressures in the presence of a catalyst. The experimental apparatus is pictured and described. Formation of MeOH from CH_4 is believed to take place as follows: $CH_4+H_2O=CO+3H_2$; $CO+3H_2=MeOH+H_2$. A yield of 57% was obtained. EtOH was also prepared from gas mixtures. 10 refs.

560. CHRISTIANSEN, J. A. Equilibrium Between Methyl Formate and Methanol and Some Related Equilibria. Jour. Chem. Soc., 1926, pp. 413–421; Chem. Abs., vol. 20, 1926, p. 1745.

For the reaction $2H_2+HCO_2Me=2MeOH$, $\log K_E=-(3{,}016/T)+3.61$ (over a range of 180°–240°); $MeOH+CO=HCO_2Me$, $\log_{10}K_E=-(1{,}880/T)+4.82$. For these values the reaction $CO+2H_2=MeOH$ is calculated: $\log K_3=-4{,}896/T+8.43$.

561. ———. Equilibrium Between Methanol and Its Decomposition Products. Jour. Am. Chem. Soc., vol. 52, 1930, p. 3165; Chem. Abs., vol. 24, 1930, p. 4981.

Christiansen's work was done in 1917–18, not in 1926.

562. CHRISTIE, J. J. German Chemicals Industry—Fischer-Tropsch Plants. Chem. Eng., vol. 57, No. 11, 1950, pp. 164–165.

Western Germany's 6 Fischer-Tropsch plants were removed from the reparations list for utilization of processes acceptable to the Allied Military Security Board. Already under way is the conversion of the Krupp-Treibstoffwerk at Wanne-Eickel to the Oxyl process. Work is being done by Lurgi in collaboration with Ruhrchemie A.-G. and is expected to be completed in the spring of 1951. It will have an output of 30,000 tons of alcohols per yr. The Oxyl synthesis (not to be confused with the Oxo process) is applied mainly to obtaining, in addition to hydrocarbons, alcohols with 2–40 C atoms. Alcohols and neutral oils are worked up and separated to yield primary alcohols with a purity of 95–98%, suitable for use as solvents or softeners or further processed into detergents. The synthesis gas used as the basic material differs from that used in the Fischer-Tropsch synthesis. Two catalysts are used: A ferrous-based catalyst in the gaseous-reaction phase, and a Co-based catalyst in the liquid phase. The final products include approximately 17% gasoline, oils, and lubricants. It is proposed to convert the Bergkamen plant of Essener Steinkohlen A.-G. to production of gas for normal heating purposes by hyperpurification and detoxification of coke-oven gases. Proposals for conversion or disposition of the other 4 Fischer-Tropsch plants have not been announced. Thesc plants are: Ruhrchemie A.-G. at Oberhausen-Holten, capacity 65,000 tons per year.; Steinkohlenberg werk Rheinpreussen at Moers, 73,000 tons capacity; Dortmunder Paraffin Werke of Dortmund, 50,000 tons capacity; Gewerkschaft Viktor at Castrop-Rauxel, 61,000 tons capacity.

CHU, P. L. *See* abs. **1269.**

CHUFAROV, G. I. *See* abs. **3326, 3327.**

563. CHUFAROV, G. I., AND ANTONOVA, M. F. [Retardation of the Bell Reaction $2\,CO = C + CO_2$.] Bull. acad. sci. U. R. S. S., Classe sci. tech., 1947, pp. 381–389 (in Russian); Chem. Abs., vol. 42, 1948, p. 3648.

Decomposition of CO by the Bell reaction on an Fe catalyst is a 1st-order reaction over a pressure range 2–200 mm. CO and a temperature range 350°–750°, and obeys the equation $-dp/dt=kp$, where p is the pressure of CO. Over a temperature range of 350°–450°, the reaction rate changes according to the Arrhenius equation $v=Ae^{-E/RT}$, where E, the activation energy, is 34,000 cal. per mol. The addition of $CuSO_4$, $Al_2(SO_4)_3$, or $MnSO_4$ to the Fe catalyst causes a marked retardation of the reaction at a temperature around 450°, 5% of $CuSO_4$ or $Al_2(SO_4)_3$ completely inhibiting the reaction. The retardation is less pronounced at higher temperatures, but the effect is still large; at 650°–750°, 5% $CuSO_4$ retards the reaction by a factor of 40, whereas 5% $Al_2(SO_4)_3$ retards it by a factor of 12. More stable sulfates, Na_2SO_4, $MgSO_4$, and $CaSO_4$, are less effective in retarding the reaction. The inhibiting effect is cuased by poisoning of the catalyst by the S-containing decomposition products of the sulfates, principally SO_2.

564. CHUFAROV, G. I., AND AVERBUKH, B. D. [Initial Rate of Reduction of Hematite and Magnetite by Hydrogen.] Ztschr. physik. Chem., vol. B–33, 1936, pp. 334–348; Chem. Abs., vol. 31, 1937, p. 24.

Reduction of hematite and magnetite by H_2 was studied between 300° and 800° and at pressures between 0.1 and 0.001 mm. Hg. The autocatalytic nature of the reaction is satisfactorily explained by the formation of active centers during the course of the reaction. Above 600°, the lower rate as compared with that at lower temperature is due to recrystallization of these centers.

———. Reduction of Iron Oxides by Gaseous Reducing Agents. II. Rate of Reduction of Magnetic Iron Oxide by Hydrogen. *See* abs. **566.**

565. CHUFAROV, G. I., AND LOKHVITZKAYA, A. P. [Reduction of Iron Oxides by Gaseous Reducing Agents. I. Velocity of Reduction of Ferric Oxide by Hydrogen.] Jour. Phys. Chem. (U. S. S. R.), vol. 5, 1934, pp. 1103–1113; Chem. Abs., vol. 29, 1935, p. 3901.

Apparatus is described. Artificial and natural Fe_2O_3 containing 98.6% Fe_2O_3, 0.35% Al_2O_3 and 1.1% SiO_2 were used. For both, an autocatalytic character of the speed of reduction by H_2 was revealed sharply. The 1st stage, reduction to magnetite, is not autocatalytic. The remaining stages, belonging to the type of inter-surface reactions, proceed autocatalytically. The anomalous course of the reduction curve above 600° is due to changes in the microporosity and ultramicroporosity of the solid product. The rates of reduction at temperatures 300°–900° are shown by a series of 11 graphs for various conditions of particle size, degree of pre-

vious reduction, etc. The porosity of the product is greater the lower the reduction temperature.

566. CHUFAROV, G. I., AND AVERBUKH, B. D. [Reduction of Iron Oxides by Gaseous Reducing Agents. II. Rate of Reduction of Magnetic Iron Oxide by Hydrogen.] Jour. Phys. Chem. (U. S. S. R.), vol. 5, 1934, pp. 1292–1298; Chem. Abs., vol. 29, 1935, p. 5336.

Samples of magnetic iron oxide of natural origin and prepared from piano wire both show on reduction strongly autocatalytic effects. The initial speeds of reduction are greater the greater the temperature, 350°–900°, but above 600° the velocity of reduction falls off very quickly with time and the curve for 800° crosses that for 400° and 600° at about 70% reduction. Above 800° this effect again is less marked. Piano wire magnetite shows this effect much more pronouncedly than does natural magnetite. The micropore and ultrapore structures are also different on reduction. Reduction proceeds in 2 stages, first to FeO then to Fe. Most rapid, about 60 minutes, 90–100% reduction is obtained at about 600° C.

567. CHUFAROV, G. I., AND TATIEVSKAYA, E. P. [Reaction Zones in the Reduction of Magnetite and Hematite With Hydrogen.] Acta Physicochim, U. S. S. R., vol. 3, 1935, pp. 957–974; Chem. Abs., vol. 31, 1937, p. 4878.

Reaction is autocatalytic. The change in porosity with temperature and degree of reduction was studied and related to the reaction rate. Magnetite is less porous than hematite, but below 600° the rate of reduction is faster. Above this temperature the porosity and the rate of reduction decrease rapidly in both cases. Microscopical investigations show the presence of the layers α–Fe–Fe_3O_4 in the case of magnetite and α–Fe–Fe_3O_4–Fe_2O_3 in the case of hematite, while FeO could not be detected, and it is suggested that $Fe_3O_4 \rightarrow Fe$ is the rate-determining process. The rate of advance of the reduction zone is linear below 500° and the activation energy for hematite is 15,700 gm.-cal.

568. ———. [Comparison of Initial Velocities of Reaction of Oxides of Iron With Hydrogen and Carbon Monoxide and Their Mixtures.] Jour. Phys. Chem. (U. S. S. R.), vol. 8, 1936, pp. 933–942; Chem. Abs., vol. 31, 1937, p. 2075.

Near 500° the reduction of hematite is much slower by CO than by H_2. At higher temperatures, 800°, the ratio of the velocities approaches the ratio of impinging molecules of the 2 gases. As a result of the smaller number of active centers at higher temperatures the absolute values of the reduction velocities are small. At 500° the presence of CO in mixtures of $CO+H_2$ decreases the reduction below that expected for the partial pressure of H_2, because of adsorption of CO on a large number of the active centers.

569. CHUFAROV, G. I., AND VILESOVA, G. F. [Influence of the Crystalline Lattice of an Oxide Upon the Speed of Reduction With Hydrogen.] Teoriya i Prakt. Met., No. 4, 1936, pp. 10–17; Chem. Abs., vol. 30, 1936, pp. 8115–8116.

Experiments were performed with grains of 0.5–1.0 mm. and with cubes of 5 x 5 x 5 mm. prepared from natural crystals of hematite and magnetite. Artificial oxides were prepared from piano wire. Reduction with H_2 was conducted at all possible temperatures up to 800°–900°. Above 600° the ultraporosity and microporosity of the magnetite reduction products is small. This blocks the penetration of the gas and the reduction is hindered. Below 600° the magnetite is sometimes reduced faster than the hematite. At higher temperatures the small crystal structure favors reduction, but at low temperatures it may hinder it because of its great adsorption of the reduction products.

CINES, M. *See* abs. **828.**

570. CLAR, —. [Improvement of Synthetic Oils by Means of Sulfuric Acid.] FIAT Reel K23, frames 2,381–2,391, Aug. 25, 1939; PB 70,214; TOM Reel 290.

Experiments on the refining of synthetic oils with H_2SO_4 have no success because of the undesirable side reactions, such as oxidation or formation of tar and esters. 7 tables.

571. ———. [Production of Oils From the Primary Products of the Gasoline Pressure-Synthesis.] FIAT Reel K28, frames 6459–6469, No. 26, 1940; PB 70,185; TOM Reel 295.

Preliminary treatment with $NaHSO_3$ + Na activated Al, $SiCl_4$, $ZnCl_2$, PCl_5, and $SnCl_4$ of the gasoline produced under pressure leads to an increase in the oil yield with simultaneous formation of contact oil. Alcohols, which interfere with oil synthesis, are likely to be split into olefins and steam. When the gasoline vapors are passed over silica gel, isomerization is effected. Describes tests on a technical scale.

572. ———. [Lubricating Oil From Synthetic Gasoline.] FIAT Reel K28, frames 6120–6145, May 11, 1941; PB 70,185; TOM Reel 295.

Fractions of a cracked gasoline boiling within a narrow range and purified over metallic Na were used for the synthesis of lubricating oil. Comparison of the oils prepared from the fractions in a single synthesis shows an improvement in the viscosity-pole height and a deterioration of the Conradson test with increasing chain length while the aniline point and the I number decrease with rising molecular weight. A higher stability of the polymerizates obtained from C_{13} and C_{14} fractions, compared with those obtained from the C_9 to C_{11} fractions, has been established by artificial aging. Acids, esters, and aldehydes are noxious; this is proved by the fact that after their elimination the viscosity-pole height and the Conradson test improve.

573. ———. [Density of Synthetic Oils and Its Dependence on the Nature of the Primary Gasoline and the Viscosity of the Oils.] FIAT Reel K29, frames 6,630–6,633, 1942; PB 70,218; TOM Reel 296.

Densities of a number of oil-test portions are tabulated according to their viscosities and their origins from cracked gasoline or from circulated gasoline. Their relations are represented graphically. Because of the large variation in the values, these curves do not have the significance of a functional relation but only of a correlation. As a rule, the densities of oils from cracked gasoline are higher than those of oils from circulated gasoline. Generally, density increases with increasing viscosity. 1 graph.

———. *See* abs. **3431.**

CLARK, A. *See* abs. **19, 20, 1399.**

574. CLARK, A., ANDREWS, A., AND FLEMING, H. W. Composition of a Synthetic Gasoline. Ind. Eng. Chem., vol. 41, No. 7, 1949, pp. 1527–1532; Chem. Abs., vol. 43, 1949, p. 7211.

8 fractions from a gasoline synthesized from CO and H_2 in the presence of a fluidized Fe catalyst of the synthetic NH_3 type at about 600° F. were percolated through silica gel. Each fraction was broken down into 4 types: Paraffins, olefins, aromatics, and oxygenated compounds. Some additional information was obtained on the character of the gasoline fractions. 40–50% by volume of the C_5, C_6, and C_7 fractions consist of straight-chain 1-olefins. 15 different aromatic compounds were identified as being present in the 1st 6 fractions. Evidence is fairly conclusive that small amounts of diolefins exist in most of the fractions.

575. CLARK, A. M. Large-Scale Production of Oxygen and Atmospheric Gases. Bib. Sci. Ind. Repts., vol. 3, No. 3, 1946, p. 158; BIOS Final Rept. 591, 1946, 29 pp.; PB 41,229.

This report reviews the production of O_2 and other gases by the Linde-Fränkl process. Altogether, 73 Linde-Fränkl units have been erected by the Linde Co. since 1930, with an average capacity of 2,378 m.³ per hr. of O_2 of 98% purity. The O_2 has been used mainly in the complete gasification of coal. Arrangement of plant and method of operation are described in some detail, with reference to the installation at Leuna. Analysis is made of available information relating to energy requirements of the process. Attempt also was made to determine the costs of O_2 production by the Linde-Fränkl process.

It is claimed that O_2 can be separated from air at a purity of 98% with an energy consumption of 0.455 kw.-hr. per m.³ of O_2. The cost of production may vary between 1.6 and 3.0 pf. per m.³ of O_2, of which 40–50% may be accounted for by the cost of power. The capital cost of large installations appears to have been around RM 500,000 per 1,000 m.³ per hr. of O_2 capacity. Gives flow diagrams.

CLARK, E. L. *See* abs. **2103.**

576. CLARK, E. L., KALLENBERGER, R. H. BROWNE, R. Y., AND PHILLIPS, J. R. Synthesis-Gas Production. Reaction of Light Hydrocarbons, Steam, and Carbon Dioxide in Commercial Equipment. Chem. Eng. Progress, vol. 45, No. 11, 1949, pp. 651–654.

Production of synthesis gas of a wide range of H_2:CO ratios in a Hygirtol-type (Girdler Corp.) furnace is described. Operating data are presented for H_2 : CO ratios of 2 : 1 and 1 : 1. H_2 and CO mixtures containing 33–90% CO are produced by the reaction of natural gas ($C_{1.17}H_{4.3}$) with steam and CO_2. No trouble was encountered at any time with C deposition on the catalyst. The catalyst used was a Ni base catalyst furnished by the Girdler Corp. under the designation F–5. The product gas has such a low CO_2 content that its removal is not required, thus reducing plant-construction cost.

CLARK, G. C. *See* abs. **2061.**

577. CLARK, R. H. Production of Liquid Fuels From Coal. Canadian Min. and Met. Bull. 190, February 1928, pp. 274–281.

This is a brief consideration of (1) production of primary tar by low-temperature carbonization; (2) hydrogenation of coal; and (3) Fischer-Tropsch process.

578. CLARK, W. New Synthetic Alcohol From Gasoline Is Developed for Plastics Industry. World Petrol., vol. 20, 1949, pp. 44–45.

Development of the process announced by Esso Standard Oil Co. is reviewed. Iso-octyl alcohol is produced by the Oxo process, in which heptene from the polymerization of unsaturated cracker-gas reacts with CO–H_2 to form octanol. Hydrogenation of the latter at 3,000 p. s. i. gives principally C_4–C_8 straight-chain alcohols with appropriate side chains. The octyl alcohols are in demand for the manufacture of plasticizers, particulary polyvinyl chloride.

578a. CLARKE, J., AND JACK, K. H. Preparation and the Crystal Structures of Cobalt Nitride, Co_2N, of Cobalt Carbonitrides, Co_2 (C, N), and of Cobalt Carbide. Chem. and Ind., 1951, pp. 1004–1005; Chem. Abs., vol. 46, 1952, p. 2948.

Co_2N was prepared by passing anhydrous NH_3 over pure Co powder (380 mesh) at 350° with the partial pressure of H_2 kept at a minimum. A Co nitride approximating Co_3N can be obtained by thermal decomposition of Co_2N. CO at 340° gradually reacts with Co_2N and Co_3N to form the corresponding Co carbonitrides. The Co_2C of Hofer and Peebles (abs. 1440) is apparently identical with that prepared by the complete replacement of N in Co_2N. X-ray powder photographs of Co_2N, $Co_2C_{0.53}N_{0.47}$ and Co_2C show that the unit-cell dimensions and the positions of the atoms within the unit cell change gradually as C replaces N. The space group is $D_{2}^{12}h$—$P\ m\ n\ n$. For Co_2N the unit cell dimensions are a=2.8535, b=4.6056, c=4.3443 A., and for Co_2C, a=2.8969, b=4.4465, c=4.3707 A.

579. CLAUDE, G. [Present Situation With Respect to the Synthesis of Ammonia in Conjunction With Coke Ovens.] Compt. rend., vol. 182, 1926, pp. 877–881; Chem. Abs., vol. 20, 1926, p. 2229.

A phenomenon peculiar to this process and not previously described is the formation of MeOH during the conversion of CO (present as an impurity in the H_2) to CH_4 thus: $CO+6H_2 \rightarrow CH_4+H_2O$. Up to 25% was found in the H_2O of the reaction, having been formed by the reaction: $CO+4H \rightarrow C_3OH$.

CLAUSMANN, P. *See* abs. **1168, 1169.**

580. CLEMENT, —., and DESORMES, —. Synthesis of Hydrocarbons and Alcohols From Water Gas. Specific Heat of Gases, Paris, 1802. In Marek and Hahn, Catalytic Oxidation of Organic Compounds, Chemical Catalog Co., New York, 1932, p. 101.

By passing steam over coke at red heat a combustible gas was produced analyzing as follows: H_2, 56.22%; CO, 28.96%; CO_2, 14.68%; CH_4, 0.49%.

581. COAL AGE. Coal for Synthesis. Vol. 54, No. 1, 1949, pp. 66–67.

Brief review of development of a synthetic liquid-fuel industry and the part that coal is playing therein. It must not be assumed that natural and synthetic gaseous and liquid fuels are or will be capable of supplying the Nation's energy demands. Coal has its present competitive difficulties, but from the standpoint of reserves, availability, and cost it is in the best position of all fuels to undergo substantial expansion.

582. COAL CARBONISATION. Petroleum and Lube Oils From Coal. Vol. 1, 1935, p. 66; Wärme, vol. 58, 1935, p. 206.

Products of the Fischer-Tropsch process for making gasoline and lubricating oils from hard-coal coke are in no way inferior and in some ways superior to natural petroleum products. For example, the cold-test of a good natural winter oil is —16° C. whereas that of a synthetic product is —42° C.

583. ———. Liquid Fuels in Germany. Vol. 3, 1937, p. 78; Tech. moderne, April 1937, p. 255.

4 plants are operating at Homberg, Castrop-Rauxel, Oberhausen-Holten, and Ruhland. The last-named plant has been enlarged to a capacity of 150,000 tons of oil per yr.

584. ———. Motor Fuels in Germany. Vol. 4, 1938, p. 65; Bull. Hamburg World's Econ. Archiv., vol. 4, No. 6, 1938, pp. 88–90.

Review of factors that have influenced the development of substitutes for petroleum products in Germany. It is stated that 50% of the light fuel-oil requirements in 1936 were covered by home production, of which the Bergius and Fischer-Tropsch processes contributed 39%. These 2 processes are also of special importance in the domestic production of diesel fuel; the latter yields a high-grade, but rather expensive, diesel fuel. Bergius benzines are claimed to be superior to imported fuel as regards antiknock qualities, and further progress is expected from new catalysts. Benzines from Fischer-Tropsch process need cracking and blending to yield a satisfactory fuel. The Fischer-Tropsch process offers the special attraction of an outlet for semicoke from the low-temperature carbonization of coal.

585. COBURN, A. E. Liquid Gas and Coal. Fuel Oil and Oil Heat, vol. 6, No. 1, 1947, pp. 57–58, 148, 150; Chem. Abs., vol. 41, 1947, p. 6385.

Sources of oil adequate for 1,000 yr. are seen in reserves of gas and coal for synthetic liquid-fuel processes. The use of O_2 in gasification, the Lurgi process, underground gasification of coal, and the Fischer-Tropsch process are described briefly.

COCKS, L. V. *See* abs. **24.**

COHEN, M. *See* abs. **2562.**

COHEN, P. *See* abs. **740.**

COHN, E. M. *See* abs. **52, 1436, 1437, 1438, 1439, 1445, 1446, 1447.**

586. COHN, E. M., AND HOFER, L. J. E. Mode of Transition From Hägg Iron Carbide to Cementite. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 4662–4664.

Reaction of Hägg carbide, Fe_2C, to yield cementite, Fe_3C, and free C is a discontinuous or heterogeneous precipitation. Hägg carbide and cementite have narrow ranges of composition and apparently do not form intermediate metastable solid solutions. The reaction $3Fe_2C\text{–Hägg} \rightarrow 2Fe_3C + C$ becomes appreciable only at about 450°, while the reaction $Fe_2C\text{–Hägg} + Fe \rightarrow Fe_3C$ starts below 300°. The unstable or labile carbide of Kölbel and coworkers is simply Hägg carbide.

587. COITH, H. S., AND ROBITSCHEK, F. O. Determination of Suitability of Paraffin Mixtures for Conversion to Fatty Acids by Catalytic Oxidation. FIAT Final Rept. 905, Sept. 3, 1946; PB 42,659; Suppl. 1, 3 pp., TOM Reel 240.

Catalytic oxidation of paraffins to fatty acids is greatly dependent upon the characteristics of the raw materials, therefore small-scale tests are important for evaluating the proposed raw materials. 2 such tests are described and compared with the actual production procedure. One of the examples given is a paraffin mixture boiling 320°–450° (Fischer-Tropsch Gatsch) using potassium permanganate as catalyst. 3 German plants used this method: The I. G. plants at Oppau and Heydebreck and the Deutsche Fettsäurewerke at Witten. Supplement 1 contains 2 drawings of apparatus for oxidation.

587a. COKE. South African Coal-to-Oil Technical Plan. Vol. 13, 1951, pp. 385–390; Fuel Abs., vol. 10, No. 6, 1951, abs. 5,219.

Production at Coalbrook at initial rate of about 200,000 ton of liquid fuels a year will be based on a combination of improved German and American versions of the Fischer-Tropsch process. The cost percentage figures of the plant are: (a) Power station 19; (b) gasification plant 30; (c) fine purification plant 9; (d) synthesis reaction vessels 6; (e) distillation, polymerization, and other finishing plant for primary and secondary products, and storage facilities 24; (f) ancillary works installations 12. The coal of ash content about 26–29% will be gasified in a Lurgi pressure plant so that the gas is generated under the actual pressure needed for the synthesis. Ruhrchemie's experimental plant has given satisfactory results. Ruhrchemie-Lurgi "Restisol" process will probably be used for the gas purification.

588. COKE AND GAS. Fluidized Technique. Vol. 9, 1947, pp. 261–266.

Details of new technique developed by the American oil industry and its application to many industrial processes, such as oil crackling, Fischer-Tropsch synthesis, and retorting of oil shale.

589. ———. Gasification Processes Compared. Vol. 9, 1947, p. 319; Rev. Gen. Gaz., vol. 69, No. 2, p. 44, 8 pp.

Summarizes information published in Germany in 1942 by Koppers concerning the complete gasification of lignite dust, coke fines, and the like. Particular attention is drawn to heat balances and cost data, and comparisons are made between the Koppers process and conventional carbonization of coal in a coking plant followed by gasification of coke in gas producers. Heat balances are shown—one for the gasification of powdered lignite using O_2, for the production of synthesis gas, and the other without O_2. The gasification efficiency for each, respectively, is 86.9% and 74.5%. These figures compare with 68.8% for synthesis gas made by gasification of pulverized coal, details of which are given in the original article. Cost comparisons indicate that the conventional method is about 10% cheaper than the Koppers method in the manufacture of fuel gas; and when reduced to standard coking coal, the fuel consumption of the Koppers process per unit volume of synthesis gas is substantially higher than that of the conventional 2-stage process. Allowing for the indirect fuel consumption in the manufacture of O_2, the efficiency of the Koppers process is said to fall below 50%.

590. ———. Iron Catalyst in the Fischer-Tropsch Synthesis. Vol. 9, 1947, pp. 125–127, 165–167.

Review of experiments carried out in Germany on the use of Fe catalyst in place of Co. The information was obtained mainly from papers already reviewed; such as BIOS Report 447, PB 77,705, CIOS Report XXXI–23, PB 12,624, and FIAT Reports 276, PB 1,291 and 426, PB 7,745. Developments sponsored by each of the following are presented: Kaiser Wilhelm Institute, Lurgi Gesellschaft, Braunkohle-Benzin A.–G., I. S. Farbenindustrie A.–G. (particularly the work of Michael on suspended catalyst, gas recycle, and catalyst for tubular reactors), Ruhrchemie, and Rheinpreussen.

591. ———. Linde-Fränkl Process for Oxygen Separation. Vol. 9, 1947, pp. 236–240.

Theory of air liquefaction is discussed and practical operating results are shown. A list of 73 units built between 1930 and 1941 is given. The working of the process is explained in some detail, and power requirements are calculated. Installation costs for early-war German conditions are given as RM 500,000/1,000 $m.^3$ of O_2/hour (English conversion rate RM 10 to 1 pound). Operating costs were divided for production up to 2,000 $m.^3$/hr. into power 40%, amortization and 5%, interest 40%, and labor and material costs 20%. Above 2,000 $m.^3$/hour the division was 50%, 40%, and 10%. In the plants with an hourly capacity of 1,000–2,000 $m.^3$ of O_2, the total cost of the gas was calculated to be 2.2–2.5 Rpfg./$m.^3$ at 0° and 760 mm.; in a 3,000-$m.^3$ plant the cost should fall to 1.5 Rpfg./$m.^3$ A fair average cost figure/$m.^3$ of 98% O_2 with power at 1.5 Rpfg./kw.-hr. would be 2.5 Rpfg. Converted into English equivalents, 98% O_2 would cost 17 d./1,000 cu. ft. with power at 0.36 d./kw.-hr.

592. ———. Manufacture of Primary Alcohols by the Oxo Process. Vol. 9, 1947, pp. 61–65.

Excellent review, with diagrams and flow sheets of the plant and operation, of the Oxo process for the manufacture of primary aliphatic alcohols from olefins and water gas. The information is adapted mainly from CIOS and BIOS reports. For the pilot plants at Holten (Ruhrchemie) and Leuna (I. G. Farbenindustrie, A.-G.) the cost of production of the alcohols was about RM. 0.90–0.95/kg. and the sales price RM. 2.5/kg. For large-scale production (12,000 tons batch process/year) the capital and operating costs were estimated at RM. 78/100 kg. of alcohol; for full-scale continuous operation RM. 60/100 kg. The potentialities of the process are briefly discussed from the viewpoint of products, and methods for increasing the production of olefins by medium-pressure, gas-recycle, and liquid-phase, fluid-catalyst are mentioned.

593. ———. Production of Hydrogen-Carbon Monoxide Synthesis Gas From Coke-Oven Gas. Vol. 9, 1947, pp. 346–349.

Review mainly of information obtained from CIOS Reports XXV–7, PB 286, XXXIII–30, PB 28,745, XXVII–55, PB 368, and FIAT 513, PB 67,564. Describes processes employed by Hibernia, Klöcknerwerke and I. G. Hoechst.

594. ———. Synthesis of Higher Alcohols. Vol. 9, 1947, pp. 273–277.

Digest of the information found in CIOS reports XXX–103, PB 23,750, XXXII–96, PB 1,366, and XXXII–107, PB 6,650. It discusses the production of alcohols up to C_9 by the I. G. Farbenindustrie, the process of the Ruhrchemie A.-G. for alcohols above C_3 and, in particular, the Synol process of the I. G. Farbenindustrie. This process involves the reaction of a gas CO : H_2=1 : 0.7–0.8 at 18–25 atm. and 180°–200° over a sintered Fe catalyst. The liquid products are mainly alcohols and hydrocarbons, the former being entirely straight-chain compounds; alcohols up to C_{20} were made successfully. The process was never operated on a full scale.

595. ———. Practical Advances in the Production of Liquid Fuels From Coal. Vol. 12, January 1950, pp. 9–17.

Account, with diagrams, of coal-to-oil demonstration plant at Louisiana, Mo.

596. Coke and Smokeless-Fuel Age. Diesel Fuels From Coal. Vol. 2, 1940, pp. 70–71; Ztschr. Ver. deut. Ing., vol. 83, No. 47, 1939, pp. 1240–1241.

Synthetic hydrocarbons of the Kogasin type, made by the Fischer-Tropsch process, have a cetene number of 120, and when about 38% is mixed with tar oil of 20 cetene number, a diesel fuel of 60 cetene number is obtained, which is equal in ignition qualities to commercial diesel oil of petroleum origin. Blended fuels must, however, be examined critically as regards miscibility, separation in storage, corrosive action, and coking qualities. Attempts to increase the ignitability of coal-tar oils by additions of ethyl nitrate and organic peroxides appear to have been abandoned for reasons of cost. H. Kölbel claims to have developed stable diesel fuels from coal-tar oil and Kogasin, utilizing the selective solvent action of the latter to remove constituents liable to cause coking. The process is said to be applicable also to low-temperature tar oils. The latter have inherently higher cetene numbers. Data relating to a 45–55 Kogasin-coal tar-oil mixture show this to have properties better than those of an unnamed petroleum fuel. An illustration compares a mixture of this type with a commercial gas oil as regards: (a) Fuel consumption in gm./metric hp.-hr. (100 gm./metric hp.–hr.=0.22 lb./hp.–hr.) in a 30- to 35-hp., 1,450-r. p. m., 4-cylinder engine; (b) exhaust temperatures; and (c) CO content of exhaust gases. The low CO content of the exhaust gases from the mixed fuel is specially interesting as it indicates the suitability of this fuel for use underground, in mine locomotives and the like.

597. ———. Turbocompressors for Hydrogenation Plant. Vol. 2, 1940, p. 120; Génie civil, vol. 116, 1940, pp. 32–34.

Turbocompressors are lighter and more compact than reciprocating compressors for high pressures of the order of 200 atm. and offer the further advantage that the gas compressed does not come into contact with lubricating oil. The author discusses gas flow in labyrinth packings and methods of reducing the losses involved. The formation of eddies in the labyrinth and the magnitude of the leakage, with different sizes of chamber between the constrictions, were investigated by hydraulic experiments on a large-scale model.

598. ———. Carbonization Research. Chemical Development. Vol. 5, 1943, pp. 151–153, 157.

Comments on an address by J. T. King before the Midland Association of Gas Engineers. The chemical development of coal utilization is likely to be based on the Fischer-Tropsch process. Gases containing CO and H_2, preferably in the ratio of 1 : 2, are purified from S to less than 0.1 grain per 100 cu. ft., and passed over a Co catalyst at temperatures between 175°–220° C. either at normal pressure or at 5–10 atm. Approximately 120 gm. of liquid product has been obtained per $m.^3$ gas treated at atmospheric pressure or 150 gm. at 10 atm. Yields are as follows, in percent by weight:

	Normal pressure	*Medium pressure*
CH_4	18	11
C_3+C_4 hydrocarbons	11	7
Oil below 200° C	43	21
200°–320° C	20	28
Wax	8	33

599. ———. Reformation of Gas. Vol. 5, 1943, pp. 111–113.

Various processes (cracking in the water-gas machine, Linde's Eismachinen, Kuhlmann, Koppers, I. G., and Kohlentechnik) are described for the reformation of gas from coke ovens and low-temperature carbonization plants into synthesis and town gas.

600. ———. Survey of German Low-Temperature Carbonization Technique. Vol. 5, 1943, pp. 68–72, 78, 84–88.

Although Germany had achieved considerable success in the low-temperature carbonization of brown coal, chiefly for the sake of the tar produced, the treatment of hard coal had been an economic failure until the development of the Fischer-Tropsch process. Hard-coal semicoke is used in quantity to make synthesis gas for the Fischer-Tropsch process, as it gives a smaller content of inerts and a better CO : H_2 ratio. The desired ratio can even be obtained by the gasification of some specially reactive semicokes. It is stated that the combination of low-temperature carbonization and the Fischer-Tropsch synthesis gives a 20–30% increase in the total yield of liquid fuels as compared with the more usual combination of high-temperature carbonization with the synthesis.

601. ———. Syntheses From Carbon Monoxide and Hydrogen. Vol. 5, 1943, pp. 208–210, 215.

Survey of recent discoveries and historical sketch. Digest and translation of a paper by F. Fischer (abs. **972**).

602. ———. German Low-Temperature Carbonization. Vol. 8, 1946, pp. 77–79.

Technical details are given of the larger installations that were operated during the war in conjunction with synthetic-oil plants. Specially described are the plant of the Krupp Treibstoffwerke at Wanne-Eickel, operated in conjunction with a Fischer-Tropsch plant, the Lurgi Spülgas plants of the A.-G. Sächsische Werke at Böhlen, and Espenhain, and the Deutsche Erdöl A.-G. plant at Regis, all carbonizing brown coal chiefly to produce tar for the Bergius hydrogenation.

603. ———. Lurgi Process. Vol. 8, 1946, pp. 49–50, 54.

Latest information about the Lurgi complete-gasification plant at Böhlen, Germany, reports a plant of 10 units, with a capacity of about 20,000,000 cu. ft. of gas per day. The complete plant cost 10,720,000 RM; the Linde-Fränkl O_2 plant 3,600,000 RM. Information is given on the modern type machinery and its operation, the gas-purifying plant, and an analysis of the fuel used. The consumption of materials per 1,000 cu. ft. of gas is: O_2 145 cu. ft., steam 90 lb., coal 90 lb.; electricity 6–7 kw.-hr.; there 0.77 lb. of tar and 0.33 lb. of light oil are produced per 100 cu. ft. of gas. Oper-

ating costs are as follows: coal 6.50 RM per ton; water 6 pf. per $m.^3$; power 1.1 pf. per kw.-hr.; labor and maintenance each 0.4 pf. per $m.^3$ of gas; oxygen 2.2 pf. per $m.^3$ The total cost of the gas was 3.8 pf. per $m.^3$ less a credit of 1.4 pf. per $m.^3$, or a net cost of 2.4 pf. per $m.^3$ or 10.9 d. per 1,000 cu. ft.

604. ———. Pintsch-Hillebrand Gasification Process. Vol. 8, 1946, pp. 218–220.

Pintsch-Hillebrand process is based on the use of heated circulating gas to supply the necessary heat for the reaction. Two plants are known: One at Hamburg gasifying brown-coal briquets and the other at the Wesseling hydrogenation plant of the Union rheinische Braunkohlen-Kraftstoff, which consists of 11 units, each of 5,500 $m.^3$ per hr. capacity, and uses brown-coal briquets with a pregasification shaft to drive off the tar. The construction and operation of the plant are illustrated and described, and operating results are tabulated. Since the plant was gravity operated, a very uniform fuel was necessary for efficient operation. The briquets were suitable if they had a specific gravity of 1.23, a moisture content of 13.5–14%, a strength of 140–180 kg. per $cm.^2$ (2,000–2,500 p. s. i.), and an ash-softening point of not less than 1,290°–1,300°. The gas produced was suitable for synthesis gas, having a CO: H_2 ratio of about 1 : 2.

605. ———. Thyssen-Galocsy Complete Gasification Process. Vol. 8, 1946, pp. 106–107.

Operating results of a 40-ton-per-day plant erected during the war at Wanne-Eickel. Due to the intermittent supply of O_2, continuous operation for more than a few days was not possible, therefore results are not conclusive.

606. ———. Winkler Gasification Process. Vol. 8, 1946, pp. 155–158.

Winkler continuous gasification process, which uses a steam and O_2 mixture as the blast, is described, and its performance in various German plants is discussed. The great economic advantage of the process is its ability to gasify low-grade, cheap fuels. In fact this is its only compensatory feature for its relatively poor thermal efficiency and the inconvenience and cost of using O_2. The capital cost of a Winkler plant is about the same as that of a complete water-gas plant of normal type.

607. Colburn, A. P., Drew, T. B., and Worthington, H. Heat Transfer in a 3 : 1 Hydrogen–Nitrogen Mixture at High Pressures. Ind. Eng. Chem., vol. 39, 1947, pp. 958–964.

Experiments were conducted for flow inside a 5-ft. length of ⅝-in.-inside diameter steel tubing heated by steam, at gas pressures of 30–900 atm. The Reynolds numbers extend from 40,000 to the unusually high value of 440,000. The results are in good agreement with the usual relations for heat transfer. In the correlations the effects of pressure on the relevant properties of the mixture are taken into account. Methods of estimating these effects, which were not pronounced over the pressure range studied, are presented. Concurrence of the data with those for better known gases is shown by inclusion of experimental data for air at 5–8 atm. and at Reynolds numbers from 9,000–50,000.

Cole, W. A. *See* abs. **178a.**

608. Colliery Engineering. Gasifying Run-of-Mine Coal. Vol. 20, 1943, pp. 237–238, 243.

Describes the Wintershall-Schmalfeldt gasification process in which synthesis gas is made from raw brown coal.

609. ———. Wintershall-Schmalfeldt Water-Gas Process. Vol. 23, March 1946, pp. 69–70, 72.

Description with diagram of the water-gas plant producing synthesis gas for the synthetic-oil works at Lützkendorf. Raw brown coal is used containing 50–54% moisture. The plant comprises 4 gasifier units, each with a pair of generators and 5 producers. The output of synthesis gas under the best operating conditions is 1.07 million cu. ft. per hr. for each gasifier unit. Operation may be with or without O_2; the usual synthesis-gas composition when using O_2 is CO, 25%; H_2, 50%; CO_2, 18%; CH_4, 3.5%; N_2, 3.5%: Without O_2, the composition is 28%, 56%, 10%, 3%, and 3%, respectively. Gives some detailed operating results.

610. Colliery Guardian. The Situation in Germany. Vol. 151, 1935, p. 861.

Capital cost of a Fischer plant is estimated at RM. 5,400 per metric ton of gasoline produced per day compared to RM. 4,000 for the I. G. coal-hydrogenation plant. Depreciation on the Fischer plant will, however, be less. The Fischer process will consume 7 tons of coke per ton of gasoline compared with 4 tons of coal for the coal-hydrogenation process.

611. ———. Production of Oils From Coke-Oven Gas—Report of Utilisation of Coal Committee. Vol. 153, 1936, pp. 380–381; Inst. Min. Eng., Mem. 19, August 1936, p. 2.

Outline of the Fischer-Tropsch process, with special reference to the modification by Fischer, Pichler, and Kölbel, whereby a suitable synthesis gas is produced by blowing a water-gas generator with a mixture of steam and coke-oven gas. For example, if 10 cu. ft. of coke-oven gas were used for every pound of steam, the resulting gas would have a composition % by volume: H_2, 60; CO, 30; N_2 and other gases, 10. For each 1,000 cu. ft. of this gas, 330 cu. ft. of coke-oven gas and 18 lb. of steam were used.

612. ———. Developments in South Africa. Vol. 156, 1938, p. 329.

Local rights in the Fischer-Tropsch process have been granted to the South African Torbanite Mining & Refining Co.

613. ———. Fischer-Tropsch Process. Production of Coal Spirit and Its Improvement by Cracking. Vol. 156, 1938, pp. 483–484.

In this process a mixture of CO and H_2 in the ratio of 1 : 2 by volume is used. Ordinary water gas, produced by passing steam over coke, seems to be the most economical source of synthesis gas. To make up the deficiency of H_2 in water gas, the producer operation is modified by operating at a low temperature or by treating the water gas with steam. The synthesis gas is treated in a 2-stage purification plant for the removal of S. The 1st stage is the usual gas-works practice at normal temperatures, and the 2d stage is the removal of organic S at elevated temperatures. Purified gas must contain less than 0.2 gm. of S per 100 $m.^3$ The catalyst is a Co salt distributed on a kieselguhr foundation. The reaction takes place in 2 stages, and the temperature and pressure must be carefully controlled. The heat released by the strongly exothermic reaction is immediately removed by the production of steam at constant temperature and pressure. The gas leaving the condensing equipment passes through an activated C absorption plant for recovering volatile oils. The theoretical yield figure is approximately 170 gm, of hydrocarbons per $m.^3$ of synthesis gas. 2 years ago the yield stood at 100–150 gm. per $m.^3$, but this has been increased and is now stated to have reached the figure of 120–130 gm per $m.^3$ Part of the product must be cracked in order to reduce the knocking properties of the fuel.

614. ———. Fischer Process, France. Vol. 159, 1939, p. 170.

Report presented by the Société des produits chimiques Courrières-Kuhlmann, a subsidiary of the Mines de Courrières and établissements Kuhlmann, mentions that in 1938 the plant for the production of

synthetic fuel contributed for the first time to the profits. The plant uses the Fischer-Tropsch process and the regular output is 30 tons of synthetic petroleum for every working day. The capacity may enable a doubled production. This installation is the only one in France that was installed and that is run without any financial assistance from the State, and the production proves beneficial. It is protected by the almost prohibitive duties imposed on all imported petroleum.

615. ———. Motor Fuels. Vol. 159, 1939, p. 727.

Australian Commonwealth Standing Committee on Liquid Fuels reports that the Government should exhaust the possibilities of accumulating large quantities of gasoline in storage and the production of other substitute fuels before embarking on the establishment of either hydrogenation or synthesis plants. The cost of producing gasoline by hydrogenation or synthesis from either bituminous or brown coal would be about 1 s. 4 d. per gal. A synthesis plant of 18,000,000 gal. per yr. capacity would cost pounds 5,000,000 and a hydrogenation unit of 45,000,000 gal. per yr. capacity pounds 12,000,000. It is estimated that the cost to the consumer of synthetic gasoline from Victorian brown coal would be 2 s. 1 d. per gal.

616. ———. Oil From Australian Brown Coal. Vol. 158, 1939, pp. 88–89; British Coal Utilisation and Research Assoc., Monthly Bull., vol. 3, No. 1, Abs. 3042.

In a report to the Victorian Government regarding the production of oil from brown-coal deposits, it is stated that the cost would be about 1 s. per gal. The cost of the plant would be about pounds 4,000,000 based on a 60,000-ton unit. It is thought that the costs could be reduced considerably if the oil is produced in conjunction with the existing electricity and briquet works. The scheme, which has been prepared by German experts, embodies many improvements enabling the proposition to be placed on a commercial basis to suit Victorian conditions, and the cost of production is much lower than any previously published figures. The report covers both the Fischer process, which is highly mechanized and involves low labor costs, and coal hydrogenation, which is at present producing greater quantities of oil.

617. ———. Production of Oil From Coal by the Fischer-Tropsch Process. Vol. 158, 1939, pp. 865–868.

Reviews history of Fischer-Tropsch process and discusses temperature control, catalysts, and fuels used in the production of the synthesis gas. It is possible to produce synthesis gas immediately from coke-oven gas by suitable treatment in a cracking plant. At the same time, the heating of coke ovens by low-grade gas is promoted, the coke-oven gas being used for the production of motor fuel while the CO_2 necessary for the conversion of the coke-oven gas can be produced from the waste gases of a coke-oven battery heated by blast-furnace gas, as this waste gas is free from S compounds because the blast-furnace is free from S. The coke-oven gas is freed from H_2S before its conversion, and the finished synthesis gas, therefore, only needs to be freed from organic S compounds. Alternatively, coke-oven gas can be transformed in a cracking plant with water gas, the latter being produced in a water-gas plant by the gasification of coke with O_2 and steam continuously. The Fischer-Tropsch process has been operated recently at pressures around 10 atm. In this way, the yield has been increased about 25–30%, mainly owing to an increase in the paraffin yield. This operation is now known as "medium-pressure synthesis," and the gas and contact material used are exactly the same as those used for normal-pressure synthesis. Below a pressure of 20 atm. there is no appreciable formation of oxygenated compounds such as fatty acids. With the medium-pressure synthesis, the catalyst has a considerably longer life than with the normal pressure operation, in fact as much as 7 times as long. The products obtained by this new method are not used directly either as motor or Diesel fuels but are cracked or polymerized by well known and existing methods. The condensible hydrocarbons consist mainly of propane-butane mixtures and are similar in composition to the Calor gas sold in this country for country-house lighting and heating. The octane number of the Fischer-Tropsch motor spirit is similar to that of straight petrol, as would be expected from the similarity in composition. The olefins from the Fischer-Tropsch process produce lubricants of a very high grade. They are adjustable to such an extent that lubricating oils suitable for any purpose whatever can be produced synthetically.

618. ———. Robinson-Bindley Process. Vol. 159, 1939, p. 203; Chem. Trade Jour., vol. 104, 1939, p. 200.

Synthetic Oils, Ltd., has issued a report on a test run of the company plant at Bedlay for producing hydrocarbon oils from blue water gas. The test substantiates the results obtained by the company's technicians in a pilot plant at the research station at Epsom. According to the report, the yield of oils during the trial was equivalent to 0.8501 gal. for every 1,000 cu. ft. of gas put through the plant, but a new method has just been devised that should bring the yield up to more than 1 gal. per 1,000 cu. ft. of gas throughput. It appears from the report that several programs of treatment of crude oils can be employed, which would mean that the products could, to some extent, be varied so as to meet current market conditions. The amounts of motor spirit, diesel, and other oils that can be produced from the crude oil are somewhat similar to those obtained from natural petroleum, but the quality of some of the oils is much better. One program of treatment mentioned in the report shows that nearly 50% of the total crude products can be converted into motor spirit and 40% into diesel oil, and by another program, nearly 40% of motor spirit and more than 40% of very high-class kerosine can be obtained. The motor spirit contains only 0.09% S, which is well within the Air Ministry's requirements. Moreover, the actual and potential gum is less than half that stipulated in the Air Ministry's specification for aviation fuels. The motor spirit, after certain normal and well established treatment, compares most favorably with No. 1 grade motor spirits. The diesel oil and kerosine are said to be vastly superior to any such oils on the market. Lubricating and transformer oils can be obtained also from the synthetic crude oil. It was found after the trial that the activity of the catalyst had not been impaired.

619. ———. German Fischer-Tropsch and Allied Processes. Vol. 172, 1946, p. 589.

Brief review of information digested from the CIOS reports on process development in the Fischer-Tropsch synthesis. The Lurgi Gesellschaft had been given all rights for the construction of future plants, and their research staff had developed and patented the recirculation of synthesis gas, pressure gasification, and the use of Fe catalysts. The advantages are stated to be: higher gas velocity and easier heat control; no hydrogenation of olefins to paraffins; and suppression of cracking by the high CO : H_2 ratio, giving less CH_4 and less C.

619a. COLTEN, O. A., AND JONNARD, A. Aliphatic Chemicals. Advances Chem. Ser. 5, 1951, pp. 287–298; Chem. Abs., vol. 45, 1951, p. 10,560.

Developments of the past 25 yr. are reviewed. Among the more recent developments are the direct oxidation of hydrocarbons to produce aldehydes, acids and alcohols; partial combustion of CH_4 to produce C_2H_2; and

the Fischer-Tropsch and Oxo synthesis to yield oxygenated chemicals.

COMAFORD, D. J. *See* abs. **1195.**

620. COMBUSTION. Fischer-Tropsch Process in United States. Vol. 14, No. 2, 1942, p. 44.

New research has been authorized by Congress. This process has certain advantages over the Bergius process. The output of the latter is a liquid that requires further refining, whereas the Fischer-Tropsch process yields a number of separated fuel and lubricant products directly. It also requires less precision machinery and is economically practicable in smaller units, about 30,000 tons annually compared with 150,000 tons for the Bergius process. Both processes yield about 1 ton or between 250–300 gal. of liquid products from 4–5 tons of coal.

621. COMPAGNIE GÉNÉRALE CONSTRUCTION FOURS. [Experimental Station for Production of Town Gas and of Synthesis Gas From Lignites of Faveau Basin.] Cahier 81; Fuel Abs., vol. 5, abs. 4703, 1949.

This plant at Digoin consists of 1 full-scale unit of Woodall-Duckham continuous vertical retorts. The lignite contains 8.5–9% moisture, 14.4% ash, 46% volatiles, and 54% fixed C on the dry ash-free basis. When making synthesis gas the central-gas offtake was used. The production of town gas was 350 $m.^3$/long ton or 12,560 cu. ft./ton at 4,000 calories or 420 B. t. u./cu. ft. The production of Syngaz was 1,030 $m.^3$ or 36,950 cu. ft./ton at 2,900 calories or 300 B. t. u./cu. ft. The Syngaz was required to have a ratio CO : H_2=2 : 1 and as little CH_4 as possible. The composition of town gas was: CO, 25.7%; H_2, 39.4%; and CH_4, 16.3%. The composition of Syngaz was: CO, 27.0%; H_2, 54.2%; and CH_4, 3.2%. This satisfactory result is attributed to the central offtake giving maximum cracking of CH_4 and an increase in steaming from 8 to 32%.

622. CONCANNON, C. C., AND SWIFT, A. H. World Chemical Developments in 1937. U. S. Department of Commerce, Bureau of Foreign and Domestic Commerce, Trade Promotion Series 177, 1938, pp. 52–53.

In 1937, Germany was able to supply over one-half of its requirements of light motor fuel from domestic sources. 3 large new synthetic-gasoline plants were brought into production, and 10 smaller ones were constructed. The 1st large-scale commercial plant for producing synthetic fatty acid by the oxidation of paraffin hydrocarbons began operations in the latter part of 1937 with a capacity of 20,000 metric tons/yr.; 2 additional plants of like capacity are under construction. When in full operation these 3 plants will supply 25% of the soap industry's requirements of fatty acid, estimated at 250,000 tons.

623. CONWAY, J. J. Equipment for Low-Cost Oxygen Production. Petroleum Meeting, Am. Soc. Mech. Eng., Tulsa, Oct. 7, 1946; Petrol. Processing, vol. 2, 1947, pp. 113–114; Petrol. Refiner, vol. 26, No. 6, 1947, pp. 557–561.

Process developed by Hydrocarbon Research, Inc., for production of O_2 and the 2,000 ton/day plant now under construction as part of the synthetic fuel installation of Carthage Hydrocol at Brownsville, Tex., are described. The plant will provide 48,000,000 cu. ft. of 95% purity O_2/day at a cost of $0.05/1,000 cu. ft., including amortization in 15 yr., maintenance at 2% of the capital investment, and operating labor at $2.00/hr., but excluding power and water costs as these are both by-products of the process. O_2 is separated from the air by new developments that treat the air as a binary mixture of N_2 and O_2, removing the latter by fractionation. The operations involved consist essentially of compression, heat exchange, refrigeration, and fractionation, as shown by a flowsheet. An estimate of the proportional effect of certain major cost items on the cost of manufactured O_2 is indicated. It is seen that a power cost of $0.05/kw.-hr. accounts for about 65% of the cost of O_2. The advent of cheap O_2 opens up possibilities for its large-scale use in 6 fields: Partial oxidation of hydrocarbon gases; gasification of coal; heavy chemical industries; iron and steel manufacture; nonferrous metal industry; and mining.

CONWAY, M. J. *See* abs. **1619.**

624. COOK, G. A. Possibilities of Power Alcohol and Certain Other Fuels in Australia. Australia Council Sci. Ind. Research, Bull. 33, 1927, pp. 7–106; Chem. Abs., vol. 22, 1928, p. 492.

Possibilities are discussed of manufacturing EtOH in Australia from cellulosic materials: Sawdust, wood, sulfite waste liquors, and straw husks. Describes the known processes of making EtOH from C_2H_4 and C_2H_2, MeOH from CO+H_2 and the Synthol and Synthin of F. Fischer.

625. COOPERMAN, J., DAVIS, J. D., SEYMOUR, W., AND RUCKES, W. L. Lurgi Process for Complete Gasification of Coals With Steam and Oxygen Under Pressure. Bureau of Mines Bull. 498, 1951, 38 pp.

An investigation was made, in an apparatus closely simulating that used in industrial-scale operation, to determine the proper fuels and operating conditions to be used in carrying out the Lurgi process of gasification. It was found that caking coals cannot be gasified, but noncaking fuels, such as anthracite and low- and high-temperature cokes can be completely gasified in a Lurgi apparatus with the production of a CO_2-free fuel gas of about 410 B. t. u./cu. ft. heating value. Low-temperature coke or char can be made from bituminous coals in various ways, particularly in batches in a rotating retort. By passing the Lurgi gas, properly purified from S, over a Ni methanization catalyst, a synthesis gas of about 950 B. t. u./cu. ft. was obtained after scrubbing out the CO_2. The catalyst was the British Gas Research Board type made by precipitating 100 parts by weight of $Ni(NO_3)_2$, 20 $Mn(NO_3)_2$, 13.6 $Al(NO_3)_3$, 25 china clay with 97 K_2CO_3 and reducing for 2 hr with H_2 at 400° and 300 p. s. i. Diagram and flow sheet of the apparatus are shown.

COQUELLE, O. *See* abs. **189.**

626. CORCORAN, W. H., ROUDEBUSH, B., AND SAGE, B. H. Temperature Gradients in Turbulent Gas Streams. Preliminary Studies. Chem. Eng. Progress, vol. 43, 1947, pp. 135–142.

Equipment is described that permits measurement of the temperature and velocity distribution in an air stream with essentially 2-dimensional flow characteristics. Preliminary results, including data describing the temperature and velocity distribution, heat transfer from the wall, and shearing stress, are submitted for 7 different sets of conditions. The data indicate that, within the accuracy of measurement, the eddy viscosity and eddy conductivity are equal, as was assumed by von Karman in his analogy between the transfer of momentum and the thermal transfer of energy. The over-all heat-transfer rate predicted by the Karman analogy agrees with the experimental results in the case of a symmetrical temperature distribution. However, significant divergences from the heat-transfer rates predicted by the analogy were experienced in the case of nonsymmetric temperature distributions. The results presented are of a preliminary nature and not of sufficient extent to permit the experimental uncertainty to be established definitely. The detailed study of temperature and velocity distribution together with the associated heat transfer and shearing stress permits a microscopic evaluation of the thermal transfer of energy through a turbulently flowing air stream. The methods employed appear to be capable of refinement, and further study of thermal transfers of energy by these and related methods should permit ultimately

the more accurate prediction of the rate of thermal transfers of energy for situations where the transfers of momentum can be predicted from the science of fluid mechanics.

CORDINER, J. B. *See* abs. **3305a, 3306.**

COREY, R. C. *See* abs. **810a, 2615.**

627. CORNUAULT, P. [Adsorbed Phase on Catalysts.] Jour, chim. phys., vol. 47, 1950, pp. 157–164; Chem. Abs., vol. 44, 1950, p. 8213.

Kinetics of desorption of H_2, CO, CO_2, and CH_4 from a Ni–Al–Mn–kieselguhr Fischer-Tropsch catalyst reduced in H_2 at 475° was measured on a sample (I) sealed off at 450° immediately after reduction, on one (II) cooled from 475° to 175° and maintained 4 hr. in H_2 at this temperature, and on one (III) kept 113 hr. in H_2 at 175°. Evolution of gas from (II) with increase of temperature is very similar to that from (III). The energy of activation of desorption up to 200° is about 19 kcal. On both samples (II) and (I), the energy of activation of desorption is about 29 kcal. at 450° Evolved gas contained 73–100% H_2; the other components were small amounts of CO_2, CO, and CH_4 coming from undecomposed carbonates of the original catalyst. Composition of the gas evolved at each temperature is given for all samples.

CORRELLI, R. *See* abs. **1135.**

CORRIGAN, T. E. *See* abs. **144a.**

628. CORSON, B. B. Industrial Catalysis. Jour. Chem. Education, vol. 24, 1947, pp. 150–155.

Nontechnical account of synthesis of gasoline and MeOH by the Fischer-Tropsch reaction.

629. COTTON, E. Germany's Fischer-Tropsch Process. Summary of Latest Developments and Operating Procedures. Nat, Petrol. News, vol. 38, No. 23, 1946, pp. R425–426, 428, 430, 432–434; Chem. Abs., vol. 42, 1948, p. 9112; PB 12,613, 1946, 16 pp.

Summary of the investigations by United States Technical Oil Mission. Discusses the commercial methods of preparing and purifying synthesis gas by the water-gas process and the CH_4–O_2 process; the preparation of the standard Co catalyst (100Co–5ThO_2–8MgO–180–200 kieselguhr) by precipitation from the nitrates and its reduction in a stream of gas (75H_2–25N_2) at 460° and a space velocity of 8,800 for 40–60 min.; the type of reactors employed for both the normal and medium-pressure processes; and the actual synthesis procedure and the products obtained. Also included is some information on the gas recycle operation and some details of the development of the Fe catalyst. The latter is made by pasting Fe powder prepared by thermal decomposition of Fe carbonyl with 1% of borax and forming into approximately 1-cm. cubes, which are sintered and reduced with H_2 at 800°–850° for 4 hr. An interesting development in the use of the Fe catalyst is the hot-gas recycle process in which gas is circulated over the catalyst and through a cooler at such a rate that the temperature rise in the catalyst bed is limited to a maximum of 10°. The reaction is carried out at a pressure of 300 p. s. i. with a gas-recycle ratio of 100 vol. of recycle to 1 vol. of fresh feed; contact time in the catalyst bed is approximately 0.5–1 sec./pass, with a gas velocity of about 1 m./sec. Another interesting development in the use of the Fe catalyst is the fixed-bed, oil-circulation process by which the heat of reaction is removed by circulating a product cut of fixed boiling range over the catalyst. The heat is removed by raising the temperature of the oil as well as by partial vaporization of the oil. The process operates at 20–25 atm. and 250°–300° in the first stage and 280°–330° in the second stage. Synthesis gas with a ratio of CO : H_2=55 : 45 is used. The throughput is controlled to yield 20–25 gm. of total product/l. of catalyst/hr. The catalyst is the same as that used in the hot-gas recycle process.

COUDRAY, R. *See* abs. **2720, 2721.**

COUFALIK, F. *See* abs. **3187.**

630. COURTY, C. [Study of Adsorption Phenomena by Means of a Weak Magnetic Field.] Proc. Pure Applied Chem. Internat. Cong. (London), vol. 11, 1947, pp. 397–409 (in French); Chem. Abs., vol. 44, 1950, p. 5166.

Review with 40 refs.

631. ———. [Magnetic Measurements Applied to Adsorption.] Compt. rend., vol. 230, 1950, pp. 745–747; Chem. Abs., vol. 44, 1950, p. 5661.

Adsorption of H_2O and air on activated charcoal was studied by measuring the magnetic susceptibility of the adsorbent containing air and H_2O. The value for pure H_2O, -0.72×10^{-6}, was found constant for adsorbed H_2O also. The value for air, $+24.16\times10^{-6}$, decreased slowly to $+14.94\times10^{-6}$ at 20°.

632. ———. [On the Evolution of the Magnetic Properties of Oxygen Adsorbed on Activated Charcoal Which Has been Activated in a Vacuum at Elevated Temperatures.] Compt. rend., vol. 230, 1950, pp. 1588–1589; Chem. Abs., vol. 44, 1950, p. 10, 403.

The coefficient of magnetization was calculated for O_2 adsorbed on charcoal activated in a vacuum and at elevated temperatures. This same measurement had been previously carried out on charcoal activated in a vacuum in the cold. In this experiment the charcoal was activated in a vacuum of 0.02 mm. for 6 hr. at 900°. When this charcoal was put into contact with O_2, the adsorption was accompanied by the release of a great amount of heat, 5.6 cal. This was attributed to the formation of CO_2. It was found that the decrease in the paramagnetism is of the same order for C that has been activated either in the cold or at high temperatures.

COUSSEMANT, F. *See* abs. **1648.**

COWAP, M. D. *See* abs. **2304, 2305.**

COWARD, H. F. *See* abs. **292, 293, 294.**

633. COWARD, H. F., AND WILSON, S. P. Equilibrium in the System Carbon, Hydrogen, and Methane. Jour. Chem. Soc., vol. 115, 1919, pp. 1380–1387. Chem. Abs., vol. 14, 1920, p. 1521.

Synthesis of CH_4 from its elements was achieved by Bone and Jerdan (abs. **296**) and confirmed by Bone and Coward (abs. **293**); the decomposition of CH_4 into C and H_2 was demonstrated by Bone and Coward (abs. **294**). Equilibrium in the system $C + 2H_2 = CH_4$ at 1,000°–1,200° showed that the mixture contained approximately 1% of CH_4. The present experiments were carried out in the apparatus described by Bone and Coward, the gaseous products being passed several times through the heated porcelain tube until analysis indicated that equilibrium was reached. The % compositions of the equilibrium mixtures of CH_4 and H_2 were respectively: At 1,100°, 0.6 and 99.4; at 1,000°, 1.1 and 98.9; at 850°, 2.5 and 97.5. Calculation of the heat of combustion of CH_4 from the experimental values, using the integrated form of the equation $d \log K/dT = -Q/RT^2$, gives 18,000 cal., with a possible error of 2,000 cal. Equilibrium was reached both by synthesis and decomposition. The use of Ni or Pt as catalyst was advantageous at the lower temperatures, the gases showing practically constant composition after the 2d passage. A steady production of CO was noted, due to a side reaction between H_2O vapor and C.

634. CRANE, J. E. Development of the Synthetic Ammonia Industry in the United States. Ind. Eng. Chem., vol. 22, 1930, pp. 795–799; Chem. Abs., vol. 24, 1930, p. 4359.

Data are also given on the production, cost, and use of synthetic MeOH.

635. CRANGLE, J., AND SUCKSMITH, W. Magnetic Analysis of Iron–Carbon Alloys. Tempering of Martensite and Retained Austenite. Jour. Iron Steel Inst. (London), vol. 168, 1951, pp. 141–151; Chem. Abs., vol. 45, 1951, p. 6559.

Pure Fe–C alloys were austenitized and quenched to convert them to martensite. Magnetic analysis indicates that hexagonal Fe carbide is present in the 1st tempering stage (100° C.); its Curie point may be considerably lower than 380° C., and its composition may differ from Fe_2C. The 2d tempering stage (150°–200° C.) is characterized by the absence of retained austenite (which decomposes into the same products that were formed in the 1st stage) and by the appearance, above 200° C., of a small amount of cementite. The shapes of the thermomagnetic curves of specimens in the 3d stage (250°–350° C.) suggest the presence of a carbide with properties similar to Hägg carbide. To eliminate this carbide completely, the temperature must be raised above 500° C. where the only remaining carbide is cementite.

CRAWFORD, R. M. *See* abs. **2154, 2155.**

636. CRAWFORD, V. A., AND TOMPKINS, F. C. Adsorption of Gases Sulfur Dioxide, Ammonia, Carbon Dioxide, and Nitrous Oxide on Barium Fluoride Crystals. Trans. Faraday Soc., vol. 44, 1948, pp. 698–708; Chem. Abs., vol. 43, 1949, p. 2485.

Adsorption was determined between —78° and 119°, and it was reversible and complete within 5 min. of gas admission at all temperatures. The Brunauer-Emmett-Teller plots are linear except at low pressures (p), where departures were anticipated. The volume adsorbed tends to be too small at high pressure (p), in keeping with the decrease in the heat of adsorption. The latter was determined by use of the Clausius-Clapeyron and the B. E. T. equations. The decrease of heats with coverage found by experiment is compared with those expected theoretically. Variation in adsorption potential over the crystal surfaces was calculated in an approximate manner and the significance discussed from the viewpoint of the applicability of the B. E. T. multilayer theory.

637. CRAXFORD, S. R. Reactions of the Fischer-Tropsch Process. Fischer-Tropsch Synthesis of Hydrocarbons and Some Related Reactions. Trans. Faraday Soc., vol. 35, 1939, pp. 946–958, 966–967; Brennstoff-Chem., vol. 20, 1939, pp. 263–270; British Chem. Abs., 1939, B, p. 1097; Chem. Abs., vol. 33, 1939, p. 9606.

At the temperature of the Fischer synthesis (~200°) CO reacts slowly with the catalyst to form Co_2C, but this reaction is always slower than the reduction of the Co_2C by H_2 at the same temperature. With CO and H_2 the catalyst forms Co_2C+H_2O and this reaction is faster than the reduction of the carbide by H_2 under the synthesis conditions. When oils are produced by the Fischer synthesis, the *o-p*-H_2 conversion is inhibited; when CH_4 is the product of the synthesis, the *o-p*-conversion occurs freely. This shows the presence of chemisorbed H on the catalyst surface in the latter case but not in the former. The water-gas reaction runs parallel to the *o-p*-H_2 conversion. It is inhibited during oil formation as is also the hydrogenation-cracking of paraffin hydrocarbons on the catalyst. Theoretical deductions are made starting with the assumption that the first step in the synthesis is the alternate formation and reduction of Co_2C to give CH_2 groups. Subsequent presence of chemisorbed H_2 yields CH_4, while the lack of chemisorbed H_2 allows the CH_2 groups to link up to give long chains.

638. ———. Function of the Promoters in the Catalysts for the Fischer-Tropsch Synthesis. Trans. Faraday Soc., vol. 42, 1946, pp. 580–585; Chem. Abs., vol. 41, 1947, p. 262.

Determinations were made on 5 catalysts to learn which of these should be the most effective catalyst for the Fischer-Tropsch synthesis. The 5 catalysts were: (1) Co; (2) Co–ThO_2 100 : 18; (3) Co–kieselguhr 1 : 1; (4) Co–ThO_2–kieselguhr 100 : 18 : 100; (5) Co–ThO_2–kieselguhr 100 : 21 : 100. They were all prepared from solutions of the nitrates of Co and Th, with addition of kieselguhr, by precipitation with K_2CO_3 and reduction by H_2 at 375°. Both the initial fast and the final slow rate of carbide formation by the reaction $2CO+2Co=Co_2C+CO_2$ was promoted most effectively by (2) followed by (4) and (5), the latter much more slowly than (4). ThO_2 and kieselguhr are found to be strong promoters for the reduction of Co_2C by H_2. Of all the catalysts used, with the exception of (1), (4) gave by far the slowest rate of reduction of the carbide and, thus, has both a relatively slow rate of carbide reduction and a relatively fast rate of carbide formation, confirming the previously expressed view about the mechanism of the Fischer-Tropsch reaction according to which the rate of formation of carbide by the reaction $2Co+H_2+CO=Co_2C+H_2O$ must be faster than the reduction of the carbide to allow for the accumulation of surface carbide during the reaction, and the consequent exclusion of chemisorbed H_2 from the surface if oils are to be formed; (2) has a very high rate of carbide formation but is not a good Fischer-Tropsch catalyst because it shows too high a rate of carbide reduction; (5) is poor in 2 respects. Its rate of carbide formation is slow compared with the normal active Fischer-Tropsch catalyst, and its rate of carbide reduction is high.

639. ———. Mechanism of the Fischer-Tropsch Reaction. Trans. Faraday Soc., vol. 42, 1946, pp. 576–580; Chem. Abs., vol. 41, 1947, p. 262.

The theory of the Fischer-Tropsch reaction has been proposed in which hydrocarbon oils are synthesized from a suitable mixture of CO and H_2 over a Co catalyst when the Co in the catalyst surface is in the form of the carbide Co_2C, and the Co in the uncombined form gives CH_4, allows the water-gas-shift reaction to take place, and is active for the hydrogenation cracking of hydrocarbons. The formation of higher hydrocarbons must be examined in greater detail to see whether the results of the synthesis can be accounted for by the above mechanism. When synthesis gas ($CO+2H_2$) is passed over the catalyst (100 Co+6 ThO+12 MgO+200 kieselguhr) at 185°, it is found that the yield of liquid hydrocarbons and the amount of CO_2 formed, both expressed in gm. per N $m.^3$ of synthesis gas, change with change of synthesis-gas rate. The oil yield is a maximum for a rate of about 1 l. per gm. Co per hr. and falls off for higher and lower rates, and the amount of CO_2 formed is small for rates higher than the above but increases rapidly at smaller gas rates. At low gas rates oil synthesis occurs only on the front part of the catalyst bed where the Co of the catalyst is largely converted to carbide and there is little chemisorbed H_2. The rest of the catalyst bed, where oil synthesis is not taking place actively, is relatively free from carbide and therefore available for the water-gas-shift reaction. Further, the small amount of CO_2 produced at the maximum gas rate for oil production shows that the formation of CO_2 and the oil-forming reaction do not occur simultaneously as $2CO+2H_2=CO_2+-CH_2$ but the former is separate and occurs later. The oil-forming reaction must, therefore, be $CO+2H_2=H_2O+-CH_2$, followed, when conditions permit, by the water-gas-shift reaction. Variation in the oil yield with the synthesis gas rate is also explained very simply on this basis. At a gas rate of 1 l. per gm. Co per hr. the entire catalyst is actively synthesizing oil. At higher gas rates the oil yield decreases as the contact

time of the gas with the catalyst diminishes, and the synthesis is not completed. At lower gas rates, the synthesis is completed on the first part of the catalyst bed and the oil formed there passes over the uncarbided second portion of the bed covered by chemisorbed H_2, and is hydrogenated-cracked with formation of CH_4.

640. ———. Chemistry of the Fischer-Tropsch Synthesis. Fuel, vol. 26, No. 5, 1947, pp. 119–123; Chem. Abs., vol. 42, 1948, p. 737.

Paper read before the 11th International Congress of Pure and Applied Chemistry. The best catalyst for the Fischer-Tropsch synthesis reaction is 100 Co : 5 ThO : 8 MgO : 200 kieselguhr, in which the ThO and the MgO play only a minor role, the Co and the kieselguhr being the active components. The kieselguhr has two functions both of which are important: To insure that the reduced Co is produced and maintained in an exceedingly finely divided form; and to establish and maintain the porosity of the individual catalyst granules. It is believed that the catalyst is not a mixture of these two constituents but rather a chemical combination of the two. The fact that these Co-kieselguhr preparations are much more difficult to reduce than Co-carbonate alone is a further indication of chemical interaction and, in particular, of silicate formation. The importance of the 2d function of kieselguhr is seen in connection with the removal of the synthesis products from the catalyst and with maintaining the catalyst surfaces in a receptive state. Active catalysts do not consist of bulk metallic Co with the normal lattice but rather with layers of Co atoms having an arrangement based on the structure of Co silicate, ordinary Co carbide thus playing no part in the reaction. When CO alone reacts with the reduced catalyst, the reaction is much faster than when it reacts with Co metal. In both cases the CO is first chemisorbed on a Co atom, and the O atom is removed by reaction with a second molecule of CO, leaving a chemisorbed C atom. In the case of bulk carbide very little CO can react in this way, and the rate is then determined by the rate of diffusion of the chemisorbed C atoms into the interior of the lattice to give Co carbide. In the case of the catalyst, on the other hand, nearly all the Co atoms are available in the surface for reaction with CO so that the rate of reaction is fast, and the final result is an array of chemisorbed C atoms. If CH_4 is added to the mixture of CO and H_2, not only is the normal formation of CH_4 by the synthesis entirely suppressed, but some of the added CH_4 enters into the reaction and polymerizes with the CH_2 groups on the catalyst surface to give higher hydrocarbons. This effect has also been observed in synthesis in 2 stages; it is believed that this effect is due to formation of a polymerization-depolymerization equilibrium.

641. ———. Fischer-Tropsch Synthesis With Cobalt Catalysts. Jour. Soc. Chem. Ind., vol. 66, 1947, pp. 440–444; Chem. Abs., vol. 42, 1948, p. 3648.

Summary of more academic aspects of the research and development work carried out in Germany and elsewhere in recent years. The composition and method of preparation of the Co catalyst are described, and the influence of the activators ThO_2, MnO, and MgO on the working of the catalyst is discussed. The importance of kieselguhr as a carrier is emphasized, and the 2 functions of maintaining the Co in a finely divided form after reduction and of preserving the porosity of the individual granules are examined. The reduction of the catalyst is considered to be the most crucial step in the entire process, and the 3 factors of temperature, time, and H_2 rates must be carefully observed. Deterioration of the catalyst during synthesis at both atmospheric and medium pressure appears to be mainly the result of wax formation on the catalyst granules, and the rate of deterioration can be closely correlated with the rate of deposition of such waxes on the catalyst. It has been concluded that ordinary Co carbide plays no part in the synthesis reaction; the Co atoms appear to be isolated and do not form part of a Co lattice. Reaction by way of chemisorbed C atoms, the so-called surface carbide, however, is thought to give an array of interacting CH_2 groups on the surface, and the composition of the products, which are obtained from this array, depends on the conditions surrounding the conversion. Some recent work has even tended to emphasize the idea of a polymerization-depolymerization equilibrium.

———. *See* abs. **1326, 1334, 1335, 1336.**

642. Craxford, S. R., and Poll, A. [Reduction of Catalysts With a Cobalt and Kieselguhr Base Utilized in the Fischer-Tropsch Synthesis.] Jour. chim. phys., vol. 47, 1950, pp. 253–257; Chem. Abs., vol. 44, 1950, p. 8086.

Catalysts having the composition Co: ThO_2: MgO: kieselguhr in the ratio 100:6:12:200 were used. The most active catalyst was obtained by carrying out the reduction at 400° in pure dry H_2 at a flow rate of 6,000 vol./vol. of catalyst/hr. When H_2 saturated with H_2O vapor at room temperature was used for reduction, the surface area of the reduced portion of the catalyst was slightly greater than that observed with dry H_2, but the amount of reduction was appreciably less. The % reduction of Co oxide after treatment with dry H_2 under the above conditions was 29.8 at 300°, 53.2 at 350°, 71.2 at 400°, 81.3 at 450°, and 91.5 at 500°. A reduction temperature of 400° caused the least diminution of the surface area after vacuum treatment at 450° for 4 hr. A reduction in surface area from 229 $m.^2$/gm. of Co to 180 $m.^2$/gm. occurred when the catalyst was used in synthesis. Along with x-ray data, the diminution in surface area suggested that appreciable agglomeration of Co occurred during use of the catalyst. Catalysts were prepared in 5 different manners to investigate the role of the formation of a hydrosilicate on the reduction. Conditions favoring the formation of a hydrosilicate appreciably decreased the ease of reduction. A catalyst that was maintained at an elevated temperature under pressure in an autoclave during preparation could not be reduced with H_2 at 800°. The minimum amount of reduction in surface area occurred under conditions of catalyst preparation that did not favor formation of a hydrosilicate.

643. Craxford, S. R., and Rideal, E. K. Mechanism of the Synthesis of Hydrocarbons From Water Gas. Jour. Chem. Soc., 1939, pp. 1604–1614; British Chem. Abs., 1940, B, p. 8; Chem. Abs., vol. 34, 1940, p. 1464.

Experiments on the rates of formation and reduction of Co_2C on Co–Th–kieselguhr catalysts under various conditions indicate that the first step in the Fischer-Tropsch synthesis of hydrocarbons from CO and H_2 is the reaction of these gases with the catalyst to give Co carbide. As indicated by the *o–p*–H_2 conversion, when carbide is reduced only CH_4 is formed and no higher hydrocarbons. Reduction by H_2 leads to formation of oils. Curves are given for the rates of the reactions between Co and CO, between Co_2C and H_2 on the Fischer catalyst, for the energies of activation of the reaction Co_2C+2H_2, and for the total reaction $CO+2H_2$. It is concluded that, in order to obtain oils, the conditions of the synthesis have to be adjusted so that only very few chemisorbed H_2 atoms are present on the catalyst surface.

644. Crentz, W. L., Doherty, J. D., and Donath, E. E. Coal Preparation for Synthetic Liquid Fuels. Min. Eng., Trans. Am. Inst. Min. and Met. Eng., vol. 187, 1950, pp. 507–510.

Principal washing problems in preparing coal for the synthetic fuel industry may be stated as: (1) Ash re-

moval for the Bergius process; and (2) S removal for the Fischer-Tropsch process. A study is made of the effect of ash on oil losses during the elimination of the nonliquefiable portions of the coal in the hydrogenation process. The oil loss increases with ash content of the coal and results in increased consumption of coal, H_2, and power. Quantitatively, it is estimated that the oil loss due to ash amounts to about 9 lb. of oil for each % of ash in 1 ton of the hydrogenated coal. Cost comparison is made of the economic advantages resulting from the use of 2.3% ash coal and a 6% ash coal in a 30,000 bbl./day hydrogenation plant. In the Fischer-Tropsch process, the quantity of ash in the raw-coal feed is not as critical as in the Bergius process. The problem here is the amount of S that the synthesis gas contains. The economic advantage, however, lies with the cleaning of the coal used to make synthesis gas to a low S content if the S can be removed by mechanical cleaning. It is estimated that it costs $1.15/ton of gasified coal to remove S from synthesis gas when the coal contains 3% S. Increase in the S content of the coal from 3 to 5% would impose an additional cost of $0.37/ton.

CRITTENDEN, E. D. *See* abs. **36, 3748.**

645. CROFT, C. M. Installation of Tower Gas Purifiers. Inst. Gas Eng., Commun. and Repts., vol. 212, 1939, 18 pp.; Chem. Abs., vol. 33, 1939, p. 6563.

Thyssen-Lenze tower gas purifiers, the first of their kind in England, as installed at the Wandsworth Works, are described. The installation, capacity 10,000,000 cu. ft./day, consists of 6 towers, together with a stocking tower and stocking frame. The purifiers have worked equally well from ½ capacity to 33% overload. To date, the spent oxide has contained 44% pure S. Costs are about ½ those of the original purifiers.

645a. CROMEANS, J. S. Hydrogenation and Hydrogenolysis. Ind. Eng. Chem., vol. 44, No. 9, 1952, pp. 2025–2036.

Review of the literature and patents occurring in 1951 on the Fischer-Tropsch process and other processes involving hydrogenation. Bibliography of 323 refs.

CROSS, A. C. *See* abs. **3303.**

CROWELL, J. H. *See* abs. **2097, 3090.**

646. CROWELL, J. H., AND BENSON, H. E. Direct Evaporative Cooling in the Synthesis of Liquid Hydrocarbons From Hydrogen and Carbon Monoxide. Am. Chem. Soc., 111th Meeting Abs., 1947, p. 14 I.

Brief summaries of the German method for heat removal from the Fischer-Tropsch converter and of such developmental processes as the hot-gas recycle, the oil slurry, and the fixed-bed oil-recycle processes. The early laboratory investigations by the Bureau of Mines upon the principle of direct evaporative cooling of the fixed bed are also described. In this method oil is allowed to trickle down over the catalyst bed, and the vaporization of this oil removes the heat of the reaction. The catalyst bed in the small unit was 3 in. diameter and 12 in. length. Mechanical operation was very smooth and temperature control was quite satisfactory. Construction and operation of a larger unit of the same diameter but 8 ft. long is described in detail. Provision was made for oil injection at various points in the column along with other improvements in design. The productivity is currently about 1 gal. of primary product/day and tabulated data are given for products, yields, and operating information for space velocities varying from 100 to 300. Future plans for study and pilot-plant development are discussed.

647. CROWELL, J. H., BENSON, H. E., FELD, J. H., AND STORCH, H. H. Fischer-Tropsch Pilot-Plant Studies of Oil-Circulation Processes at Bureau of Mines. Am. Chem. Soc., 117th Meeting Abs., March–April 1950, p. 5–J.

Summary of Fischer-Tropsch process development is given in which the essential features of the German fixed-bed system, the hot-gas recycle and oil-circulation processes, and the oil-slurry and fluidized-bed system are briefly described. Most of the pilot-plant experimentation at the Bureau of Mines has been directed toward the development of the oil-circulation process since a simple converter design could be used and precise operating control could be attained in such a system. Several moderately successful experiments were performed that employed a cooling-oil circulation through a fixed catalyst bed. However, shutdowns were necessary after 3 or 4 months of synthesis because the catalyst particles became cemented together and an excessive pressure drop developed across the catalyst bed. This problem of catalyst cementing was circumvented by employing a moving-bed catalyst in which the lifting action of the circulating oil was used to expand the catalyst bed and keep the particles in motion. Details of induction and synthesis operations, operating data, analyses of gas and liquid streams, tables of calculated yields, and a typical product distribution are given for various experiments. Calculations are made for a 2-stage process, with interstage scrubbing of CO_2, showing the C_1, C_2, and C_3 yields, which could be expected at a 91% overall synthesis-gas conversion.

648. ———. Fischer-Tropsch Oil-Circulation Processes. Ind. Eng. Chem., vol. 42, No. 11, 1950, pp. 2376–2384.

See abs. **647.**

CRUMLEY, P. *See* abs. **1326a.**

649. CRUTCHFIELD, J. W., AND PRUETT, H. T. Engineering Developments in Southwest Texas. Petrol. Eng., vol. 18, No. 1, 1946, pp. 208, 210; Chem. Abs., vol. 41, 1947, p. 261.

Brief account of the Carthage Hydrocol, Inc., development at Brownsville utilizing a modified Fischer-Tropsch process. The plant will process 64,000,000 cu. ft. of dry gas/day, yielding 3.84 and 0.78 gal. respectively of gasoline and Diesel fuel/1,000 cu. ft. of gas. Development of the process is traced with special reference to the production of cheap O_2 and the conversion of CH_4 into CO and H_2 by the direct reaction of CH_4 and O_2.

CRYDER, D. S. *See* abs. **1103.**

CRYDER, D. S., AND FROLICH, P. K. Catalyst for the Formation of Alcohols From Carbon Monoxide and Hydrogen. IV. Decomposition and Synthesis of Methanol by Catalysts Composed of Zinc and Chromium Oxides. *See* abs. **1101.**

650. CUELLAR, F. T. Organic Bases and Salts for the Purification of Gas. Ion, vol. 5, 1945, pp. 755–760; Chem. Abs., vol. 41, 1947, p. 2863.

Review of substances used in the removal of undesirable constituents of gases used in the synthesis of NH_3, the Fischer synthesis, and hydrogenation. 12 refs.

651. CUMMINGS, A. D. Oil From Coal: How Germany Synthesized Petrol for War. Discovery, vol. 9, February 1948, pp. 54–57; Fuel Abs., No. 3062, 1948.

Two processes, hydrogenation and the Fischer-Tropsch synthesis, are outlined. The Pintsch-Hillebrand, Wintershall-Schmalfeldt, and Winkler systems for utilizing brown coal in the synthesis are described, and the compositions of the gas mixtures from the 3 are compared.

652. CURIE, P. [Magnetic Properties of Materials at Various Temperatures.] Ann. chim. phys., Ser. 7, vol. 5, 1895, pp. 289–405.

653. CZERMAK, A. [Utilization by Processing of Low-Grade Coals As Well As Liquefaction of Coals.] Montan. Rundschau, vol. 19, 1927, pp. 283–290, 309–316, 337–344, and 371–375; Chem. Abs., vol. 21, 1927, p. 4047.

Outline of the chemical properties of C and several series of hydrocarbons is followed by a discussion of the methods for utilizing brown coals, lump coal, and lignites. Effects upon the coal, its byproducts, and heating values are given of the following: Improvements in byproduct oven design; drying of the coals by applying steam under pressure; the Bertinierung process; the carburization or Delkeskamp method; and the swelling processes. Descriptions of these processes, sectional diagrams of a Rolle-Oven installation, several tables of data obtained using different kinds of coals, and manufacture and uses of producer gas and Grudekok are included. The distribution and economics of the petroleum industries are discussed from the national and world standpoints. The experiments of Bergius and of Fischer in making liquid fuels from coal are reviewed, and compared, and the importance of these processes to countries that do not possess petroleum fields is emphasized. Gives number of refs. to recent articles on liquefaction.

D

654. DAHM, —. [Influence of the Iron Content of Kieselguhr on the Properties of Catalysts for the Hydrocarbon Synthesis.] FIAT Reel K29, 1939, frames 6,945–6,948; TOM Reel 296; PB 70,218.

Object of the work was to determine whether a favorable influence on the course of the synthesis with regard to an important reduction in the formation of CH_4 can be obtained by extracting the Fe from the kieselguhr used for catalysts. The answer is negative. 2 graphs.

654a. DALE, B., LEACH, J. R., BECKETT, C. W. AND JOHNSTON, H. L. Survey of the Scientific Literature on the Fischer-Tropsch Process. Ohio State Univ. Research Foundation, Tech. Rept. Project RF-319, 1950, 78 pp.

Review with 474 refs.

655. DAL PRATO, L. [Transformation of Heavy Mineral Oils Into Benzine.] Rass. min. met. chim., vol. 61, 1924, pp. 118–122, 153–158; vol. 62, 1925, pp. 12–14; Chem. Abs., vol. 19, 1925, p. 1492.

General review of present developments in the conversion of oils to benzine by cracking, by heating under pressure with H_2, and by catalytic decomposition and of attempts to synthesize hydrocarbons from H_2 and CO. Describes a new process developed by Dal Prato, consisting of the catalytic decomposition of complex molecules of the heavy hydrocarbons to benzine and gases and the catalytic synthesis of these gases to benzine. Process does not include hydrogenation.

656. ———. [Synthetic Petroleum.] Rass. min, met. chim., vol. 62, 1925, pp. 64–67, 91–93, 113–116; Chem. Abs., vol. 19, 1925, p. 2873.

Describes processes for synthesizing hydrocarbon fuels from C, H_2, and simple gaseous compounds of these elements, including industrial preparation of illuminating gas, water gas, CH_4 and H_2; polymerization of CH_4, C_2H_4, and C_2H_2; hydrogenation of C_2H_2 and C of Sabatier, Berthelot, Fischer, and Bergius and their transformation to liquid hydrocarbons; oxidation of C and of CH_4 to liquid fuels by the Fischer process; and synthesis of petroleum by the Olivier and Burgeois process.

657. DAMKOHLER, G. [Excess Temperature in Catalyst Grains.] Ztschr. physik. Chem., vol. 193, 1943, pp. 16–28; Chem. Abs., vol. 39, 1945, p. 2689.

The maximum excess temperature, $\theta_{max.}$ in a stationary catalyst grain during reaction is independent of the chemical reaction velocity, as well as the radius of the grain and is determined solely by the heat of reaction Q, the internal diffusion coefficient D_{ji}, the internal thermal conductivity λ_i, and the external concentrate c of the reactants. The following equation was derived:

$$\theta_{max.} \approx QD_{ji}(c_{jr}-c_{jo})/v_j\lambda_i \text{ where } c_{jo}$$

is the equilibrium concentration of reactants and v_j is the stoichiometric coefficient of constituent j. Calculated $\theta_{max.}$ for SO_2 oxidation was 0.42°, for NH_3 synthesis 0.20° at 200 atm. and 0.57° at 1,000 atm., for MeOH synthesis 1.0°, for butane synthesis from CO and H_2 3.0°. This behavior of an individual catalyst grain is quite different from that of a converter where chemical reaction velocity and dimensions of the reaction vessel are of importance.

658. DAMM, P. [Synthetic Alcohols—Manufacture of Synthetic Ethyl and Methyl Alcohol by the Mining Company of Bethune.] Mon. produits chim., vol. 11, No. 114, pp. 1–5; Chem. Zentralb., 1928, II, p. 2208; Chem. Abs., vol. 23, 1929, p. 4668.

Report on synthetic manufacture of EtOH and MeOH from coke-oven gases, consisting chiefly of H_2 CH_4, C_2H_4, CO, and N_2. H_2 is separated by liquefaction of the rest of the gases. C_2H_4, CH_4 and CO can be separated by the same method. C_2H_4 is converted into EtOH by means of H_2SO_4. A suitable mixture of H_2, CO, and N_2 serves for the synthesis of MeOH according to the equation: $CO+2\ H_2=CH_4O$. For this reaction a catalyst is used whose composition is kept secret. NH_3 is synthesized from the remaining mixture of H_2 and N_2. It is still more advantageous to make MeOH from water gas. MeOH should have a promising future because it is an excellent motor fuel.

659. DĂNĂILĂ, N., AND BOLTUS-GORUNEANU, M. [Preparation of the Higher Fatty Acids From Mineral Oil and Paraffin by Oxidation With Air at Ordinary and at High Pressures With and Without Catalysts.] Bul. Chim. Soc. Română Stiinte, vol. 31, 1929, pp. 133–200; British Chem. Abs., 1932, B, p. 790; Chem. Abs., vol. 24, 1930, p. 2282.

Detailed review of the literature from 1855. At ordinary pressure the oxidation of paraffin in the presence of Cu gave solid fatty acids, while mineral oil yielded only semisolid fatty acids resembling humic acids. Only the acids from paraffin can have practical application. Oxidation at ordinary temperature produces colored, malodorous byproducts and hydroxy acids, which diminish the value of the Na soaps. Better yields, 53%, were obtained by repeating the oxidation of the paraffin at increased pressure in the Bergius bomb and still better, 75%, by threefold oxidation. The fatty acids are colorless and odorless, and their molecular weights are not far from that of stearic acid. The Na salts are solids that foam freely. They could be employed in soap making. Na salts of acids made from mineral oils are liquids that foam readily. They could be employed as liquid soaps. A preliminary treatment of the mineral oils for removing the unsaturated aromatic and naphthene hydrocarbons increases the yields of fatty acids.

660. DANCKWERTS, P. V. Absorption by Simultaneous Diffusion and Chemical Reaction. Trans. Faraday Soc., vol. 46, 1950, pp. 300–304; Chem. Abs., vol. 44, 1950, p. 8706.

Equations are derived for the rate of absorption and the concentration when a solute of limited solubility diffuses into a semi-infinite medium with which it undergoes a 1st-order reaction. Consideration is given to the case where the medium is a mixture only 1 component of which reacts. Examples are the absorption of a gas into a liquid or solid, the solution of a solid into a supernatant liquid, or the absorption of 1 solid or liquid material into another.

661. DANNEFELSER, W. [Knock Measurements on Synthetic Gasoline.] Oel u. Kohle Erdoel Teer, vol.

38, 1942, pp. 363–365; Chem. Abs., vol. 37, 1943, p. 6442.

Virtually no resin formation occurs when gasoline obtained by the Fischer-Tropsch synthesis process is stored, and the mono-olefin content (30–40%) remains unchanged. In general, peroxides are not formed during prolonged storage of large batches of gasoline. Signs of peroxidation have been observed with small batches, for example, the octane number of a sample stored for 15 months in a sealed can was lowerd by 3 units. *o*-Cresol is recommended as a peroxide inhibitor. Samples when tested for knock rating after being taken from a refrigerator gave an octane number 1 unit higher than when tested at room temperature.

662. ———. [Notes on the Examination of Synthetic Benzine.] Oel u. Kohle Erdoel Teer, vol. 39, 1943, pp. 903–910; Chem. Zentralb., 1944, I, p. 199; Chem. Abs., vol. 38, 1944, p. 6066.

Evaporation losses in synthetic benzine amounting to a loss of weight of 2% and a reduction in the Reid pressure of 0.04, caused a fall in octane number. Peroxide formation during storage from the effect of daylight or ultraviolet rays also affected the octane number considerably. The tendency of different synthetic benzines to form peroxide varies. Other factors than the above 2 mentioned also caused changes in the octane number, but the author was unable to determine them.

663. DANULAT, F. [Gasification of Solid Fuels by Oxygen Under Pressure.] Mitt. Metallges., No. 13, 1938, pp. 14–22; Ind. Eng. Chem., news ed., vol. 16, 1938, p. 535; Braunkohle, vol. 37, 1937, pp. 200–202; Chem. Abs., vol. 33, 1939, p. 1471.

Description of commercial manufacture of city gas in Germany by the gasification of brown coal in a plant having two generators of 3.9 ft. diameter, 47,300 lb. of coal is gasified per 24 hr., yielding 563,000 cu. ft. of gas (at 0° and 760 mm.). It is claimed that any noncoking solid fuel can be used for gasification. O_2 is introduced at approximately 300 p. s. i.; this pressure is maintained during gasification of coal. Before entering the generator, the O_2 is mixed with superheated steam at 500°. After purification and CO_2 reduction, the gas has the following composition: CO_2, 3.0; illuminants, 0.5; O_2, 0.1; CO, 22.8; H_2, 48.7; CH_4, 22.6; N_2, etc., 2.3%. For certain synthetic purposes, it is possible to limit the CO production to 15% and increase H_2 to as much as 75% by suitable control of steam input, temperature, and pressure and by use of proper fuels.

664. ———. [Pressure Gasification of Solid Fuels With Oxygen.] TOM Reel 195, pt. 8, item 5 (*see* items 3 and 4); Gas- u. Wasserfach, vol. 84, 1941, pp. 549–552; Chem. Abs., vol. 36, 1942, p. 4315.

Concise description of total pressure gasification of solid fuel by means of pure O_2 and superheated steam. The advantages of this method over previous processes are presented. The operation takes place under a pressure of 20–30 atm., with extensive formation of CH_4, which renders the process so exothermic that consumption of O_2 is greatly reduced. The throughput is increased 5-fold over previous methods because of the reduced amount of gas necessary. Gives some results of pressure gasification of various fuels and includes flowsheets and diagrams of plant with operating data.

DAS, P. P. *See* abs. **166a.**

DAUR, R. *See* abs. **1110.**

665. DAVEY, W. Synthetic Lubricants. Sci. Lubrication, vol. 2, No. 6, 1950, pp. 10–13; Fuel Abs., vol. 8, No. 6, 1950, abs. 4595.

Polymers of high viscosity index may be prepared by polymerizing C_2H_4, C_3H_6, and C_4H_8 or olefins having more than 8 C atoms in the chain. One process involves cracking a straight-chain wax for a short time at high temperatures and polymerizing the resultant high proportion of olefins. The product is largely a steam-cylinder oil. Moderately viscous oils can also be produced by polymerizing olefins from the 150°–200° Fischer-Tropsch fraction from water gas. A German process uses the chlorination of a Fischer-Tropsch middle oil to give a 20–25% Cl content and reaction of this product with about half its weight of naphthalene in the presence of naphtha and an $AlCl_3$ catalyst. The product yields spindle and turbine oils and a residue of cylinder stock. CO and H_2 may be added to olefins to give aldehydes, which can be reduced to alcohols and oxidized to acids. The esters obtained by combining the long-chain alcohols and acids have high viscosity index and low pour point.

DAVIDSOHN, A. *See* abs. **666.**

666. DAVIDSOHN, J., AND DAVIDSOHN, A. Fatty Acids for the Soap Industry. Soap. Sanit. Chemicals, vol. 15, No. 8, 1939, pp. 21–23, 70; Chem. Abs., vol. 33, 1939, p. 8047.

Oxidation of fatty acids and use of products in soap making are discussed. Some mention is made of production of fatty acids by Fischer-Tropsch process.

DAVIDSON, R. L. *See* abs. **1100**

667. DAVIES, V. Treatment of Liquid Products From Water-Gas Synthesis. Ind. Chemist, vol. 13, 1937, pp. 442–446; Chem. Abs., vol. 32, 1938, p. 1072.

True vapor-phase process was used to crack Fischer synthetic oil. High pressures are not required, and there is no coke formation. High yields of good-quality motor spirit and 5% residue are produced. Gives flow sheets and photographs of plant.

668. DAVIN, E. [Practical Test of Synthol.] Mat. grasses., vol. 17, 1925, p. 7267; Chem. Abs., vol. 19, 1925, p. 3155.

Crude synthol rectified to 200° gave 87% of distillate suitable as light fuel having d_{20}, 0.8289%; C, 69.29%; H_2, 12.25%, calorific value, 8,200 cal./kg.; the cold test begins to set at —30° and is completely solidified at —90°. Road tests with a 4-hp. motorcycle having a carburetor adjusted for C_6H_6 and running at 25 km./hr. showed the following distances/100 cm.^{3} of fuel: C_6H_6, 2.9 km.; synthol 3; 1:1 C_2H_5–synthol 3.2, 1:1:1 C_6H_6–alcohol-synthol 2.9. With synthol alone the motor knocks, but with synthol–C_6H_6 it runs quite smoothly.

DAVIS, H. S. *See* abs. **2816.**

DAVIS, J. D. *See* abs. **625, 3159, 3213.**

669. DAVIS, R. T., JR., DEWITT, T. W., AND EMMETT, P. H. Adsorption of Gases on Surfaces of Powders and Metal Foils. Jour. Phys. and Colloid Chem., vol. 51, 1947, pp. 1232–1248; Chem. Abs., vol. 42, 1948, p. 1102.

Adsorption isotherms for N_2, Kr, *n*–C_4H_{10}, 1–C_4H_8, and $CHCl_2F$ were measured at temperatures at or below their boiling points and found to be S-shaped on Ag foil, monel ribbon, glass spheres, W powder, ZnO pigments, Al_2O_3, and SiO_2 gel. Cross-sectional areas that had to be assigned to the various adsorbates to bring the calculated surface areas for the last 5 of these adsorbents into agreement with those obtained from adsorption isotherms for N_2 by assigning an area of 16.2 Å.^{2} to the N_2 molecule were: Kr, 20.8 Å.^{2} at —195°; C_4H_{10}, 43.4 Å.^{2} at —78° and 46.9 Å^2 at 0°; $CHCl_2F$, 37.5 Å.^{2} at —78° and 40.1 Å.^{2} at 0°; and 1–C_4H_8, 42.7 Å.^{2} at 0°. For Ag foil and monel ribbon, these same molecule area assignments yielded absolute areas that were 10% to 60% larger than the geometric surface area when $CHCl_2F$, *n*–C_4H_{10}, and Kr were used as adsorbates. With molecule area, assignments calculated for these 3 adsorbates from liquid density in the usual way (abs. **827**) the surface areas of the Ag foil and

monel ribbon obtained from Kr, C_4H_{10}, and $CHCl_2F$ were smaller than the geometric area by as much as 25%.

670. DAVIS, S. G. Evaluation of Catalysts Used in the Synthesis of Hydrocarbons. Canadian Chem. Process Ind., vol. 31, 1947, p. 644.

Abstract of a paper presented at the 3d annual meeting of the Chemical Institute of Canada. A preliminary report is made indicating a method and the apparatus used in the evaluation of catalysts for the reaction of CO and H_2. The apparatus consists of 6 semi-pilot-scale catalyst-testing units. Shows some typical results. Also describes apparatus on which the surface area, the rate of carbiding with CO, and the rate of reduction of the carbide with H_2, are measured on the catalysts.

———. *See* abs. **3747.**

671. DAZELEY, G. H., AND GALL, D. Lubricating Oils From Fischer-Tropsch Olefins Using Water Gas as Raw Material. Petroleum (London), vol. 9, 1946, pp. 208–210; Chem. Abs., vol. 41, 1947, p. 2562.

Products obtained by the Fischer-Tropsch process using water gas ($CO:H_2=1:1$) have a considerably higher olefin content than products of similar boiling range obtained from synthesis gas ($CO:H_2=1:2$) and are therefore more promising raw materials for polymerization to lubricating oils. The aim of this investigation was to examine the effects of chain length of olefins and of reaction temperature on the properties of the resulting lubricating oils and on the yields obtained. For a given chain length of olefins, the absolute viscosity of the lubricating oil decreases with increase of reaction temperature, but the V. I. remains approximately constant. Under given temperature conditions, the absolute viscosity of the oil decreases with increase in the chain length of the hydrocarbons in the starting material. The V. I. of all oils prepared from a higher-boiling fraction of gasoline are greater than those of oils from a lower-boiling fraction. The yield of oil calculated on the weight of starting material is less for the higher-boiling gasolines. Calculated on the weight of olefins present, the yield appears to increase with increase in chain length of the hydrocarbons. A marked decrease in yield occurs where a high reaction temperature is employed, but otherwise the effect of reaction temperature on yield is not significant. Reaction temperature and chain length have very little effect on stability to oxidation. The oils are superior in general properties to those obtained from synthesis gas. The V. I. is higher and the oxidation numbers are lower (2.4–2.9, but still too high to comply with Government specification, which requires one below 2). If oils of moderate viscosity and good viscosity-temperature properties are required, it would seem that the most suitable ones are obtained by polymerizing the olefins in the fraction of water-gas gasoline boiling 140°–200°, although the yield is somewhat less than with lower-boiling fractions.

672. DAZELEY, G. H., AND HALL, C. C. Polymerization to Lubricating Oils of 1–Heptene and 1–Pentadecene. Jour. Soc. Chem. Ind., vol. 67, 1948, pp. 22–23; Chem. Abs., vol. 42, 1948, p. 4738.

1–Heptene and 1–pentadecene obtained by synthesis from allyl bromide and the appropriate Grignard reagents were each polymerized with 3–5% $AlCl_3$ at 0°–20° without diluent and also at 80° in a solution in the related paraffin. No sludge formed in the low-temperature polymerization, and the polymerizates had slightly higher viscosity indexes. This suggests that some isomerization occurred at the higher temperature. The yields of lubricating oil were 73–93%. All oils had viscosity indexes in the range 108–132. The oxidation stabilities were independent of the chain length of the original olefin and were significantly better than for the polymerizates from cracked Fischer-Tropsch diesel oil previously described (abs. **673**).

673. ———. Preparation of Lubricating Oils From Hydrocarbon-Synthesis Products. I. II. Petroleum (London), vol. 11, 1948, pp. 14–15, 26, 41–44; Chem. Abs., vol. 42, 1948, p. 3943.

Fischer-Tropsch diesel oil may be cracked to yield products containing olefins. Material obtained by thermal cracking at 600° and atmospheric pressure polymerizes in the presence of 5% $AlCl_3$ to give good yields of satisfactory lubricating oil. The products derived from cracking in an autoclave at 450° and over an Al–Si catalyst at 600° give poor yields of lubricating oil on polymerization. The differences in the products are said to be due to the presence of mainly straight-chain α-mono-olefins in the thermally cracked gasolines but not in those formed by other methods of cracking.

674. ———. Production of Olefins by the Cracking of Fischer-Tropsch Waxes and Their Conversion Into Lubricating Oils. Fuel, vol. 27, No. 2, 1948, pp. 50–55; Chem. Abs., vol. 42, 1948, p. 7515.

Total waxes, boiling above 300° at 760 mm., produced at atmospheric pressure and at 10 atm. pressure by synthesis from CO and H_2 in the presence of a Co catalyst were subjected to noncatalytic, vapor-phase cracking at temperatures ranging from 500°–640° and at a throughput of 50 gm. wax per 40 ml. of cracking space/hr. It was found that substantial amounts of α olefins of fairly high purity can be readily recovered from the cracked products. For example, 54 gm. of material, boiling 85°–105°, gave on distillation 36 gm. of *n*-heptene-1. At a given temperature, the total yield of cracked products is less than for the diesel-oil fraction (200°–300°), but the yield of liquid products is higher. In the range C_5–C_{12} the liquid products from wax contain about 95% of olefins, mainly of the straight-chain α type. The yields and composition of the liquid- and gaseous-cracked products are virtually the same for both waxes. Approximate C-number and olefin-distribution curves for the total products of cracking have been constructed. Polymerization of the olefins with 2–3% of $AlCl_3$ at 80° gives greater yields of lubricating oil with a high viscosity index than are obtained from the products of cracking the diesel-oil fraction, owing to the greater production of long-chain olefins from the waxes. All the oils obtained had B. A. M. oxidation numbers above 2.0.

675. DAZELEY, G. H., GALL, D., AND HALL, C. C. Production of Olefin-Polymer Lubricating Oils of Satisfactory Oxidation Stability. Jour. Inst. Petrol., vol. 34, 1948, pp. 647–653.

Attempts have been made to increase the oxidation stability (as measured by the B. A. M. oxidation-number test) of olefin-polymer lubricating oils derived from the products of the Fischer-Tropsch synthesis. A controlled hydrogenation of the oils in the presence of MoS_2 at 200° and 200 atm. pressure yields an oil with an oxidation number of 1.8. The effect is the result of saturation by H_2 coupled with the formation of S-containing inhibitors and can be accurately reproduced by hydrogenation in the presence of Ni catalyst followed by heating with MoS_2 in the absence of H_2. Treatment of the oil with $AlCl_3$ at 180° produces some improvement in oxidation stability, but the effect is small and is accompanied by a serious loss of oil. Naphthalene added to the olefins before polymerization is chemically incorporated in the resulting oil and leads to an increase in oxidation stability, an increased conversion of the olefins to lubricating oil, and a decrease in the viscosity index of the oil. About 15% napthalene is required to produce an oil with an oxidation number below 2.0; this causes a fall in viscosity index from 100 to a value in the range 80–85.

676. DEAN, R. S. Colloidal Behavior in Metals and Alloys. Colloid Chem., vol. 6, 1946, pp. 561–578; Chem. Abs., vol. 40, 1946, p. 2427.

I. Gasses in metals: Physicochemical nature of metallic interfaces; gas-metal systems as colloids; degasification of metals; grain-size control; H. embrittlement. II. Slag-metal systems: Aston wrought-iron process; steel-making reactions; powder metallurgy; magnetic, electric and mechanical properties of metal compacts. III. Dispersions of metals in metals: Solid metals in solid metals; ordering in alloys; dispersion hardening; internal friction or vibration-damping capacity of metals. 78 refs.

677. DE BRUIJN, H., WESTRIK, R., AND VAN LOON, W. Dutch Report on Visit to I. G. Farbenindustrie, A.-G., Ludwigshafen and Oppau and Raschig Werke Mundesheim BIOS Miscell. Rept. 104, no date, 126 pp.; PB 96,352.

Some of the subjects reported are: I. Conversion of CO at 25 atm. pressure, the catalyst Fe_2O_3–Cr_2O_3–Na_2SO_4; conversion of CH_4, catalyst Ni on magnesite. II. Conversion of CH_4 to synthesis gas for CH_3OH. III. Synthesis of CH_3OH, procedure, converter, catalyst, temperature, coke-oven gas—the raw material. IV. Manufacture of formaldehyde from CH_3OH. V. Preparation of C_2H_2 from CH_4 by partial combustion and from CaC_2. VI. Preparation of C_2H_4 from C_2H_6 by partial oxidation and by dehydrogenation. VII. Synthetic phenol by Raschig process.

DECARRIÈRE, E. *See* abs. **62.**

678. DECARRIÈRE, E., AND ANTHEAUME, J. [An Iron Catalyst for Hydrogenation of Carbon Dioxide at Ordinary Pressures.] Compt. rend., vol. 196, 1933, pp. 1889–1891; Chem. Abs., vol. 27, 1933, p. 4632.

Catalyst containing less Cu than that of Fischer is more active than his original composition. Omission of Cu entirely, however, lowers the activity almost to zero.

DECHAMPS, G. *See* abs. **2541.**

DEGODON, F. *See* abs. **2161.**

679. DE HEMPTINNE, A. [Synthesis of Organic Compounds by Means of the Dark Electric Discharge.] Bull. Acad. roy. Belg. (3), vol. 34, pp. 269–277; Jour. Chem. Soc., vol 1, 1898, p. 461; Chem. Zentralb., 1897, II, p. 1044.

When mixtures of CO and H_2 are subjected to the silent electric discharge, CH_2O and its polymers are produced. CO and CH_4 yield an aldehydic substance and CO and C_2H_6 form a ketone and an aldehyde.

680. DELAUNAY, R. [Methanol Synthesis From Wood by the Lacotte Process.] Chim. et ind., vol. 58, No. 4, October 1947, pp. 335–340; Chem. Abs., vol. 42, 1948, p. 1041.

Describes first plant-scale operation of the Lacotte process for the manufacture of synthetic MeOH from wood. The particular originality of the process, as carried out at the Decazeville plant, lies in the Lacotte gas producer, which directly and continuously produces synthesis gas of such high purity that its purification is unnecessary before use. The catalytic synthesis of MeOH utilizes as a catalyst a mixture of the oxides Zn and Cr deposited on a carrier. The operation takes place at a temperature of 425° and a pressure of 650 kg./cm.^{2} The plant processes 20 tons of wood of 25% water content/day and produces 6,000 l. of MeOH of 99.9% purity. Each l. of MeOH requires 2.7 m.^{3} of synthesis gas, 3.3 kg. of wood of 20–25% moisture, 0.8 m.^{3} of 98% O_2, 2.8 kw.-hr. of electricity, and 0.7 kg. of steam. 1 ton of dry wood gives 3 hl. of MeOH.

DELION, R. *See* abs. **1604.**

DELLE, V. A. *See* abs. **2431.**

681. DELLEY, E. [Substitute and Synthetic Motor Fuels.] Schweiz. Techztg., 1938, pp. 59–66, 75–80; Chem. Zentralb., 1938, II, p. 234; Chem. Abs., vol. 34, 1940, p. 3469.

Exhaustive report of methods of production, possibilities for use, and production figures for the hydrogenation products of coal (Bergius-I. G. and Fischer-Tropsch processes) and C_2H_2; for EtOH and MeOH, benzene, and vegetable oils; for the products of distillation of asphalt and bituminous shales; for gaseous fuels such as compressed city gas from sludge digestion, coke-oven gas and CH_4, C_2H_2, NH_3, and H_2; and for gaseous fuels such as coal gas. Discusses their utilization in Switzerland.

682. DEMANN, W. [Semicoke for Chemical and Metallurgical Processes.] Glückauf, vol. 73, 1937, pp. 1101–1106; Coal Carbonisation, vol. 4, 1938, p. 16.

A general survey of the use of semicoke is followed by notes on the results of various large-scale trials, including the manufacture of synthesis gas by the Ruhrbenzin A.-G.; the direct manufacture of synthesis gas in water gas producers at the Grasbrook (Hamburg) gas works; and the manufacture of ferrosilicon, CaC_2, and other products.

683. ———. [Status of Low-Temperature Coking in Germany and Its Relation to the German Power Situation.] Gas- u. Wasserfach, vol. 85, 1942, pp. 375–381; Chem. Abs., vol. 37, 1943, p. 4551.

Review of low-temperature coking processes, with 52 refs. Tar obtained by low-temperature coking of bituminous coal differs from that obtained from brown coal by its aromatic-naphthenic structure; gasoline obtained from this tar has an octane number of 80–90. Coke from low-temperature carbonization of bituminous coal of an ash content of 2% or less is used for metallurgical purposes, for example, the manufacture of ferrosilicon. To obtain tars suited for the manufacture of motor fuels several German gas works have installed special coking apparatus in their gas generators. The Müller process (abs. **2337**), which combines low-temperature coking with the Fischer-Tropsch hydrocarbon synthesis increases the oil yield of the synthetic process by 20–30%.

684. DEN OTTER, H. P. [Mersol and Sodium Mersolsulfonic Acid.] Chem. Weekblad, vol. 43, 1947, pp. 211–217, 276–282; Chem. Abs., vol. 41, 1947, p. 5327.

Describes manufacture of Mersol by reaction of SO_2 and Cl with hydrocarbons produced by the Fischer-Tropsch synthesis. Depending upon the reaction conditions, this produces Mersol D (50–60% of monosulfonyl chloride, 10–20% of di- and higher sulfonyl chlorides, and about 20% of unchanged hydrocarbon) or Mersol H_2 (about 50% monosulfonyl chloride and 50% of unchanged hydrocarbon). Unchanged hydrocarbon is best removed by extraction with benzine; steam distillation is too expensive. Production of Mersolat and its use as a detergent are described.

685. ———. [Soap From Synthetic Fat Acids. I.] Chem. Weekblad, vol. 43, 1947, pp. 37–42.

Review and discussion of the literature, with 76 refs.

686. ———. [Soap From Synthetic Fat Acids. II.] Chem. Weekblad, vol. 43, 1947, pp. 120–122, 131–134; Chem. Abs., vol. 41, 1947, p. 3310.

Review and discussion of the literature, with 153 refs.

687. ———. [Soap From Synthetic Fat Acids. III] Chem. Weekblad, vol. 43, 1947, pp. 740–747; Chem. Abs., vol. 43, 1949, p. 7241.

Review and discussion of the literature, with 105 refs.

688. ———. [Soap From Synthetic Fat Acids. IV.] Chem. Weekblad, vol. 43, 1947, pp. 740–747; Chem. Abs., vol. 42, 1948, p. 1439.

Sample of synthetic fat acids as used in Germany in 1943–1944 was found to have a composition approximately similar to that of a mixture of 50% coconut-oil-fat acids and 50% lard-fat acids but to contain little oleic acid. On preparation of the Na soap-fat acid, losses of 5% were observed. The soap contained 0.71% NaCl. Compared with soaps made from natural-fat acids it lacked plasticity; it suffered greater loss in use; its foam was equal in quantity but less stable; its cleaning power was inferior; and its odor was disagreeable.

689. DENT, F. J. Use of Oxygen for Town-Gas Manufacture. Gas World, vol. 128, 1948, pp. 384–385.

Proposal for pressure gasification of coal linked with a synthetic-oil process for the production of town gas. Data so far available indicate that pressure gasification might assume the basic position in the gas industry that carbonization now occupies provided the demand for gas outstrips that for coke; the process also would have the advantage of flexibility in operation during peak periods. As compared with the Fischer synthesis process, gasification under pressure, with withdrawal of part of the gas for oil synthesis, shows many advantages. Assuming an overall thermal efficiency of about 70%, the gas cost is reduced to 0.65 d. per therm.

———. *See* abs. **2302.**

690. DENT, F. J., AND HEBDEN, D. Catalytic Synthesis of Methane as a Method of Enrichment in Town-Gas Manufacture. Gas Research Board Rept. 51; Gas World, vol. 130, 1949, pp. 1938–1939; vol. 131, pp. 69–75.

Experiments were carried out to demonstrate that catalysts can be operated successfully at the high space velocities necessary on gas-production plants by suitably controlling the temperature of the catalyst surface and by using catalysts of suitable composition. Temperature control was maintained by recirculation of the heating gases. Operating with blue water gas at a space velocity of 2,000 vol. per vol. per hr., a final gas of approximately 500 B. t. u. per cu. ft. was made at atmospheric pressure, and with a H_2-rich gas of more than 700 B. t. u. it was made at 20 atm. During a 4-month run with no appreciable deterioration in the calorific value and with a catalyst life of this length, the catalyst cost should be no more than 0.3 d. per therm. There are two possible applications of the synthesis reaction that are worth consideration: As an alternative to oil for enrichment of blue water gas at times when the maximum thermal output of gas is not required from the water gas plant, and for enrichment of gas produced by the gasification of coke breeze at moderate pressure with O_2 and steam. In the first case, the margin between the cost of the raw material and the value of the synthesized product should be enough to cover the installation and operation of the synthesis plant. Determination of the efficiency of the gasification of breeze under pressure and of the outputs obtainable is to be made soon under pilot-plant conditions.

DENT, F. J., BLACKBURN, W, H., AND MILLETT, H. C. Investigation of the Use of Oxygen and High Pressure in Gasification. II. Synthesis of Gaseous Hydrocarbons at High Pressure. *See* abs. **692.**

———. Investigation of the Use of Oxygen and High Pressure in Gasification. III. Synthesis of Gaseous Hydrocarbons at High Pressure. *See* abs. **693.**

DENT, F. J., BLACKBURN, W. H., MILLETT, H. C., AND MOIGNARD, L. S. Investigation of the Use of Oxygen and High Pressure in Gasification. IV. Synthesis of Gaseous Hydrocarbons at High Pressure. *See* abs. **694.**

691. DENT, F. J., BLACKBURN, W. H., WILLIAMS, N. H., AND MILLETT, H. C. Investigation of the Use of Oxygen and High Pressure in Gasification. I. Gasification With Oxygen. Rept. 39, Joint Research Committee, Institution of Gas Engineers and University of Leeds; Inst. Gas Eng. Commun. and Repts., Commun. 141, 1936, 76 pp.; Trans. Inst. Gas Eng., vol. 86, 1936–1937, p. 118; Chem. Abs., vol. 31, 1937, p. 7225.

Discusses results for Lurgi plant using lignite. Coke from Sharlston and Warrenhouse coals were studied in a laboratory apparatus described. The Warrenhouse was a more reactive and, therefore, a better product than the Sharlston coke, giving lower outlet temperature, lower O_2 consumption, and less sensible-heat loss, and allowing the use of a lower steam : O_2 ratio. Addition of Na_2CO_3 improved the reactivity of Warrenhouse coke. Preheating of steam and O_2 also gave improved results. Use of air-steam mixtures instead of O_2-steam increased the heat losses. The influence on the results of rate of gasification and size of coke was studied. Gives results for gasification using O_2–N_2 and O_2–CO_2 mixtures. Blowing O_2 instead of air through a heated coke bed reduced CO formation and sensible-heat losses.

692. DENT, F. J., BLACKBURN, W. H., AND MILLETT, H. C. Investigation of the Use of Oxygen and High Pressure in Gasification. II. Synthesis of Gaseous Hydrocarbons at High Pressure. Rept. 41, Joint Research Committee, Institution of Gas Engineers and University of Leeds; Inst. Gas Eng. Commun. and Repts., Copyright Pub. 167/56, 1937, 58 pp.; Trans. Inst. Gas Eng., vol. 87, 1937–1938, p. 231; Gas Jour., vol. 220, 1938, pp. 470, 473–475, 658–659; Gas World, vol. 107, 1938, pp. 424–425, 545–546; Chem. Abs., vol. 32, 1938, p. 6435.

Preliminary experiments showed that it was possible to gasify all types of bituminous coals and lignite in steam under pressure with synthesis of hydrocarbons in the fuel bed and the production of a gas of calorific value high enough for general supply. Various types of fuels were heated to 800° (1½–2¾ hr.) in a stream of H_2 or gas contg. H_2 at 1–100 atm. pressure and held for 1½ hr.; similar tests in N_2 were run for comparison. Results with a coke prepared at 450°–500° from Yorkshire coal are typical. In N_2, yields at atm. pressure were H_2 23.0; CH_4, 14.7; and total gaseous hydrocarbons 16.3 therms per ton of coke. In H_2, yields at atm. pressure were H_2 1.3 and gaseous hydrocarbons 33.8 therms. At 5 atm., yields of gaseous hydrocarbons were 92.1 therms; at 10 atm., 132.9 therms; at 25 atm., 202.5 therms; at 50 atm., 276.0 therms; and at 100 atm., 311.2 therms. CH_4 still was being formed at the end of the tests. At 50 and 100 atm., tar yields increased. Maximum calorific value of outgoing gas in B. t. u. per cu. ft. was 345 at 1 atm., 429 at 5 atm., 500 at 10 atm., 589 at 25 atm., 719 at 50 atm., and 914 at 100 atm. Calorific value increased with increasing rate of heating or decreasing rate of H_2 supply, although there was an accompanying decrease in yield of hydrocarbons. H_2 absorption, in therms per ton, was 32.9 at 5 atm., 60.8 at 10, 107.7 at 25, 153.5 at 50, and 193.5 at 100. The coke contained 19.8% volatile matter, but % losses in weight were 18.6 at 1 atm., 27.7 at 5, 34.9 at 10, 44.6 at 25, 62.4 at 50, and 72.0 at 100. At low pressure, hydrogenation was most rapid at 500°–550°; at higher pressure, 700°–750°. These are temperatures related to thermal decomposition of coke; hence H_2 merely modifies the course of the decomposition. The thermal yields of gaseous hydrocarbons were not reduced by substitution of

CO–H_2 mixtures for H_2 if the rate of supply and pressure were increased to allow for lower H_2 in the mixture; CO dilution reduced the calorific value of gas.

693. ———. Investigation of the Use of Oxygen and High Pressure in Gasification. III. Synthesis of Gaseous Hydrocarbons at High Pressure. Rept. 43, Joint Research Committee, Institution of Gas Engineers and University of Leeds; Inst. Gas Eng., Copyright Pub. 190/73, 69 pp.; Gas Jour., vol. 224, 1938, pp. 442–445, 627–628; Gas World, vol. 109, 1938, pp. 364–365, 401–404; Trans. Inst. Gas Eng., vol. 88, 1938–39, p. 150; Chem. Abs., vol. 33, 1939, pp. 6561–6562.

In a continuous plant, coals and cokes prepared at temperatures up to 800° could be virtually completely gasified in H_2 at 50 atm. if the temperature of the fuel bed were maintained around 900° and if, with coals, caking properties did not occasion difficulties on the larger scale of operation. Rate of gasification was accelerated by alkalies, but the effect was most marked in hydrogenating at low temperatures. A coke prepared from an intimate mixture of coal and 3% Na_2CO_3 gave 463 therms of gaseous hydrocarbons/ton when hydrogenated at 800°, but gave only 140 therms in absence of alkali; at 900° the coke gave 520 therms without alkali, but alkali accelerated the rate toward the end of hydrogenation. Alkali reduces the tendency of coal to cake during treatment. Highest percentages of CH_4 obtained at 50 atm. were 57.3 at 800°, 43 at 900°, and 36.3 at 950°; therefore, gas of 600 B. t. u. cannot be prepared above 915°; of 700 B. t. u., above 810°; of 800 B. t. u., above 700°. If higher temperatures of treatment are necessary to secure proper reactivity of coke, the lower limit of pressure must be increased. Data are also given for H_2 containing CO, CO_2, and N_2. There are 2 periods in the hydrogenation: (1) Thermal decomposition of coal while temperature is raised and (2) thermal stability of the solid residue at a steady temperature. During (2), rate of formation of hydrocarbons was limited and depended on final temperature maintained. During (1), high rates of heating gave high hydrocarbon production. For example, heating at 12°/min. and using 58,000 cu. ft. of H_2/hr./ton produced the first 200 therms at an average rate of 220 therms/hr., corresponding on dilution to gas of 500 B. t. u. with a rate of 415 therms/hr./ton (normal carbonization 7 therms/ton/hr.). Complete gasification of coals in H_2 to simple hydrocarbons involves breaking down 6-membered C rings. With benzene under the above experimental conditions, gaseous hydrocarbons were formed at 750°; at 850°, ⅔ was decomposed to CH_4 in 1 min. Anthracene was more readily decomposed. With xylene, CH_4 formation was appreciable at 550°–600°; hydrogenation of side chains was complete at 700°.

694. Dent, F. J., Blackburn, W. H., Millett, H. C., and Moignard, L. S. Investigations of the Use of Oxygen and High Pressure in Gasification. IV. Synthesis of Gaseous Hydrocarbons at High Pressure. Rept. 50, Joint Research Committee, Institution of Gas Engineers and University of Leeds; Inst. Gas Eng. Commun. and Repts., Commun. 26, 1946, 52 pp.; Gas World, vol. 125, 1946, pp. 680–682; Chem. Abs., vol. 41, 1947, p. 3277.

In the light of the knowledge gained in the laboratory, consideration is given to 4 processes: (1) The Lurgi process for complete gasification; (2) a 2-stage process for complete gasification involving the production of gaseous hydrocarbons by hydrogenation; (3) a process of gasification at high pressure combined with CH_4 formation by catalytic synthesis; and (4) a process of carbonization in which internal heating is obtained by the exothermic hydrogenation and decomposition of the coal. It is doubtful whether the Lurgi process would produce, from British coals, a gas with as high a heating value as that normally supplied, and it would probably require some pretreatment of the fuels to render them noncaking. When complete gasification is required the 2d process is more suitable for bituminous coals. A detailed analysis of the mechanism by which gaseous hydrocarbons are produced indicates that, in this process also, the yield of enriching hydrocarbons would be limited. It appears that gas of approximately 500 B. t. u./cu. ft. might be readily obtained by synthesis without the need of additional gaseous hydrocarbons from hydrogenation. The solid residue from the hydrogenation of coal is particularly combustible; although in the laboratory it had not been obtained as yet in large strong pieces. Coals were hydrogenated in a vessel of 6⅜ in. internal diameter, which was not externally heated. All coals except anthracite fused under high pressure; and, unless they were first rendered noncaking, difficulty was encountered in securing uniform gas flow and reaction throughout the charge. Coals that were not pretreated could be hydrogenated if the sizes below ⅛ in. were separated and charged down the side of the vessel. With such a graded charge it was possible to treat satisfactorily a wide range of coals, including semianthracites, caking coals, and high-volatile, weakly caking coals. When coals were heated under controlled temperature conditions and under pressure in a 1-in.-diameter reaction tube the gas arising from the decomposition of the fuel was high in hydrocarbons, even when the atmosphere supplied was rich in hydrocarbons. At 50 atm. and 800°, gas containing 30% CH_4 was prepared from C and H_2 at space velocities as high as 20,000 with Ni supported on porous pot as the catalyst. CH_4 was decomposed rapidly and almost completely at a high temperature, high pressure, with excess steam, and in the presence of a Ni catalyst.

695. de Pauw, F., and Jungers, J. C. [Kinetics of Hydrogenation of Acetylene on Nickel.] Bull. soc. chim. Belg., vol. 57, 1948, pp. 618–630; Chem. Abs., vol. 44, 1950, p. 915.

Hydrogenation of C_2H_2 (I) to C_2H_4 (II) or C_2H_6 was observed in a static system by means of pressure drops. Catalyst (A) was prepared by reducing $NiCO_3$ precipitated on kieselguhr; (B) was prepared by reducing oxide from the calcination of $Ni(NO_3)_2$ at 350°. With (A) and equimolar H_2 and (I) there was no reaction at 29°–100°, but if H_2 was admitted first, there was rapid reaction. With equimolar H_2 and (II) there was reaction. It was concluded that (I) by forming polymers poisoned the catalyst. Using the less active catalyst (B) tempered by heating in a H_2+(I) mixture at 300°, and an excess of H_2 over (I) (ratios 2–20), it was possible to make kinetic experiments. The catalyst was periodically regenerated with H_2 at 300°. At 29°–30°, an initial reaction of steady rate continued until about 1 mol. of H_2 was used per mol. of (I); the rate then increased. For the initial period, rate $=k(H_2)/(I)^{1/2}$. The reaction was faster for D_2 than for H_2. The activation energy (16°–57°) for (I) hydrogenation was 14 kg.-cal.; for (II) it was 10 kg.-cal. Results are explained by strong adsorption of (I), which inhibits hydrogenation of (II) as long as (I) is present. The rate laws are fitted by means of Langmuir adsorption formulas. The adsorption coefficient of (I) is estimated to be 100 times that of H_2 at 30°, whereas that of D_2 is about 1.5 times that of H_2.

Derrig, M. J. *See* abs. **3599.**

696. Dersin, H. [Synthesis of Higher Alcohols From Carbon Monoxide and Hydrogen.] Chem.-tech. Rundschau, vol. 44, 1929, p. 310; Chem. Abs., vol. 23, 1929, p. 3661.

By passing CO and H_2 over the same catalyzers, but at a slower rate than for MeOH, alcohols of higher molecular weight may be obtained. These are con-

taminated with MeOH, aldehyde, amines, and small quantities of liquid hydrocarbons. By suitable variation in the operating conditions formation of higher alcohols is favored. Patent literature is reviewed.

697. ———. [Synthetic Production of Methanol From Carbon Monoxide and Hydrogen.] Chem.-tech. Rundschau, vol. 44, 1929, pp. 146–148, 176–178; Chem. Abs., vol. 23, 1929, p. 3661.

Review of periodical and patent literature on production and purification of initial materials, apparatus, catalyzers, and purification of the crude methanol.

DESORMES, —. *See* abs. **580.**

698. DEVILLE, H. S. [Dissociation of Carbon Monoxide.] Compt. rend., vol. 59, 1864, p. 873; vol. 60, 1865, pp. 317–325.

Discovery is made that the reaction $CO_2+C=2CO$ is reversible. Only a small degree of dissociation was observed at temperatures a little lower than the melting point of Ag, while at temperatures above 1,000° none could be observed.

699. DEW, W. A., AND TAYLOR, H. S. Adsorption and Heat of Adsorption of Ammonia Gas on Metallic Catalysts. Jour. Phys. Chem., vol. 31, 1927, pp. 277–290; Chem. Abs., vol. 22, 1928, p. 1074.

Measurements of the specific adsorption and heats of adsorption of NH_3 on Cu, Ni, and Fe catalysts have been made by methods previously used in order to study the reaction: $2NH_3=N_2+3H_2$. Values for the specific adsorption of NH_3 and H_2, and some figures for N_2 on Na, Cu, Ni, and Fe and 50–50 Fe-Mo at 0°, 110°, 218°, 305°, and 444.6°, with a number of exceptions, are given, which show that the catalysts adsorb NH_3, that the adsorption is reversible at low temperatures, and that decomposition occurs at higher temperatures. Differential heats of adsorption for NH_3 at 0° on Cu, Ni, and Fe and integral heats for NH_3 at 0° on Cu and Ni have been given. The beneficial effect of low-temperature preparation of catalysts upon the adsorption effect is stressed, and indication is found that the higher the heat of adsorption the greater the possibility of catalytic activity.

700. DEWAR, J., AND JONES, H. O. New Iron Carbonyl and the Action of Light and Heat on the Iron Carbonyls. Chem. News, vol. 95, 1907, pp. 97, 109; Chem. Abs., vol. 1, 1907, p. 1226.

701. DEWEY, D. R. Hydrocarbon Synthesis. Wartime Work of the Kaiser Wilhelm Institut für Kohlenforschung. Ind. Chemist, vol. 21, 1945, pp. 681–683; Chim. et ind., vol. 55, 1946, pp. 327–328; CIOS Rept. XXV/27, 1945; U S. Naval Tech. Mission Rept. (in Europe), 110–45; TOM Reel 196; PB 289, 890, L 86,445; Chem. Abs., vol. 40, 1946, p. 7,557.

Supplements the disclosures made by F. Fischer on his retirement as Director in 1943 (abs. **972**). Co remains the best catalyst for the normal-pressure synthesis; the Fe catalyst was found to be unsuitable. In the medium-pressure synthesis, use of the Co catalyst gives a low yield of olefins and a high yield of paraffins, whereas the contrary is true with the Fe catalyst. The Fe can be combined with 2–3% Cu and up to 1% of alkali; the higher the proportion of alkali, up to this limit, the higher the average molecular weight of the hydrocarbons made. A pressure of 20 atm. gives the highest factor of conversion and the best yield of high-molecular compounds. Below 10 atm. the life of the catalyst decreases rapidly and above 20 atm. the formation of O-containing compounds begins. The best composition for the synthesis gas is 1 CO : $1H_2$. Typical yields with Fe catalyst are as follows: C_3–C_4 compounds containing 50% olefins; 20% gasoline fraction containing 50% olefins; 40% fraction boiling 200°–300°; 20% waxes m. p. above 15° 20%. The temperature for the Co catalyst is about 190°, for the Fe 240°. Evidently Fe was used in the commercial process to save the available Co for the Kogasin synthesis; Fe produces the waxes in satisfactory quantity, and that was the main point regardless of the nature of the lower products and the smaller yield of waxes than with Co. The direct synthesis of iso-compounds dates only from 1940–41 and began with the production of C_3H_8–C_4H_{10} mixtures with up to 90% of iso-C_4H_{10} in the C_4 fraction. It is thought that the formation of iso-compounds arises from the chain of reactions: water gas to higher alcohols; dehydration of alcohols to olefins; hydrogenation of olefins to isoparaffins. Catalysts capable of promoting the simultaneous progress of these reactions include ThO_2, Th and Al oxides, Zn and Al oxides, Al_2O_3, and ZnO with Th, Ce, or Zr oxide. The reaction is best carried out with a gas 1.2 CO : 1 H_2 at 450° and 300 atm. With a ZnO–Al_2O_3 catalyst the composition of the products from C_4 upward is: C_4H_{10} (90% iso-C_4H_{10}), 60–70% by weight; C_5H_{12} (96–98% iso-C_5H_{12}), 20–30% by weight; C_6, C_7, and C_8 small amounts. Up to about 10% of alcohols, mostly isobutyl, is produced also. The proportion of compounds with different numbers of C atoms in the molecule may be varied by altering the composition of the catalyst; if the ZnO is increased the proportion of higher compounds rises, and vice versa. The ZnO–Al_2O_3 catalyst seems to be the best commercial proposition, because of its cheapness, but a catalyst of Al_2O_3 and ThO_2 (4 : 1) gives less alcohol and permits a faster gas rate. Above 300 atm. (the best operating pressure) O-containing compounds are formed in increasing amounts. At 400° the yield includes a high % of alcohols; at a slightly higher temperature dimethyl ether is produced; there is quite a narrow band around 450° where iso-C_4H_{10} is produced; above this temperature the deposition of C becomes excessive. The synthesis is generally insensitive to S. Catalysts are known to be good for 6 months without any decrease in activity. With the Ru catalyst, chiefly solid paraffins of high melting point are produced at over 100 atm. pressure. It is now known that a catalyst life of 2 yr. or more can be expected at an operating pressure around 100 atm. and that increased pressure gives an increase in both yield and molecular weight of the paraffins produced. The reaction has been operated at 1,000 atm. with complete success. The catalyst is very sensitive to S; the concentration of S must be as low as 0.01 gm. per 100 $m.^3$ to prevent rapid poisoning. At 475°–500° and 30 atm. pressure with a catalyst of Cr oxide or Mo oxide, a gas 1 CO : 1 H_2 yields aromatic compounds. The factor of conversion is poor, and much CH_4 is formed; each $m.^3$ of synthesis gas yields up to 10 gm. of liquid containing about 50% aromatics and 50% naphthenes. The aromatics are chiefly xylene and toluene. At the high temperatures, C deposition is troublesome; an improvement can be secured by adding 5–10% of K_2CO_3 to the catalyst, but this slows the reaction rate. By means of methylation, with a catalyst of methyl chloride, Al chloride and Al metal, any lower paraffin may be converted into a more highly branched paraffin containing 1 more C atom. Thus far, success has been achieved only with the conversion of iso-C_4H_{10} to neopentane. This reaction proceeds to completion and *n*-C_4H_{10} isomerizes catalytically into iso-C_4H_{10} during the reaction, thus again giving neopentane; but iso-C_5H_{12} and the other butanes all yield neopentane again, being evidently decomposed into iso-C_4H_{10}.

701a. DEWITT, C. C., AND HEIN, L. B., Partial Oxidation of Light Hydrocarbon Gases at Atmospheric Pressure. Michigan State Coll. Agr., Eng. Expt. Sta., Bull., vol. 106, 1946–1947, 40 pp.; Chem. Abs., vol. 42, 1948, p. 857.

Partial oxidation of CH_4, C_2H_6, C_2H_8, and natural gas to HCHO and HCOOH was investigated over

the range 350°–650° at 739 mm. pressure. Catalysts employed were electrolytic Cu, SiO_2 gel, CuO–SiO_2, V oxides on SiO_2, Mo oxides on SiO_2, and bronze tubing. The yield from the oxidation of natural gas in the presence of a Mo oxide catalyst at 650° was of the order of 3%, calculated as the % of O_2 input resulting in useful product. Data on the effects of flow rates of the various reactants in the presence of different catalysts are given. The most active catalysts were found to be Mo oxide–SiO_2 and V oxide–SiO_2 in that order.

DEWITT, T. W. *See* abs. **377, 669, 2009, 2718.**

DEWLING, W. L. E. *See* abs. **2831.**

D'HONT, M. *See* abs. **2460.**

DIDENKO, P. D. *See* abs. **2.**

DIEBOLD, R. *See* abs. **3436, 3437.**

DIECKMANN, T. *See* abs. **1420.**

DIENST, W. *See* abs. **1036.**

702. DIEPSCHLAG, E. [Reduction of Iron Ore by Employing Higher Pressures.] Arch. Eisenhüttenw., vol. 10, 1936, pp. 179–181; Chem. Abs., vol. 31, 1937, p. 635.

Complete separation of the O from the Fe in the ore is possible only at temperatures over 1,000°. Lower temperatures can, however, be used with fully the same efficiency and economy if the reduction is carried out at higher pressures, which increases velocity of reduction as the reduction gases penetrate faster into the interior. The reduction is greatest for pressures up to 3 atm. and more efficient in an atmosphere of CO than of H_2. The following reactions take place: $3Fe_2O_3+H_2=2Fe_3O_4+H_2O$; $Fe_2O_3+H_2=2FeO+H_2O$; $Fe_2O_3+3H_2=2Fe+3H_2O$; $3Fe_2O_3+CO=2Fe_3O_4+CO_2$; $Fe_2O_3+CO=2FeO+CO_2$; $Fe_2O_3+3CO=2Fe+3CO_2$.

DIETER, W. E. *See* abs. **1448.**

DIETHELM, A. *See* abs. **1616.**

DILTHEY, P. *See* abs. **978, 979, 980, 981, 1043.**

DIMOCK, W. R. *See* abs. **3747.**

DINERSTEIN, R. A. *See* abs. **3767, 3768.**

DINGMANN, T. *See* abs. **3052, 3053, 3055, 3057, 3059, 3061.**

DITTRICH, E. *See* abs. **3456.**

703. DOBYCHIN, D. P., ROGINSKIĬ, S. Z. AND TSELLINSKAYA, T. F. [Increasing the Activity of Nickel Formate Catalysts.] Jour. Phys. Chem. (U. S. S. R.), vol. 13, 1939, pp 1367–1388; Chem. Abs., vol. 35, 1941, p. 373.

Activities of $Ni(CHO_2)_2$ catalysts obtained at various temperatures, 150°–300° in vacuo and in a stream of H_2, were determined by means of the I numbers of the oils obtained by hydrogenation in their presence. Catalysts obtained in a stream of H_2 were as much as 5 times as active as those obtained in vacuo. Up to 245°, a higher temperature yields a more active catalyst, 2–3-fold at 220°–245°; further heating again yields less active catalysts because of rapid aging. The temperature should be brought up to the optimum as rapidly as possible. Similar results should be found for other catalysts produced by endothermic reactions. Catalysts prepared from $Ni(HCO_2)_2$ suspended in oil are more active than those prepared from the dry salt; the oil produces a more disperse catalyst by hindering recrystallization and sintering. Experimental data under various conditions and the activity of catalysts obtained are shown in 9 tables and 17 figures. In the initial stages the rate is given by the equation for a topochemical reaction, $\sqrt[3]{p}=\alpha+\beta t$. After a surface layer of Ni covers the formate crystal, the rate of decomposition is given by $v=k(a-x)^{2/3}$. For decomposition in oil, the initial rate is given by $v=At^3-Bt^4$.

704. DODGE, B. F. Note on the Methanol Equilibrium. Ind. Eng. Chem., vol. 22, 1930, pp. 89–90; Chem. Abs., vol. 24, 1930, p. 1018

Discrepancies between calculated values for K_p and those experimentally determined for the MeOH synthesis may be accounted for by lack of extreme accuracy for heats of reaction, since the quantity sought is the result of differences of larger quantities. Thus, if the value for heat of combustion for MeOH were in error 0.1%, K_p for the reaction at 298.1°, K would be in error 33%.

———. *See* abs. **1511, 2303, 2456, 2457, 2458, 3583.**

705. DOEHLEMANN, E. [Rates of Decarburization and of Carburization of Iron, Nickel, and Cobalt in Carbon Monoxide–Carbon Dioxide Mixtures.] Ztsch. Elektrochem., vol. 42, 1936, pp. 561–569; Chem. Abs., vol. 30, 1936, p. 8120.

Velocities of carburization and decarburization of Fe, Co, and Ni foils in stagnant CO–CO_2 mixtures at 920°–970° were determined by following the change in electrical resistance with a Kelvin bridge. Under the experimental conditions employed, the reaction at the metallic surface is the rate-determining factor. Diffusion within the metal proceeds rapidly. Data from the experimental curves show that the decarburization velocity is independent of the C content of the metal and increases linearly with the total pressure for a constant ratio of the partial pressures P_{CO2}/P_{CO}. Carburization or decarburization velocities can be expressed as $-dc/at=[K_1P_{CO2}+K_2(P_{CO2}/P_{CO})]\ [1-(c_t/c)]$, where K_1 and K_2 are graphically determined velocity constants while c_t and c are the C contents in weight % in the metal at equilibrium and at time t. From the 1st bracketed expression it can be seen that the reaction CO_2 (gas)$\rightleftharpoons$CO+O (adsorbed) determines the velocity of the process, while the reaction O (adsorbed)+C$\rightleftharpoons$CO is essentially in equilibrium. Values of 0.078, 0.155, and 0.308 for the CO_2: CO ratio were employed. These corresponded to solubilities of 0.42, 0.20, and 0.087 gm. C: 100 gm. Fe. Carbides do not precipitate at these temperatures until a solubility of C in Fe of 1 gm.: 100 gm. is obtained. As the solubilities of C in Co and Ni at these temperatures are smaller than for Fe, CO_2: CO ratios of 0.036, 0.082, and 0.108 were used for these metals. Plots of $dc:dt$ *vs.* reaction pressure for Co and Ni were similar to those for Fe, and the curves for all 3 metals can be similarly expressed. Different carburization rates may be found for 2 samples of Fe otherwise considered to be identical.

706. ———. [Mechanism of the Water-Gas Reaction on an Iron Catalyst.] Ztschr. Elektrochem., vol. 44, 1938, pp. 178–183; Chem. Abs., vol. 32, 1938, p. 4060.

Velocity of the reaction $CO_2+H_2\rightarrow CO+H_2O$ on an Fe-foil catalyst at 910° is essentially proportional to the CO_2 pressure and increases with H_2 pressure somewhat more slowly than corresponds to a direct proportionality. The stationary C concentration of the Fe catalyst in a water-gas mixture, which is reacting in the direction $CO_2+H_2\rightarrow CO+H_2O$, is greater than corresponds to the equilibrium : C (dissolved in γ-Fe)+CO_2 (gas)$\rightleftharpoons$2 CO (gas). This qualitative result agrees with the working hypothesis that the catalytic water-gas reaction can be explained as a transfer of an O atom from CO_2 to H_2 through the formation of adsorbed O on Fe as an intermediate product; thus, (1) formation of O (adsorbed) as a relatively slow reaction: CO_2 (gas)$\rightleftharpoons$CO (gas)+$O_{(ads)}$: It is followed by (2) a rapid reaction (practically at equilibrium); $O_{(ads)}+H_{2\,(gas)}\rightleftharpoons H_2O_{(gas)}$: Then (3) a rapid reaction of C dissolved in Fe; $C_{\text{(dissolved in }\gamma\text{-Fe)}}+O_{(ads)}\rightleftharpoons CO_{(gas)}$. The data obtained did not confirm

this mechanism quantitatively, probably because of simultaneous reactions.

DOHERTY, H. G. *See* abs. **3154.**

707. DOHERTY, J. D. Synthetic Fuels Development. Oil Gas Jour., vol. 47, No. 28, 1948, pp. 207, 419; Min. Eng., vol. 1, No. 4, 1949, pp. 116–124; Am. Inst. Min. and Met. Eng., Tech. Pub. 2562 **F.**

Paper was presented at the annual Fuels Conference of the American Society of Mechanical Engineers and the American Institute of Mining and Metallurgical Engineers. Because "synthetic liquid fuels are not going to do us very much good in an emergency if we have to start from scratch," construction of commercial plants for the production of 1,000,000 bbl. per day should begin at once. The planned program calls for a total investment in plant and equipment of 8.7 billion dollars as compared with the 7.5 billion dollars that the petroleum industry will spend between 1947 and 1951 to maintain its present production rates. In general 2 processes would be used about equally: The Fischer-Tropsch gas-synthesis process and the Bergius coal-hydrogenation process. The cost of production per gallon of total products would be 12.4 or 12.6 cents depending on the process used. The production of 1,000,000 bbl. per day would consist of 86,000 bbl. liquefied propane and butane, 648,000 bbl. high-grade motor gasoline, and 266,000 bbl. Diesel and furnace oils. The coal requirement would be 575,000 tons per day, a 34% increase over the average 1947 production. Of this consumption, 213,000 tons would be bituminous coal from east of the Mississippi River and 362,000 tons would be coal and lignite from the West. Steel requirements are estimated at 6.3 million tons, the peak consumption occurring 5 or 6 years after starting the program. Employment would be given to about 160,000 men, including miners.

———. *See* abs. **644.**

708. DOHERTY, T. B. Hydrocarbon Synthesis. Eng. Jour., vol. 31, 1948, pp. 425–429; Chem. Abs., vol. 42, 1948, p. 9116.

Possibilities of producing synthetic liquid fuels from coal or natural gas are discussed. German methods and plants are described as well as the American methods of preparing synthesis gas and the proposed method of processing coal for its production. The long-range United States development of synthetic fuels is most likely to be from coal. While in Canada the gas process is economically more attractive, it is unlikely that synthesis will be started in Canada in the near future. Reasons are given for this conclusion.

709. DOHSE, H. [Heterogeneous Decomposition Reactions. III. Decomposition of Methanol on Zinc Oxide.] Ztschr. physik. Chem., vol. 8, Abt. B, 1930, pp. 159–180; Chem. Abs., vol. 24, 1930, p. 4452.

CH_3OH dissociates in 2 steps; 1st. into HCHO and then to $CO+H_2$. This can be seen with certainty only when studied from monomolecule films, and both steps are then of 1st. order. The reaction constants grow somewhat smaller as the reaction proceeds as a result of lessening activity of the reaction centers. The heat of activation for the 1st. is 22,500 cal. and for the 2d. 35,000 cal., the latter being in good accord with the direct determination for HCHO.

710. ———. [Catalytic Gas Reactions.] Chem. Fabrik, vol. 11, 1938, pp. 133–139; Chem. Abs., vol. 32, 1938, p. 4060.

Gaseous, liquid, and solid catalysts are discussed briefly, with examples to illustrate the reacting materials, temperature, pressure, catalyst, and products. The mechanism of catalysis, catalyst formation, and loss of activity by contraction from overheating and from poisoning are explained. A flow diagram, 5 views, and a model of a 75,000-ton plant for the manufacture of motor fuel from coal by the Fischer and Tropsch method are shown, and also cuts of apparatus for H_2SO_4 manufacture, including the Lurgi apparatus for direct conversion of H_2S into H_2SO_4.

DOKKUM, T. *See* abs. **3043.**

711. DOLCH, M., AND KOLLWITZ, J. [Reaction of Water Vapor Upon Glowing Coke. Contribution to the Oxidation of Coal.] Braunkohle, vol. 31, 1932, pp. 607–610, 628–632, 645–649; Chem. Abs., vol. 26, 1932, p. 5735.

In studying effects of rate of steam flow upon composition of gas formed, the reaction $C+H_2O=CO+H_2$ with bituminous cokes is found to be more rapid, and the reaction $C+2H_2O=CO_2+2H_2$ is more rapid with brown-coal cokes. With cokes of intermediate coals, this distinction is not noted. Thus, not only temperature and time, but the constitution of coal determine gas consumption. Apparatus for coke gasification with measured amounts of steam is described.

712. DOLCH, P. [Action of Steam on Coal. Study of Superimposed Equilibria.] Ztschr. Elektrochem., vol. 38, 1932, pp. 596–601; British Chem. Abs., 1933, B, p. 5; Chem. Abs., vol. 26, 1932, p. 5193.

Action of steam on coal leads to the formation of CO and H_2. The formation of CO_2 is a secondary reaction ($CO+H_2O=CO_2+H_2$), the extent of which depends on the active coke surface. There is no evidence for the reaction $C+2H_2O=CO_2+2H_2$. Experiments with CO_2 and H_2, which were passed over coke, confirm this.

713. ———. [Water-Gas Generation From Coke and Coal.] Gas- u. Wasserfach, vol. 75, 1932, pp. 807–811; Chem. Abs., vol. 27, 1933, p. 399.

Calculations from the experiments of Bunte and Dolch show that the reaction of water vapor on C and the formation of CO_2 is determined by the water-gas equilibrium rather than by the water-gas reaction. The degree of attainment of the water-gas equilibrium depends on the reactivity of the coke on which the reaction takes place. No evidence is found for the direct action of water vapor on C according to the reaction $C + 2H_2O = CO_2 + 2H_2$. Experiments with mixtures of CO_2 and H_2 over wood charcoal at temperatures of 600°–1,000° indicated that CO_2 and H_2 first react to form CO and H_2O at about 600°, while CO_2 first begins to react with C at about 750°; with coke the corresponding temperatures are 800° and 980°. The significance of coke reactivity for technical water-gas manufacture is outlined, showing that a very reactive coke is desirable for the run, but that it leads to an excessive CO content during the blow period. Special adjustments of blow and run periods are required with the very reactive brown-coal coke. High reactivity is desirable, however, for the newer continuous water-gas processes using recuperators. The use of cokes from young coals should permit the manufacture of gas high in H_2 and CO_2, from which the CO_2 can readily be washed out to give a gas with high H_2 content for synthesis purposes.

714. ———. [Water-Gas Generation From Coal and Coke.] Gas- u. Wasserfach, vol. 75, 1932, p. 974; Chem. Abs., vol. 27, 1933, p. 827.

Reply to abs. **1412** and **2436.** The attainment of the water-gas equilibrium depends more on the reactivity of the carbonization product than on the ash content. In general the degree attainment of this equilibrium parallels the reactivity of various cokes with respect to water vapor as given by Bunte (abs. **407**). Experiments at 800° with a beechwood charcoal containing 2.3% ash indicated substantial attainment of the water-gas equilibrium as did experiments with a coke containing 5.3% ash. Both charcoal and coke were prepared by carbonizing the wood or coal at 1,000°

715. ———. [Influence of the Reactivity of Cokes on the Behavior of Carbon Dioxide-Hydrogen Mixtures at 600°–1,200°.] Brennstoff-Chem., vol. 14, 1933, pp. 261–263; British Chem. Abs., 1933, B, p. 772; Chem. Abs., vol. 27, 1933, p. 5173.

Both bituminous coke and wood charcoal accelerate the reaction $CO_2+H_2 \rightarrow CO+H_2O$. Equilibrium was not reached during passage of a 3 : 7 mixture over the coke even at 970°; above this temperature interaction of the coke with the gases began, but even at 1,100° there were still appreciable quantities of steam in the efflux gases; below 820° with 34 : 66 mixtures with coke or charcoal, respectively, solid C does not enter into the reaction. Equilibrium in the gaseous reaction was reached over the charcoal at 750°; above 820° the gases reacted with it, and at about 1,000° only CO and H_2 were produced.

716. ———. [Chemical Principles of Synthesis-Gas Production. I. Water-Gas Equilibrium.] Feuerungstech., vol. 27, 1939, pp. 1–5; British Chem. Abs., 1939, B, p. 684; Chem. Abs., vol. 33, 1939, p. 3997.

In a discussion of the water-gas equilibrium as the chemical basis of synthesis-gas production, $H_2 : CO = 2$, the author compares the direct method of production in which all the water gas is passed through the catalyst vessel and conversion with steam continues until $H_2 : CO = 2$, and the indirect method in which some of the water gas is converted with steam into a gas with a low proportion of CO (2–4%) and this gas is mixed with the remaining water gas to obtain the desired ratio $H_2 : CO = 2$. The quantity of synthesis gas produced by the 2 methods is the same, but the steam consumption differs considerably.

717. ———. [Chemical Principles of Synthesis-Gas Production. II. Composition of Synthesis Gases. III. Yield of Synthesis Gas.] Feuerungstech., vol. 27, 1939, pp. 41–51; British Chem. Abs., 1939, B, p. 684; Chem. Abs., vol. 33, 1939, p. 3997.

Discusses the composition of synthesis gas and its dependence on the H_2 available. Explains ternary diagrams and derives equations to determine the effect of the H_2 available on the yield of synthesis gas. Discusses effects of methods of procedure and the CH_4 content of the gas.

718. ———. [Production of Synthesis Gas by Oxygen-Steam Gasification.] Feuerungstech., vol. 27, 1939, pp. 103–108; British Chem. Abs., 1939, B, p. 684; Chem. Abs., vol. 33, 1939, p. 5157.

After a general discussion of the chemical theory and the consumption of heat and O_2, the author describes briefly technical processes for producing synthesis gas by gasification with O_2-steam mixtures; that is, the Winkler producer, O_2-steam gasification in vertical ovens, the Lurgi process under pressure, and also the effect of the formation of CH_4 on the yield and composition of the gas. It is claimed that gasification in vertical ovens at atmospheric pressure with O_2-steam mixture produces a synthesis gas containing little CH_4 with the smallest O_2 consumption.

719. ———. [Synthesis Gas From Brown Coal. Fundamentals.] Brennstoff-Chem., vol. 20, 1939, pp. 101–111; Chem. Abs., vol. 33, 1939, p. 9592.

Brown coal as a raw material for producing synthesis gas is examined in detail in low-temperature assays, composition, and yield of products from 3 mid-German and 1 Bohemian brown coals of varying tar contents. Data obtained were analyzed in material balances and presented graphically. From the calculated proportions of the various constituents in the products, behavior of these coals in the Bubiag-Didier process with (1) simultaneous tar degasification, (2) tar removal and return of detarred gases, (3) complete gasification with outside heat, and (4) gasification with tar recovery and outside heating; in the Wälz gas process of Pintsch-Hillebrand and Koppers; and in the O_2-steam gasification of the Winkler suspension and pit processes, has been predicted with detailed yield data. Comparison indicates that the last-named process, in which heat-requirements of the gasification are met by separate gasification of part of the fuel, is far superior in yield of synthesis gas, particularly $CO+H_2$.

720. ———. [Development of the Koppers Continuous Vertical Retort in the Past 25 Years.] Gas- u. Wasserfach, vol. 86, 1943, pp. 27–33; British Chem. Abs., 1945, I, B, p. 118.

Kopper's installation for producing synthesis gas for noncoking Japanese long-flame coal of low ash-melting point is described.

720a. ———. [Reactions in Water-Gas and Synthesis-Gas Generation and Their Presentation in the Terbeck Diagram.] Gas- u. Wasserfach, vol. 93, 1952, pp. 234–238; Chem. Abs., vol. 46, 1952, p. 7,737.

Terbeck diagram has been shown to be useful for operational control and in the interpretation of gas analyses for synthesis gas plants. This diagram is also of value in planning, developing and placing such plants in operation. The graphic method presented in this article is simple and gives close agreement with practice.

721. Dolgov, B. [Synthesis of Liquid Fuel From Gases Obtained in Underground Gasification of Coal.] Podzemnaya Gazifikatsiya Uglei, No. 5, 1935, pp. 10–18; Chem. Abs., vol. 30, 1936, p. 1541.

Review. 19 refs.

722. Dolgov, B. N. [Methanol Synthesis. I.] Jour. Chem. Ind. (U. S. S. R.), vol. 8, 1931, pp. 457–472; Chem. Abs., vol. 25, 1931, p. 5139.

Review of well-known methods for industrial production of synthetic MeOH.

723. ———. [Methanol Synthesis. II.] Khim. Tverdogo Topliva, vol. 3, 1932, pp. 185–204; Chem. Abs., vol. 28, 1934, p. 5211.

Synthesis was carried out in a steel bomb lined with Cu and having a Cu insert to hold the catalyst. The process was effected at a cold pressure of 100–150 atm. and 350°–400°. Pure Kahlbaum CO and H_2 were used containing H_2, 97.2; CH_4, 0.4; unsaturated compounds, 0.2; N_2, 2.6; and O_2, 0.3%. Cu catalysts are not recommended, but good results were obtained with Zn chromates. Among the best tricomponent catalysts were $Cu_{46}Zn_{46}Cr_8$ and $Cu_{50}Zn_{40}Bi_{10}$, the yield of MeOH amounting to 86–87% and 75%, respectively, at temperatures of 360° and 400°. The product contained MeOH 89–92%, unsaturated compounds 2–4%, aldehydes and ketones 0.05–0.2%, and H_2O and other admixtures 9–4%. Various reactions are described. The difficulties in determining the amount of H_2O accompanying MeOH were overcome by the construction of a special apparatus, the product being treated with CaO.

724. Dolgov, B. N., and Karpov, A. Z. [Methanol Synthesis. III. Synthesis From Commercial Gas and a Long-Life Catalyst.] Khim. Tverdogo Topliva, vol. 3, 1932, pp. 282–288; Chem. Abs., vol. 28, 1934, p. 5212.

Synthesis was carried out in the presence of 4ZnO. Cr_2O_3 catalyst was prepared from 324.0 parts ZnO and 304.0 parts Cr_2O_3 by shaking in 5 l. of H_2O for 24 hr. The mass then was filtered through a Büchner funnel and pressed into long strips. The gas was a technical water gas containing varying amounts of H_2 and CO. Therefore H_2 was added to the required ratio. The process was carried out at a constant pressure, the best pressure being 250 atm., and 370°. The product was contaminated with Fe carbonyl, which precipitated

out through the influence of air. The degree of conversion with each cycle amounted to about 9%, with a total yield of 63%.

725. DOLGOV, B. N., AND BOCHAROVA, E. M. [Methanol Synthesis. IV. Catalytic Oxidation of the Synthetic Methanol to Formaldehyde]. Khim. Tverdogo Topliva, vol. 3, 1932, pp. 406–418; Chem. Zentralb., 1934, I, p. 2652; Chem. Abs., vol. 28, 1934, p. 5805.

According to the experiments described in detail, passage of the gas mixture over porous surfaces (glass, porcelain, C) yields minute amounts of HCHO. The metallic catalysts, except Ag and Cu, are of little use. The yields are slightly higher when the catalysts are compressed in the reaction tube. Metal oxides cannot be used, while catalysts prepared from Cu disks, which are placed close together, give a HCHO yield up to 42%. A catalyst composed of CuO alone or together with an activator gives CH_2O yields of 21–42%. The best results were obtained with Th and U catalysts, which yielded up to 41–42% of CH_2O. The apparatus used is described, and the numerical data are tabulated.

726. DOLGOV, B. N., AND KARPINSKIĬ, M. N. [Methanol Synthesis. V. Influence of Activators on the Zinc-Chromite Catalyst.] Khim. Tverdogo Topliva, vol. 3, 1932, pp. 559–568; Chem. Zentralb., 1934, I, p. 2652; Chem. Abs., vol. 28, 1934, p. 5805.

Following promotors were used in conjunction with the $4ZnO.Cr_2O_3$ catalyst: W, V, Th, Ce, La, Ta, and Zr. The experiments were carried out with a decreasing pressure, each being carried out for 60 min. with 500 cc. of the catalyst. The highest MeOH yields were obtained with the promotors (1%) ThO_2, ZrO_2 and TaO_2. The results are tabulated and plotted.

727. ———. [Methanol Synthesis. VI. Synthesis From Carbonic Acid and Hydrogen.] Khim. Tverdogo Topliva, vol. 4, 1933, pp. 69–79; Chem. Zentralb., 1934, I, p. 2652; Chem. Abs., vol. 28, 1934, p. 5805.

These experiments were carried out with a decreasing pressure and the activity of the catalysts was investigated at 226°–400°. In another synthesis carried out at constant pressure and with introduction of additional portions of gases during the process, a circulating Fischer retort of 4.5-l. capacity was used. The gas mixture was prepared by mixing CO_2 and H_2, compressing it, and keeping it in steel bottles. The reaction $CO_2+3H_2\rightarrow CH_3OH+H_2O$, as shown by the experiments, proceeds in 2 stages (1) $CO_2+H_2\rightarrow CO+H_2O$ and (2) $CO+2H_2\rightarrow CH_3OH$. The velocities of the reactions differ, depending upon the ratio of gases, temperature, catalyst, etc. 19 different catalysts and their mixtures were investigated, and it was found that the maximum lies at 300°–325°, that is, 75° lower than that for MeOH from CO and H_2. The following catalysts were used in various combinations: MgO, Fe_2O_3, ZnO, ThO_2, V_2O_5, Ce_2O_3, CuO, Ni_2O_3, CdO, MnO, and Cr_2O_3. The highest MeOH yields were obtained with ZnO+4.5% CdO+5% Fe_2O_3 and ZnO+2% Fe_2O_3+1% CuO, reaching 51.5% and 50%. However, when maintaining a constant pressure by the introduction of new portions of gas, working at 325°, 200–210 atm., and using the catalyst ZnO+5% CdO, the yield of CH_3OH could be raised to 63% by weight. Changes in the velocity of the flow of the gas mixture caused lower yields of MeOH because of the slowing down of the conversion of CO_2 to CO. The crude MeOH contained C_nH_{2n} traces, C_nH_{2n+2} none, HCHO none, AcH traces, AcOEt none, AcOH about 0.05–0.06%, and $Fe(CO)_5$ none. A pure 98% MeOH is obtained by distillation and rectification. The gas used in the synthesis consisted of 1 vol. CO_2/3–3.5 vol. H_2 with the admixture of 0.2–0.8% CO and 0.4–3.0% N_2.

728. DOLGOV, B. N., KARPOV, A. Z., AND VELTISTOVA, M. V. [Methanol Synthesis. VII.] Khim. Tverdogo Topliva, vol. 4, 1933, pp. 492–499; Chem. Abs., vol. 28, 1934, p. 6279.

Catalyst that was used previously (*see* abs. **724**) and that still retained its activity was analyzed after 186 experiments. It contained ZnO, 78.1, Cr_2O_3, 18.3; Fe_2O_3, 0.3; and S, 2.0%. The missing 1.1% includes admixtures such as $ZnCO_3$ and $ZnSO_4$. The influence of the volume velocity of the mixture of gases on the MeOH yield was investigated; at 350 l./hr. the volume velocity is 35,600, the duration of contact 10.4 sec., and the yield of MeOH 750 gm./hr. The frequency of the discharge of the MeOH from the apparatus affects the yields considerably; on discharging every 5 min. during 1 hr., 457 $cm.^3$ of MeOH is obtained; in discharging every 30 min., the yield is only 373 cc. In the experiments carried out with water gas alone, without the addition of H_2, an appreciable decrease in the activity of the catalyst takes place. With the increase of the amount of the H_2, through conversion of the CO and consequent formation of H_2O, the activity of the catalyst increases, remaining, nevertheless, below that existing in the presence of enough H_2. Small amounts of AcOH, EtOAc, AcH, allyl alcohol, acetone, Fe carbonyl, S, and H_2O are formed, in addition to 96% MeOH.

729. DOLGOV, B. N., KARPINSKIĬ, M. N., AND SILINA, N. P. [Methanol Synthesis. VIII.] Khim. Tverdogo Topliva, vol. 5, 1934, pp. 470–474; Chem. Abs., vol. 29, 1935, p. 7275.

ZnS as such, or with the addition of 5% of CdS, MoS_2, and CuS, decomposes MeOH 100% at 300°–375°. ZnS, with the addition of 1% of the above admixtures and Sb_2S_5 decomposes MeOH 100% at 300°–325°. ZnO decomposes MeOH completely at a temperature exceeding 400°. The composition of the gas obtained is near the stoichiometric ratio CO : H_2=0.5 only for ZnS, further additions considerably increase the H_2 ratio, particularly the 1% admixtures (1.5–2.5 times). An addition of 1% of activators increases the activity of the catalyst noticeably, but it lowers the amount of CO in the gas. The catalysts may be suitable for MeOH synthesis carried out under pressure.

730. DOLGOV, B. N. [Synthesis of Hydrocarbons From Carbon Oxide and Hydrogen Under Atmospheric Pressure.] Khim. Tverdogo Topliva, vol. 8, 1937, pp. 901–922; Chem. Abs., vol. 32, 1938, p. 4308.

Review in which 22 catalysts used in the synthesis are tabulated and their merits discussed.

———. *See* abs. **277, 278, 279, 280, 281, 282, 1578, 3557.**

DOLGOV, B. N., AND BOCHAROVA, E. M. [Methanol Synthesis. IV. Catalytic Oxidation of the Synthetic Methanol to Formaldehyde.] *See abs.* **725.**

DOLGOV, B. N., AND KARPINSKIĬ, M. N. [Methanol Synthesis. V. Influence of the Activators on the Zinc–Chromite Catalyst.] *See* abs. **726.**

———. [Methanol Synthesis. VI. Synthesis From Carbonic Acid and Hydrogen.] *See* abs. **727.**

DOLGOV, B. N., AND KARPOV, A. Z. [Methanol Synthesis. III. Synthesis From Commercial Gas and a Long-Life Catalyst.] *See* abs. **724.**

DOLGOV, B. N., KARPINSKIĬ, M. H., AND SILINA, N. P. [Methanol Synthesis. VIII.] *See* abs. **729.**

DOLGOV, B. N., KARPOV, A. Z., AND VELTISTOVA, M. V. [Methanol Synthesis. VIII.] *See* abs. **728.**

731. DOMENICALI, C. A. Magnetic and Electric Properties of Natural and Synthetic Single Crystals of Magnetite. Phys. Rev., vol. 76, 1949, p. 460; vol. 78, 1950, pp. 458–467; Chem. Abs., vol. 44, 1950, p. 7104.

732. DOMINIK, W. [Catalysts for the Reaction $CO+H_2O \rightleftarrows CO_2+H_2$.] Przemysl Chem., vol. 11, 1927, pp. 557–562; Chem. Abs., vol. 23, 1929, p. 1997.

Process of preparing the catalyst was based on the equation: $3FeCO_3+HNO_3+4H_2O=3Fe(OH)_3+NO+3CO_2$. Its activity was still great at a temperature as low as 390° working with a gas composed of CO_2, 7.5, CO, 17, and H_2, 55%. The hypothesis was substantiated that only metal that possesses the least alkaline properties, and the sulfide of which is readily hydrolyzed by water vapor, can be a permanent activator in presence of S gases. Thus, it was possible to reactivate the Fe catalyst with Cr or Al but not with Co or Mn.

733. ———. [Catalysts for the Reaction $CO + H_2O \rightleftarrows CO_2 + H_2$.] Przemysl Chem., vol. 12, 1928, pp. 229–235; Chem. Abs., vol. 22, 1928, p. 4334.

From theoretical considerations the following equation for $CO + H_2O \rightleftarrows CO_2 + H_2$ is derived:

$$\frac{x-x_2}{x-x_1}=\frac{x_0-x_2}{x_0-x_1}\cdot e^{-b(K-1)(x_1-x_2)1/V}.$$

This is like that for bimolecular reactions in homogenous systems. b is a constant that characterizes the useful surface of the catalyst at a given temperature, $K = [CO_2]\,[H_2] : [CO]\,[H_2O]$ = equilibrium constant at a given temperature, V = space velocity of the gas vapor mixture in cc. per hr. per gm. of catalyst, x = partial pressure of CO_2 in the reaction mixture, x_0 = partial pressure of CO_2 before the reaction, x_1 and x_2 the 2 roots of the equation

$$\frac{x(P_0H_2+x-x_0)}{\{P_0CO-(x-x_0)\}\{P_0H_2O-(x-x_0)\}}-K=0,$$ in which

P_0H_2, P_0CO and P_0H_2O represent the partial pressures of the respective components before the reaction, and only x_2, the root with the negative radical, represents the pressure of CO_2 at equilibrium. To test this experimentally the extent of the reaction was measured after the gaseous mixture had passed over 1 and over 2 equal portions of the catalyst under the same conditions. A whole series of determinations shows that the catalysis of water gas does proceed according to the derived equation, but that possibility of small differences of temperature lowers the accuracy of the determinations.

734. ———. [Processes for the Synthetic Production of Liquid Fuels.] Przeglad. Chem., vol. 2, 1938, pp. 14–17; Chem. Zentralb., 1939, I, p. 1698.

Review of processes for the production of fuels from coal, with comparative costs for the construction of plants in Poland.

DONATH, E. E. *See* abs. **644, 3311.**
DONN, L. *See* abs. **3392.**
DORCAS, M. J. *See* abs. **1488.**
DORING, W. *See* abs. **3570.**

735. DORSCHNER, O. [Gas Pipeline Transmission of Methane Derived From Pressure Gasification and Synthesis.] Erdöl u. Kohle, vol. 2, 1949, pp. 59–65; Chem. Abs., vol. 43, 1949, p. 4832.

For obtaining a gas of high calorific value from the residual Fischer-Tropsch synthesis, a process has been developed that combines pressure gasification of coal with Fischer-Tropsch synthesis. Pressure gasification may be carried out with lignite or coal (moisture and ash content up to 35%, particle size 2–40 mm.) and an O_2-steam mixture at 10–30 atm. The exothermic CH_4 reaction reduces the O_2 consumption to ½ of that used in similar processes. The percentage compositions of the raw gas, synthesis gas (after removal of CO_2), and CH_4 gas (residual gas from Fischer-Tropsch synthesis) follow, respectively: CO_2, 28.6, 1.0, 3.9; C_nH_m, 0.9, 1.2, 1.8, CO, 18.7, 25.5, 2.7; H_2, 38.1, 53.3, 3.2; CH_4, 12.4, 17.2, 82.1; N_2, 1.3, 1.6, 6.3; heats of combustion in kcal. per m.^{3} were 3,150, 4,350, 8,450. There is no reduction in yield of liquid products nor in catalyst activity. The heat balance for ordinary synthesis gas: 3,066 kcal. = 100%; liquid hydrocarbons, paraffin 1,385 kcal. = 45%; residual gas 1,062 kcal. =34.7%; steam 414 kcal. = 13.6%; loss 205 kcal. = 6.7%. Heat balance for pressure gasification 4,135 kcal. = 100%; liquid products 1,240 kcal. = 30%; CH_4 gas 2,290 kcal. = 55.4%; steam 400 kcal. = 9.7%; loss 202 kcal. = 4.9%. The gas also may be utilized as fuel for motor vehicles, locomotives (gas turbines), or raw material for C_2H_2 manufacture. Diagram of process.

736. DOTTERWEICH, F. H. Report of Subcommittee. I. On New Developments. Proc. Am. Gas Assoc., vol. 26, 1944, pp. 316–318.

Perfection of the steam conversion process for transformation of natural gas to blue gas or H_2 as end products has been of importance. The former is available for MeOH and HCHO production or as the first steps in the Fischer-Tropsch process. To date, research on this subject suggests the production of 1 bbl. of hydrocarbon liquid/10,000 cu. ft. of natural gas, including fuel for the process.

737. ———. Intrinsic Value of Natural Gas, a National Asset. Am. Gas Jour., vol. 165, No. 6, 1946, pp. 11–14, 58.

The role of natural gas in the national economy is presented, with brief mention of its utilization in producing liquid fuel by way of the Fischer-Tropsch and the Hydrocol processes.

———. *See* abs. **2661, 2662.**

738. DOTTERWEICH, F. H., AND HUFF, W. J. Colloidal Properties of Iron Oxide in Hydrogen Sulfide Removal. Proc. Am. Gas Assoc., vol. 20, 1938, pp. 699–717; Gas Age, vol. 82, No. 9, 1938, pp. 43–44, 54, 56–58; Chem. Abs., vol. 33, 1939, p. 1473.

Adsorption capacity, activity, and colloidal content of a number of Fe oxides used for removing H_2S from gas were measured. These oxides were divided into 2 groups, (1) those containing more than 11% Al_2O_3 and (2) those containing less than that amount. Oxides of group (1) showed increasing capacity and activity for H_2S absorption with decreasing particle size; those of group (2) showed greater activity but diminishing capacity with decreasing particle size. Also oxides of the latter group are affected markedly in their activity by changes in alkali content. Heating the oxides to 550° caused the particle size of all oxides to increase; this resulted in correspondingly lower activity.

739. D'OUVILLE, E. L., AND HOWE, K. E. Use of Thermal Conductivity Cells for Gas Analysis in Studying the Fischer-Tropsch Synthesis of Hydrocarbons. Petrol. Refiner, vol. 26, No. 6, 1947, pp. 526–531.

Method is described with the help of 11 figs. for analysis of both synthesis gas and product gas from a bench-scale Co-catalyst Fischer-Tropsch unit. A single thermal conductivity cell unit is used for binary mixtures and for other mixtures that can be so considered. For complex mixtures of as many as 5 components a multiple cell unit is described. A complete description of the cells, auxiliary equipment, and technique is given. The advantages and limitations of the method are discussed with special reference to Fischer-Tropsch gases.

740. DOWD, J. J., ELDER, J. L., CAPP, J. P., AND COHEN, P. Experiment in Underground Gasification of Coal, Gorgas, Ala. Bureau of Mines Rept. of Investigations 4164, 1947, 62 pp.

Using various methods of operation, it was determined that gases could be generated specifically for use in generating power or for synthesis purposes. It is estimated that 236 tons of coal were burned completely and 164 tons coked during the combustion period. 5 types of blasting were used: Gas-air, O_2-air, O_2-air-steam, O_2-steam, and steam. Comparative heating val-

ues for each of these methods per cu. ft. of gas were, respectively: 47, 50, 110, 135, and 200 B. t. u. It was also determined that the first 2 methods produced gases suitable for power generation, while the last 3 yielded gases suitable for synthesis purposes.

741. DOWNS, C. R. Impact of Tonnage Oxygen on American Chemical Industry. Chem. Eng., vol. 55, No. 8, August, 1948, pp. 113–117, 121.

The paper was presented before the Chemical Market Research Association. Tonnage O_2 of 90–95% purity is being produced experimentally, and enormous plants for its production are being constructed. It will largely supplant 99.5% O_2, except for metal cutting and welding. Production of 99.5% O_2 now amounts to about 15.5 billion cu. ft./yr. 7 plants for production of 95% O_2 are now being built, the estimated production of which is 40 billion cu. ft./yr. The composition of 95% O_2 by vol. is approximately 95% O_2, 3.2% A, and 1.8% N_2. Plant and operating costs for a plant of 1,000 tons/day capacity should be $4,000,000 and $3.67/ton, respectively, whereas the cost of 99.5% O_2 is approximately $64–$120/ton, depending upon a monthly volume of 190–10 tons respectively. Several uses for tonnage O_2 are presented and discussed, such as synthetic fuels, chemicals, iron and steel production, roasting of ores, and city gas and chlorine production.

742. DOWNS, C. R., AND RUSHTON, J. H. Tonnage Oxygen. Chem. Eng. Progress, vol. 1, 1947, pp. 12–20; Chem. Abs., vol. 41, 1947, p. 2213.

Potential examples for the use of tonnage oxygen are discussed at some length: Gasification of coal, synthesis gas production, synthetic liquid fuels, chemical products (Synthine process), H_2SO_4 and SO_2, and metallurgical uses. Costs are calculated as follows:

Estimated total plant and operating costs, October 1946, for producing 95% O_2

Plant capacity——tons per day	120	240	360	480	1,000
Plant capacity——tons per hr	5	10	15	20	42
95% O_2——million cu. ft. per day	2.88	5.76	8.64	10.52	24.00
Approx. plant cost——million dollars	.9	1.3	1.7	2.0	3.4
Total utility cost——dollars [1] per ton	1.29	1.27	1.25	1.22	1.20
Operating labor per ton, $80 per day	.68	.34	.23	.17	.08
Maintenance per ton, 2.5%	.54	.39	.34	.30	.25
Fixed charges per ton, 12.5%	2.70	1.95	1.70	1.50	1.22
Total operating cost per ton	5.21	3.95	3.52	3.19	2.75
Total operating cost per 1,000 cu. ft——cents	21.7	16.5	14.7	13.3	11.5
Kw.-hr. per 1,000 cu. ft. for compression	13.4	13.1	12.8	12.7	12.5
Kw.-hr. per 1,000 cu. ft. for auxiliaries	2.2	2.2	2.2	2.2	2.2
Total kw.-hr. per 1,000 cu. ft	15.6	15.3	15.0	14.9	14.7

[1] Includes water, 1 cent per 1,000 gal.; incidental electric power, 0.4 cent per kw.-hr.; steam, 30 cents per 1,000 lb.

742a. DRAIN, J., AND MICHEL, A. [Structure and Thermomagnetic Properties of the Cobalt Carbide Co_2C.] Bull. soc. chim., 1951, pp. 547–549.

By passing CO over Co at 210° Co_2C was formed. Its structure appears to result from the insertion of C atoms into an orthorhombic, almost compact hexagonal, network of Co atoms. This insertion gives rise to a series of solid solutions which may deviate from the composition Co_2C. The carbide Co_2C is only the upper limit. The paramagnetic carbide Co_2C is transformed under vacuum into a compact hexagonal phase which is a solid solution of C in α–Co, this phase being progressively decarburized by heating to give a pure hexagonal Co. The gases, H_2, N_2, CO, in accordance with their nature, react upon Co_2C and cause an evolution analogous to that which the hexagonal Ni carbide undergoes under the same conditions.

743. ———. [Thermomagnetic and Structural Study of the Cobalt Carbide Co_2C.] Bull. soc. chim., January–February 1951, p. 23.

Reduced Co, supported on ThO_2, was carburized with CO at 210° C. to form paramagnetic, orthorhombic Co_2C (abs. **1440**) similar to Co_2N, with a=2.904Å, b=4.465Å, c=4.368Å. The crystalline parameters varied slightly with the mode of preparation, probably because of differences in composition. The carbide decomposed in vacuo at about 260° into a ferromagnetic hexagonal close-packed solid solution of C in α–Co, which was subsequently decarburized to hexagonal close-packed α–Co. Reaction set in at 298° in N_2, at 198° in H_2, and at 364° in CO.

744. DRAWE, R. [High-Heating-Value Gas From the Oxygen Gas Producer.] Gas- u. Wasserfach, vol. 76, 1933, pp. 541–545; Chem. Abs., vol. 27, 1933, p. 5172.

At Tegel, brown coal was gasified at atmospheric pressure in an O_2 gas producer at the rate of 200 kg. per $m.^2$ producer area. Higher rates were not possible because of limited O_2 supply. The O_2 was saturated at 89°–93°. No slagging was noted. With O_2 saturated at 90°, 1 $m.^3$ O_2 gave 16,000–17,000 cal. in the form of gas having the following analysis: CO_2, 13.2%; O_2, 1.1%; illuminants, 2.3%; CO, 32.9%; H_2, 42.8%; CH_4, 1.1%; and N_2, 6.6%. 1 $m.^3$ of O_2 was enough to gasify 4 kg. brown-coal briquets. Experiments with an O_2 gas producer at elevated pressures by the Lurgi Gesellschaft für Wärmetechnik were limited by the O_2 supply to 900 kg. throughout per $m.^2$ of producer area per hr. at an operating pressure of 20 atm. The back pressure with a 3-m. fuel bed was less than 50 mm. At the higher pressure tar oils and light oil were easily separated by cooling. The O_2 used had a purity of 72–73%, but calculations as to O_2 requirements were made on a basis of 90% O_2, indicating that requirements per 4,000 cal. in the form of gas were 0.202 $m.^3$ at 1 atm., 0.110 $m.^3$ at 10 atm., and 0.80 $m.^3$ at 20 atm. operating pressure. The calculated heating value of the CO_2-free gases reached a maximum of 534 B. t. u. per cu. ft. at 20 atm., so that this gas should be satisfactory for city gas. An O_2 price equivalent to about $0.10 per 1,000 cu. ft. is assumed in estimating that this gas could compete with other sources of city gas.

745. ———. [Increasing the Form Value of Fuels.] Gas- u. Wasserfach, vol. 80, 1937, pp. 806–810; Chem. Abs., vol. 32, 1938, p. 1071.

Continuous gasification of brown coal with O_2 and superheated steam at 20 atm. is described. The town of Zittau has been supplied during the past year with gas of calorific value 4,280 kcal. per $m.^3$ and d. 0.448. Modification of the process to produce liquid fuel by the Fischer-Tropsch synthesis could be made by operating at 8–10 atm.

746. ———. [Results of Pressure Gasification With Oxygen.] Arch. Wärmewirt., vol. 19, 1938, pp. 201–203; Chem. Abs., vol. 32, 1938, pp. 7700.

Plant of Zittau gasifying brown coal with mixed steam and O_2 at 20 atm. is briefly described with a heat balance. Curves are given to show that as the pressure increases the CH_4 and CO_2 in the products rise, while the H_2 and CO fall.

747. ———. [Evaluation of Fuels.] Glaser's Ann., vol. 73, No. 5, 1949, pp. 80–85; Gas- u. Wasserfach, vol. 90, 1949, pp. 212–217.

Discusses evaluation of solid, liquid, and gaseous fuels. Presents data on performance and heat consumption of various power gases and heat balance of the Fischer-Tropsch synthesis and of high caloric gas production.

DRESSLER, R. G. *See* abs. **155, 156, 1431, 1677a, 3549.**

DREW, T. B. *See* abs. **607.**

748. DRIGO, A., AND PIZZO, M. [Magnetization of Thin Ferromagnetic Films.] Nuovo cimento, vol. 5, 1948, pp. 196–206; Chem. Abs., vol. 42, 1948, p. 7587.

Preliminary paper. Theories of magnetism predict that the properties of thin films should differ from those of massive samples. Experiments with thin films of Fe, Co, and Ni show that the characteristics of the magnetization curve vary with film thickness. Barkhausen discontinuities disappear at a thickness of 1.2×10^{-5} cm. for Co, 0.8×10^{-5} for Ni, and 1.3×10^{-5} for Fe.

DRIKAS, G. *See* abs. **3140.**

748. DUBROVSKAYA, A., AND KOBOZEV, N. I. [Adsorption Properties of Promoted Iron Oxide in Relation to the Distribution of the Promoter in the Oxide Form of Ammonia Catalysts.] Acta Physicochim., U. R. S. S. (in German), vol. 4, 1936, pp. 841–858; Chem. Abs., vol. 30, 1936, p. 7987.

Adsorption isotherms of O_2 on pure Fe_2O_3 and on Fe_2O_3 that contained 10% Al_2O_3 were determined at −190° and +400°. X-ray photographs of Fe_2O_3 samples heated to various temperatures showed that the adsorbing power of Fe_2O_3 decreased as the crystals became larger. The kinetics of O_2 desorption from promoted and nonpromoted Fe_2O_3 studied at various temperatures, showed that the activation energy of desorption is independent of the presence of a promoter and averages 10,860 cal. Thus, even in the case of the promoted Fe_2O_3, the adsorption centers are the Fe_2O_3 mols. It was found that the addition of 10% Al_2O_3 to Fe_2O_3 lowers the specific adsorption of O_2. This proves that the dissolved Al_2O_3 is strongly adsorbed on the surface of the Fe_2O_3 crystals. From the data found, the equilibrium constant between the dissolved and adsorbed Al_2O_3 was calculated and an equation derived. Using this equation, it was shown that with relatively large Fe_2O_3 crystals, 1% Al_2O_3 shielded 50% of the surface of the Fe_2O_3.

750. DUCHENE, G., AND MARTIN, R. M. [French Experimental Station for the Production of City Gas and Synthesis Gas From Fuveau Lignites.] Chaleur et ind., vol. 29, No. 274–275, May–June 1948, pp. 113–125, 149–156; Chem. Abs., vol. 42, 1948, p. 6514.

Description with diagrams and operating data of an experimental plant for the production of city gas and synthesis gas by the Syngaz process developed by G. Szigeth of Hungary. It appears to be a modification of the Woodall-Duckham system. The process is continuous and includes the phases of carbonization, water-gas production, and gas conversion in the same apparatus. The last step involves a reversal of the gas stream and cracking of the hydrocarbons and the CH_4 by contact with the incandescent coke. The results of two Syngaz runs reveal the production of synthesis gas with the correct CO : H_2 ratio of 1 : 2.

DUDASH, A. P. *See* abs. **1987.**

DUDLEY, J. F. *See* abs. **1677.**

751. DUFF, D. M. Coal Gasification Rather Than Hydrogenation Urged. Oil Gas Jour., vol. 46, No. 40, 1948, pp. 39, 129.

P. C. Keith, in a recent talk at a meeting of the Natural Gasoline Association of America, proposes, "coal gasification rather than expensive, inefficient coal hydrogenation," as a means of meeting the existing shortage of fuels. Use of 100,000,000 tons of coal per year in a noncatalytic, relatively simple, gas-from-coal process originally developed by the Germans and now under pilot-plant operation in Trenton, N. J., would replace the 350,000,000 bbl. of petroleum fuels, which the residual and distillate heating market is estimated to require annually by 1950. This shift, coupled with the 650,000 bbl. of liquid fuels per day considered as available from natural-gas conversion, might bridge the 2,000,000-bbl. daily gap, which has been mentioned by Government authorities. A program for the wholesale conversion of coal to liquid fuels, either by high-pressure hydrogenation or low-pressure Hydrocol process is unwise and ill-advised at present. Thermal efficiency of the coal-to-liquid-fuel processes is basically low (not over 45%) and there is a serious question if the tremendous quantities of coal required are readily available.

752. ———. Synthesis Fuels Competitive With Crude-Based Fuels. Oil Gas Jour., vol. 46, No. 37, 1948, p. 57.

According to E. V. Murphree, president of the Standard Oil Development Co. and principal speaker at the dedication of a new research building at Baton Rouge, motor fuel produced from natural gas is now generally competitive with that produced from petroleum. The hydrocarbon-synthesis process employing the fluid-catalyst technique is still undergoing improvement, and commercial plants are being considered. Comparative plant costs under present prices are about as follows: For a conventional refinery, $2,000–$2,500 per bbl. of product per day; for a natural-gas synthesis plant, $4,000–$4,500; and for a synthesis plant using coal, $8,000. A pilot-plant demonstration of the 2-vessel system of shale retorting using the fluid technique will soon be inaugurated. Pilot plants devoted to synthesis study including a 10-bbl. per day unit from which data are being obtained through more than 60 recording instruments are under operation. A former hydrogenation unit is being converted to the production of higher molecular-weight alcohols, the process, therefore, being based on the reaction between synthesis gas and certain petroleum fractions with subsequent hydrogenation.

753. DUMANOIS, P. Utilization of Methanol as a Possible Automobile Fuel. Oil Gas Jour., vol. 25, No. 28, 1926, p. 142; Proc. Internat. Conf. Bituminous Coal, 1st Conf., 1926, pp. 161–164; Chem. Abs., vol. 21, 1927, p. 2179.

Objections to the use of MeOH as fuel are its low calorific value and the tendency to form aldehydes on incomplete combustion. At compression ratios above 6, the alcohol caused self-ignition. Detonation may be eliminated by the use of an antidetonant such as $PbEt_4$.

DUNNING, R. G. *See* abs. **2035.**

754. DUNSTAN, A. E. Fluid Fuels. Gas and Oil Power, vol. 22, No. 253, 1926, pp. 6–7.

Deals with Bergius process and synthol.

755. ———. Refining of Petroleum. III. Synthol and Synthetic Petroleum. Fuel, vol. 8, 1929, pp. 502–504. Chem. Abs., vol. 24, 1930, p. 2587.

Excerpt from the Cantor lecture. Briefly reviews work of Badische Anilin- und Soda-Fabrik, Patart, Fischer, and Tropsch on the synthesis of hydrocarbons from CO and H_2.

756. ———. Fluid Fuels Today and Tomorrow. Chem. and Ind., vol. 51, 1932, pp. 822–831, 846–855; Chem. Abs., vol. 27, 1933, p. 176.

Second jubilee memorial lecture. Discusses liquid fuels from various sources: Petroleum, natural gas, bottled gas, coal carbonization, and synthetic oils.

757. DUNSTAN, A. E., AND SHATWELL, H. G. Liquid Fuels Other Than Petroleum. Jour. Inst. Petrol. Technol., vol. 14, 1928, pp. 64–77; Chem. Abs., vol. 22, 1928, p. 1845.

Consideration of liquid fuels obtainable from low-temperature carbonization, coal hydrogenation, and gas reactions is shown. Results from low-temperature carbonization have been disappointing. Of the 16-gal. primary tar per ton of coal obtained, about ⅓, which is tar acids and bases, must be removed, unless the tar is to be used in boilers or Diesel engines. The remaining tar contains paraffins, wax, pitch, and unsaturated hydrocarbons. The latter resist detonation in internal-combustion engines and are thus especially useful in blending. In hydrogenation, the technical validity of the Bergius process is established, 1 ton

of coal producing 140 gal. of liquid product resembling low-temperature primary coal tars. Recovery of H_2 is important economically, and methods for doing this are mentioned. Gas reactions afford many possibilities and variations. Catalytic reduction of CO at high pressures yields oxygenated compounds. At atmospheric pressure and high temperature, CH_4 is the sole product. Synthetic MeOH can be obtained with almost theoretical yield by using ZnO at 400° and 150 atm. For this purpose other catalysts mentioned are metals and metallic oxides or their mixtures, salts, oxides of Cu, Ag, Zn, Pb, or Cd, chromates, vanadates, molybdates, and tungstates, but Fe, Ni, and Co must be rigorously excluded. For products other than MeOH, iron metals and alkalies are essential. Synthol, a mixture of higher alcohols, fatty acids, aldehydes, ketones and esters, but no hydrocarbons, is obtained by passing water gas over Fe borings impregnated with a strong base at 410° and 50 atm. Fischer and Tropsch have obtained gaseous liquid and solid homologs of CH_4 by low-temperature reduction of CO. Gives references to literature and to patents.

DUNVILLE, T. C. *See* abs. **3549.**

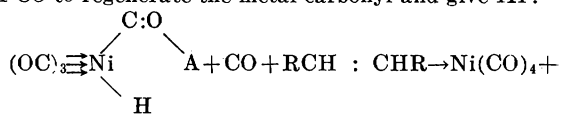
758. DUPAS, M. R. [Lubricant Synthesis.] Bull. assoc. franç. techniciens petrole, No. 69, 1948, pp. 1–16; Jour. Inst. Petrol., vol. 34, 1948, p. 265 A; Chem. Abs., vol. 43, 1949, p. 1952.

After a brief review of the chief methods for lubricating-oil synthesis, describes (with flow sheet) the process used at the Standard-Kuhlmann plant at Estaque. Lubricating oil is produced by a Friedel-Crafts condensation of benzene with dichlorethane and a Fischer-Tropsch gas oil (180°–320°) chlorinated to a Cl content of 22–24%. Production is effected continuously in 3 steel vessels; in the 1st vessel (at 80°) benzene, dichlorethane, and Al powder are mixed. The chlorinated gas oil is added in the 2d stage (at 100°), and the reaction is concluded in the 3d vessel (at 120°). Flow through the plant takes 6 hr. The supernatant oil is separated from the $AlCl_3$ residue, neutralized with Na_2CO_3 solution, and the excess benzene is removed by distillation. Following a clay treatment to eliminate traces of $AlCl_3$ the product is vacuum distilled yielding 2 side streams (transformer and light engine oils) and a residual bright stock. Gas oil is removed overhead and recycled. A further quantity of secondary oil, together with benzene and gas oil, is recovered by hydrolysis of the $AlCl_3$ residue. The yields (as % on the hydrocarbon charge) are: primary oil, 45%; secondary oil, 10%; recycle, 27%; and loss, 18%. The viscous oils (35–330 cs. at 50°) obtained have high density (0.942–0.950) and good viscosity index.

DUPONT, G. *See* abs. **1260.**

759. DUPONT, G., PIGANIOL, P., AND VIALLE, J. [The Oxo Reaction and Its Mechanism.] Bull. soc. chim., France, 1948, pp. 529–532; Chem. Abs., vol. 42, 1948, p. 7232.

Instead of the formation of the intermediate $RCH\cdot CHR\cdot CO$ (I) when CO reacts with olefins in the presence of metallic carbonyls, the authors propose the existence of a combination of Ni or Co carbonyl with a reactive compound, A.H (H_2, H_2O, ROH, R_2NH, etc.). This complex (II) reacts with the olefin in the presence of CO to regenerate the metal carbonyl and give III:



$RCHCH_2R$ (III). It is stated that number I has been
|
AC : O

isolated from these reactions and that they do not occur unless A.H is present. C_2H_2, CO and $Ni(CO)_4$ in the presence of a little HCl and alcohol at 50° give a 50% yield of polymers of CH_2 : $CHCO_2Et$ and CH_2 : $CHCO_2H$. 1-Hexene, alcohol, CO, and $Co(CO)_4$ at 180° and 300 kg. pressure for 7 hours give 70% of a mixture of $Me(CH_2)_5CO_2Et$ and $Me(CH_2)_3$ $CHMeCO_2Et$. Cyclohexene under similar conditions gives 37% $C_6H_{11}CO_2Et$. Replacing the alcohol with H_2O gives the acid. Methendecenoate gives a mixture of diesters. Compounds with double bonds next to a tertiary C (carvomenthene and pinene) give little, if any, reaction.

760. DURAND, J. F. [Double Decomposition of Metallic Acetylides and Salts in an Aqueous Medium.] Compt. rend., vol. 177, 1923, pp. 693–695; Chem. Abs., vol. 18, 1924, p. 657.

CaC_2, when added to aqueous solutions of salts, precipitates acetylides, which can be purified by washing with dilute HOAc. Thus, with $CuCl_2$, CuC_2; with $NiCl_2$, NiC_2; with $MnCl_2$, MnC_2; $FeCl_2$, FeC_2.

761. DUTTA ROY, R. K. Synthetic Gasoline in India. Jour. Indian Chem. Soc., Ind. News Ed., vol. 12, No. 2, 1949, pp. 28–48; Chem. Abs., vol. 44, 1950, p. 2729.

Discusses available processes for the production of synthetic liquid fuels and their status in various countries. Gasoline production in India can meet only 10% of the demand. The Bergius and Fischer-Tropsch processes are reviewed concerning their requirements for raw material and synthesis-gas manufacture. Describes plant layout.

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761a. EASTMAN, D. Preliminary Report on Coal Gasification. Am. Inst. Min. and Met. Eng., 173d Meeting, February 1952.

According to the Texas Co., any type of coal can now be processed into synthesis gas under high pressure. A slurry of finely ground, raw coal containing 40–60% coal and 60–40% H_2O is pumped through a heater, where the coal suspension is raised to several hundred pounds pressure and temperatures exceeding 1,000° F., into the reaction chamber where it meets a stream of pure O_2. The ash which has become molten is drawn off at the bottom of the reaction chamber into a reservoir of cold H_2O where it disintegrates and is removed as a finely divided solid suspended in H_2O. The product gas passes through a waste-heat boiler. The reactor, a pressure shell fitted with an internal coil, has H_2O circulating through it. The generator is normally operated at a temperature above the fusion point of the ash. If the fusion temperature is higher than the desired reaction temperature, a fluxing agent may be added to the coal-H_2O feed to help melt the ash. Gasification has been as high as 95%. O_2 consumption rates are expected to be 15,000–20,000 ft.^{3} per ton of dry coal with 80–90% of the heating value of the coal appearing as H_2 and CO in the synthesis gas.

293793°—54——8

762. EASTMAN, E. D. Equilibria in the Systems: Fe–C–O and Fe–H–O, and the Free Energies of the Oxides of Iron. Jour. Am. Chem. Soc., vol. 44, 1922, pp. 975–998; Chem. Abs., vol. 16, 1922, p. 1901.

Summary of the widely scattered and often discordant data relating to the oxides of Fe and to the equilibria in which they are involved, with an attempt to appraise and interpret the results. For each of the reactions: $3FeO+CO_2\rightleftharpoons Fe_3O_4+CO$, $Fe+CO_2\rightleftharpoons FeO+CO$, and $3Fe+4CO_2\rightleftharpoons Fe_3O_4+4CO$ the equilibrium con-

stant (CO_2) : (CO) has been plotted for different temperatures. The lines for the 3 reactions meet in the invariant point, where there are 3 solid phases and a gas phase (theoretically the C occurs only in the gas phase) at about 560° and (CO_2) : (CO)=1. Similarly for the reactions: $FeO+H_2 \rightleftharpoons Fe+H_2O$, $Fe_3O_4+H_2 \rightleftharpoons 3FeO+H_2O$, and $Fe_3O_4+4H_2 \rightleftharpoons Fe+4H_2O$ the lines meet at about 560° and where (H_2) : (H_2O)=4. The free energies of the oxides of Fe have been calculated by means of the relation, $\Delta F = -RT\ln K$.

763. EASTMAN, E. D., AND EVANS, R. M. Equilibria Involving the Oxides of Iron. Jour. Am. Chem. Soc., vol. 46, 1924, pp. 888–903; Chem. Abs., vol. 18, 1924, p. 1418.

Compositions of the gas phase in equilibrium with solid phases varying in average composition between pure Fe and Fe_3O_4 have been determined at 772° in the system Fe : H_2 : O_2. The results indicate the existence at this temperature of solid solutions in the composition ranges O–5% O_2, 20–24% O_2, and above about 27% O_2. Equilibrium constants in the divariant equilibrium in this system represented by the equations, $FeO+H_2=Fe+H_2O$, and $Fe_3O_4+H_2=3FeO+H_2O$ have been determined between about 657° and 1,025°; and a series of measurements has been made of the constant of the divariant equilibrium $Fe_3O_4+CO=3FeO+CO_2$, between 816° and 1,039°. From the values obtained for the equilibrium constants, the equilibrium constant of the water gas reaction has been calculated. The values of I in the free-energy equation, calculated from the values of this constant, show a satisfactory constancy. Corrections to the free-energy data relating to CO and CO_2 have been made on the basis of the new results.

EASTWOOD, A. H. *See* abs. **1742.**

EBERT, W. *See* abs. **3052, 3053.**

764. ECHARD, —. [Petroleum Industry and Chemical Industry. Evolution in Germany.] Bull. assoc. franç. techniciens pétrole, No. 62, 1947, pp. 23–46; Chem. Abs., vol. 41, 1947, p. 7082.

Review of German developments in the utilization of paraffins and olefins as raw materials for the manufacture of synthetic lubricants, plasticizers, detergents, fatty acids, and alcohols (Oxo process).

765. ECKELL, J. [Relations Between Structure of Catalyst and Chemical Change. I.] Ztschr. Elektrochem., vol. 39, 1933, pp. 423–432; Chem. Abs., vol. 27, 1933, p. 4996.

Historical review of previous work on this problem, with many refs.

766. ———. [Relations Between Structure of Catalyst and Chemical Change. II.] Ztschr. Elektrochem., vol. 39, 1933, pp. 433–439; Chem. Abs., vol. 27, 1933, p. 4996.

Effect of cold working on the catalytic activity of Ni foil used in the hydrogenation of C_2H_4 was studied. After the foil was rolled to a thickness of 0.1 mm., the strip was divided into 2 sections; 1 section was tested for catalytic activity without further treatment while the other was recrystallized by heating for 5 hr. in a high vacuum at 900°. The recrystallized strip was always inactive. The untreated strip decreased in activity after the 1st run. The recrystallized strip after being polished became as active as the untreated cold-rolled strip. The catalytic action was independent of the size of the surface area but depended on the structure. The activity of the Ni is attributed to deformation of the space lattice of the surface crystals by cold rolling or polishing.

767. ECKSTROM, H. C., AND ADCOCK, W. A. New Iron Carbide in Hydrocarbon-Synthesis Catalysts. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 1042–1043.

During the course of hydrocarbon-synthesis investigations, X-ray diffraction patterns of certain catalyst samples have indicated the presence of a new Fe carbide phase. The new carbide appeared along with Fe_3O_4 and Fe_2C (Hägg) during a fluidized synthesis run at 27 atm. pressure and 360°, and eventually it constituted approximately 90% of the total catalyst charge. The X-ray diffraction pattern is shown in comparison with those of Fe_3O_4 and Fe_2C (Hägg). The d/n values and relative line intensities are given also. The new carbide is ferromagnetic; and, within the limits of experimental error, its Curie temperature is the same as that of Fe_2C (Hägg), (250°+ or —3°). After heating the sample for 10 min. at 600°, an X-ray diffraction pattern showed that the carbide had been converted partly to cementite, Fe_3C; after 30 min., all the carbide had been converted into Fe_3C. A chemical analysis gave 77.4% Fe and 17.4% C. This gives an Fe : C ratio of 0.96, so that the new phase could be equivalent to FeC.

EDEBURN, P. W. *See* abs. **3150, 3151, 3152.**

768. EDEBURN, P. W., SCHMIDT, L. D., MCGEE, J. P., AND BONAR, F. Pulverized Fuel Process for Synthesis-Gas Experimental Unit Operating on Entrained Powder. Am. Chem. Soc., 112th Meeting, Symposium on Production of Synthesis Gas, September 1947, pp. 123–136.

Description of an experimental unit designed for the dual purpose of obtaining data for the design and construction of a large-scale unit to develop a new process using entrained powder for making synthesis gas from pulverized fuel, and for testing cokes, chars, and coal from various sources for their synthesis-gas-making properties. A literature investigation disclosed that reactivity tests would not give the desired information because of the narrow reactivity range of solid fuels at gas-making temperatures. The apparatus as designed includes a generator and a purification train. The heat insulated reaction chamber of the generator is a 3-inch-i. d. refractory tube 4 ft. long placed inside a concentric 6-inch tube of the same material, the latter extending 6 in. below the lower end of the inner tube. The reacting materials and the flames for heating pass down the inner tube and then up the annular space between the tubes and out at the top to the purification train. A novel and simple O_2 : steam ratio controller is described. Data obtained in 2 initial runs are included.

EDWIN, B. *See* abs. **161.**

EGLESON, G. C. *See* abs. **3023.**

769. EGLOFF, G. [Modern Hydrocarbon Syntheses.] Brennstoff-Chem., vol. 18, 1937, pp. 115–117; Chem. Abs., vol. 31, 1937, p. 4789.

Brief account of production of high-octane motor fuels by cracking petroleum, Fischer's Kogasin, etc., and by the polymerization of gaseous olefins.

770. ———. Manufacture and Use of Substitute Motor Fuels Is Proving Costly in Europe. Oil Gas Jour., vol. 37, No. 17, 1938, pp. 56, 58–59, 62–64, 67.

In 1937, consumption of substitutes composed of synthetic gasoline and benzol from coal, alcohol, and oil shale amounted to about 18% of the total gasoline consumption. Gives retail prices, import duty, and taxes on motor fuel in principal cities in Europe.

771. ———. Motor-Fuel Economy of Europe. Ind. Eng. Chem., vol. 30, 1938, pp. 1091–1104; Chem. Abs., vol. 33, 1939, p. 343.

Coal is converted into liquid motor fuel by carbonization, hydrogenation, and the water-gas reaction. Alcohols from farm products and MeOH from hydrogenation of CO and from wood distillation also are used. CH_4, C_2H_6, C_3H_8, butanes, and city gas are used in compressed form in steel cylinders (3,000–4,000 p. s. i. pressure) in gas-driven motor vehicles. These

gases are derived from coal carbonization, coal hydrogenation, and from hydrogenation of CO and natural gas. There are about 26,000 of this type of motor vehicles in use. Other types of gas-driven vehicles manufacture their own combustible gas en route from wood and charcoal. There are about 9,000 such motor vehicles in Europe consuming about 450,000,000 lb. of wood yearly. These vehicles are heavily subsidized by governments by direct payments, elimination of taxes on the wood and vehicle, and taxes on imported gasoline. Total consumption of power alcohol in Europe in 1937 amounted to 510,000 tons compared with 646,000 tons during 1936. The 510,000 tons of EtOH (some MeOH) represented 4.3% of the total 11,882,600 metric tons of motor fuel consumed during 1937 in Europe. It is estimated that the 510,000 tons of alcohol used in Europe cost the consumer and state in additional expenditures on the order of about $100,000,000 in subsidies, tax losses, and higher operating costs of vehicles. Figures on the cost of production of gasoline from coal hydrogenation or from water gas are taken from the reports of the Committee of Imperial Defense (Falmouth Committee) and the Labor Party; from coal hydrogenation, $0.156 and $0.183 per gal., and from synthesis, from CO, $0.217 and $0.21 per gal.

772. ———. Motor Fuels of the Present and Future. Jour. Inst. Fuel, vol. 13, 1940, pp. 175–188; Chem. Abs., vol. 34, 1940, p. 8233.

Reviews source and characteristics of various natural and synthetic motor fuels

773. ———. Petroleum Looks Ahead. Chem. and Eng. News, vol. 23, No. 11, 1945, p. 987.

This address was given before the 10th annual petroleum meeting of the Wichita section, Am. Chem. Soc. Development work on the production of gasoline by coal hydrogenation is commendable for use, but requires 4 tons of coal per ton of gasoline produced. It is a costly operation. There are greater potentialities in the hydrogenation of shale oil of which there are large reserves. The Fischer-Tropsch process is probably the most versatile reaction known, with capabilities of producing many oxidized compounds, alcohols, diesel fuel, and other products.

774. ———. Fuel Developments in Midwest. Chem. Eng., vol. 55, No. 9, 1948, pp. 142–144.

Brief review of current developments in catalytic cracking of petroleum, synthesis of oil from natural gas, coal burning and gasification, and oil from coal by hydrogenation.

———. *See* abs. **204, 2164, 2326.**

775. EGLOFF, G., AND VAN ARSDELL, P. M. Substitute Fuels as a War Economy. Jour. Inst. Petrol., vol. 28, 1942, pp. 115–132.

Fischer-Tropsch plants in Germany [1]

Plant	Date placed in operation	1938	Production, bbl, 1939	1940
Schwarzheide	1937			
Wanne Eickel	1939		425,000	1,700,000
Bochum	1939		425,000	1,700,000
Rauxel	1938	340,000	425,000	1,700,000
Sterkrade-Holten	1938	255,000	637,500	850,000
Moers-Moerbeck	1936 and 1939	255,000	765,000	765,000
Koln Neussen	1938	255,000	425,000	425,000
Dortmund	1939			
Deschowitz	1939		212,500	425,000
Essen	1938 and 1939	212,500	425,000	1,870,000
Essen	1939	255,000	425,000	425,000
Recklinghausen [2]	1936	850,000	1,062,500	1,275,000
Total		2,422,500	5,227,500	11,135,000

[1] From La Revue pétrolifère, 1941, p. 237.
[2] Intern. Hydrogenation Patents Process.

These data are incomplete as to the actual number of plants operating.

776. EGLOFF, G., NELSON, E. F., AND MORRELL, J. C. Motor Fuel From Oil Cracking-Production by the Catalytic Water-Gas Reaction. Ind. Eng. Chem., vol. 29, 1937, pp. 555–559; Brennstoff-Chem. vol. 18, 1937, pp. 260–263; Chem Abs., vol. 31, 1937, pp. 4482.

Synthetic gasoline produced by the Kogasin process is claimed to be produced in 81.6% yield and is principally a straight-chain or slightly branched-chain mixture of saturated and unsaturated hydrocarbons, having the fractions: gasoline, 30°–220°; diesel oil, 220°–350°; and wax separated from the diesel-oil fraction. The gasoline fraction is water-white and S-free, and olefins are present to over 50%. The octane number is below 50. Experiments are reported on the reforming of this naphtha and cracking the bottoms from the distillation operation. The final gasoline product, obtained by blending the low-boiling products from the topping and cracking with a high antiknock gasoline that is obtained by catalytically polymerizing the olefinic gases obtained by cracking, had an octane value of 66, which could readily be increased by more drastic cracking. The possibility of producing a good aviation gasoline by blending low-boiling straight-run with the polymer gasoline is indicated.

777. EGUCHI, T. Synthesis of Methanol From Coal. Fuel Econ., vol. 11, 1936, pp. 417–420; Trans. World Power Conf., 3d Chem. Eng. Cong., London, 1936; Chem. Zentralb., 1936, II, p. 3467; Chem. Abs., vol. 30, 1936, p. 7816.

With reduced Cu as catalyst, 87% of the gas $CO+H_2$ is converted to CH_3OH at 250° and 100 atm. S compounds, hydrocarbons of the C_2H_2 series, and gaseous Fe-group compounds are poisonous to Cu oxide catalysts but have less effect on Zn oxide catalysts. A special catalyst operating at 230° and 100 atm. has been in use over a month with but slight decrease in CH_3OH yield. The gas is obtained directly from a gas generator with coal as a raw material.

778. EHRHARDT, U. [Literature Survey on the Synthetic Production of Mineral Oils From Gases.] Ges. Abhandl. Kenntnis Kohle, vol. 4, 1919, pp. 471–506.

EHRMANN, —. *See* abs. **2264, 2265.**

EICHNER, C. *See* abs. **2743, 2744.**

779. EICHNER, C., PERRIN, M., AND PRETTRE, M. [Controlled Catalytic Combustion of Methane.] Compt. rend., vol. 218, 1944, pp. 621–623; Bull. soc. chim., 1944, p. 388; Chem. Abs., vol. 40, 1946, p. 1643.

With a limited O_2 supply, possible reactions are: (1) $2CH_4+O_2=2CO+4H_2$; (2) $CH_4+2O_2=CO_2+2H_2O$; (3) $2CH_4+3O_2=2CO+4H_2O$; (4) $CH_4+O_2=CO_2+2H_2$; residual CH_4 and reaction products may give (5) $CH_4+H_2O=CO+3H_2$ and (6) $CO+H_2O=CO_2+H_2$, 2 independent reactions. A mixture of O_2 and CH_4 entering a catalytic column previously brought to constant temperature produces an initial rise followed by a drop in temperature; this indicates at least 2 steps to the reaction; only (5) is endothermic. Equilibria (1) and (5) give very poor yields below 1,000°. Composition of gases after reaction indicates (4) does not occur. Calculated and experimental results for equilibria (5) and (6) compare well at 725°–870°. When equilibrium is not attained, analyses show (2) to be the preferred mechanism; an excess of H_2O and CO_2 is found in the gas mixture leaving the column; (3) sometimes occurs.

780. EIDUS, Y. T. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Uspekhi Khim., vol. 7, 1938, pp. 1714–1754 and 1801–1857; Chem. Zentralb., 1939, II, p. 359.

Comprehensive review.

781. ———. [Mechanism of the Synthesis of Aliphatic Hydrocarbons by the Contact Hydrogenation of Carbon Monoxide.] Uspekhi Khim., vol. 9, 1940, pp. 673–681; Chem. Abs., vol. 35, 1941, p. 1023.

Carbide theory in connection with Co catalysts is explained, and photochemical data are cited on the nature of the CO bonds. (*See also* abs. **780.**)

782. ———. Reactions of Some Oxygen-Containing Organic Compounds Over the Cobalt Contact Catalysts Used for the Synthesis of Gasoline From Water Gas. Bull. acad. sci. U. R. S. S., classe sci, chim., 1943, pp. 65–73 (English summary); Nat. Petrol. News, vol. 37, No. 14, 1945, pp. R-302, 304, 306; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 439; Chem. Abs., vol. 38, 1944, p. 1342.

MeOH decomposes almost completely over a Co–ThO_2–kieselguhr catalyst at 170°–200°, forming CO and H_2. These react further to form a mixture of liquid hydrocarbons similar in properties to, but smaller in amount than, the mixture obtained directly from water gas over this catalyst. HCO_2H similarly decomposes, chiefly to H_2 and CO_2, somewhat less to H_2O and CO, and very slightly to HCHO, CO_2, and H_2O. EtOH gives a series of products, of which the chief are CH_4, CO, and H_2. In both cases liquid hydrocarbons are formed, but always as secondary products from CO and H_2. Thus, MeOH, HCO_2H, and EtOH cannot be intermediates in the synthesis of hydrocarbons from water gas.

783. ———. [Catalysts for Hydrogenation of Carbon Monoxide by Joint Application of the Dynamic and Static Methods. I. Activity of the Complex Fe-Cu-ThO_2-K_2CO_3-Kieselguhr Catalyst.] Bull. acad. sc. U. R. S. S., classe sci. chim., 1944, pp. 255–262; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 492A; Chem. Abs., vol. 39, 1945, p. 2391.

Reaction was studied in a current of gas and also, by rate of change of pressure, in a closed system. On Fe-type catalysts, in contrast to the Co-type catalysts, the intermediate step in the synthesis is the formation of carbides. The change in the activity of the catalyst Fe–Cu–ThO_2–K_2CO_3–kieselguhr at the different moments of the contact process of formation of hydrocarbons from CO_2 and H_2 was studied by simultaneous application of the dynamic and static methods; the reaction of this contact mass to H_2, CO, and CO_2 separately and to water gas with addition of CO was also investigated.

784. Eidus, Y. T., and Altshuller, S. B. [Investigation of Catalysts for Hydrogenation of Carbon Monoxide by Simultaneous Use of the Dynamic and Static Methods. II. Activity of Catalysts Containing Various Components of the Catalyst Fe–Cu–ThO_2–K_2CO_3–Kieselguhr.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1944, pp. 249–357; U. O. P. Co. Survey Foreign Petroleum Literature Transl., May 1945, No. 507; Chem. Abs., vol. 39, 1945, p. 3142.

12 Catalysts containing varying combinations of the components of the complex catalyst Fe–Cu–ThO_2–K_2CO_3–kieselguhr made up in proportion of 100 : 25 : 2 : 2 : 125 have been investigated by a combined method with respect to their activity in hydrogenation of CO and interaction of CO with the catalytic surface at 258°. It was established that only those catalysts that contain both Fe and Cu as well as one of the promoters, either ThO_2 or K_2CO_3, are active in the process discussed. However, addition of the 2d promoter brings about a sharp rise in the activity of the catalyst. In both processes studied, the change in the initial velocity of the process is well correlated with the composition of the catalyst. These data, in conjunction with those previously reported (abs. **783**) justify an assumption that synthesis of hydrocarbons from CO and H_2, over Fe catalysts, involves carbide formation as an intermediate step, which does not take place over Co or Ni catalysts. The dependence of the velocity of the total process of hydrogenation of CO to hydrocarbons on the Fe–Cu–ThO_2–K_2CO_3–kieselguhr catalyst in the above proportions upon the temperature was studied in a static system. The apparent energy of activation within 245° and 265° was found to amount to 28.7 calories per mole. The pre-exponential member of the Arrhenius equation is diminished at temperatures above 255°, which may be due to formation of new reaction products resulting in a decrease of the number of active centers on the surface of the catalyst that participate in the basic reaction.

785. Eidus, Y. T. [Investigation of Catalysts for Hydrogenation of Carbon Monoxide by Simultaneous Application of the Dynamic and Static Methods. III. The Part Played by the Alkaline Activator in the Formation of the Surface of the Catalyst Fe–Cu–ThO_2–K_2CO_3–Kieselguhr.] Bull. acad. sci. U. R. S. S., classe sci. chim., No. 1, 1945, pp. 62–70; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 537; Chem. Abs., vol. 39, 1945, p. 4792.

Catalyst Fe–Cu–ThO_2–K_2CO_3–kieselguhr, composed in the proportion of 100 : 25 : 2 : 2 : 125, was investigated for the reaction of hydrogenation of CO_2; 4 catalysts made up of various components of this catalyst were likewise studied for their interaction with CO_2 at 258°. It was found that no catalytic hydrogenation of CO_2 takes place under the conditions used. Data were obtained showing that the interaction of CO_2 with the surface of the catalyst is due to K_2CO_3 and that addition of ThO_2 promotes this process. The alkaline activating agent, while contained in only slight amount in the catalyst, accumulates on the surface of the latter and occupies a substantial portion of its active part. The accumulation of the activator on the surface of the catalyst is the cause of the activity of the latter with respect to carbide formation, hydrogenation of CO and interaction of CO_2 with the catalytic surface.

786. ———. [Investigation of Catalysts for Hydrogenation of Carbon Monoxide by Simultaneous Application of the Dynamic and Static Methods. IV. Kinetics of Carbide Formation and of Hydrogenation of Carbon Monoxide on Co, Ni, and Fe Catalysts.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1946, pp. 447–453; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 656, 1946, 7 pp.; Chem. Abs., vol. 43, 1949, p. 6063.

By the simultaneous application of the dynamic and static methods, a comparative study was carried out of the kinetics of hydrogenation of CO and of the interaction of the latter with the surface of Co–Th–marshallite catalysts (100 : 18 : 100), of Ni–Mn–Al–marshallite (100 : 20 : 10 : 100), and of Fe–Cu–Th–K_2CO_3–marshallite (100 : 25 : 2 : 2 : 125). With the Co and Ni catalysts, the reaction temperatures were 180°–210° with a gas mixture 1 CO : 2 H_2; in the case of Fe catalyst, 230°–260° and 1 CO : 1 H_2. The carbide formation and the hydrogenation of CO were studied at identical temperatures in the same catalytic furnace. The kinetic data obtained show that the ratio of the initial velocities of hydrogenation of CO to the carbide formation is much lower in the case of the Fe catalyst than for the Co and Ni catalysts. The lower ratio for the Fe catalyst results from the reduced hydrogenation velocity of CO on this catalyst as compared with the velocity of this process on the Co and Ni catalysts. This is in agreement with the carbide theory of synthesis of hydrocarbons from CO and H_2. On Co and Ni catalysts, the rate of hydrogenation of CO materially exceeds that of interaction of CO with the catalyst, which contradicts the carbide theory of catalytic synthesis of hydrocarbons from CO and H_2 on these catalysts. If formation of liquid and solid

hydrocarbons by hydrogenation of CO involves the carbide mechanism

$$(1)\quad 2CO \rightarrow CO_2 + C(\text{carbide}) \quad (a)$$

$$(2)\quad \begin{array}{l} C(\text{carbide}) + H_2 \rightarrow CH_2 \quad (b) \\ \hline 2CO + H_2 \rightarrow CO_2 + CH_2 \quad (c) \\ \downarrow \\ (CH_2)_n \end{array}$$

then the conclusion can be drawn from the experimental data obtained that equality of the reaction velocities of (*a*) and (*c*) is in accord with the carbide theory only in the case of Fe catalysts; for the Co and Ni catalysts, the velocity of the process is considerably in excess of that in the process (*a*). All this speaks against the applicability of the carbide-formation mechanism for the explanation of the chemical process occurring on the Co and Ni catalysts and in favor of this mechanism of synthesis of hydrocarbons from CO and H_2 in the case of Fe catalysts. This is also supported by data previously reported by the author.

787. ———. [Reduction of Catalysts for the Synthesis of Aliphatic Hydrocarbons From Mixtures of Carbon Monoxide and Hydrogen.] Jour. Gen. Chem. (U. S. S. R.), vol. 16, 1946, pp. 875–883; Chem. Abs., vol. 41, 1947, p. 1824.

A comparative study was made on reduction of the following water-gas catalysts: Co–ThO_2–kieselguhr (100 : 18 : 100), Fe–Cu–ThO_2–K_2CO_3–kieselguhr (100 : 25 : 2 : 2 : 125), and Fe–Cu–ThO_2–K_2CO_3–marshallite (100 : 25 : 2 : 2 : 125). The general course of reduction was similar in both catalyst types, with the maximum reduction rate occurring at the beginning of reduction. Reduction with H_2 at 375° proceeds more rapidly and results in twice as great a loss in weight in the 1st catalyst as was observed for the 2d and 3d catalysts at 250°; the latter catalysts are reducible with H_2 only to the extent of 82%. Interaction of these catalysts with CO first results in further reduction of the former (loss in weight) followed by carbide formation (weight gain). CO is adsorbed on the 1st catalyst 4 times more effectively than on the 2d or 3d, after H_2 reduction. Slow heating-up of the latter catalysts during H_2 reduction gives the most active catalysts.

788. ———. [Synthesis of Liquid and Solid Hydrocarbons from Water Gas at Atmospheric Pressure on a Precipitated Fe–Cu–ThO_2–K_2CO_3–Marshallite Catalyst.] Jour. Gen. Chem. (U. S. S. R.), vol. 16, 1946, pp. 869–874; Chem. Abs., vol. 41, 1947, p. 1987.

Precipitated Fe–Cu–ThO_2–K_2CO_3–marshallite catalyst was shown to have a rather high effectiveness in the synthesis of hydrocarbons from water gas at 250° and atmospheric pressure. The best catalyst contained a 1 : 2 ratio of ThO_2 : K_2CO_3, which was used in 2% amount relative to Fe. Yields of solid paraffins as high as 13.6% are reported.

789. ———. [Progress in the Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Uspekhi Khim., vol. 19, 1950, pp. 32–58; Chem. Zentralb., 1950, II, p. 1173.

Summary of progress during the last 10 yr. Following points are discussed: (1) Role of the various components in the catalysts of CO–H_2 synthesis; (2) precipitation of Co–Ni catalysts; (3) Fe catalysts; (4) Ru catalysts; (5) technical Co catalyst; (6) synthesis in the liquid phase; (7) the decline in catalyst activity; (8) isosynthesis; (9) synthesis of aromatics; (10) Synol process; (11) Oxo synthesis; (12) hydrocondensation of Co, H_2, and olefins (pressureless). 121 literature refs.

789a. ———. [Mechanism of Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen.] Uspekhi Khim., vol. 20, 1951, pp. 54–70; Chem. Zentralb., 152, I, p. 3430.

Following subjects are discussed: Carbide formation, carbide formation as the intermediate step in the synthesis, oxygenated compounds as the intermediate step and methylene radicals as the intermediate step. 90 literature refs.

———. [Investigation of Catalysts for Hydrogenation of Carbon Monoxide by Simultaneous Application of the Dynamic and Static Methods. III. Part Played by the Alkaline Activator in the Formation of the Surface of the Catalyst Iron-Copper-Thoria-Potassium Carbonate-Kieselguhr.] *See* abs. **785.**

———. [Investigation of Catalysts for Hydrogenation of Carbon Monoxide by Simultaneous Application of the Dynamic and Static Methods. IV. Kinetics of Carbide Formation and of Hydrogenation of Carbon Monoxide on Cobalt, Nickel, and Iron Catalysts.] *See* abs. **786.**

———. *See* abs. **802a.**

EIDUS, Y. T., AND ALTSHULLER, S. B. [Investigation of Catalysts for Hydrogenation of Carbon Monoxide by Simultaneous Use of the Dynamic and Static Methods. II. Activity of Catalysts Containing Various Components of the Catalyst Iron–Copper–Thorium Dioxide–Potassium Carbonate–Kieselguhr.] *See* abs. **784.**

790. EIDUS, Y. T., AND ELAGINA, N. V. Activity and Stability of Fe–Cu–ThO_2–K_2CO_3 Catalyst in the Synthesis of Liquid Hydrocarbons From CO–H_2 Mixture as Influenced by Composition of the Catalyst and the Nature of the Carrier. Bull. acad. sci. U. R. S. S., classe sci. chim., 1943, pp. 305–311 (English summary); U. O. P. Co. Survey Foreign Petroleum Literature Transl. 468; Chem. Abs., vol. 38, 1944, p. 5648.

18 catalysts of composition Fe–Cu–ThO_2–K_2CO_3–carrier were examined in the synthesis of liquid hydrocarbons from 1 CO : 2H_2 mixture. The catalyst Fe 100 : Cu 25 : K_2CO_3 2 : kieselguhr 125 shows a sharp optimum for ThO_2 content at 1%. Slight maximum in efficiency is found at 2% K_2CO_3 in Fe 100 : Cu 25 : ThO_2–kieselguhr catalyst. In this catalyst, the best results were obtained with the carrier of Insen diatomite and marshallite, the latter support being somewhat more stable. The results contradict the view of catalyst support as an inert mass. The Fe catalysts investigated showed poor stability, which was not improved with variations of ThO_2 content.

791. EIDUS, Y. T., AND GUSEVA, I. V. [Effect of Ammonia in the Incoming Gas on the Catalytic Hydrogenation of Carbon Monoxide to Higher Hydrocarbons.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1950, pp. 287–290; Chem. Abs., vol. 44, 1950, p. 8087.

In 5-hr. runs with a mixture of 1 CO : 2 H_2 flowing at 80–90 l. per l. catalyst per hr. at 190° and atmospheric pressure over a Co catalyst (5 gm. metal over 35 cm.), addition of NH_3 resulted in marked decrease of the yield of higher hydrocarbons without any increase in the amount of CH_4; the % of CO reacted is decreased in the same degree as the yield of hydrocarbons. A precipitate of $(NH_4)_2CO_3$ is formed at the end of the reactor. The effect of NH_3 is reversible; as soon as the NH_3 is shut off, the yield reverts to its original high level. Judging by the absence of $MeNH_2$ (also of Me_2NH, Me_3N, and CO $(NH_2)_2$) in the products, the inhibition by NH_3 is not due to a reaction $NH_3 + CH_2 \rightarrow MeNH_2$. The formation of $(NH_4)_2CO_3$ can be attributed only to enhanced occurrence of the reaction $CO + H_2O \rightarrow CO_2 + H_2$, with CO_2 reacting further with NH_3; in the absence of NH_3, that reaction ordinarily

ceases as soon as the catalyst is formed, but not with NH_3 present.

792. EIDUS, Y. T., AND PUZITSKII, K. V. Catalytic Hydrocondensation of Carbon Monoxide With Ethylene. Compt. rend. acad. sci. U. R. S. S., vol. 54, 1946, pp. 35–38 (in English); Chem. Abs., vol. 41, 1947, p. 3741.

Using the same method of preparation as described previously (Eidus and Zelinskii, abs. **793**), but using Co(I) and Co(II), differing in preparation, as catalysts, the catalytic interaction of C_2H_4 with CO in the presence of H_2 at 760 mm. pressure was studied. (I) was not stable enough; (II) was more stable. Results show that a hydrocondensation reaction of CO with C_2H_4 in the presence of H_2 takes place; 75% by volume of liquid product is formed at the expense of the initial C_2H_4. The presence of a considerable amount of O_2-containing compounds was detected, particularly alcohols. PrOH was detected as the 3-nitrophthalate.

793. EIDUS, Y. T., AND ZELINSKIĬ, N. D. [Intermediate Formation of Methylene Radicals During the Catalytic Synthesis of Aliphatic Hydrocarbons From Carbon Monoxide and Hydrogen.] Bull. acad. sci. U. R. S. S., classe sci. chim, 1940, pp. 289–293; Chem. Abs., vol. 35, 1941, p. 4744.

A very highly purified mixture of CO and H_2 (1 : 2) was allowed to react over a Ni–Co–Al catalyst in the presence of C_6H_6(I) at 190°; small quantities of toluene (II) and xylene (?) were formed (detected as nitrotoluene and nitroxylene (?), respectively). The formation of (II) was explained through the action upon (I) of methylene radicals, intermediately formed during the contact hydrogenation of CO.

794. ———. [Carbide Formation as an Intermediate Stage in the Catalytic Synthesis of Hydrocarbons From Water Gas.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1942, pp. 190–194; U. O. P. Co. Survey Foreign Petroleum Literature Transl. No. 385; Chem. Abs., vol. 39, 1945, p. 2391.

The Co carbide formed by the action of CO on the Co–ThO_2–kieselguhr catalyst is neither an intermediate product nor a catalyst of the synthesis of gasoline from CO and H_2. Intermediate formation of methylene radicals during this synthesis appears to be confirmed.

795. ———. [Reaction of Carbon Monoxide With Cobalt Catalysts Used in the Synthesis of Gasoline From Water Gas.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1942, pp. 45–54; Chem. Zentralb., 1943, II, p. 1770; Chem. Abs., vol. 37, 1943, p. 2909.

When CO is passed over a mixture of 100 parts Co, 18 parts ThO_2, and 100 parts kieselguhr at 192°–272°, 2 reactions occur, forming, respectively, Co_2C and C. At 192°–212°, a carbide formation predominates; but, as the temperature rises, more free C is formed, and at 272°, 5 gm.-atoms C form per gm. atom Co. At this temperature, decomposition of Co_2C also occurs. Poisoning of the catalyst with SO_2 also reduces Co_2C formation. Reduction of Co_2C by H_2 goes faster and at a lower temperature on this catalyst than on pure Co.

796. EĬDUS, Y. T., ELAGINA, N. V., AND ZELINSKIĬ, N. D. [Synthesis of Olefin Hydrocarbons From Primary Alkyl Magnesium Halides and Carbon Monoxide Under Pressure.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1945, pp. 672–674; Chem. Abs., vol. 42, 1948, p. 5838.

Effect of changing the halide in 2 examples of Fischer and Stoffers's reaction between Grignard reagents and CO under pressure is studied. The substitution of BuMgBr and iso–AmMgCl for BuMgCl and iso–AmMgBr yields the same products, 4–nonene and 2–8–dimethyl–4–nonene, respectively, but the yields are 25.4% and 51% instead of 51% and 53.6%, respectively.

797. EIDUS, Y. T., KAZANSKII, B. A. AND ZELINSKIĬ, N. D. [Influence of the Type of Carrier on the Synthesis of Liquid Hydrocarbons Over Ni–MnO–Al_2O_3 Catalysts at Atmospheric Pressure.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1941, pp. 27–33; Chem. Zentralb., 1942, II, p. 642; U. O. P. Co. Survey Foreign Petroleum Literature Transl. No. 325–B; Chem. Abs., vol. 37, 1943, p. 5306.

Effect of using supports of kieselguhr from different parts of Russia for the (5 Ni+Mn) +10% Al_2O_3 catalyst used in preparing hydrocarbons from CO and H_2 is reported. The degree of washing the catalyst after precipitation has great influence on its activity, and the separation of Fe and ignition are not always required.

798. EIDUS, Y. T., ZELINSKIĬ, N. D., AND ERSHOV, N. I. [Condensing Action of Methylene Radicals on Ethylene.] Compt. rend. acad. sci. U. R. S. S., vol. 60, 1948, pp. 599–601; Chem. Abs., vol. 43, 1949, p. 108.

In hydropolymerization of C_2H_4, the most important role is played by the CH_2 radicals. Using, as a source of CH_2 radicals, molecules of CO in the course of hydrogenation, a new reaction of catalytic hydropolymerization of C_2H_4 was discovered, which proceeds only in the presence of small amounts of CO. With an equimolecular mixture of C_2H_4 and H_2, containing 4–7% CO, and a space velocity 100 at 190° at atmospheric pressure, intensive hydropolymerization takes place on the catalyst surface; selection of the conditions may restrict hydrogenation of C_2H_4 to 25–30% of the total reaction. The yields of liquid hydrocarbons reach 400–500 ml. per $m.^3$ or 30–45 ml. per hr. Distillation of a typical run showed the presence of 54% butylene, 4.1% butane, 19% propylene, 3.3% propane, 18.2% ethane, and 1.1% C_2H_4, in addition to which appreciable amounts (up to 60–65%) of C_5–C_8 hydrocarbons are formed. Increase of the CO content 0.06–6.1% increases the amount of heavy oil (in ml. per $m.^3$) 0–61.3. The light oil reaches a maximum of 193.5 ml. per $m.^3$ at 4% CO, while gas oil (C_4 and lower) reaches a maximum of 153.9 ml. per $m.^3$ at 1.5% CO. Complete absence of CO led to the failure of formation of any higher oil; only hydrogenation to C_2H_6 took place.

799. EIDUS, Y. T., ZELINSKIĬ, N. D. AND PUZITSKIĬ, K. V. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. I. Hydrocondensation of Carbon Monoxide With Ethylene.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1949, pp. 110–114; Associated Tech. Services, Transl. RF–24, April 1950; Chem. Abs., vol. 43, 1949, p. 4829.

Mixtures of CO, H_2, and C_2H_4 passed over a catalyst under atmospheric pressure at 190°–200° undergo hydrocondensation, mainly into aliphatic hydrocarbons. The following data give the composition of the gaseous mixture, space velocity in l. per l. catalyst per hr., duration in hours, yields (in mil. per $m.^3$ of total gas passed) of heavy oil, light oil, total oil, H_2O; mean yield of total oil in ml. per l. catalyst per hr.: 1 CO : $2H_2$: $3C_2H_4$, 93, 90, 130.8, 212.5, 343.3, 29.6, 30.2; 1 CO : $2H_2$: $1.5C_2H_4$, 106, 71, 107.5, 88.1, 195.6, 19.4, 85.1. On a particularly active catalyst, a mixture 1 CO : $2H_2$: $3C_2H_4$ gave, at a space velocity of 114–135, in 49 hr., total oil 333–465 ml. per $m.^3$ total gas passed, or 33–49 ml. oil per l. catalyst per hr., with a maximum of 465.2 ml. per $m.^3$ or 49.2 ml. per l. per hr., at a space velocity of 118. The yield of H_2O was 55–96 ml. per $m.^3$, and the volume ratio of light to heavy oil decreased during the operation from 1.42 to 0.85. The balance of the C_2H_6 formed and of the amounts of each component spent in the reaction shows that C_2H_4 reacts to the extent of 80–93% and that only 15–22% of the C_2H_4 that reacts is spent on formation of C_2H_6; H_2 reacts to the extent of 87–99%, with only 20–33% of

the reacting H_2 being spent on formation of C_2H_6. Of the CO, 71.4% enters the reaction at its initial stage; at later stages, about 48–51% of the CO enters the reaction. Formation of the liquid and solid products consumes, on the average, 2–3 vol. H_2 and 3–4.5 vol. C_2H_4 per vol. CO. Preliminary study of the oily and aqueous products showed only a small amount of oxygenated compounds, mainly alcohols; among these, iso-PrOH was identified. The oil is a mixture of saturated and unsaturated aliphatic hydrocarbons.

800. ———. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. II. Liquid Products of Hydrocondensation of Carbon Monoxide With Ethylene.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1949, pp. 326–332. Chem. Abs., vol. 44, 1950, p. 4409.

Hydrocondensation of CO–3 C_2H_4–2 H_2 at 190° yields the oil layer, which was separated into components conventionally. These comprised 2–3% O_2 derivatives (10% in the aqueous layer of catalyzate). The aldehyde content was 0.9% in the oil and 1.9% in the aqueous layer. Of these only EtCHO was identified. Ketones are absent. The aqueous layer contained 1.5% organic acids, of which 70% was EtCOOH. The hydrocarbons formed in the reaction represent a very wide boiling range and are a complex mixture of paraffins and olefins containing C_6, C_9, C_5, and C_7 members; the latter probably form by intermediacy of CH_2 radicals, which are believed to be the principal hydrocarbon-forming agency. The nonparticipation of CO in this reaction is confirmed by lack of condensation of CO with C_2H_4 in the absence of H_2. Small amounts of PrOH were isolated from the summary reaction product (identified as the 3-nitrophthalate).

801. ———. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. III. Polymerization and Hydropolymerization of Ethylene Under the Conditions of Hydrocondensation Catalysis.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1950, pp. 98–107; Chem. Abs., vol. 44, 1950, p. 6100.

(1) C_2H_4 alone and in mixture with H_2 was passed at 190°, under atmospheric pressure, over catalyst (III) after it had been used for 120 hr. in hydrocondensation of $1CO:2H_2:3C_2H_4$. Its activity in that reaction is expressed by the production of 218–237 ml. per m.^{3} oil, or 21.1 ml. per l. per hr. at space velocity S=101–114; gas contraction, c=31.3%, H_2O yield, w=20.8–39.5 ml. per m.^{3}. In a subsequent run with C_2H_4 alone (86% pure), c was 12%, oil initially 62.7 ml. per m.^{3} (6.0 ml. per l. per hr.), falling to 32.8 (2.9), extent of reaction 13% of the C_2H_4 passed, w=15.7–32.8 ml. per m.^{3}. This shows that, in $CO+H_2+C_2H_4$ the liquid products cannot be due to a polymerization of C_2H_4 itself. (2) In a subsequent run with $2C_2H_4:1H_2$, the oil yield rose to 118.2 ml. per m.^{3} (9.7 ml. per l. per hr.), c to 32.2%, extent of reaction 46.7% of the C_2H_4 passed, with 53.7% of the C_2H_4 reacted spent on formation of liquid and solid products; H_2 reacted to the extent of 71.8%, with 34.1% of the H_2 reacted spent in the formation of liquid and solid. In a subsequent run with $1C_2H_4:1H_2$, the oil yield was 202.0 (20), c 48.3%, extent of reaction 87.7, and 72.7% of C_2H_4 and H_2 passed, respectively, with 45.4 and 28.5%, respectively, of the C_2H_4 and H_2 reacted gone into the liquid and solid product. In two following runs with $1C_2H_4:1.2H_2$, the C_2H_4 reacted completely (100%), but only 20–25% of it went into the oil the yield of which fell to 49.6 (3.5). The same results were obtained in an analogous series of runs, on catalyst (IV). As a rule, the proportion of light oil in the liquid product is markedly higher with $H_2+C_2H_4$ than with $CO+H_2+C_2H_4$ and increases in consecutive runs. (3) Passage of H_2 alone over a catalyst having been used in runs with $CO+H_2+C_2H_4$, produces no significant amounts of liquid and no light oil. This proves that the hydrocondensation products obtained with $H_2+C_2H_4$ are not due to a hydrogenation of the solid deposit formed on the surface of the catalyst. (4) Passage of $1H_2:1C_2H_4$ on a fresh catalyst produced practically no oil, only hydrocarbons C_4, with a yield of 5.2–14.0% with respect to C_2H_4 passed, or 35–90.5 liquid ml. (at −80°) per m.^{3} gas passed. The main mass of the C_2H_4 is hydrogenated to C_2H_6. (5) These results are interpreted as being due to the presence of CH_2 radicals at certain points of the lattice of the metallic catalyst surface having been used with $CO+H_2+C_2H_4$. Wherever a CH_2 group happens to be located in a suitable position between the ends of 2 molecules of C_2H_4 adsorbed on the same surface, it serves as a bridge linking the C_2H_4 molecules and leading to the formation of higher polymerization products. Such CH_2 groups being absent at the surface of a fresh catalyst, the probability of higher polymerization is very slight and there can only be dimerization of adjacent C_2H_4 molecules into C_4 products.

802. Eidus, Y. T., Zelinskiĭ, N. D., Ershov, N. I., and Batuev, M. I. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. IV. Hydrocondensation of Ethylene With Carbon Monoxide at Low Concentrations of the Latter.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1950, pp. 377–385; Chem. Abs., vol. 45, 1951, p. 1495.

At 190° under atmospheric pressure, mixtures of C_2H_4 and H_2 with small amounts of CO gave with 3 different catalysts the following yields (vol. % C_2H_4, H_2, CO in the initial gas, space velocity, length of run in hours, yield (ml. per m.^{3}) of heavy oil, light oil, gas oil, and H_2O): 52.6, 37.5, 5.7, 104 l. per l. catalyst per hr., 12.2 hr., 86.3, 199.1, 285.4, 7.0; 48.9, 36.9, 7.6, 78, 47.0, 77.4, 224.8, 96.3, 21.3; 47.9, 38.5, 6.5, 85, 69.5, 38.7, 162.3, 100.4, 36.7. The composition of the outgoing gas (vol. %) in these 3 experiments was C_2H_4, H_2, CO, and C_2H_6, respectively: 2.4, 35.7, 0.8, 42.9; 19.1, 20.0, 9.7, 38.8; 12.8, 18.3, 8.6, 53.0 (balance N_2). The yield of liquid condensate (gas oil included) attains 30–45 ml. per l. per hr. C_2H_4 reacts to the extent of 77.7–98.5%, H_2 to 62.3–96.9%; CO is consumed mainly (up to 94.9%) in the beginning of the run, less at later stages. The fraction of the reacted C_2H_4 converted to C_2H_6 varies 27.6–56.6%. At constant space velocity, 100 l. per l. catalyst per hr., with a gas mixture containing about 7% CO, the optimum temperature, in the 100°–250° range, is 190°–210°. By fractionation of the products from an equimolecular mixture of C_2H_4 and H_2, containing 4–7% CO, the gas oil constitutes about 36% of all organic products in the condensate, and consists, in wt. % (not including CH_4) of C_2H_4, 1.1, C_2H_6, 18.2; C_3H_6, 19.0; C_3H_8, 3.3; C_4H_8, 54; C_4H_{10}, 4.1; or in % of the organic matter in the condensate, respectively, 0.35, 6.1, 6.3, 1.1, 18.1, 1.4. More than half of the gas oil, 54 wt. %, is the nonhydrogenated dimer of C_2H_4, namely C_4H_8; the hydrogenated dimer, C_4H_{10}, is 4.1% (with respect to the weight of the condensate, C_4H_8 is 18.1, C_4H_{10}, 1.4%). The presence of a $C_3H_8+C_3H_6$ fraction (22.3% of the gas oil, 7.4% of the condensate), with a C_3H_8 : C_3H_6 ratio of 0.2 : 0.3, indicates condensation of CH_2 radicals with C_2H_4. Fractions C_6 and C_8 (trimers and tetramers of C_2H_4) constitute, respectively, 18.8% and 12.6% of the condensate (with the gas oil separated); the presence of the fractions C_5, C_7, and C_9 constituting, respectively, 12%, 16.5%, and 8.5% of the gas oil-free condensate, indicates reaction with CH_2 radicals. Unsaturated compounds attain up to 70% of the condensate. By Raman spectra of the hydrogenated catalyzate, the fractions b. 69°–126.5° contain only the corresponding normal hydrocarbons, the fraction b. 66°–68.5°, beside C_6H_{14}, also contains about 15% 2-methylpentane and about 25% 3-methylpentane; the fraction b. 27°–36° contains, beside C_5H_{12}, about 15% 2-methylbutane.

802a. ZELINSKIĬ, N. D., EĬDUS, Y. T., PUZITSKIĬ, K. V., AND BATUEV, M. I. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. V. Hydrocondensation of Carbon Monoxide and Propylene.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1950, pp. 647–653; Chem. Abs., vol. 45, 1951, p. 8,437.

As shown earlier, in the complete absence of CO, C_2H_4 with H_2, under catalytic conditions, yields only C_2H_6, but in the presence of CO polymers and hydropolymers of odd and even number C atom hydrocarbons are formed. A similar reaction between propene and 5.7–7.0% CO at 190° and atmospheric pressure of H_2 with the previously described catalyst gives 85–90% conversion of the propene, of which 35% is C_3H_8; the yield of liquid condensate is 550–600 ml. per $m.^3$. The yield of butylenes is 2.7%, that of C_4H_{10} 2.6%. The condensate freed of C_3 and C_4 products boils over a very wide range (30°–325°) and contains about 35% unsaturates, mostly of lower molecular weights. After hydrogenation over Raney Ni 75% of the condensate b. 28°–340°, and contains about 12–14% each of C_5, C_7, C_8, and C_9 products, about 20% C_6. The C_5–C_8 fractions contain some branched-chain products (Raman method), possibly 2- and 3-methylpentane, while the rest are *n*-hydrocarbons C_5–C_7.

802b. EIDUS, Y. T., ERSHOV, N. I., BATUEV, M. I., AND ZELINSKIĬ, N. D. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. VI. Hydrocondensation of Carbon Monoxide With *n*-Butylene.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1951, pp. 722–727; Jour. Inst. Petrol., vol. 38, 1952, p. 215A.

Experiments were carried out on equimolecular mixture of H_2 and C_4H_8+2.6–6% of CO, under the same conditions as previously. At 2.6% CO 100% of CO and 97.1% of C_4H_8 react, at 6% CO, 100%, and 70.4% respectively. 30–35% of the C_4H_8 is reduced to C_4H_{10}. Liquid products, $>C_4$, have b. p. 28°–276° C. and consist of aliphatic hydrocarbons, unsaturates 28%. After hydrogenation liquid condensate was fractionated; analysis (Raman spectra) showed 24% C_5 (about half of which is isopentane), 15% C_6, 8% C_7, 8% C_8, 9% C_9, as well as higher hydrocarbons.

802c. EIDUS, Y. T., ZELINSKIĬ, N. D., PUZITSKIĬ, K. V., AND ERSHOV, N. I. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. VII. Effect of Carbon Monoxide Concentration on Its Hydrocondensation With Propylene and *n*-Butylene.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1952, pp. 145–151; Chem. Abs., vol. 46, 1952, p. 11,095.

CO concentration was varied 0–22% for propylene and 0–15.8% for *n*-butylene. In both cases hydrocondensation of olefin–H_2 mixtures did not occur in absence of CO and was at maximum for CO content in feed gas of 6–8%. Reactions occurring at low, 6–8%, and high, >approximately 14%, CO content are quite distinct. Rapid decrease of hydrocondensation reaction at CO 15–20% is in contrast to behavior with ethylene, where hydrocondensation still occurs at these concentrations.

EIDUS, Y. T., ERSHOV, N. I., BATUEV, M. I., AND ZELINSKIĬ, N. D. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. VI. Hydrocondensation of Carbon Monoxide With *n*-Butylene.] *See* abs. **802b**.

803. EIDUS, Y. T., FEDITSCHKINA, T. L., KAZANSKII, B. A., AND ZELINSKIĬ, N. D. [Effect of Lowering the Reduction Temperature of the Catalysts Used in the Synthesis of Hydrocarbons from CO and H_2 at Atmospheric Pressure.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1941, pp. 34–40; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 329; Chem. Zentralb., 1942, II, p. 642.

Of the Ni catalysts produced from the oxalate and reduced at 200°, 230°, and 280°, that one reduced at 230° gives the highest contraction. A Ni catalyst obtained from the formate and without previous reduction gave liquid hydrocarbons, but only in small amounts. Ni–Mn–Al_2O_3 catalyst with 6% Cu and 6% Ag is wholly inactive. A Co–Mn catalyst with 10% Cu and without previous reduction gave good results. Catalysts precipitated with soda gave liquid hydrocarbons as well as solid paraffins but deteriorated rapidly.

EĬDUS, Y. T., ZELINSKIĬ, N. D., ERSHOV, N. I., AND BATUEV, M. I. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. IV. Hydrocondensation of Ethylene With Carbon Monoxide at Low Concentrations of the Latter.] *See* abs. **802**.

EIDUS, Y. T., ZELINSKIĬ, N. D., PUZITSKIĬ, K. V., AND ERSHOV, N. I. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. VII. Effect of Carbon Monoxide Concentration on Its Hydrocondensation With Propylene and *n*-Butylene.] *See* abs. **802c**.

804. EIDUS, Y. T., EPIFANSKII, P. F., PETROVA, L. V., ELAGINA, N. V., AND ALTSHULLER, S. B. [The Activating Effect of Oxides of Some Metals on the Iron-Copper Contacts Used for Synthesis of Gasoline From Water Gas.] Bull. acad, sci. U. R. S. S., classe sci. chim., 1943, pp. 145–151; U. O. P. Co. Lib. Bull., No. 48, Nov. 29, 1944; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 441; Chem. Abs., vol. 38, 1944, p. 4117.

Investigation of the activating effect of certain metal oxides on the Fe–Cu catalyst under the conditions previously reported in studies of Co and Ni catalysts. The ratio of C to H_2 was 1 : 1. All catalysts tested contained 100 parts Fe, 25 of Cu, 2 of K_2CO_3, and 125 of kieselguhr, plus promoters consisting of oxides of Mn, Mg, Al, and Th used in amount of 2% on the Fe. A catalytic glass tube of 10 mm. diameter containing a layer of catalyst 40 cm. long was used. The experiments were continued from 8–12 hr. at temperatures of 240°–260° in the case of Fe, about 50° lower (180°–210°) with Co or Ni. The latter require a preliminary high-temperature (250°) reduction with H_2 whereas the Fe–Cu catalysts do not. The experimental data show that the activity of the catalyst is affected not only by the method of preparation but by the nature of the metal oxide promoter. The most active catalysts were those precipitated with K and promoted with ThO_2 and MnO. A yield of 79–80 ml. liquid and solid per $m.^3$ initial gas was obtained in presence of a potash-precipitated catalyst promoted with Mn. This was the highest yield obtained. The catalyst promoted with MgO was an exception to the rule in that Na was a more favorable precipitant than K. Another exception was the catalyst promoted with MnO, which was more active when produced by thermal decomposition than by precipitation with Na. Addition of 2 oxides did not raise the activity. The literature reports that Al_2O_3 and ThO_2 inactivate precipitated Fe–Cu catalysts were not confirmed. On the contrary, Al_2O_3 is able to activate Fe–Cu–Mn catalysts if it is added after precipitation of these catalysts. Fe–Cu catalysts are characterized by low stability. The cause may be connected with wax formation. A similar connection was observed for some Co and Ni catalysts.

804a. EISCHENS, R. P. Exchange Between Chemisorbed and Gaseous Carbon Monoxide on Reduced Iron. Am. Chem. Soc., 120th Meeting Abs., September 1951, p. 15 G.

Exchange between chemisorbed and gaseous CO at —78° goes at markedly different rates on various portions of the Fe surface. There are relatively few of these portions and the rate within each is constant. The exchange goes fastest on the portions where the chemisorption bond is weakest. The most strongly bonded CO is easiest to oxidize to CO_2; however, this observation must be qualified to take into account the

effect of temperature. CO is taken up by "slow chemisorption" or carbonyl formation exchanges at a measurable rate. There is no appreciable difference in the properties of $C^{14}O$ and CO in the chemisorption on Fe.

805. EISENHUT, O., AND KAUPP, E. [Radiographic Investigation of the System, Iron–Nitrogen.] Ztschr. Elektrochem., vol. 36, 1930, pp. 392–404; Chem. Abs., vol. 24, 1930, p. 4207.

Phase boundaries, solubility lines, eutectoid lines, and temperatures of Fe–N are definitely fixed by radiograms. The results agree well with data from magnetic analysis. The existence of 4 phases, α, γ, γ' and ϵ is established. There is continuous absorption of N_2 during regular changes of the crystal-lattice constants. Nitrogen martensite is formed. Bibliography included.

806. ———. [Röntgenographic Researches on Iron Catalysts for Ammonia Synthesis.] Ztschr. physik. Chem., vol. 133, 1928, pp. 456–471; Chem. Abs., vol. 22, 1928, p. 3073.

Debye-Scherrer method of powder analysis was used for synthetic NH_3 catalysts, which were prepared according to the patent of the Badische Anilin & Soda-Fabrik (German **249,447**, abs. **86**), and from complex Fe salts $KAlFe(CN)_6+\chi KCl$. All of these showed principally pure α-Fe, independently of the method of formation or use. The Badische Anilin u. Soda-Fabrik catalyst consisted primarily of Fe_3O_4 in the beginning. The catalyst from the complex salts after reduction also contained Fe_2N, Fe_3C, C, etc. in small quantities.

EISENSTECKEN, F. *See* abs. **3051.**

ELAGINA, N. V. *See* abs. **790, 796, 804.**

ELDER, J. L. *See* abs. **740.**

807. ELEY, D. D. Catalytic Activation of Hydrogen. Advances in Catalysis, Academic Press, Inc., New York, 1948, vol. 1, pp. 157–199.

Report of experimental and theoretical studies on the chemisorption of H_2 on metals. The parahydrogen conversion with reference to the Fischer-Tropsch synthesis is discussed.

808. ELEY, D. D., AND RIDEAL, E. K. Catalysis of the Parahydrogen Conversion by Tungsten. Proc. Roy. Soc. (London), vol. 178, A, 1941, pp. 429–451; Chem. Abs., vol. 36, 1942, p. 22.

The p–H_2 conversion was measured on the surface of W as a function of the surface concentration of adsorbed O acting as a poison. The O decreases the fraction of the metal surface available for reaction and affects the reactivity of the neighboring chemisorbed hydrogen. Dipole-dipole interaction between the adsorbed atoms may be an important factor in this. A part of the O adsorbed on W can be removed at room temperature by reaction with H_2. Films of CO, N_2, and C_2H_4 also act as poisons, and it appears that the small conversion that takes place when they are present is due to the formation of a hydride surface on top of the film rather than on gaps in it. Constants for the reaction are calculated, including the temperature-independent factor for the zero order reaction. The reaction is considered in terms of the activated complex theory and is shown to be more in accordance with a conversion mechanism based upon an interchange between loosely adsorbed H_2 molecules and chemisorbed H than with the original idea of the recombination of chemisorbed H_2 atoms. The H_2+D_2 reaction has the same rate as the p–H_2 conversion; hence tunneling in the potential barriers plays an unimportant part in this H_2 reaction, even at −150°. The H_2+D_2 reaction has about the same activation energy as the parahydrogen conversion. This, measured at 1.3 mm., is 3,070 cal. The 2 reactions are kinetically identical and go through the same mechanism.

ELFSTROM, N. *See* abs. **1623.**

809. ELIAN, J. [Synthesis of Liquid Hydrocarbons by the Induschimie-Carsyn Process.] Induschimie Fabricators for the Chemical Industries, Brussels, 1941, 23 pp.

Prospectus briefly reviews development of the Fischer-Tropsch process, discusses reaction mechanism based on the carbide theory, and gives an economic study of the process with calculations on the cost of production of primary oil. The conclusions are based largely on the results of experiments carried out over a period of time at the University of Liège. The chief modification resulting from the research is in the use of active metal carbides as catalysts. It is stated that yields have been increased thereby by about 45%, and a more precise control of the nature of the product is obtained. A flow sheet of the process illustrates the synthesis of liquid hydrocarbons from natural gas or byproduct gases from petroleum refining. The process is patented, and the Ruhrchemie A.–G. controls the rights in Germany for utilization of the patent on catalysts. (*See* U. S. Patent 2,369,548.)

810. ELIOT, T. Q., GODDIN, C. S., AND PACE, B. S. Chemicals From Hydrocarbon Synthesis. Oil Gas Jour., vol. 48, No. 1, 1949, p. 112.

Abstract of paper presented at American Institue of Chemical Engineers meeting, Tulsa. Commercial hydrocarbon-synthesis plants in this country, based upon a modified Fischer-Tropsch reaction, will produce a variety of aliphatic oxygenated compounds as byproducts. Typical yields of chemicals are presented for a commercial hydrocarbon plant designed to produce 7,000 bbl. per day of liquid hydrocarbons from natural gas. The distribution of these chemicals, ranging from low-molecular weight, water-soluble materials to high-molecular-weight, oil-soluble materials, is reviewed. Recovery of the byproduct chemicals as crude mixtures from the several synthesis product streams is described. Emphasis is placed upon problems relating to the separation and manufacture of specification-grade chemicals from these crude mixtures. The need for additional fundamental data on physical properties and equilibrium behavior of the individual components and mixtures is indicated.

ELKIN, E. M. *See* abs. **3264, 3265, 3266.**

ELLIOTT, M. A. *See* abs. **53, 2615.**

810a. ELLIOTT, M. A., PERRY, H., JOHAKIN, J., COREY, R. C., AND KHULLAR, M. L. Gasification of Pulverized Coal With Oxygen and Steam in a Vortex Reactor. Ind. Eng. Chem., vol. 44, 1952, pp. 1,074–1,082.

An experimental study has been made of the gasification of pulverized bituminous C coal with O_2 and steam in a vortex-type reactor at atmospheric pressure. The potentialities of this type of reactor for producing synthesis gas were investigated. The unit was operated downflow with continuous removal of slag. Most of the data was obtained in coal throughputs of 100 lb. per hr., steam : coal ratio of about 0.5 lb. per lb. of coal, and O_2: coal ratio ranging 7–11 ft.^{3} per lb. of coal. The O_2 and steam feed streams could be preheated to 1,300° F. All tests were made at a constant reactor diameter of 2 ft. with a 4-in.-diameter outlet, but with reactor depths of 8, 24 and 36 in. In most of the tests, all of the O_2 entered the reactor through tangential slots at the periphery. In some tests, part of the O_2 entered the vortex just beneath the coal stream. The coal was always fed to the reactor from a rotating, H_2O-cooled plate at the top. The effect of ratio of O_2: coal and depth of reactor on C conversion, production of $CO+H_2$ per lb. of coal and per ft.^{3} of O_2, are shown and discussed in detail. The best gasification results were obtained when part of the O_2 was admitted with the coal. For example, in the 36-in. vortex the C conversion ranged 78–94% for the range of O_2: coal ratio of 8–11 ft.^{3} O_2 per lb of coal. At

8 ft.^{3} of O_2 per lb. of coal, approximately 41 lb. of coal and 329 ft.^{3} of O_2 were required for the production of 1,000 ft.^{3} of $CO+H_2$, even with heat losses from the shell of about 1,000 B. t. u. per lb. of coal. This heat loss is thermodynamically equivalent to an O_2 consumption of about 80 ft.^{3} per 1,000 ft.^{3} of $CO+H_2$. The critical factors to be considered in interpreting experimental results on the suspension gasification of coal with O_2 and steam are discussed.

811. ELLIS, C. Hydrogenation of Organic Substances. Van Nostrand Co., New York, 1930, 3d ed., chap. LIII–LV, 986 pp.

Reduction of C oxides: MeOH, synthol, and synthine.

812. ———. Lecture Notes on a Visit to Plants of the I. G. Farbenindustrie A.-G. During 1930. Trans. Am. Inst. Chem. Eng., vol. 25, 1930, pp. 16–41; Chem. Abs., vol. 25, 1931, p. 4636.

Illustrated description of the I. G. plants at Oppau and Ludwigshafen with a discussion of the production of synthetic NH_3 and MeOH and the hydrogenation of mineral oils.

813. ———. Chemistry of Petroleum Derivatives. Reinhold Publishing Corp., New York, 1937, vol. II, chap. 52, pp. 1223–1255.

Reduction of CO to hydrocarbons is reviewed, giving 175 refs.

814. ELOVICH, S. Y., AND ZHABROVA, G. M. [Mechanism of the Catalytic Hydrogenation of Ethylene on Nickel. I. Kinetics of the Process.] Jour. Phys. Chem. (U. S. S. R.), vol. 13, 1939, pp. 1761–1764; Chem. Abs., vol. 35, 1941, p. 373.

815. ———. [Mechanism of the Catalytic Hydrogenation of Ethylene on Nickel. II. Role of the Activated Adsorption of Ethlyene and Hydrogen in the Hydrogenation Process. General Scheme of the Process.] Jour. Phys. Chem. (U. S. S. R.), vol. 13, 1939, pp. 1775–1786; Chem. Abs., vol. 35, 1941, p. 373.

Within the temperature region in which hydrogenation occurs, both H_2 and C_2H_4 undergo activated adsorption on a Ni catalyst prepared by reduction of NiO. The equation $dq/dt=ae^{-\alpha q}$ holds for all 3 processes. The energy of activation for the activated adsorption for H_2 is 16±1 cal. and for C_2H_4, 9 cal. The initial hydrogenation velocity is 40–60 times as great as the rate of activated adsorption. When the reaction is carried out stepwise, that is, adsorption of H_2 and then of C_2H_4, or the reverse, no hydrogenation takes place. The experimental results can be explained by the following mechanism: $H_2+Ni=H_2Ni$ (molecular adsorption); $C_2H_4+Ni=C_2H_4Ni$ (molecular adsorption); $C_2H_4Ni=C_2H_4Ni^*$ (active state); $C_2H_4Ni^*=C_2H_4Ni$ (activated adsorption); $C_2H_4Ni^*+H_2Ni=C_2H_6+Ni$ (reaction). As the temperature rises, the rate of activated adsorption of C_2H_4 increases, relatively, more rapidly than the rate of hydrogenation, until finally its absolute rate is greater also; poisoning of the surface results, and above a certain temperature of maximum rate of hydrogenation the latter decreases. The temperature for this maximum rate of hydrogenation is lower the more active the catalyst, with respect to activated adsorption and is characteristic for the given catalyst.

816. ELVINS, O. C. Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen. Jour. Soc. Chem. Ind., vol. 46, 1927, pp. 473–478T; Chem. Abs., vol. 22, 1928, p. 3130.

Interaction of CO and H_2 was investigated at atmospheric pressure and in presence of catalysts at temperatures of the order of 280°. A catalyst prepared from a mixture of 60 parts of Co, 30 parts of CuO, and 45 parts of MnO was used in conjunction with varying gas mixtures. Contrary to the original statements of Fischer and Tropsch that only aliphatic hydrocarbons are formed by this reaction definite amounts of water-soluble oxygenated compounds and olefins were found among the reaction products. Gives detailed account of the experimental work, and describes preparation of the catalyst from precipitated hydroxides, by ignition of nitrates, and from fused oxides. The size of the granule was also investigated from the point of view of the inherent fouling effect of the waxy products of reaction.

817. ELVINS, O. C., AND NASH, A. W. Reduction of Carbon Monoxide. Nature, vol. 118, 1926, p. 154; Chem. Abs., vol. 20, 1926, p. 3684.

Formation of hydrocarbons by passing a mixture of CO and H_2 at atmospheric pressure over catalysts has been described by F. Fischer (abs. **1021**). Elvins and Nash have confirmed the formation of liquid hydrocarbons and also have shown the possibility of the synthesis of oxygenated compounds. A mixture of 53.9% CO and 44.6% H_2 at atmospheric pressure was passed over reduced oxides of Mn, Co, and Cu impregnated with 0.5% Li_2CO_3, at 302°. 1.2 m.^{3} of gas mixture gave 0.5 gm. of solid and 1.4 gm. of yellow oil insoluble in H_2O and H_2O-soluble acids equivalent to 0.33 gm. KOH. Steam distillation from the K salts of the acids gave 0.5 cc. liquid, boiling at 74°–80°, which gave the CHI_3 reaction in the cold. Fischer's theory of intermediate carbide formation does not explain the formation of oxygenated compounds. The production of oxygenated compounds and hydrocarbons may be regarded as being preceded by the hypothetical formation of MeOH, which gives CH_4 and other substances according to the conditions. The reaction may proceed in stages, or the catalyst may accelerate one or more of the possible reactions of CO and H_2. When a mixture of aldehydes, ketones, acids, and hydrocarbons is obtained, both courses may be followed. Most of the products are probably formed simultaneously rather than consecutively.

818. ———. Synthetic Fuel From Carbon Monoxide and Hydrogen. Fuel, vol. 5, 1926, pp. 263–265; Chem. Abs., vol. 20, 1926, p. 2572.

Review of recent work with preliminary notes on new experiments on the conversion of CO and H_2 to a liquid fuel. The catalyst was prepared by mixing, drying, and reducing a mixture of moist hydrated Co, Cu, and Mn oxides with H_2 at 400°. A mixture of equal volumes of CO and H_2 was washed with aqueous KOH and then H_2SO_4 and passed over the catalyst. The amount of CO_2 increased rapidly with the temperature, reaching 10% at 284°. The gases were cooled and led through active charcoal to a gasometer. An oil accumulated on the water, and the charcoal yielded a liquid composed of saturated hydrocarbons.

819. ELWORTHY, R. T. Synthetic Methanol. Canadian Chem. and Met., vol. 9, 1925, pp. 139–140; Chem. Abs., vol. 19, 1925, p. 2403.

Résumé of the Badische (abs. **1014**, **1015**), Patart, and Audibert processes for preparing MeOH from water gas and H_2, with a short bibliography. The first process mentioned employs purified water gas containing 60% H_2, and 30% CO, together with CO_2 and N_2, at 200 atm. pressure, over a catalyst maintained at about 400°. Catalysts are mixtures of metal oxides belonging to different groups in the periodic system, as 90 parts ZnO and 10 parts Cr_2O_3; 85 parts ZnO and 15 parts V oxide, or 90 parts CdO and 10 parts Cr_2O_3. Gases used must be purified carefully, particularly for S and volatile Fe compounds. The Merseberg plant produces about 10–20 tons per day at $0.20 per gal. The Patart process (abs. **2141**) uses as catalyst 90% CuO and 10% ZnO at temperatures of 400°–420° and at pressures of 150–250 atm. It gives a product at $0.22-$0.32 per gal. Audibert uses catalysts contain-

ing suboxides of V, Mn, W, Pb, and Bi. Emphasizes economic importance of these processes.

EMERT, O. *See* abs. **2297.**

820. EMMETT, P. H. Studies on the Mechanism of Ammonia Synthesis Over Iron Catalysts. Jour. Chem. Education, vol. 7, 1930, pp. 2571–2583; Chem. Abs., vol. 25, 1931, p. 453.

Résumé of all published work on the mechanism of catalytic synthesis of NH_3 and on the effect of promoters on the activity of Fe catalysts.

821. ———. Surface-Area Measurements—a New Tool for Studying Contact Catalysts. Advances in Catalysis, Academic Press, Inc., New York, 1948, vol. I, pp. 65–90.

Critical discussion is presented of new developments in the theory and application of surface area measurements in connection with catalytic work. Its application to the preparation of Fischer-Tropsch catalysts is introduced.

821a. ———. Radioisotopes. Oil Gas Jour., vol. 50, No. 21, 1951, pp. 82, 84, 87, 89, 90, 93.

Uses that have been made of radioactive isotopes in the petroleum industry are discussed under 3 headings: (1) Exploration and production of petroleum, (2) refining and distribution of petroleum products, and (3) chemical research as applied to process development or improvement of petroleum products. Experiments on the application of radioactive tracers to the study of the Fischer-Tropsch mechanism of reaction are described. 47 references.

EMMETT, P. H. *See* abs. **42, 376, 377, 386, 387, 388, 389, 390, 669, 1358, 1359, 1470, 2006, 2007, 2008, 2009, 2010, 2717a, 2718.**

822. EMMETT, P. H., AND BRUNAUER, S. The Poisoning Action of Water Vapor at High Pressure on Iron Synthetic Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 2682–2693; Chem. Abs., vol. 24, 1930, p. 4693.

Poisoning of synthetic NH_3 catalysts by water vapor was studied at 450° at pressures as high as 100 atm. and at various partial pressures of H_2O vapor between 0.08 and 0.64%. The amount of O retained by the catalyst is proportional to $\sqrt{P_{H_2O} : P_{H_2}}$ Very active catalysts are capable of retaining more O than less-active catalysts. The poisoning of both doubly and singly promoted catalysts by water vapor is almost entirely reversible, although a slight permanent injury to the catalyst results. A probable mechanism of NH_3 synthesis consists in the reduction by H_2 of surface Fe_4N formed by the reaction of N_2 with surface Fe atoms having average free energies sufficiently in excess of those of normal Fe atoms.

823. ———. Adsorption of Nitrogen by Iron–Synthetic-Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 56, 1934, pp. 35–41; Chem. Abs., vol. 28, 1934, p. 1243.

Rates of adsorption of N_2 by promoted and by pure Fe catalysts were measured over the temperature range 273°–450°. The energy of activation of the adsorption process is about 16,000 cal. Isotherms at 400° and 450° indicate a heat of adsorption of about 35,000 cal. Isotherms taken at —189° are linear with respect to pressure 100–760 mm.

824. ———. Application of Polanyi's Potential Theory to the van der Waals Adsorption of Gases on Iron–Synthetic-Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 57, 1935, pp. 2732–2733; Chem. Abs., vol. 30, 1936, p. 1291.

Potential-volume curves for the adsorption of N and A on a single promoted Fe synthetic–NH_3 catalyst are given. They seem to represent the isotherms very closely throughout the entire pressure range covered including the region concave to the pressure axis where probably less than a molecule layer of gas exists, the linear portion that has been postulated to represent the building up of a 2d layer of gas on the catalyst surface, and the higher-pressure portion, which is convex to the pressure axis and, which, it is generally believed, represents the condensation of the gas to liquid in the capillaries of the adsorbent. The potential curves exhibit no variation with temperature, the —183° and —195.8° points falling on the same curve.

825. ———. Accumulation of Alkali Promoters on Surfaces of Iron–Synthetic-Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 59, 1937, pp. 310–315; Chem. Abs., vol. 31, 1937, p. 2915.

By comparing the adsorption isotherms for N_2 at —183°, CO at —183°, and CO_2 at —78° on various Fe–synthetic-NH_3 catalysts, evidence was obtained to show that a % or so of K_2O in the catalysts will actually cover more than 50% of the surface of the reduced catalyst. Apparently the chemisorption of CO at —183° occurs principally on surface Fe atoms, whereas the chemisorption of CO_2 at —78° occurs on such surface promoter molecules as contain alkali.

826. ———. Use of Adsorption Isotherms for Measuring the Surface Areas of Catalysts and Other Finely Divided Materials. Trans. Electrochem. Soc., vol. 71, 1937, 12 pp. (preprint); Chem. Abs., vol. 31, 1937, p. 3371.

Describes method for measuring the surface areas of catalysts, and of other finely divided substances, by using low-temperature adsorption isotherms of gases such as N_2, A, CO, O_2, and CO_2. Representative isotherms for 2 promoted Fe–synthetic–NH_3 catalysts, pumice, Ni on pumice, and NiO on pumice are presented. In the case of the Fe catalyst, it is shown that if the beginning of the linear portion of the isotherms is interpreted as the point of completion of a unimolecular layer, surface areas can be calculated that are approximately the same for all gases tried. Furthermore, the surface areas so calculated are large enough to accommodate the observed chemisorption of CO at —183° and the largest irreversible adsorption of H observed at —78°–100°. Only in the case of O at —183° is the volume taken up irreversibly by the catalyst several fold greater than a monomolecular layer. Presumably O reacts chemically with the outer layers of Fe atoms even at —183°. The method has so far been applied with apparent success to the catalysts and catalyst supports mentioned above and in addition to 4 other synthetic NH_3 catalysts, 2 Cu catalysts, glaucosil, 2 soils and 2 soil colloids, samples of dry powdered bacteria, Cr oxide gel, and Cr oxide gel that had been glowed at 400°.

827. ———. Use of Low-Temperature van der Waals Adsorption Isotherms in Determining the Surface Area of Iron–Synthetic-Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 59, 1937, pp. 1553–1564; Chem. Abs., vol. 31, 1937, p. 7322.

Adsorption isotherms of N_2 and A at —195.8°; N_2, A, CO, and O_2 at —183°; CH_4 and NO at —140°; N_2O and CO_2 at —78°; NH_3 at —36°; and *n*-butane at 0° on 6 different Fe synthetic–NH_3 catalysts were determined. These isotherms together with data on the chemisorption of CO on the catalysts at —183° and —78° and for the activated adsorption of H_2 appear to afford a means of measuring the absolute and the relative surface areas of the Fe catalysts. Al_2O_3 promoters appear to concentrate on the surfaces of the Fe catalysts.

828. EMMETT, P. H., AND CINES, M. Surface-Area Measurements on Metal Spheres and Carbon Blacks. Jour. Phys. and Colloid Chem., vol. 51, 1947, pp. 1329–1341; Chem. Abs., vol. 42, 1948, p. 1104.

Comparison of areas obtained by adsorption isotherms for N_2 at 195° on metal powders with those calculated from photomicrographs yields roughness factors in the range 1.1–1.8. Areas determined by the adsorption isotherms for CS_2 and for C_4H_{10} are 20–50% lower than those obtained by using N_2 as adsorbate. Pelletizing carbon black produces no appreciable changes in its surface area per gm.

829. EMMETT, P. H., AND HARKNESS, R. W. Adsorption of Hydrogen by Iron-Synthetic-Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 57, 1935, pp. 1631–1635; Chem. Abs., vol. 30, 1936, p. 369.

Experimental evidence is presented to show that the two types of activated adsorption of H_2 that occur on Fe-synthetic-NH_3 catalysts are, in part at least, adsorptions on the surface of the catalysts rather than any type of solution within the metal. The rate of the lower temperature-activated adsorption (type A) agrees closely with that calculated by assuming that all H_2 molecules are adsorbed that strike the catalyst with the observed energy of activation, 10,400 cal.

830. ———. Catalytic Interconversion of *o-p* Hydrogen Over Iron, Platinum and Nickel Catalysts. Jour. Am. Chem. Soc., vol. 57, 1935, pp. 1624–1631; Chem. Abs., vol. 30, 1936, p. 369.

The *o-p* interconversion of H_2 over Fe-synthetic-NH_3 catalyst was studied as a function of the temperature, pressure, time of contact, and presence of various poisons. Both types of activated adsorption of H_2 on Fe are poisons for the conversion of *o-p*-H_2 at liquid-air temperature. The low-temperature *o-p* conversion over Ni and Pt is also inhibited by the activated adsorption of H_2.

831. EMMETT, P. H., AND KUMMER, J. T. [Physical and Chemical Adsorption Studies on Catalysts.] Jour. chim. phys., vol. 47, 1950, pp. 67–73; Chem. Abs., vol. 44, 1950, p. 6711.

Theory for the multilayer adsorption of gases on solids (abs. **389**) still appears to yield reliable values for the surface area of porous and finely divided solids, though according to Halsey (abs. **1340**, it is doubtful if the assumptions of the theory are valid. N_2^{28} and N_2^{30} react rapidly to form N_2^{29} over Fe catalysts at 450°–500°, contrary to previous conclusions (abs. **1639**). Singly promoted Fe-synthetic-NH_3 catalysts rapidly catalyze the reaction $H_2+D_2=2HD$ at —195°, even though D_2 does not remove H adsorbed at —78° or 100° from the surface at —195°. Adsorption measurements indicate the existence of a new type of activated adsorption on Fe capable of occurring rapidly at —195°. Chemisorption measurements, using normal CO as well as radioactive CO, indicate that Fe-synthetic-NH_3 catalysts behave as though half the surface was homogeneous and half heterogeneous. The measurements were made by covering part of the surface with radioactive CO and the remainder with normal CO at low temperatures and then collecting and analyzing the evolved CO for radioactivity as the temperature was slowly raised.

831a. ———. Mechanism Studies of Fischer-Tropsch Synthesis. Proc. 3d World Petrol. Cong., 1951; Fuel Abs., vol. 11, No. 2, 1852, abs. 1299; Fuel, vol. 31, 1952, p. 370.

Tracer experiments using Fe_2C^{14} lead to the conclusion that most of the hydrocarbon synthesis over Fe and Co catalysts does not occur through formation of metallic carbides as intermediates. Adsorption experiments suggest that the carbides by themselves probably are not good catalysts. The use of radioactive CH_4 is recommended as a sensitive means of ascertaining whether or not this gas can be converted into higher hydrocarbons during synthesis. Results on Fe and Co catalysts showed that in synthesis fewer than 0.1% of the C atoms in the higher hydrocarbons came from CH_4, even though radioactive CH_4 was present in a high concentration (about 50%). Measurements of the free energy of formation of Fe_2C and Fe_3C show that the direct reduction of these carbides by H_2 to form olefins or paraffins by hydrocarbons with more than 6 C atoms is thermodynamically unfavorable. This confirms the tracer experiments in indicating that the carbides of Fe and Co are not intermediates in Fischer-Tropsch synthesis. Use of radioactive O-containing organic molecules is useful for obtaining information relative to the nature of the surface complexes serving as intermediates in the Fischer-Tropsch synthesis. Two such experiments using radioactive EtOH as tracer have shown that either this compound or some surface complex formed from it is capable of acting as an intermediate in the synthesis of higher hydrocarbons. Furthermore, about 90% of the added C atoms that transform the C_2 complex to C_3 hydrocarbon add to the C in the CH_2 rather than to the C of the CH_4 group of the adsorbed alcohol. It seems certain that at least over Fe catalysts, and probably over Co, the higher hydrocarbons are built up by successive adsorption of CO molecules on to the catalyst surface adjacent to some intermediate complex. The CO then attaches itself to the intermediate to form momentarily an O-containing complex which in turn is hydrogenated to remove O and then either escapes from the surface as a hydrocarbon or adds another CO to form a complex containing 1 more C atom. It seems improbable that the synthesis over either Fe or Co results from polymerization of CH_2 groups on the surface or from the reduction of carbides as intermediates.

832. EMMETT, P. H., AND LOVE, K. S. Reduction by Hydrogen and Thermal Decomposition of Nitrides Made by the Reaction of Ammonia With Various Promoted and Unpromoted Iron-Synthetic-Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 55, 1933, pp. 4043–4050; Chem. Abs., vol. 28, 1934, p. 29.

Fe_4N prepared from active catalysts decomposes more rapidly than that prepared from rather inactive catalysts. The energy of activation of the decomposition is about 50,000 cal. Gives rates and nature of the reduction and decomposition of the nitrides from the various Fe catalysts.

833. EMMETT, P. H., AND SHULTZ, J. F. Equilibrium in the System: Carbon Monoxide–Water–Cobalt Oxide–Hydrogen. Free-Energy Changes for the Reaction $CoO+H_2=Co+H_2O$ and the Reaction $Co+1/2\ O_2=CoO$. Jour. Am. Chem. Soc., vol. 51, 1929, pp. 3249–3262; Chem. Abs., vol. 24, 1930, p. 774.

The object was to determine at several temperatures the equilibrium ratio of $H_2O:H_2$ in the presence of Co. CoO, reduced by H_2 at the temperature desired, was subjected to various mixtures of H_2+H_2O, and the effluent gases were analyzed for H_2 and H_2O. A second catalyst was prepared by reducing Co_3O_4 to CoO. Equilibrium was approached at each temperature from both the H_2 and H_2O sides. A modification of the flow system of Pease and Cook, was used. The ratio $H_2O:H_2$ at 335° was 85±5; at 450°, 67±1; at 515°, 57.0±0.3; and at 570°, 50.5±0.2. $\Delta F°_{298}$ for the reaction $CoO+H_2=H_2O+Co$ was calculated as —3,678 calories. ΔH_{298} was calculated as —1,646 calories, as compared with —300 calories calculated from the heats of formation of CoO and H_2O. X-ray photographs indicated that at 500° H_2O did not form Co_3O_4 from CoO. $\Delta F°_{1373}$ for the formation of CoO from Co and O_2 was calculated as 32,050 calories, and from this, partial pressure of O_2 in equilibrium with CoO and Co at 1,100° was calculated as 0.5×10^{-7} mm. Transformation of hexagonal to cubic Co takes place at 340°–360°.

834. ———. Equilibria in the Iron–Hydrogen–Oxygen System. Indirect Calculation of the Water-Gas

Equilibrium Constant. Jour. Am. Chem. Soc., vol. 52, 1930, p. 4268–4285; Chem. Abs., vol. 25, 1931, p. 453.

The equilibrium constant $K=P_{H_2O}/P_{H_2}$ for the reaction $FeO+H_2=Fe+H_2O$ was determined by a flow method. At 600°, 700°, 800°, 900°, and 1,000°, K is, respectively, 0.332, 0.422, 0.499, 0.594, and 0.669. For the reaction $Fe_3O_4+H_2=3FeO+H_2O$, K is 1.18 at 700° and 2.37 at 800°. The water-gas constants, calculated by combining these Fe–H–O equilibrium values with those for the Fe–C–O system, agree excellently with constants measured directly by Neumann and Kohler.

835. ———. Equilibrium in the System: Co–CO_2–CoO–CO. Indirect Calculation of the Water-Gas Equilibrium Constant. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 1782–1793; Chem. Abs., vol. 24, 1930, p. 3157.

The value of the equilibrium constant $K_1=CO_2/CO$ for the reaction $CoO+CO=Co+CO_2$ was determined by a flow system at 450°, 515°, and 570° to be 489.6, 245.9, and 148.4, respectively. Combination of these values with the previously determined constant $K_2=H_2O/H_2$ for the reaction (abs. **833**) $CoO+H_2=Co+H_2O$ gives indirect values for the water gas constant $K=(CO)(H_2O)/(CO_2)(H_2)$ that agree well with the values determined directly by Neumann and Kohler (abs. **2436**).

836. EMMETT, P. H., HENDRICKS, S. B., AND BRUNAUER, S. Dissociation Pressure of Fe_4N. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 1456–1464; Chem. Abs., vol. 24, 1930, p. 2940.

By a flow method, it was determined that at 1 atm. pressure the % NH_3 in a gaseous H_2–NH_3 mixture in equilibrium with an Fe–Fe_4N mixture is 36 at 420°, 30 at 444°, 28.5 at 460°, and 17 at 525°. The dissociation pressures of Fe_4N at these respective temperatures are calculated to be 4,250, 4,300, 5,400, and 5,600 atm.

837. ENGELHARDT, A. [Recovery and Chemical Utilization of Gaseous Hydrocarbons From Fuel Beneficiation and Motor-Fuel Synthesis.] Internat. Cong. Pure Appl. Chem., 10th Conf., Rome, 1938; Brennstoff-Chem., vol. 19, 1938, pp. 297–304; Chem. Abs., vol. 32, 1938, p. 9444.

Address deals with the sources and relative amounts of gaseous hydrocarbons, methods of their recovery, and possibilities of utilization. Because of the short contact time in the benzine synthesis of Fischer-Tropsch, olefinic hydrocarbons are formed. After recycle over the catalyst, the composition of the synthesis gases in volume % is as follows: CO_2, 29; N_2, 15; H_2, 22; CO, 14.4; CH_4, 16; C_2H_4, 0.6; C_nH_{2n}, 1.5–1.8; C_nH_{2n+2}, 1.7–2.1. Changing the reaction conditions might, naturally, yield a gas of different composition. In general the gaseous hydrocarbons with 2 or more C atoms make up 15–20% of the liquid product; their complete utilization is therefore greatly desired, particularly since they are wholly free from S impurities.

ENGELHARDT, F. *See* abs. **1947, 1951, 1952, 1953, 1953a, 1955.**

838. ENGELS, W. H. [Production of Hydrogen by the Interaction of Carbon Monoxide and Calcium Hydroxide and Acceleration of the Water-Gas Reaction by Means of Iron.] Jour. Gasbeleucht., vol. 62, 1919, pp. 477–483, 493–500; Chem. Abs., vol. 14, 1920, p. 599.

Engels has investigated the conditions under which the reaction between CO and $Ca(OH)_2$ will best serve for the technical production of H_2. An investigation with the purpose of determining whether the course of the reaction for the production of H_2 is represented by the equation $CO+H_2O\rightarrow H_2+CO_2$ or by the equation $Ca(OH)_2+CO_2\rightleftharpoons CaCO_3+H_2$ is detailed. The results indicate that the course of the reaction is determined principally by the latter equation, a little of the H_2, however, resulting from the reaction represented by the first equation. The reaction is best carried out at about 500°. The use of more steam in the water-gas mixture than that corresponding to the vapor pressure of $Ca(OH)_2$ at the temperature employed is to be avoided. The reaction between Co and CaO is accelerated at least elevenfold by the catalytic action of Fe in consequence of the acceleration of the water-gas reaction by this catalyst. The effect of temperature upon the equilibrium of the water-gas reaction is well represented by the thermo-dynamic relation previously deduced by Haber.

839. ENGINEERING. Fischer-Tropsch Hydrogenation Process. Vol. 146, 1938, p. 517; Chem. Age, vol. 38, 1938, p. 164.

The importance of pilot-plant operation to bring out various difficulties not apparent in laboratory investigation is pointed out. It is important to keep the catalyst at the correct temperature. The various ranges of fuels that may be treated and the different types of products obtained are described in detail, and it is stated that Fischer-Tropsch products have a high H_2 content. The primary products may be used for the synthetic production of lubricants. Recent developments have given greater elasticity to the process with respect to the products obtained.

840. ———. Synthetic Liquid Fuels. Vol. 161, 1946, p. 422.

Summary of progress in the United States in producing liquid fuel synthetically by coal hydrogenation, gas synthesis, shale retorting, and distilling agricultural residues.

841. ———. American Synthetic Liquid Fuel Production. Vol. 165, 1948, p. 398.

Review of United States plans for developing a synthetic fuel industry.

EPIFANSKII, P. F. *See* abs. **804.**

842. EPSTEIN, S. Alloys of Iron and Carbon. I. Constitution. McGraw-Hill Book Co., New York, 1936, 476 pp.

ERCOLE, R. *See* abs. **2401a, 2706c.**

843. ERDELY, A., AND NASH, A. W. Catalysts Used in the Synthesis of Higher Hydrocarbons From Water Gas. Jour. Soc. Chem. Ind., vol. 47, 1928, No. 32, pp. 219–223T; Chem. Abs., vol. 22, 1928, p. 3818.

A continuation of Elvin's experiments (abs. **816**). From the experiments with different unpromoted catalysts at 285°, and with a gas mixture containing equal parts of CO and H_2, a Co–Cu–ZnO catalyst appears to be most suitable. After the initial period, its activity was very constant, causing a contraction of about 50% for several days continuous operation. A Co–Cu–Al_2O_3 catalyst gave nearly as satisfactory a performance, although less oil and more H_2O was formed in its presence. The oil yield was highest with an unpromoted Co–Cu catalyst, although the activity of this catalyst decreased most rapidly. A Co–Cu–CeO_2 catalyst gave the lowest yield of H_2O and a fair yield of oil, but although the initial activity of this catalyst was the greatest, its activity decreased about as rapidly as that of the Co–Cu. Catalysts supported on silica gel were as active as the Co–Cu–Mn catalyst only in 1 instance. In this connection, the importance of the relative proportions of catalyst to support was shown. The optimum temperature for the formation of liquid hydrocarbons was found to be 280°–290° for the Co–Cu–Al_2O_3 catalyst. Above 290° CO_2 and CH_4 are the chief products, and below 230° no reaction was observed. An excess of H_2 in the initial gas mixture increased the H_2O formation, while an excess of CO rapidly decreased

the activity of the catalyst. The gas velocity exerts a marked influence on the yield of products. The optimum space velocity for the Co–Cu–ZnO catalyst was about 120 vol. of gas per hr. per unit vol. of catalyst.

844. ERDÉLYI, S. [Production of Liquid Fuels From Gases.] Magyar Mernök-Epiteszegylet Közlönye, vol. 62, 1928, pp. 73–78; Chem. Abs., vol. 23, 1929, p. 2010.

Summarizing description of the methods of Fischer and the I. G. Farbenindustrie.

845. ERDMANN, E. Production of Methane From Carbon Monoxide and Hydrogen. Gas World, vol. 55, 1911, pp. 195–197; Jour. Gasbeleucht., vol. 54, 1911, pp. 737–741; Chem. Trade Jour., vol. 49, 1911, p. 175; Chem. Abs., vol. 5, 1911, pp. 3618, 3726.

Commercial process (the Cedford gas process) is described of converting water gas into CH_4 as follows: $CO+3H_2=CH_4+H_2O$. In practice it is necessary to use 5 vol. H_2 : 1 CO. A water gas containing 40% CO, 4% CO_2, 52% H_2, and 4% N_2 after going through the process, contained traces of CO and CO_2, 30% CH_4, 62% H_2 and 6–7% N_2. The total cost was 8.5 d. per 1,000 cu. ft.

845a. ERDÖL U. KOHLE. Patent Report. Vol. 5, 1952, pp. 585–589; Chem. Abs., vol 47, 1953, p. 290.

List of German and foreign patents on the general subject of coal and oil production and manufacture.

846. EREMENKO, V. Y., AND MIROSHNICHENKO, G. K. [Thermoanthracite and the Chemical Industry.] Coke and Chem. (U. S. S. R.), No. 2, 1939, pp. 41–46; Khim. Referat. Zhur., No. 8, 1939, pp. 90–91; Chem. Abs., vol. 34, 1940, p. 5625.

During the production of thermoanthracite in the Miroshnichenko furnaces up to 20% of the anthracite is gasified. By blowing with steam–O_2 or air–steam–O_2, the contents of CO and H_2 can be increased to yield a gas suitable for the synthesis of NH_3 or of MeOH. Combined production of thermoanthracite and gas for the synthesis lowers the cost.

ERIKSEN, A. *See* abs. **2782.**

847. ERKKO, E. O. [Liquid Fuels.] Suomen Kemistilehti, vol. 8A, 1935, pp. 103–108; Chem. Zentralb., vol. I, 1936, p. 1152; Chem. Abs., vol. 30, 1936, p. 265.

Survey of synthetic methods for the production of liquid fuels.

848. ERNST, F. A. Equipment for High-Pressure Reactions. Ind. Eng. Chem., vol. 18, 1926, pp. 664–669; Chem. and Met. Eng., vol. 33, 1926, pp. 413–414; Chem. Abs., vol. 20, 1926, p. 2765.

Sketches and brief description of various pieces of high-pressure (100–1,000 atm.) equipment for research or experimental work. The apparatus described has been operated satisfactorily at the Fixed Nitrogen Research Laboratory, Washington, D. C. The equipment described includes materials, hydraulic pump, deadweight gage, converter head, electrical connection, tubing and connectors, gas-circulating pump, magnetic pressure-regulating valve, and high-pressure relief valve.

———. *See* abs. **928.**

EROFEEV, B. V. *See* abs. **1806.**

849. EROFEEV, B. V., RUNTSO, A. P., AND VOLKOVA, A. A. [Kinetics of the Catalytic Reduction to Hydrocarbons of Carbon Monoxide by Hydrogen on a Cobalt-Thorium Catalyst.] Acta Physicochim. U. R. S. S., vol. 13, 1940, pp. 111–122 (in German); Chem. Abs., vol. 35, 1941, pp. 1690–1691.

Kinetics of the reaction $nCO + 2nH_2 = C_nH_{2n} + nH_2O$ at 200° were studied on a Co : Th : SiO_2 = 100 : 15 : 100 catalyst prepared by treatment of the nitrates with K_2CO_3, addition of ethyl orthosilicate, and reduction with H_2 at 400°. With carefully purified H_2 and CO the yield of liquid C_nH_{2n} was 60–70 cc. per $m.^3$ gas. The experimental data satisfy the equations, $A = a+(b/u_o)$, $u_k = cu_o - b$, $\pi = Au_o = au_o + b$, where u_o and u_k = volume velocity of gas entering and leaving, A = contraction, π = capacity and a, b, c are constants. These results indicate that the reaction is of zero order on a catalytic surface of the first kind. The capacity increases with increasing streaming velocity; this fact indicates that the adsorption of the reaction products depends strongly on their partial pressures; greater streaming velocity increases the surface available for reaction.

ERSHOV, N. I. *See* abs. **798, 802, 802b, 802c.**

850. ESKREIS, A. [Conversion of Carbon Monoxide: $CO+H_2O=CO_2+H_2$.] Plyn, Voda zdravotni Technika, vol. 17, 1937, p. 176; Chem. Zentralb., vol. II, 1937, pp. 1486–1487; Chem. Abs., vol. 33, 1939, p. 4763.

For this reaction there is a definite proportion of water vapor that gives the optimum yield. The introduction of superheated steam increases the amount of water vapor and thus improves the effect. The temperature must be maintained within narrow limits. The conversion is retarded not only by the reaction products but also by an excess of one of the reacting substances, that is, the water vapor. The optimum concentration of steam at a given temperature can be calculated from the relation: $(100-q : 100)\eta W' = Q_p - Q_s + Y(\eta A - B) + (B - B')X$. Here q=the percentage heat loss in the reaction space; η=the thermal capacity of the apparatus; W'=the theoretical heat effect of the reaction; Q_p=heat of the products after the reaction at the final temperature of the process; Q_s=the heat of the reactants before the reaction at the initial temperature of the reaction; Y=the theoretical percentage completion of the reaction; B=the molecular specific heat of water at the final temperature; B'=the molecular specific heat of water at the temperature of steam entering the furnace; X=the molecules of water vapor to be added; and A=the molecular specific heat of CO_2 at the final temperature.

851. ESTIVAL, J. Gasification of Low-Grade Fuels for the Synthesis of Gasoline and Methanol. Coal Carbonisation, vol. 2, 1936, p. 222; Génie civil, vol. 109, 1937, pp. 405–407; Chem. Abs., vol. 31, 1937, p. 8884.

Philipon gas producer and the installation at Saint Etienne are described. Tests were made in a small gas producer, treating 100–150 kg. per hr., on a lignite from the collieries of Bouches-du-Rhone. A slag suitable for cement manufacture, an iron containing less than 0.10% S, a gas particularly rich in CO and H_2, and some tar were obtained. Results indicate that any fuel, crude, carbonized, or semicarbonized, can be used to produce a gas suitable for the manufacture of MeOH or gasoline. Adaptation to large-scale production and means of reducing costs are discussed. Suggestions for using the gas to make gasoline or MeOH and a drawing of equipment for the manufacture of MeOH are given.

ETH, —. *See* abs. **3728.**

852. EUCKEN, A. [Contact Catalysis.] Naturwissenschaften, vol. 36, 1949, pp. 48–53, 74–81; Chem. Abs., vol. 44, 1950, p. 3777.

Review dealing with general principles, dehydration and dehydrogenation of alcohols on metal oxides, and hydrogenation of unsaturated hydrocarbons on metals; many curves and tabulated data.

852a. ———. [Hydrogenation of Unsaturated Hydrocarbons on Nickel Contact Catalysts. I. Adsorption of Hydrogen on Nickel.] Ztschr. Elektrochem., vol. 53, 1949, pp. 285–290; British Abs., 1951, I, A, p. 52.

Adsorption of H_2 on Ni powder is investigated at constant temperature and also at constant pressure. The

differential or intermediate heat of adsorption is determined calorimetrically. The results agree with the assumption that H_2 is dissociated and is adsorbed in the atomic state. The adsorption velocity is determined. There are 2 maxima in the adsorption velocity isobars, 1 at about 200° abs. and the other at about 270° abs. At higher pressures the 1st maximum disappears. This is not due to the presence of 2 regions of the surface with different activities. It is more likely that changes take place in the whole surface on heating, and that the activity therefore alters. The heat of adsorption decreases relatively strongly with increasing cover density.

853. EUCKEN, A., AND HUNSMANN, W. [Calorimetric Study of Physical and Activated Adsorption of Hydrogen on Nickel.] Ztschr. physik. Chem., vol. B 44, 1939, pp. 163–184; Chem. Abs., vol. 34, 1940, p. 666.

Heat of adsorption of H_2 on Ni was studied calorimetrically, 20°–273° K. Desorption was also measured in the same temperature range with a hot-wire manometer. 2 heats of activation for desorption were detected: 1 corresponds to 14% of the adsorbing centers and amounts to 9–10 kcal. per mol; the other accounts for the remaining 86% and is 18–22 kcal. per mol. The heat of adsorption increases linearly from 4–21 kg.-cal. per mol. The van der Waals heat of adsorption is about 800 cal. per mol. and depends strongly on the density of coverage of the surface. Low-temperature tunnel effects could not be detected.

EVANS, G. M. *See* abs. **3657.**

854. EVANS, H. P., AND HAYES, A. Graphitizing Behavior of Iron Carbide in Pure Iron–Carbon Alloys in the Critical-Range. Trans. Am. Soc. Steel Treating, vol. 11, 1927, pp. 691–707; Chem. Abs., vol. 21, 1927, p. 3878.

Fe–C alloys of high purity have been graphitized in the presence of a CO–CO_2 gas mixture at a pressure of 5 atm. within the temperature interval 1,292°–1,875° F. Fe_3C in Fe–C alloys of high purity and containing about 2.3% C is metastable at temperatures below 1,292° F. and above 1,562° F. in the presence of this CO–CO_2 gas mixture when it is applied at a pressure of 5 atm.

EVANS, R. M. *See* abs. **763.**

855. EVANS, R. M., AND NEWTON, W. L. Hydrogen From Water Gas. Ind. Eng. Chem., vol. 18, 1926, pp. 513–517; Chem. Abs., vol. 20, 1926, p. 2242.

Catalysts for the Bosch or "catalytic water gas" process for H_2 production by interacting the CO of the water gas with steam (and later removing the CO_2 thus formed) have been studied in detail. With an oxide catalyst containing 97% Co, 2% Al, and 1% K and a space velocity per hr. of 1,000 at 450° and at 350°, the % CO in the dry effluent gas was reduced to 1.1 and 0.3, respectively, these corresponding to the equilibrium values. Substitution of the Co, partly or wholly, by Fe produced only slightly less efficient catalysts. The Co catalysts are slowly poisoned even by small quantities of H_2S, CS_2, or COS, so that careful purification would be necessary in operation, but the Fe catalysts are less sensitive and probably could function continuously on unpurified water gas from a good grade of coke.

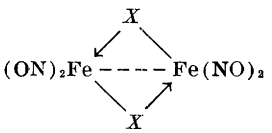
EVENTOVA, M. S. *See* abs. **306.**

856. EWELL, R. H. Calculation of Chemical Equilibrium at High Pressures. Ind. Eng. Chem., vol. 32, 1940, pp. 147–153; Chem. Abs., vol. 34, 1940, p. 3158.

Starting with the 3d law of thermodynamics, the general expression for equilibrium constants is derived and applied to the synthesis of MeOH from CO and steam. Fugacities and activity coefficients are reviewed, and Berthelot's equation of state and a new modification of the van der Waals equation are brought out. The use of Raoult's law in calculating high-pressure equilibrium in the manufacture of MeOH is indicated.

857. EWENS, R. V. G. Constitution of Certain Binuclear Metallic Carbonyls and Nitrosyls. Nature, vol. 161, 1948, pp. 530–531; Chem. Abs., vol. 42, 1948, p. 4484.

Discussion of the resonance structure proposed by Jensen and Asmussen for $Fe_2(CO)_9$. A covalent Fe–Fe link is preferred on the basis of X-ray and diamagnetic data, as well as color (*see* Powell and Ewens, abs. **2736**). Structures of a similar nature are proposed for $Co_2(CO)_8$, Fe nitrosyl compounds, $Fe(NO)_2X$, where X is SK, Cl, I, SC_2H_5, SC_6H_5, or S_2O_3K.



———. *See* abs. **2736.**

EWIG, K. *See* abs. **3324.**

858. EYBER, G. [Photochemical Decomposition of Iron Pentacarbonyl.] Ztschr. physik. Chem., vol. 144 A, 1929, pp. 1–21; Chem. Abs., vol. 24, 1930, p. 553.

Eyber has investigated the absorption spectrum of hexane solutions of $Fe(CO)_5$ and finds strong absorption below about 4,600 Å. U. The decomposition of the vapor by radiation of wave length, 4,000 Å. U., has been studied. A quantum efficiency of 2 is found. This is explained by the postulation of the formation of an activated molecule that reacts with a normal molecule to give CO and $Fe_2(CO)_9$. Foreign gases (CO_2, A, N_2 and CO) inhibit the decomposition; a deactivation of the excited molecule may be the reason.

$$d(\mathrm{CO})/dt = \frac{K_1(I_{\mathrm{abs.}})}{1+(K_3/K_2)\cdot[(G)/(C)]}$$

where (G) is foreign gas and (C) is pentacarbonyl, satisfies the data. O_2, if present, alters the reaction. The vapor-pressure curve from −14° to +20° has been determined.

859. EYRAUD, I. [Automatic Adsorption Balance.] Jour. chim. phys., vol. 47, 1950, pp. 104–107; Chem. Abs., vol. 44, 1950, p. 7095.

Details of construction for a sensitive adsorption balance capable of automatically recording and plotting a curve for the rate of adsorption of a gas by a solid.

F

860. FABER, A. [Natural and Artificial Mineral Oils in Germany, 1914–17.] Petrol. Ztschr., vol. 24, 1928, pp. 644–652; Chem. Abs., vol. 23, 1929, p. 267.

German oil production, consumption, and import statistics. A general discussion of the possible future supply from coal points to the most economical production by coal distillation to produce tar oil and coke, the coke being gasified with steam to produce water gas, which may be used in the production of synthetic motor fuel. The coal tar serves as a basis for diesel and fuel oils.

861. FABRE, R. [Synthetic Methanol.] Jour. pharm. chim. (8), vol. 2, 1925, pp. 113–117; Chem. Abs., vol. 20, 1926, p. 1216.

Review.

FAIRFIELD, R. G. *See* abs. **202, 1708.**

FAIRLIE, D. M. *See* abs. **2749, 2750, 2751.**

862. FALCKE, V. [Reaction Between Ferrous Oxide and Carbon and Between Carbon Monoxide and Iron. I.] Ber. deut. chem. Gesell., vol. 46, 1913, pp. 743–750; Jour. Soc. Chem. Ind., vol. 32, 1913, p. 365; Chem. Abs., vol. 7, 1913, p. 2525.

The above reaction was studied to ascertain whether or not any difference could be detected between the various kinds of amorphous C, the method being to determine the equilibrium pressure. Experiments showed that FeO prepared by heating FeC_2O_4 at 300° is not pure, and that gas is still given off after the solid has been heated to 700°. Addition of amorphous C has no effect on the pressure produced when FeO, containing 0.5% C, and Fe are heated together at 530°–660°; further, the reaction between FeO and CO is different when the CO is passed over the FeO and when the 2 are heated together in a closed vessel, in the 1st. case much C being deposited, in the 2d, none. When the product obtained in the latter case is dissolved in HCl, no C is deposited, but much CO_2 is evolved.

863. ———. [Reaction Between Ferrous Oxide and Carbon and Between Carbon Monoxide and Iron. II.] Ztschr. Elektrochem., vol. 21, 1915, pp. 37–50; Jour. Soc. Chem. Ind., vol. 34, 1915, p. 554; Chem. Abs., vol. 9, 1915, p. 1883.

The author has studied these reactions at temperatures ranging from 600° upward, and has examined the gaseous products obtained when the reaction mixtures were dissolved in HCl. 3 varieties of graphite and 5 of amorphous C were used. After thorough purification these were analyzed and their densities determined. The apparatus was one used in previous work (abs. **862**). The solid mixtures were introduced in the form of compressed pellets. Below 650° the highly purified varieties of C do not react with FeO, and above this temperature the several varieties of C do not behave alike and may be classed in 3 groups. Sugar charcoal and that obtained by the action of CO on Na are quite inactive up to 800°. C obtained by burning C_2H_2 in Cl and that from petroleum reacted with vigor at 650°. It is not known whether the different in behavior is a property of the different modifications or the result of catalytic action. The graphites reacted vigorously also. The products of the reaction of C and FeO contained pure Fe, and no hydrocarbons resulted from solution in HCl. When Fe was permitted to absorb a large quantity of CO and the equilibrium pressure set up at 600°, the product of the reaction that took place yielded large amounts of saturated hydrocarbons, chiefly C_2H_6, when treated with HCl. No solid C remained. On the contrary, when Fe was heated in a stream of CO or allowed to absorb CO in large amounts, and then heated in a vacuum, the product treated with HCl gave no hydrocarbons and a residue of C resulted.

864. ———. [Reactions Between Ferrous Oxide and Carbon and Between Carbon Monoxide and Iron. III.] Ztsch. Elektrochem., vol. 22, 1916, pp. 121–133; Jour. Chem. Soc., vol. 110, II, p. 484; Chem. Abs., vol. 10, 1916, p. 3041.

Continuation of experiments already described (abs. **863**). Experiments are made to compare the author's values directly with those of Schenck (abs. **3064, 3073**).

865. ———. [Reactions Between Ferrous Oxide and Carbon and Between Carbon Monoxide and Iron. IV.] Ztschr. Elektrochem., vol. 27, 1921, pp. 268–278; Chem. Abs., vol. 15, 1921, p. 3017.

Previous investigations on the equilibrium of the reactions between FeO and C and between CO and Fe are discussed briefly. It has been found experimentally that at temperatures under 700° the equilibrium constant,

$$\zeta = \frac{p^2CO}{pCO_2 \cdot RT \cdot 760}$$

of the reaction $C+CO_2 \rightleftharpoons 2CO$, does not coincide with that obtained from measurements of the equilibrium of the reaction between FeO and C and between CO and Fe. From both this and analytical data it would appear that in this equilibrium the C does not play a role as a definite phase. The most probable explanation of this phenomenon is the previously accepted surmise that the equilibrium is determined by the formation of carbide.

866. ———. [Equilibrium $C+CO_2 \rightleftharpoons 2CO$. Thermodynamics of the Blast-Furnace Process.] Ztschr. Elektrochem., vol. 33, 1927, pp. 1–11; British Chem. Abs., 1927, B, p. 191.

Values recorded in the literature for the equilibrium constant, $k=[CO]^2/[CO_2]$, at various temperatures (523°–1,150°) have been collected and compared by plotting on a log k–T diagram: Corresponding values for the heat of reaction, q, have been calculated from those of k. Independent sets of values for k and q have been calculated from specific heat data and figures for the heats of combustion of C and CO. At a given temperature 2 values of k (calculated), and similarly of q (calculated), are obtained according to whether graphite or amorphous C is regarded as participating in the reaction; but for k (calculated) the difference becomes inappreciable at the higher temperatures. Above 750° values of k (experimental) agree well among themselves and with the corresponding calculated values, but at lower temperatures they are somewhat irregular. Comparison of values of q (from experimental k) with those of q (calculated) shows that above about 750° the former fit in with the assumption that graphite participates in the equilibrium, whereas, at lower temperatures they correspond more closely to values for amorphous C. Values of k (experimental) obtained from equilibria reached from the CO side in the presence of Fe powder diverge notably from those obtained in other ways when the equilibrium temperature is below 750°. This discrepancy is ascribed to the abnormal condition of the C in the iron; it is markedly reduced if the Fe is previously treated with CO for a long time so that free C may be deposited in it. In any case, the establishment of equilibrium is undoubtedly slow at the lower temperatures, and is not well-defined. Measurements of k derived from the composition of blast-furnace gases have also been collected on log k–T diagrams. They are very irregular at lower temperatures, but correspond approximately with the experimental and calculated values at temperatures above about 750°. Thus the equilibrium $C+CO_2 \rightleftharpoons 2CO$ is only attained in the blast furnace gases at these higher temperatures.

867. ———. [Reactions Between Ferrous Oxide and Carbon and Between Carbon Monoxide and Iron.] Ztschr. Elektrochem., vol. 34, 1928, pp. 393–398; Chem. Abs., vol. 23, 1929, p. 2086.

Polemical. Criticism of the work of R. Schenck (abs. **3049**).

———. *See* abs. **3073.**

868. FALCKE, V., AND FISCHER, W. [Equilibrium Between Carbon Monoxide, Carbon and Carbon Dioxide. Reaction Between Ferrous Oxide and Carbon, and Between Carbon Monoxide and Iron.] Ztschr. Elektrochem., vol. 32, 1926, pp. 194–201; Chem. Abs., vol. 20, 1926, p. 3626.

Numerous determinations of the equilibrium constant for the reaction $C+CO_2=2CO$ may be expressed $\log K_p = -(8351/T)+0.242 \log T - 5.65\times10^{4T} + 4.60\times10^{-8T^2} - \log T + 9.504$. The heat of the reaction (van't Hoff equation) is 36,600 cal. at $T=958$. In the presence of excess free Fe the reaction is not $CO_2+Fe=CO+FeO$. Fe_3C is formed and hence in presence of Fe, not saturated with C, the equilibrium constants deviate from the above equation decidedly.

FALLOT, M. *See* abs. **1279.**

869. FALMOUTH, VISCOUNT (Chairman). Falmouth Report on Oil From Coal. Rept. of Comm. of Imperial Defense, Subcomm. on Oil from Coal. H. M. S. Office, London, 1938, 71 pp; Engineering, vol. 145, 1938, pp. 211–212; Engineer, vol. 165, 1938, pp. 215–216, 223, 241–243; Chem. Age, vol. 38, 1938, pp. 141–143; Colliery Guard., vol. 156, 1938, pp. 307–309, 346–347; Iron and Coal Trades Rev., vol. 136, 1938, pp. 326, 356.

870. FALTIN, H. [Problems of Heat Transmission in the Construction of Contact Synthesis Furnaces.] Die Technik, vol. 3, 1948, pp. 457–464; Chem. Abs., vol. 43, 1949, p. 2475.

Effect of the heats of reaction in both endothermal and exothermal processes on the requirements of available space in the reaction chamber and arrangements for carrying away the heat developed or supplying any heat required to make the process isothermal are discussed. Furnace design is explained. Endothermal processes comprise disintegration of CO_2 into CO and O, or dehydration. Exothermal processes are oxidation, hydration, chlorination, polymerization, etc.

FANKUCHEN, I. *See* abs. **1617.**

871. FANNING, L. M. Gasoline Substitutes Gain in Europe. Oil Gas Jour., vol. 34, No. 34, 1926, pp. 142, 150; Chem. Abs., vol. 20, 1926, p. 1706.

General discussion of the synthetic fuel situation.

FANO, U. *See* abs. **3027.**

FARAGHER, W. F. *See* abs. **1494, 1495, 3393.**

872. FARAGHER, W. F. AND HORNE, W. A. Interrogation of Dr. H. Pichler and Professor Ziegler at Kaiser Wilhelm Institut für Kohlenforschung, Mülheim. FIAT Rept. 276; PB 1,058, 1291.

Gives further information on isosynthesis and the results of comparative tests on Fe Fischer-Tropsch catalysts conducted at Schwarzheide-Ruhland. Supplements information previously given in abs. **1302.**

873. FARAGHER, W. F., HORNE, W. A., HOWES, D. A., SCHINDLER, H., CHAFFEE, C. C., WEST, H. L., AND ROSENFELD, L. Supplemental Report on Ruhrchemie A.-G., Sterkrade-Holten, Ruhr. CIOS Report XXXII–96, 1945, 92 pp. TOM Reel 196; PB 1366; British Abs., 1948, B II, p. 287.

Contains information on the manufacture of toluene from n-heptane, synthetic lubricating oil from Fischer-Tropsch olefins, a laboratory test for activity of the Fischer Co catalyst, an estimate of the operating costs of the Oxo process, the direct synthesis of higher alcohols from water gas, preparation of the Fe Fischer catalyst, the methanization of coke-oven gas-catalyst and process, oxidation of paraffin wax with N oxides to produce fatty acids, product testing and utilization of fuels and lubricating oils produced by Ruhrchemie A.-G.

874. ———. Supplemental Report on Ruhrchemie A. G., Sterkrade-Holten, Ruhr. Synthetic Lubricating Oil Manufacture. CIOS Rept. XXXII–96, 1945, pp. 5–13; TOM Reel 196; PB 1366.

Raw material for the manufacture of synthetic lubricating oil by the Ruhrchemie process consists of olefins in the gasoline boiling range having 1 double bond at the end of the chain that are obtained by cracking Fischer-Tropsch gas oil and sweet oil from Fischer-Tropsch wax. Gas oil from plants operating at atmospheric pressure or at 10–15 atm. is suitable. The gas oil has a boiling range of about 230°–320°. The feed stock, thus obtained, and containing not more than 0.015% of H_2O, is polymerized in the presence of 1.2–1.5% of $AlCl_3$, the temperature being gradually raised from 40° to 100° over a period of 4–6 hr. The synthetic oil product is separated from the catalyst-complex oil by settling; dechlorinated by treatment with 1.5% each of Tonsil, HCl activated clay, and ZnO at 180° for 3 hr.; and double distilled, yielding about 33% gasoline, naphtha diesel oil and spindle oil and 64% lubricating oil, 3% being lost. The finished motor oil has a density at 20° of 0.855, viscosity at 50° 7E° and pole height 1.75. Owing to the unsaturated character of the synthetic oil, it was very unstable toward oxidation and only a temporary improvement was obtained by subjecting it to a second treatment with 1% $AlCl_3$ at 180° for 3 hr. A more permanent improvement was obtained by adding 0.2–0.5% by weight of phenthiazin to the olefins before polymerization. Another method was to add 0.3–0.5% by weight of S to the feed stock before polymerization and then treating the oil with 1% by weight of $AlCl_3$ at 250° for 5 hr. The viscosity of the finished oil could be changed by changing the conditions of polymerization. Using 1.5% by weight of $AlCl_3$ and keeping the temperature at 100° from the start of the reaction gave an oil of low viscosity, 4° E at 50°, whereas when 4–6% $AlCl_3$ is used and the temperature kept at 15° for 12–20 hr. followed by heating to 60° for 2 hr., an oil of 38° E at 50° is obtained. The viscosity index and resistance to oxidation were also improved by using olefins with longer chains. In making aviation grade bright stock by the so-called Synthol process, a different feed stock had to be used; only olefins from C_9 to C_{18} were to be used and these supplemented with C_6 to C_{10} olefins obtained directly by the Recycle process and by the C_{15} to C_{18} paraffins, which remain unreacted in the Oxo process. The Recycle process, designed for the manufacture of olefins, consists in using 1 vol. of water gas containing 87% of CO and H_2 ($CO : H_2 = 1 : 1.23$–1.25) with 3 vol. of recycle gas from the synthesis so that the $CO : H_2 = 1 : 0.8$. The catalyst is 100 Co, 15 MgO, 200 kieselguhr, the temp. of the synthesis 200°–220°, pressure 10–15 atm., the space velocity 800 $m.^3$ gas per 10 $m.^3$ catalyst per hr. The total yield of liquid products and gasol amounts to 160 gm. per $m.^3$ of ideal gas. The polymerization procedure varied somewhat from that followed in the manufacture of motor lubricant; it was planned to use 4–6% by weight of $AlCl_3$, react the olefins for 10 hr. with the catalyst at 15° and then heat for 2 hr. at 60°. Phentiazen was to be added to the olefins before polymerization. A flowsheet shows the complete process.

875. ———. Supplemental Report on Ruhrchemie, A. G., Sterkrade-Holten, Ruhr. Laboratory Test for Activity of Fischer Catalyst. CIOS Rept. XXXII–96, 1945, pp. 14–16; TOM Reel 196; PB 1366.

About 4 gm. of catalyst in a glass tube are reduced for 2 hr. at 450° with a mixture of H_2 and N_2 (3 : 1) at the rate of 300 l. per hr. or with pure H_2 at 400°. The final catalyst contains 40–50% of the Co as oxide. After reduction, the tube is placed in an Al-block furnace and treated with synthesis gas (4 l. $CO : H_2 = 1.0 : 1.8$–1.9) for 500 hr. Contraction of the gas volume and yield of liquid products are measured and serve as measures of activity. The liquid products are expressed as cc. per N $m.^3$ of synthesis gas and comprise oil that condenses at room temperature in the receiver and the liquid removed from the activated C adsorber by steaming at 150° and 15–20 mm. Hg. Water formation can also be used in appraising the catalyst activity. A diagram of the apparatus is shown, and typical test data for a normal Co catalyst and its contraction curve are attached.

876. ———. Supplemental Report on Ruhrchemie A.-G., Sterkrade-Holten, Ruhr. Oxo Process. CIOS Rept. XXXII–96, 1945, pp. 17–19; TOM Reel 196; PB 1366.

Economic estimate as of Mar. 4, 1943, is given of the operating costs for 12,000 tons per yr. of fatty

alcohols based on pilot-plant operation, 1/10 commercial size. Material input was 12,000 tons olefins at RM 0.40 per kgm., 6,000,000 *N* m.³ water gas at RM 0.04 per *N* m.³, 3,000,000 *N* m.³ H_2 at RM 0.075 per *N* m.³ with total material, operating and capital costs of RM 9,387,070 or RM 78.23 per 100 kg. fatty alcohol. 2 flow sheets of the process are attached.

877. ———. Supplemental Report on Ruhrchemie A.-G., Sterkrade-Holten, Ruhr. Direct Synthesis of Higher Alcohols From Water Gas. CIOS Rept. XXXII–96, 1945, pp. 20–21; TOM Reel 196; PB 1366.

Direct synthesis of alcohols was being studied in the small unit show schematically. The process involves passing a mixture of fresh water gas and recycle gas compressed in 2 stages to 10–100 atm. at a space velocity of 100–150 *N* l. per l. of catalyst per hr. over 5 l. of a promoted Fe catalyst (100 Fe, 5 Cu, 10 Ce, 50 kieselguhr) contained in an oil-heated tubular reactor. The reaction products are passed through a hot separator at 110° and thence to a condenser. The gas flow is started at a reactor temperature of 200°, which is raised degree by degree to the desired conversion temperature, 220°–240°. At the higher pressure the olefin content of the product is small and the O-containing products are of shorter chain length, whereas at medium pressure higher molecular compounds are formed with a higher proportion of olefins. From 1 *N* m.³ of gas, 80–100 gm. of a mixture of alcohols, esters, and olefins, to about C_{18}, are obtained in a single pass operation. The alcohol content of the total product averages 50–60% and the alcohols are all primary and predominantly of iso-structure.

878. ———. Supplemental Report on Ruhrchemie A.-G., Sterkrade-Holten, Ruhr. The Ruhrchemie Iron Fischer Catalyst. CIOS Rept. XXXII–96, 1945, pp. 22–26; TOM Reel 196; PB 1366.

Preparation of a new Fe catalyst to replace the previously used dense sintered Fe catalyst is described. The new catalyst is made by dissolving the components, Cu, Fe, and CaO in that order in a 50% concentration of technical HNO_3, heating the solution to boiling for several hours and then cooling it to room temperature. Thus prepared, the solution contains little free HNO_3, is stable and does not form a deposit; the content of the components is within the following ranges: Fe, 115–125; Cu, 5–7; and CaO, 11–13 gm. per l. Total HNO_3 is 510–450 gm. Before precipitation, the concentration of the Fe is brought to 50–55 gm. per l. Precipitation from the mixed nitrates is accomplished by introducing the solution heated to 98° into a boiling solution of Na_2CO_3 of a concentration of 90–100 gm. per l. while stirring intensively. The amount of Na_2CO_3 used is such that, at the end of the precipitation, the *p*H is 6.8. Total time of precipitation must not exceed 5 min. After evolution of CO_2 is ended, the calculated amount of kieselguhr is stirred into the mixture, the suspension is filtered and washed with hot condensate down to 0.4–0.6% of $NaNO_3$, the cake is impregnated with 3.0–3.5% of KOH based on the Fe, the filter is pressed again, and then is dried at 110°. The catalyst thus prepared is hard and resistant to abrasion. The finished catalyst has the following proportions: 100 Fe; 5 Cu; 8 CaO; 30 kieselguhr. Reduction of the catalyst takes place with a mixture of H_2 and N_2 (3 : 1) for 30 min. at a maximum temperature of 300°. When H_2 only is used the time is much shorter. The rate of gas flow is about 2,000 m.³ per hr. per m.² of cross section. A content of more than 5–8% of metallic Fe in the finished reduced catalyst must be avoided as higher contents give an inactive catalyst. Furthermore, the Fe soluble in 2% solution of acetic acid shall be 60–70% of the total Fe. After reduction the catalyst is treated in the usual manner with cold N_2 and then saturated with CO_2. The saturation must be conducted slowly since considerable heat is liberated.

FARCAS, T. *See* abs. **2755.**

879. FARISH, W. S. Manufacture of Gasoline and Oil From Coal. Synthetic Liquid Fuels Hearings Before a Subcommittee of the Committee on Public Lands and Surveys, U. S. Senate, 78th Cong., 1st Sess., on S. 1243, 1944, pp. 51–59.

Survey of the economics of the Bergius coal hydrogenation and the Fischer-Tropsch synthesis processes for the production of gasoline. The paper summarizes the raw material and overall steel requirements, as well as investments and operating costs. Figures are on the basis of 1942 estimate.

Cost estimates on synthetic liquid fuel processes if operated in the United States in 1942

	Approx. plant investment per bbl. gasoline per day	Approx. tons steel per bbl. gasoline per day	Approx. cost of gasoline per gal. without depreciation	Approx. gasoline total cost, including depreciation
1. High-pressure coal hydrogenation	$12,800.00	14.1	$0.159	$0.226
2. Fischer process, Europe design, from coal	7,600.00	8.9	.147	.192
3. Fischer process, Europe design, natural gas at $0.05 per 1,000 cu. ft.	4,750.00	6.5	.06	.088
4. Modern high-pressure hydrogenation of petroleum	1,150.00	1.4	.048	.055
5. Modern oil refinery crude at $1.20 per bbl. thermal cracking	700.00	.7	.051	.053
6. Modern oil refinery crude at $2.00 per bbl. thermal cracking	700.00	.7	.083	.085

Items 1 and 2 are for plants of 2,950 bbl. and 3,960 bbl. production capacity/day, respectively. For larger plants, that is, 30,000 tons, the costs would be slightly lower, probably about $0.15–$0.16/gal. and $0.155/gal., respectively.

880. FARKAS, A., AND FARKAS, L. Ortho-, Para- and Heavy Hydrogen. MacMillan Co., New York, 1935, 215 pp.

In certain cases a relationship is known to exist between magnetic properties and catalytic activity. For example, the conversion of *o*- and *p*-hydrogen is catalyzed by paramagnetic ions, the rate of conversion increasing with increasing magnetic moment of the ions. The so-called magnetocatalytic effect is based on similar phenomena.

FARKAS, L. *See* abs. **880.**

881. FARRAR, L. D. Acres of Promise for Synthetic Fuels. Public Utilities Fortnightly, vol. 46, 1950, pp. 210–222.

Economy of the synthetic liquid fuel processes is discussed. The cost of H_2 constitutes about 50% of the total cost of liquid products from the Bergius process, while the cost of synthesis gas represents 60–70% of the total cost of Fischer–Tropsch products. Underground gasification of coal is being investigated as a lower cost method of producing gases suitable for both processes.

882. FARUP, P. [Catalytic Influence of Ores on the Decomposition of Carbon Monoxide.] Tids. Kjemi Bergvesen, vol. 6, 1926, pp. 1–6, 15–17; Chem. Abs., vol. 21, 1927, p. 1243.

Catalytic decomposition of CO in the presence of Fe oxides has been studied experimentally at 400°–500°, the interval of maximum efficiency of this re-

action. Pieces of different species of Fe ore, concentrates, and briquets were heated in a current of pure CO and the formation of CO_2 and C was observed and measured. Briquetted ore has a catalytic effect several times greater than that of fresh ores and concentrates. The burning temperature of the briquets could not be seen to have an influence upon the catalytic efficiency, nor was this considerably reduced in briquets burned with a small addition of $CaCO_3$ or NaCl.

883. FAST, E. Spectrographic Determination of Potassium in Iron Catalysts by Fractional Distillation. Anal. Chem., vol. 22, 1950, pp. 320–322.

Spectrographic method for determining K in Fe catalysts has been developed. K was found to distill quantitatively from a sample pellet during the initial arcing period. By photographing the spectrum during this period only, interference due to Fe was eliminated. The length of the log sectored K line was found to be a linear function of the log concentration of K. An average deviation of 5–10% of the amount present is indicated by repeated determinations on the same sample. Na and Li can be determined in the same manner. The method is not applicable to catalysts containing several percent of C.

884. FAUSER, G. [Synthetic Gasoline.] Energia Termica., vol. 7, 1939, pp. 30–37.

Characteristics are given of the Fischer-Tropsch process for synthesis of gasoline from H_2 and CO and of catalytic hydrogenation under high pressure by the Bergius process. Data on world development in technique of hydrogenation and production of synthetic gasoline in Italy are given.

885. FEDERAL POWER COMMISSION. Natural-Gas Investigation by the Federal Power Commission. Oil and Gas Jour., vol. 45, No. 8, 1946, pp. 60–61.

Abstract of testimony by P. C. Keith, president of Hydrocarbon Research, Inc., on the development of processes for making gasoline from natural gas and for gasifying and liquefying coal. (*See* abs. **1780.**) Fuel reserves as of Jan. 1, 1946, if converted into crude oil, would make a total of 6,326 billion bbl. divided: 21 billion bbl. from crude, 25 billion from natural gas, and 6,280 billion bbl. from coal synthesis. It is predicated that commercial production of gasoline from natural gas and from coal will take place within 5 yr. Experiments had been made in the production of city gas from coal, and a gas had been obtained of 600–900 B. t. u. at a cost of $0.17/1,000 cu. ft. It is estimated that gas could be produced at West Virginia coal mines and transported to New York for $0.242/1,000 cu. ft. By this process 10,000 tons of coal would produce about 200 million cu. ft. of gas. It is also stated that gasoline can be made from coal for $0.06/gal., assuming the cost of coal at $2.00/ton. The time will probably come in the not too distant future when this price will be competitive with petroleum and natural gas.

886. ———. Prospects for Production of a Substitute for Natural Gas. Natural-Gas Investigation Docket G. 580, 1947; Chem. Eng., vol. 54, No. 8, 1947, pp. 104–106.

Four methods to manufacture high-B. t. u. gas from coal are described: Fischer-Tropsch hydrocarbon synthesis; pressure gasification and hydrogenation (Lurgi plant); coal hydrogenation with gas byproduct (Bergius process); underground gasification and catalytic enrichment. Each process is illustrated by flow charts. Economic factors are discussed.

FEDITSCHKINA, T. L. *See* abs. **803.**

887. FEHLING, H. R. Adiabatic Temperature and Equilibrium of the Gasification Process. Jour. Inst. Fuel, vol. 14, 1940, pp. 39–46; Chem. Abs., vol. 35, 1941, p. 3415.

Ideal gasification, wherein the reaction products are in thermodynamic equilibrium and no heat is lost, is illustrated by a diagram showing the interdependence of temperature, calorific value, steam saturation, and steam decomposition. It also shows the theoretical limits of the process. Analysis of experimental results with this diagram indicates that with low steam saturation nearly complete decomposition of CO_2 and H_2O is attainable. At saturation temperatures above 45° the reaction velocity sets a limit and prevents complete decomposition when the temperature falls below a critical point that depends chiefly on reactivity. Thermodynamic efficiency, as opposed to thermal efficiency, is defined as the degree of approach to the theoretical limit of a producer. Experimental results show that gas quality and thermal efficiency may be improved only by increasing the amount of steam in conjunction with more reactive fuels, preheating the air and steam, and providing special aerodynamic conditions. The so-called "wall effect" observed in producer practice is explained thermodynamically.

FEISST, W. *See* abs. **1042, 2874.**

FELDMAN, J. *See* abs. **42a.**

888. FELDMAN, J., PANTAZOPLOS, P., PANTAZOPLOS, G., AND ORCHIN, M. Design, Construction, and Operation of a Distillation Laboratory for the Synthetic Liquid Fuels Program. Bureau of Mines Rept. of Investigations 4764, February 1951, 4 pp.

Detailed description, with numerous diagrams and figures, of the distillation laboratory at Bruceton, Pa., which was established to aid in the separation and identification of the products produced in the synthetic liquid fuel processes. Compounds present in synthetic liquid fuels may include aliphatics C_1–C_{60} or greater. Alcohols, ketones, esters, aliphatic carboxylic acids, saturated hydrocarbons, olefins, and diolefins are all found in Fischer-Tropsch products. Coal hydrogenation products contain, in addition to aliphatic compounds, a large proportion of naphthenic material and aromatic compounds ranging from benzene to coronene; in addition, appreciable amounts of tar acids and bases are present. In designing the laboratory, provision had to be made for the greatest amount of flexibility and versatility. A great deal of standardization of basic equipment had also to be designed to permit interchange of parts and services.

889. FELDMAN, O. Synthesis of Petroleum. South African Min. and Eng. Jour., vol. 46, pt. 1, 1935, pp. 361–362; Chem. Abs., vol. 29, 1935, p. 7055.

Fischer process for the synthesis of liquid and solid hydrocarbons from CO and H_2 at atmospheric pressure and 200°–250° is described. The yields are gasol, b. 30°, 4% (50% olefins); gasoline, b. 30°–200°, 62% (30% olefins); oil, b. +200°, 23% (10% olefins); paraffin wax, m. p. 50°, 7%; and paraffin deposits, m. p. +70°, in catalyst, 4%.

890. FELDMAN, Y. A., AND ALLISON, E. [Crude Methanol.] Jour. Chem. Ind. (U. S. S. R.), vol. 12, 1935, pp. 1237–1240; Chem. Abs., vol. 30, 1936, p. 2170.

The lower boiling portion of the byproducts distilled from synthetic MeOH consists mostly of ethers and esters, of which MeOAc is the main representative. Me_2S, Me_2CO, and aldehydes are also present. About half the higher-boiling fraction is iso-BuOH. The rest consists of other higher alcohols and acids.

891. FELDMAN, Y. A., AND KHAĬKOVA, N. A. [Production of Synthetic Methanol from Water Gas.] Jour. Chem. Ind. (U. S. S. R.), vol. 13, 1936, pp. 970–975; Chem. Abs., vol. 31, 1937, p. 240.

Corrosion in Fe apparatus is chiefly due to formation of $Fe(CO)_5$ by CO in the presence of H_2O, although S compounds are also harmful. Cr–V and Cr–Ni steels are also easily attacked by CO.

892. FELDMAN, Y. A., AND NIKITIN, V. M. [Use of Higher Alcohols Obtained in the Synthesis of Methanol.] Jour. Chem. Ind. (U. S. S. R.), vol. 13, 1936, pp. 922–924; Chem. Abs., vol. 30, 1936, p. 7538.

Higher boiling fraction from synthetic MeOH is treated with 475–500 kg. of HOAc per ton of alcohols and 4–5% of the weight of HOAc of H_2SO_4 and refluxed for 1.5–2 hr. The MeOAc distilled off in yields of 1–20% up to 72°. Distillation is continued to 87°, yielding a mixture of iso–BuOH, iso–BuOAc, and H_2O. The H_2O is separated and the other components returned to the still and redistilled. In this way 40–60% of iso–BuOAc is obtained. The H_2O solution is salted out with 25% its weight of NaCl and gives 3–3.5% iso–PrOAc and iso–BuOAc.

893. FELDMAN, Y. A., IVANOV, K. N., AND NAUMOVA, A. I. [Use of Siderite as a Source for Catalysts for the Synthesis of Ammonia.] Jour. Chem. Ind. (U. S. S. R.), vol. 12, 1935, pp. 1036–1038; Chem. Abs., vol. 30, 1936, p. 1190.

When Bakal siderite is fused without removing any impurities, most of the Fe_2O_3 becomes Fe_3O_4, and a good catalyst for NH_3 synthesis is obtained. Addition of Al_2O_3 or K_2O does not improve it.

894. FENSKE, M. R. Unit Processes in Organic Synthesis, by P. H. Groggins. McGraw-Hill Book Co., New York, 3d ed., 1947, chap. VIII, pp. 488–562.

General discussion of hydrogenation with special emphasis on the following industrial applications: Hydrogenation or hardening of vegetable or marine oils; the synthesis of MeOH, higher alcohols, and hydrocarbons from water gas; the reduction of long-chain fatty acids to alcohols; hydrogenation of hydrocarbons, mineral oils, and coal.

———. *See* abs. **1098, 1099, 1100, 1104, 1105.**

FENSKE, M. R., AND FROLICH, P. K. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. V. Decomposition and Synthesis of Methanol With a Zinc-Copper-Chromium Oxide Catalyst. *See* abs. **1102.**

895. FERGUSSON, R. R., AND BARRER, R. M. Derivation and Development of Huttig's Multilayer Sorption Isotherm. Trans. Faraday Soc., vol. 46, 1950, pp. 400–407; Chem. Abs., vol. 44, 1950, p. 9768.

Statistical derivation is given of a generalized sorption isotherm based on evaporation-condensation properties of a sorbed molecule. Characterictic isotherm equations were obtained analogous to the various modifications of the Brunauer, Emmett, and Teller isotherm (abs. **389**). Isotherms of types I, III, and to some extent V, are obtained but not types II and IV. A major objection to this and the Brunauer, Emmett and Teller treatment of multilayer sorption is the lack of interaction laterally with molecules in adjacent columns, although interaction with molecules in the same column is permitted.

896. FERRERO, P. [Chemical Evaluation of Coal.] Rev. univ. mines, vol. 9, 1933, pp. 453–458, 487–493; Chem. Abs., vol. 27, 1933, p. 5935.

Utilization of coal in the coking process and the products obtained by different processes are reviewed. Methods of obtaining aromatic substances, coloring materials, pharmaceutical products, explosives, CH_4, NH_3, HNO_3, HCN, different alcohols, formaldehyde, synthol, coke-oven gas, EtOH, acetone, and glycol are discussed and their reactions explained.

897. ———. [Present Chemical Syntheses Starting From Petroleum.] Rev. univ. mines, vol. 6, 1950, pp. 121–133.

Among other topics, the Fischer-Tropsch synthesis is discussed.

897a. ———. [Chemical Utilization of Gas Collected in Coal Mines.] Pubs. assoc. ing. faculté polytech. Mons, 1952, No. 1, pp. 74–78. Chem. Abs., vol. 46, 1952, p. 7736.

Many ways might be found to chemically utilize the gas (grisou) emanating in coal mines. Grisou contains 90% CH_4, 8% air, and small amounts of C_2H_4, H_2 and CO_2. Processes are reviewed for converting grisou to town gas and to synthesis gas for manufacture of NH_3 or MeOH by steam reaction in the presence of catalysts or by partial oxidation. Also mentioned are the manufacture of C_2H_2, HCN by various methods, chlorination, nitration, Oxo reaction, Fischer-Tropsch process.

898. FERRIS, S. W. Limiting Compositions in Hydrocarbon Conversion. Ind. Eng. Chem., vol. 33, 1941, pp. 752–759; Chem. Abs., vol. 35, 1941, p. 7163.

Several investigators have attempted to show that the process of cracking hydrocarbons tends to approach an equilibrium. This term is not used in the present paper. Instead, attention is called to the tendency for a synthetic crude to be formed in the cracking reactions. The synthetic crude oil includes all the liquid material resulting from a reaction, under such conditions of condensation that vapor pressure approximates 10–15 lb./sq. in. From very different stocks the curves of distillation of the products of cracking are seen to approach a limiting band. The same tendency can be traced from the literature in catalytic as in thermal cracking, in destructive hydrogenation, alkylation, the Fischer-Tropsch synthesis from CO and H_2, catalytic reforming, and even in polymerization. The effect was similar when a naphthenic petroleum and successive synthetic crude oils from it were subjected to thermal cracking. The 3 passes after the 1st made little differences in the approach of the synthetic crude oils to the limiting band. It was found that if the distillation curve of the original stock lay to the right of the limiting band, the synthetic crude oil could not be forced to the left of it. Petroleums of this character were probably residual crude oils from which the light fractions had escaped in the course of geologic change. The petroleums whose distillation curves started at the left of the limiting band were regarded as distillate crude oils. If pyrolysis is pushed far enough, a 2d limiting composition can be detected in which benzene and napthalene predominate. This is a conclusion based on the data reported by Rittman, Dutton, and Dean. The conditions for the production of the limiting band depend upon an original specific gravity of 0.800–0.930. At higher specific gravities the available supply of H_2 is so limited that the tendency is toward benzene-naphthalene limiting composition.

899. FESTER, G. [Catalytic Reduction of Carbon Monoxide.] Brennstoff-Chem., vol. 3, 1922, pp. 244–245; Chem. Abs., vol. 17, 1923, p. 1745.

An observation by Orlov has been confirmed, that is, that CO when reduced at 100° by H_2 in presence of a catalyst of Ni and Pd asbestos yields unsaturated hydrocarbons and not CH_4. The catalyst rapidly loses its activity.

900. FESTER, G., AND BRUDE, G. [Decomposition of Carbon Monoxide.] Ber. deut. chem. Gesell., vol. 56B, 1923, pp. 2245–2249; Chem. Abs., vol. 18, 1924, p. 1095.

It has been previously shown that the equilibrium $2\ CO \rightleftharpoons CO_2 + C$ (1) is displaced but slightly to the right at low temperatures for want of a suitable catalyzer (abs. **2219, 3001,** and **3222**), but that the equilibrium $CO + H_2O \rightleftharpoons CO_2 + H_2$ (2) in the presence of Pd black is displaced considerably to the right at low temperatures (abs. **3688**). By using Pd adsorbed on active charcoal as catalyzer, CO, either alone or mixed

with an equal volume of H_2, was decomposed at low temperatures in the presence of so small an amount of H_2O that reaction (1) took place and not (2). To prove that reaction (1) occurred, active charcoal was replaced by active SiO_2 whereby the free C formed in (1) was easily detected. By varying the amount of H_2O vapor present, H_2 in small or large amount was formed, owing to reaction (2). Contrary to Orlov (abs. **2532**), no C_2H_4 could be detected in the products, though under certain conditions small amounts of saturated hydrocarbons and $Ni(CO)_4$ were detected.

901. ———. [Reactions of Carbon Monoxide.] Brennstoff-Chem., vol. 5, 1924, pp. 49–53; Chem. Abs., vol. 18, 1924, p. 2480.

During various attempts to reduce CO by H_2 catalytically, it has been observed that at low temperatures appreciable amounts of CO_2 are formed. A study is made of the formation of CO_2 from CO–H_2 mixtures and CO alone at temperatures 35°–240° with Pd precipitated on active C and on silica gel as catalysts. 2 reactions were considered: 2 $CO=CO_2+C$ and $CO+H_2O=CO_2+H_2$. Both were found to take place to a limited extent. Concentrations of 1 to 55% CO_2 in exit gases were obtained, the higher results being obtained at 240°, corresponding to 71% of the pure CO used. With CO : H_2 mixtures 1 : 1 the H_2 appeared to have no reducing action, presumably because of strong preferential adsorption of CO by active C and silica gel. Moist CO gave higher concentrations of CO_2, indicating that $CO+H_2O \rightarrow CO_2+H_2$ took place. Preferential oxidation of CO in mixtures of H_2, O_2, and small amounts of CO with V_2O_5 as catalyst was tried without success, although with equal concentrations of CO and H_2, 2½ times as much CO as H_2 was oxidized.

FETTERLY, L. C. *See* abs. **2441, 2442.**

FIELD, J. H. *See* abs. **647, 648.**

902. FIELDNER, A. C. Gasoline Substitutes From Coal. Jour. Western Soc. Eng., vol. 31, 1926, pp. 306–315; Jour. Soc. Auto. Eng., vol. 20, 1927, pp. 98–104; Chem. Abs., vol. 20, 1926, p. 3557.

General review of the situation, and the status of research in the manufacture of gasoline substitutes from coal. 4 methods are described briefly and the physical and economic possibilities of each discussed: high-temperature carbonization; low-temperature carbonization; coal hydrogenation; and synthesis of alcohols from CO and H_2.

903. ———. Motor Fuel From Coal. Nucleus, vol. 4, No. 5, February 1927, pp. 20–25; Chem. Abs., vol. 21, 1927, p. 1175.

Approximate economic analysis is made of the Lander (low-temperature carbonization for production of smokeless semicoke and tar oils), Franz Fischer (synthetic hydrocarbons from water gas), Patart (catalytic synthesis of MeOH and higher alcohols from water gas under pressure), and Bergius (liquefaction of coal by direct hydrogenation at high pressure) processes for obtaining liquid fuels from coal under American conditions, to provide some basis for predicting when they may come into use for augmenting the supply of gasoline from petroleum. Low temperature carbonization is considered of minor interest, while the other processes cannot compete with petroleum gasoline until its refinery price rises to $0.30–$0.40 per gal.

904. ———. Use of Off-Peak Water-Gas Capacity for Methanol Production. Am. Gas. Jour., vol. 126, 1927, pp. 179–181; Chem. Abs., vol. 21, 1927, p. 1699.

An estimate based on data taken from a paper by G. Patart in the Proceedings of the International Conference on Bituminous Coal, 1926 (abs. **2589**). The cost of production of MeOH by a large plant in the United States would probably be only $0.30 per gal., but the situation with regard to the use of off-peak water gas is less favorable.

905. ———. Recent Developments in the Production of Motor Fuels From Coal. Bureau of Mines Inf. Circ. No. 6075, 1928, 18 pp.; Fuel, vol. 7, 1928, pp. 492–501; Chem. Markets, vol. 23, 1928, pp. 375–378; Chem. Abs., vol. 23, 1929, p. 1245.

Review of the production of motor fuel by: (1) Carbonization of coal; (2) the Bergius process; and (3) the complete gasification of coal and conversion of the gases by pressure synthesis. It is believed that the Bergius process, or some modification of it, will prove most economical.

906. ———. Recent Developments in the Production of Motor Fuels From Coal. Canadian Chem. and Met., vol. 12, April 1928, p. 99.

Digest of a paper given before the Montreal Section of the Society of Chemical Industry. The 2 processes, Bergius and Fischer, are still in the semiexperimental stage, the former being about ready for actual commercial production and the latter still in the laboratory. It is predicted that the Bergius process will prove the more economical for motor fuel production from coal, while the synthesis of liquid fuels from gas will be limited to the utilization of byproduct gases and natural gas.

907. ———. Recent Developments in Coal Utilization. Synthesis of Chemical Products From Gases Produced From Coal or Coke. Bureau of Mines Minerals Yearbook, 1932–33, pp. 447–450; Chem. Abs., vol. 28, 1934, p. 284.

Production of gasoline by passing mixtures of H_2 and CO at atmospheric pressure over Fe or Co catalysts at approximately 260° C. has not reached commercial realization, although a semicommercial-scale plant at the Mülheim Coal Research Institute has been operating experimentally during the past few years. The earlier Co catalysts have been superseded by Ni-Mn-Al oxide on kieselguhr. This catalyst gave yields of 100–120 cc. of liquid products per $m.^3$ of gas during 4 weeks of continuous operation. The yield had then decreased to 30% of the initial value. The catalyst must be regenerated by removing the accumulated paraffin. The maximum reaction temperature ranges from 190° at the beginning of a run to 210° C. at the end. The principal difficulties in large-scale commercial operation of the process are to dissipate the high heat of reaction and keep the catalyst at the proper temperature; also, the gases must be purified carefully to remove S. The solution of these problems is nearing completion.

908. ———. Developments in Coal Preparation and Utilization. Synthetic Hydrocarbons From Gases. Bureau of Mines Minerals Yearbook, 1934, pp. 627–643; Chem. Abs., vol. 29, 1935, p. 318.

At present, the production of synthetic motor fuel from gases does not have as good commercial prospects as production from coal or coal tar by hydrogenation.

909. ———. Recent Developments in Coal Preparation and Utilization. Bureau of Mines Minerals Yearbook, 1935, pp. 691–709; Fuel, vol. 15, 1936, pp. 173–179, 204–211.

Brief statement with bibliography of Fischer process for making synthetic products from gases.

910. ———. Recent Developments in Coal Preparation and Utilization. Bureau of Mines Minerals Yearbook, 1936, pp. 625–648; Fuel, vol. 16, 1937, pp. 160–176.

Review includes bibliography.

911. ———. Recent Developments in Coal Preparation and Utilization. Bureau of Mines Minerals Yearbook, 1937, pp. 935–954; Fuel, vol. 17, 1938, pp. 272–280, 300–307; Chem. Abs., vol. 31, 1937, p. 8062.

Review with extensive bibliography.

912. ———. Developments in Coal Research and Technology in 1937 and 1938. Synthetic Products From Gases. Bureau of Mines Tech. Paper 613, 1940, pp. 77–86; Chem. Abs., vol. 34, 1940, p. 7574.

Survey with bibliography. Economic data on the Fischer-Tropsch process are quoted from the Falmouth Committee report and the Labor Party Committee report with money, weights, and volumes converted into United States figures by G. Egloff. On the basis of these reports the cost for American conditions of synthetic gasoline would be about $0.14–$0.16 per gal.

913. ———. Production of Liquid Fuels From Coal and Lignite. Bureau of Mines Statement, Aug. 4, 1943; U. O. P. Co. Lib. Bull., No. 34, 1943.

Review of developments in the production of liquid fuels from coal by low-temperature carbonization, shale oil, and coal hydrogenation, both direct and indirect. It is estimated that the direct hydrogenation requirements for steel for plant and equipment are from 8.8–14.1 ton per bbl. of gasoline per day. Aside from the amount of steel, multi-stage compressors, special alloy-steel pressure vessels, and special electrical equipment would be required. The Fischer-Tropsch process does not need as much special equipment but must have more steel per barrel of gasoline, 8.9–14.3 tons.

914. ———. Production of Liquid Fuels From Coal and Lignite. Synthetic Liquid Fuels Hearings Before a Subcommittee of the Committee on Public Lands and Surveys, U. S. Senate, 78th Cong., 1st sess., on S. 1243, 1944, pp. 168–178.

Review of the production of liquid fuels by the Bergius coal hydrogenation and the Fischer-Tropsch synthesis processes. Estimated costs of production are taken from the paper by W. S. Farish (abs. **879**). Bureau of Mines estimates for steel requirements differ somewhat from those stated in the above paper: 8.8 tons per bbl. of gasoline, as compared to 14.1 tons for a coal-hydrogenation plant; and 14.3 tons, as compared to 8.9 tons for a Fischer-Tropsch plant.

915. ———. Liquid Fuels From Sources Other Than Petroleum. Hearings Before a Special Committee Investigating Petroleum Resources, U. S. Senate, 79th Cong., 1st Sess., S. Res. 36, June 19–25, 1945, pp. 336–349; Nat. Petrol. News, vol. 37, No. 36, Sept. 5, 1945, R709, 711, 712, 714, 715.

Report made before the Senate Petroleum Investigating Committee on June 22, 1945, of the progress already made in the direct hydrogenation of coal and lignite; the conversion of coal, coke, natural gas, and other carbonaceous material to liquid fuels by the gas-synthesis process; and the recovery and refining of oil from shale. The early development and pilot-plant work is for the purpose of providing new and improved procedures for demonstration plants of up to 200 bbl. per day capacity. The program for the next fiscal year is summarized.

916. ———. Synthetic Liquid Fuels Program. Nat. Petrol. News, vol. 37, No. 36, Sept. 5, 1945, pp. R709, 711, 712, 714, 715.

Report before the Senate Petroleum Investigating Committee on June 22, 1945, of the progress already made in the direct hydrogenation of coal and lignite; the conversion of coal, coke, natural gas, and other carbonaceous material to liquid fuels by the gas-synthesis process; and the recovery and refining of oil from shale. The early development and pilot-plant work is for the purpose of providing new and improved procedures for demonstration plants of up to 200-bbl. per day capacity. The program for the next fiscal year is summarized.

917. ———. Nation's Reserve of Solid Fuels and Its Relation to the Future Supply of Gaseous and Liquid Fuels. Rept. to Federal Power Commission, June 1946, 12 pp.; Gas, vol. 22, 1946, pp. 70, 75, 78; Gas Age, vol. 98, No. 6, 1946, pp. 37–40, 42; Coal-Heat, vol. 50, November 1946, pp. 30–34; Mech. Eng., vol. 69, 1947, pp. 221–226, 228.

Reserves of mineral fuels in the United States are estimated as follows: Coal, 3.2 trillion tons; petroleum, 20.8 billion bbl.; natural gas, 135 trillion cu. ft. In terms of equivalent heating value, (coal taken at 13,000 B. t. u.), coal comprises 98.8% of the mineral-fuel energy reserves, oil shale 0.8%, petroleum 0.2%, and natural gas 0.2%. The coal reserves are distributed among the different ranks of coal on the basis of energy content in the following proportions: Anthracite, 0.6%; low-volatile bituminous coal, 2.2%; high-volatile bituminous coal, 54.2%; subbituminous coal, 23.1%; lignite 18.7%. The ultimate reserves of oil and gas are, therefore, very small as compared to the reserves of coal and lignite, and as the supply of oil and natural gas declines, it will be necessary to resort to coal either by direct substitution or by conversion of it to liquid and gaseous form. Fuel gases from coal by carbonization or complete gasification have been in commercial use for a long time, and recently processes have been developed for the conversion of coal to liquid fuel by the direct hydrogenation of coal or hydrogenation of tars or gases produced from coal. For coal hydrogenation by the Bergius process, most of the high-volatile bituminous coals, the subbituminous coals, and the lignites are suitable, while for the Fischer-Tropsch process, almost any carbonaceous material that can be reacted with steam to produce CO and H_2 is a potential source of liquid fuel. Furthermore it is not believed that the cost of producing liquid fuels by either of these processes will be in any sense prohibitive. From reports of German developments and from British and American estimates, it appears that, in general, gasoline can be produced by the hydrogenation of solid fuels for about $0.10–$0.15 per gal. more than from petroleum, and by the Fischer-Tropsch process for $0.06–$0.08 per gal. more.

918. ———. Synthetic Liquid Fuel Investigations of the Bureau of Mines. Science Counselor, vol. 10, No. 1, 1947, pp. 8–10, 24–26; Chem. Abs., vol. 41, 1947, p. 3937.

Survey including discussions of United States sources of supplementary liquid fuels, alcohol by vegetable fermentation, conversion of oil shale, liquefaction of coal or lignite by high-pressure hydrogenation, and conversion of water gas from coal or lignite; also European developments and their application to American conditions, synthetic gas production, and the cost of synthetic liquid fuels.

919. ———. Frontiers of Fuel Technology. Chem. and Eng. News, vol. 26, 1948, pp. 1700–1701; Fuel, vol. 28, No. 1, 1949, pp. 19–21.

Paper presented during the dedication of the Bureau of Mines synthetic fuels laboratories at Bruceton, Pa. It traces briefly the upward trend in the last 2 decades of new developments and improvements in the mining, preparation, and utilization of coal and predicts a new era in the processing of coal for the production of gaseous and liquid fuels. The basic German processes for the production of liquid fuels by coal hydrogenation and gas synthesis are already undergoing technical improvement toward a greater economy of operation in respect to American conditions.

———. *See* abs. **1370, 3121.**

920. Fieldner, A. C., and Brewer, R. E. Tenth Annual Report of Research and Technologic Work on Coal for the Fiscal Year 1945. Electron-Microscope Studies of Fischer-Tropsch Catalyst. Bureau of Mines Inf. Circ. 7352, 1946, pp. 15–18; Chem. Abs., vol. 40, 1946, p. 5898.

Fischer-Tropsch catalyst consisting of Co–ThO_2–MgO–kieselguhr was studied by the electron microscope. Co oxide and several types of kieselguhr also were studied. A micrograph of the mixed catalyst shows the characteristic open structure of kieselguhr. Its effectiveness as a carrier is probably the result of this open structure, which permits the reacting gases to penetrate freely to the active components. The particles and aggregates are seen on the micrograph range in size from several microns down to 0.01 micron. Calculations from the effective surface area of this catalyst measured by an N_2-absorption method indicate that, if the material were composed of nonporous particles, their average diameter would be 0.015 micron. Apparently the larger particles are either aggregates of these very small ones or are porous enough so that gases can readily penetrate them. Since calculations of surface area from electron micrographs depend on the visually apparent particle size, such measurements obviously would not show the area effective in catalyzing the Fischer-Tropsch synthesis. Measurements made on a number of micrographs of the Co oxide gave an area of 4 $m.^2$ per gm., compared to 62 $m.^2$ per gm. obtained by the N_2 absorption method. For use in a proposed small-scale Fischer-Tropsch experimental plant, a CO generator was developed utilizing pitch coke or petroleum coke as fuel and having an O_2 blast. The raw gas leaving the generator contains approximately 97% CO, 1.6% N_2, 1% H_2 and 0.5% CO_2 and O_2. Most of the ash in the fuel is volatilized and is present in the gas as smoke necessitating electric precipitation methods for cleaning. Although the experimental unit had a capacity of 25,000 cu. ft. per day of CO, extension of the same principle to larger units seems warranted.

921. FIELDNER, A. C., AND BROWN, R. L. Complete Utilization of Coal and Motor Fuel. Oil, Paint and Drug Reptr., vol. 108, 1925, pp. 12–13; Blast Furnace and Steel Plant, vol. 14, 1926, pp. 138–140, 148; Chem. and Met. Eng., vol. 32, 1925, p. 799.

Processes for obtaining motor fuel from coal may be grouped in 3 classes: (1) Carbonization of coal including gas manufacturing and low-temperature carbonization; (2) hydrogenation and liquefaction of coal by the Bergius process; (3) complete gasification of coal and conversion of the gases by pressure synthesis into MeOH, synthol, and other liquid combustibles.

922. ———. Comparative Study of Values Obtained in Synthesis of Methanol. Ind. Eng. Chem., vol. 20, 1928, pp. 1110–1112; Chem. Abs., vol. 22, 1928, p. 4461.

Values for the equilibrium constant in the Nernst equation have been calculated for the reaction: $CO+H_2=MeOH+Q$ calories, with the experimental data, which have been reported by different independent observers. In spite of probable variation in the exact conditions of the experiments from different laboratories, there is close agreement in the values of the constant.

923. FIELDNER, A. C., AND FISHER, P. L. Bibliography of Bureau of Mines Investigations on the Production of Liquid Fuels From Oil Shale, Coal, Lignite, and Natural Gas. Bureau of Mines Inf. Circ. 7304, 1945, 18 pp.

List of 236 refs. to papers written by the Bureau of Mines staff. (*See* abs. **1217.**)

924. FIELDNER, A. C., AND GOTTLIEB, S. Thirteenth Annual Report of Research and Technologic Work on Coal, Fiscal Year 1948. Bureau of Mines Inf. Circ. 7518, 1949, 87 pp.

Summary of papers already published. The following subjects are noted: Electron-diffraction and electron-microscope studies of Fischer-Tropsch catalysts (p. 13); underground gasification of coal (pp. 71–73); production and purification of synthesis gas (pp. 73–76) and 4 diagrams; synthesis of liquid fuels from H_2 and CO, Oxo process, process mechanism, catalysts, internally cooled process (pp. 76–82); hydrogenation of coal, function of solvents and catalysts, Sn catalyst, hydrogenation of asphalt (pp. 83–86).

925. ———. Annual Report of Research and Technologic Work on Coal, Fiscal Year 1949. Bureau of Mines Inf. Circ. 7565, 1950, 97 pp.

This report, based largely upon publications issued during the fiscal year, summarizes research and technologic work of the Bureau of Mines on coal and coal products with continued emphasis on coking-coal reserves, conservation and mining safety, anthracite problems, and synthetic liquid fuels production.

926. FIELDNER, A. C., AND SCHROEDER, W. C. Oil and Gasoline From Oil Shale and Coal. Fuel, vol. 23, No. 2, 1944, pp. 34–36; Chem. Abs., vol. 38, 1944, p. 3445.

Review of processes with estimates of costs. The Fischer-Tropsch process offers a convenient means of converting natural gas to liquid fuel. In spite of the attractive possibilities, however, for the use of natural gas in this way, it is not desirable to encourage this development from the long-range national conservation viewpoint.

927. FIELDNER, A. C., BELTZ, J. C., AND FISHER, P. L. Eighth Annual Report of Research and Technologic Work on Coal for 1943. Synthesis of Hydrocarbons From Water Gas. Bureau of Mines Inf. Circ. 7272, 1944, p. 56.

Experimental work on Fe and Co catalysts has been completed. Methods for the preparation and reactivation of Fe catalysts have been developed, and 1 Fe catalyst has been in operation for 3 months with no loss in activity. Fe catalysts yield a highly olefinic product and a larger proportion of solid paraffins than is obtained with the Co catalyst. Cheaper methods of preparation of Co catalysts have been investigated and a very promising method has been developed. Interpretation of available data on the steam-carbon reaction corroborates the generally accepted conclusions that the primary products are CO and H_2 and that CO_2 is formed subsequently by way of the water-gas reaction.

928. FIELDNER, A. C., ERNST, F. A., AND BROWN, R. L. Use of Off-Peak Gas for Methanol and Hydrocarbon Synthesis, With Notes on the Bergius Process. Proc. Am. Gas Assoc., vol. 9, 1927, pp. 1031–1033.

Theoretical requirement of blue gas to make 1 ton of MeOH, with 70% conversion, is put at 100,000 cu. ft. A plant of 20-ton-per-day capacity will thus require 2,000,000 cu ft. The total investment-per-ton-per-yr. for the gas plant plus the MeOH plant is calculated at $107.00–$128.00. On such a basis it is not considered that either MeOH or synthol could be produced to compete with gasoline as a motor fuel.

929. FIELDNER, A. C., FISHER, P. L., AND BREWER, R. E. Ninth Annual Report of Research and Technologic Work on Coal in 1944. Synthesis of Liquid Fuels by Hydrogenation of Carbon Monoxide. Bureau of Mines Inf. Circ. 7322, 1945, pp. 75–79; Chem. Abs., vol. 40, 1946, p. 5897.

Critical discussion on the preparation and properties of metal carbides and the reaction mechanism between CO and Co or Fe or their oxides to form carbides was published. (*See* abs. **1434**). The reaction is stated to be much too slow to account for the rate of synthesis of hydrocarbons by reduction of carbides with H_2 when a mixture of CO and H_2 is used. It is known that the presence of H_2 with CO markedly accelerates the formation of C, which appears to proceed by way of the metal carbide. Since Co is a much more active catalyst than Fe for the water-gas reaction and because

the most active Fe catalysts catalyze this reaction to only a slight degree at temperatures below 300°, it appears probable that H_2O and CO_2 are primary products on Co and Fe catalysts, respectively. Although metal carbides are formed on both Co and Fe, there is evidence that the mechanism of the synthesis on Co catalysts differs from that on Fe catalysts. An investigation has been made on the correlation of the physical properties, particularly X-ray diffraction pattern and ferromagnetism, of Fe catalysts with their mode of preparation and activity. An analysis of published data shows that the reaction rate in the Fischer-Tropsch synthesis is directly proportional to the partial pressure of the synthesis gas and inversely proportional to that of the products. The retardation of the rate by the products is large enough so that only little advantage is obtained, so far as space-time yield is concerned, by increasing the operating pressure from 5 to 20 atm. Under a total pressure of about 1 atm., dilution of the synthesis gas with N_2 decreases the yield of liquid hydrocarbons per unit volume of gas but does not decrease the % conversion. In fact, such a dilution results in a conversion somewhat greater than would be calculated on the basis of a first-order reaction. Photographs illustrate some of the development work being accomplished. The type of converter used in the Ruhrchemie plants to regulate the heat-transfer problem is illustrated. The catalyst is packed in narrow spaces between steel sheets through which cooling tubes are interlaced. Water under pressure is circulated through the tubes. The cost of such a converter is relatively high because of the large amounts of steel used per unit of oil produced. A promising method of removing the heat of reaction has been tested by the Bureau. It consists of flushing a cooling oil of proper boiling range over the catalyst particles, the heat of vaporization of this oil being supplied by the heat of the synthesis reaction. It has been found possible to maintain virtually complete adiabatic conditions in the converter, and precise temperature control has been readily obtained.

930. FIELDNER, A. C., GAUGER, A. W., AND YOHE, G. R. Gas and Fuel Chemistry. Ind. Eng. Chem., vol. 43, No. 5, 1951, pp. 1039–1048.

Outline study of the development and growth of gas and fuel chemistry over the past 75 years or of the active initiation of the synthetic liquid fuels program by the Bureau of Mines.

931. FILHOL, J. [Petroleum and Substitute Motor Fuels.] Sci, et ind., Tech. ind. pétrole, No. 284 bis, 1939, pp. 110–112; Chem. Abs., vol. 33, 1939, p 7531.

World petroleum production and consumption is reviewed along with French laws favoring (1) vehicles provided with gas generators or compressed gas, (2) those driven electrically, (3) products derived from bituminous schists, (4) alcohol fuels, (5) synthetic fuels, such as those produced by hydrogenation, and (6) benzene.

FINGAS, E. *See* abs. **2436.**

FINK, W. L. *See* abs. **424.**

932. FINKELSHTEIN, V. S., AND RUBANIK, M. Y. [Kinetics of Ammonia Synthesis by Technical Iron Catalysts.] Jour. Phys. Chem. (U. S. S. R.), vol. 6, 1935, pp. 1051–1058; Acta physicochim. U. S. S. R., vol. 3, 1935, pp. 945–956; Chem. Abs., vol. 30, 1936, p. 7286.

Apparent energy of activation of NH_3 formation was 21 cal. per mol. Considering the various reaction energies required, it seems that the primary step in NH_3 synthesis is not nitride but imide formation by direct union of N and H.

933. FINZEL, T. G. Pyrophoric Iron. I. Preparation and Properties. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 142–149; Chem. Abs., vol. 24, 1930, p. 1275.

Pyrophoric Fe can best be prepared by the reduction of Fe_2O_3 in H_2 at 500° for 3 hr. The Fe_2O_3 was precipitated from Fe $(NO_3)_3$ solutions of different concentrations to produce oxides of different degrees of dispersion, which, in turn, would influence the pyrophoric activity of the reduced Fe. The pyrophoric Fe was inactivated by heating in H_2, N_2, or He. Oxides of the highest degree of dispersion yield pyrophoric Fe most easily inactivated—the ease of inactivation depending upon the degree of dispersion. The time factor of inactivation for the different gases varied in the order: $He > N_2 > H_2$. Inactivation is accompanied by a decrease in total surface. Samples were produced that displayed pyrophoric activity at −78° and in air that had been thoroughly dried.

934. ———. Pyrophoric Iron. II. Adsorption of Carbon Dioxide and Ammonia and the Use of Pyrophoric Iron in the Ammonia Synthesis. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 150–156; Chem. Abs., vol. 24, 1930, p. 1275.

Relations between pyrophoric activity and adsorptive and catalytic properties were investigated. Adsorption of CO_2 by pyrophoric Fe is no criterion for pyrophoric activity; adsorption seems to depend primarily upon the amount of residual oxide contained in the Fe. Sensitivity and ease of inactivation of pyrophoric Fe may be due to rapid recrystallization, the processes of which are hindered by the presence of cores of Fe_2O_3 in the particles. Fe prepared from colloidal Fe_2O_3 is worthless as a catalyst in the synthesis of NH_3.

935. FIRSANOVA, E. N. [Chemical Composition of Synthin. I.] Khim. Tverdogo Topliva, vol. 8, 1937, pp. 892–901; Chem. Zentralb., 1938, II, p. 1523; Chem. Abs., vol. 32, 1938, p. 4308.

Products of the reaction of CO and H_2 in the presence of the catalysts Ni–Al, Ni–Co–Si and catalyst "*a*" (composition not disclosed) at 180°–200° were analyzed. The mixture of gasoline and oil can yield a product boiling up to 200° in amounts of 60%. The synthin consisted mainly of paraffin hydrocarbons with smaller amounts of unsaturated compounds and no naphthenes nor aromatic compounds, therefore, the synthin had a low antiknock value. The residue boiling over 250° contained 57% of solid paraffin. n–C_5H_{12}, C_6H_{14}, C_7H_{16}, C_8H_{18}, C_9H_{20}, $C_{10}H_{22}$ and $C_{11}H_{24}$ were found in the paraffin-hydrocarbon fraction. Iso compounds were not found in the fractions boiling up to 200°. No cycloolefins nor diolefins were found. 12 refs.

936. ———. [Investigation of the Chemical Composition of Synthin. II. Analysis of Water Formed in the Synthesis of Hydrocarbons.] Jour. Appl. Chem. (U. S. S. R.), vol. 18, 1945, pp. 367–371; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 589; Chem. Abs., vol. 40, 1946, p. 3246.

Results of this work show that the products of interaction of CO with H_2 under atmospheric pressure in the presence of a Ni–Co–Al catalyst at 180°–190° contain not only hydrocarbons and small amounts of acids but also aliphatic alcohols and aldehydes soluble in H_2O. From the reaction water 0.15–0.37% neutral oxygenated compounds have been isolated, for the most part alcohols. Methyl, ethyl, n–propyl, and n–butyl alcohols were isolated and identified; amyl alcohol also is present apparently. In addition to alcohols, an aldehyde was isolated but could not be identified. In contrast to literature data, only a small amount of acetone was found among the oxygenated compounds, about 2%. The acids isolated from the water and identified comprise acetic, propionic, and butyric. The presence of formic acid was shown by only a qualitative test.

937. FIRTH, F. G. X-ray Diffraction. I. Basic Principles and Theory. II. Constitution of Matter. III.

Application of X-ray Diffraction. Petrol. Refiner, vol. 24, No. 4, pp. 114–120; No. 5, 1945, pp. 117–119; No. 6, 1945, pp. 111–114.

Brief statement as to its applicability to the study of Fischer-Tropsch catalysts.

938. FISCHBECK, K., AN SALZER, F. [Change of the Catalytic Effect of Metals at the Transition Point.] Ztschr. Elektrochem., vol. 41, 1935, pp. 158–169; Chem. Abs., vol. 29, 1935, p. 3958.

Sharp decrease of the catalytic activity with the change into the high-temperature form was shown for (1) the decomposition of NH_3 on Fe and (2) the hydrogenation of CO_2 on catalysts of Ni 5–Co 95%, and Ni 10–Co 90%. At the demagnetization temperature of Ni and Ni–Cu alloys, no discontinuous change of the catalytic activity was observed. They conclude that, per unit surface, the catalytic activity of 2 forms of the same substance is different.

939. FISCHER, F. [New Possibilities of Obtaining Oil From Coal.] Ges. Abhandl. Kenntnis Kohle, vol. 4, 1919, pp. 458–470; Brennstoff-Chem., vol. 2, 1921, pp. 386–387.

Introductory remarks on the synthesis of oils from gas with special reference to the work already done by the Badische Co. and by Uhde. Occurrence of carbides as the intermediate product is discussed.

940. ———. Conversion of Coal Into Oils. Colliery Guard., vol. 128, 1924, pp. 87–88; Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 287–297; Ztschr. Ver. deut. Ing., vol. 69, 1925, pp. 15–17; Chem. Abs., vol. 18, 1924, p. 3470.

Address before the World Power Conference, including a discussion of destructive distillation in general, the hydrogenation of coal, and the synthesis of oils from gases.

941. ———. Umwandlung der Kohle in Öle. Berlin, Gebrüder Borntraeger, 1924, 367 pp.; Chem. Abs., vol. 19, 1925, p. 1622.

942. ———. Conversion of Coal Into Oils. Transl. by Lessing. D. Van Nostrand Co., New York, 1925, 284 pp.

Book has 5 chapters dealing, respectively, with the production of oil from coal by extraction with solvents, low-temperature carbonization, hydrogenation, synthetic processes, and by way of carbides. The 1st and last chapters are negligible, the other 3 making up the bulk of the book.

943. ———. Liquid Fuels From Water Gas. Ind. Eng. Chem., vol. 17, 1925, pp. 574–576; Chem. Abs., vol. 19, 1925, pp. 2119–2120.

Reactions with CO and various catalysts are discussed. Processes are developed for the formation of MeOH, and from this a mixture of alcohols is made called synthol. By heating synthol at 400° in an autoclave, there is formed synthin, a petroleumlike liquid, about ½ of which is saturated hydrocarbons similar to benzine or gasoline, the other ½ being soluble in concentrated H_2SO_4.

944. ———. [Methanol and Synthol Made From Carbon Monoxide as Motor Spirit.] Brennstoff-Chem., vol. 6, 1925, pp. 233–234; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 215–217; Chem. Abs., vol. 19, 1925, pp. 3361–3362.

Road tests were made with a 4-cylinder truck motor, 12-hp., 75-mm. bore, and 130-mm. stroke, the weight of the truck being 1,600 kg. Compression of the motor was raised from 4.6 to 6.0 atm. by change of pistons. Fuels used on the test were: (a) Pure MeOH, (b) national fuel (benzine: EtOH=1:1), (c) benzine with 20% kerosine and 2% lead tetraethyl, (d) benzine with 30% kerosine and 2% lead tetraethyl. Fuel required per 100 km., maximum speed on the level, and average speed, respectively, for the different fuels: (a) 22 l., 80 km. per hr. and 46 km.; (b) 11.6 l., 85 km. and 50 km.; (c) 12.7 l., 93 km. and 62 km.; (d) 11.7 l., 90 km. and 55 km. With pure MeOH and 6 atm. compression there was trouble from preignition without detonation; with 5% H_2O the MeOH ignited properly.

945. ———. [Coal Liquefaction and Complete Gasification.] Naturwissenschaften, vol. 14, 1926, pp. 1213–1214; Chem. Abs., vol. 21, 1927, p. 1342.

Short review without details of modern gasification processes. Purified water gas is treated with Fe or Co catalyzer at 200°–300° and atmospheric pressure. Benzine, petroleum, and paraffin formed are removed. The gas remaining has a heating value of 6,000–7,000 cal. per $m.^3$ and is a valuable byproduct of the process.

946. ———. Synthesis of Petroleum. Nat. Petrol. News, vol. 18, No. 47, 1926, pp. 49–51; Chem. Age, vol. 15, 1926, pp. 610–611; Chem. Abs., vol. 21, 1927, p. 2182.

Progress of the hydrogenation of CO is discussed. The hydrogenation of CO under high pressure with an excess of H_2 produces O_2-containing compounds only. At pressures above 130 atm. and at temperature below 400°, MeOH only is formed when ZnO is used as a catalyst. Petroleum hydrocarbons are produced at ordinary pressure and 200°–300° temperature with finely divided Co and Fe as the catalyst. The process may be so conducted that in addition to higher hydrocarbons, the uncondensed gases have the proper ratio for further reaction after the removal of CO_2. The product most simply produced is gasol, a mixture of C_2H_6, C_3H_8, and C_4H_{10}. In order to produce gasoline it is necessary to achieve a nice balance in the catalyst because the polymerization tends to go on to the formation of solid paraffins, especially when strong bases are used. A yield of 100 gm. of solid liquid and liquefiable hydrocarbons can be obtained from each $m.^3$ of water gas which is led several times over the catalyst. The theory of the process indicates that intermediate carbides are formed that react with H_2 and CO.

947. ———. Synthesis of Petroleum. Proc. Internat. Conf. Bituminous Coal, 1st Conf., 1926, pp. 234–246; Chem. Abs., vol. 21, 1927, p. 2378.

General review and discussion of the synthesis of hydrocarbons from water gas.

948. ———. [Chemistry and Coal.] Brennstoff-Chem., vol. 8, 1927, pp. 226–231; Ztschr. angew. Chem., vol. 40, 1927, pp. 799–804; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 415–425; Chem. Abs., vol. 21, 1927, p. 3116.

Lecture touching upon the development of coal hydrogenation and the production of hydrocarbons by synthesis from water gas.

949. ———. [Progress in the Field of Chemical Gas Purification and Conversion, Particularly With Reference to the Production of Synthetic Products From Gases.] Brennstoff-Chem., vol. 8, 1927, pp. 221–225; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 439–449.

950. ———. [Synthesis of Petroleum Hydrocarbons.] Brennstoff-Chem., vol. 8, 1927, pp. 1–5; Fuel, vol. 6, 1927, pp. 89–94; Proc. Internat. Conf. Bituminous Coal, 1st Conf. 1926, pp. 234–246; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 384–393; Canadian Chem. and Met., vol. 11, 1927, pp. 7–10; Fuel Econ., vol. 2, 1927, pp. 335–338, 616–617; Chem. Abs., vol. 21, 1927, p. 1537.

Refers briefly to recovery of hydrocarbons from coal by low-temperature carbonization and by hydrogenation under pressure, Bergius process. The last process carried out at 200 atm. and 400°–500° converts about half the coal into oil. Hydrogenation of CO may be

carried out at both high and low pressures. At high pressures with an alkalized Fe catalyst, a mixture of acids, alcohols and aldehydes is obtained (synthol, abs. **101, 944, 3198**); with a ZnO catalyst MeOH is obtained. At atmospheric pressure with Fe metals as catalysts, hydrocarbons (abs. **1018, 1020, 1021**) from butane to solid paraffin are obtained. Co is more active than other metals of the series; the temperature should be 200°–300° and the ratio H_2 : CO about 1 : 1. Temperatures higher than 300° favor CH_4 formation; strong bases in the catalyst favor solid paraffin. A yield of 100 gm. of liquids was obtained by several passages of the gas. Water gas may be used, but it must be especially purified and freed from organic S. With pure gas the catalyst retains its activity indefinitely. Fischer proposes to use his process as an adjunct to water-gas plants where it can be used to produce motor spirit or to enrich gas for distribution as required.

951. ———. [Twelve Years of Coal Investigation.] Ztschr. angew. Chem., vol. 40, 1927, pp. 161–165; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 338–348; Chem. Abs., vol. 21, 1927, p. 1340.

Review of the researches conducted on the hydrogenation of coal and water gas.

952. ———. [Formation at Relatively Low Temperatures of Carbides Yielding Acetylene.] Brennstoff-Chem., vol. 9, 1928, pp. 328–333; Chem. Abs., vol. 23, 1929, p. 2662.

BaC_2 is prepared from BaO by heating with C in an electric porcelain-tube furnace in a stream of CH_4, with or without the addition of a small quantity of Fe_2O_3 and CaO. BaC_2 yielding 60% of the theoretical C_2H_2, was obtained by heating a mixture of 2 gm. BaO+1 gm. CaO+0.2 gm. Fe_2O_3 for 30 min. at 1,150° in CH_4 at 35 mm. pressure. Carbides were not formed below 850° and yields fell sharply above 1,150°. The highest yields were obtained in an atmosphere of CH_4. The carbide formed at these low temperatures yields both H_2 and C_2H_2 with H_2O. Fischer believes that free Ba is first formed by reduction, and this is partly converted into BaC_2 and partly into BaH_4.

953. ———. Formation of Benzene and Hydrocarbons by the Action of Heat on Methane. Chem. Markets, vol. 23, 1928, pp. 587–591; Chem. Abs., vol. 23, 1929, p. 1119.

By conducting CH_4 of various origins through tubes at certain temperatures, pressure, rate of flow, and cooling speeds, it was shown that C_6H_6, $C_{10}H_8$, and other aromatic hydrocarbons could be formed, whereas earlier investigators had pointed to the formation of C (carbon black) and H_2 as the chief or only products. Experimental conditions and results are detailed, and the suggestion is made that in some countries where carbon black is now made by wasteful processes it may be feasible to resort to CH_4 as raw material for synthesizing C_6H_6.

954. ———. [Synthesis of Aromatic Hydrocarbons From Methane at Atmospheric Pressure and Without Catalysts.] Brennstoff-Chem., vol. 9, 1928, pp. 309–316; Chem. Abs., vol. 23, 1929, p. 2694.

Pure CH_4 from various sources and CH_4 with other gases (coal gas) is decomposed by passage through porcelain or quartz tubes heated 900°–1,200°. The tar formed is precipitated by a Cottrell precipitator, and light oils are absorbed by active charcoal. The time of contact is fully as important as the temperature. For example, 346 l. CH_4 89% with 8% N_2 passed through the 1-mm. annular space between concentric 14- and 16-mm. tubes 22 cm. long at 63 l. per hr. gave 7 gm. oil, 3 gm. tar, and 0.2 gm. C. Higher temperatures with the same gas flow favor precipitation of C. Tar and oil do not form to an appreciable extent below 900°. The tar is aromatic; naphthalene, anthracene, and phenenthrene being isolated. The oils contain mostly benzene with xylene and $C_{10}H_8$. SiO_2, W, Mo, and Sn as catalysts did not favor oil yields; Fe, Cu, and graphite favored C precipitation.

955. ———. [Solved and Unsolved Problems in Coal Investigation.] Brennstoff-Chem., vol. 10, 1929, pp. 444–447; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 450–459; Chem. Abs. vol. 24, 1930, p. 2859.

Chemical and biological problems encountered in the study of coal constitution are touched upon, and work on the complete gasification of coal is mentioned. The ideal here, not yet realized, is practical conversion of coal into O_2-free (except for CO) combustible gases. Recent research at Mülheim has aimed at complete technical purification, mainly desulfurization, of water gas and catalytic conversion of this into liquid hydrocarbons. Considerable work also is being done on the re-forming of fuel gases.

956. ———. [Development of the Benzine Synthesis From Carbon Monoxide and Hydrogen at Atmospheric Pressure.] Brennstoff-Chem., vol. 11, 1930, pp. 489–500; Ges. Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 501–533; Chem. Abs., vol. 25, 1931, p. 796.

Motor benzine, colorless, S-free, and requiring no further refining, has been prepared on a semicommercial scale from industrial-gas mixtures, containing CO and H_2, in a train of apparatus consisting of purifiers, heaters, contact units, etc. Gas liquefaction has been increased from 20 to 50% with a Co–Cu–Th catalyst, and the possible use of a cheaper Ni catalyst is indicated. From 1 m.^{3} of a mixture of CO–H_2–C_2H_2, prepared by incomplete combustion of CH_4 and O_2, as much as 100 cc, benzine and 50 cc. oil have been obtained. The apparatus is shown schematically and detailed drawings are given of a number of the various designs of contact units employed in the tests. Questions involved in commercial utilization of the process with reference to necessary costs and feasible mixtures of coal, water, fuel, producer, and blast-furnace gases for use in the synthesis are discussed. A boiling-point composition curve for the benzine is given, together with a bibliography for 1926 to date.

957. ———. [Origin of Petroleum.] Brennstoff-Chem., vol. 11, 1930, pp. 352–354; Ges. Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 583–594; Chem. Abs., vol. 25, 1931, p. 476.

Recent work and its relation to theories of inorganic and organic origin and secondary formation from fossil matter are discussed. It is postulated that under certain favorable conditions, synthetic petroleum could be produced from subterranean gases having the correct ratio of CO: H_2 through contact of steam with glowing C and catalyzed by Fe or alkaline earths.

958. ———. [Ruhr Coal as a Chemical Raw Material.] Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 724–730; Chem. Abs., vol. 26, 1932, pp. 3899.

959. ———. Utilization of Coal by Conversion to Gases. Jour. Indian Chem. Soc. Prafulla Chandra Ray Commemoration, vol., 1933, pp. 331–362; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 655–681; Chem. Abs., vol. 27, 1933, p. 5513.

Review of research and development on production of liquid fuel by benzine, synthol and MeOH synthesis.

960. ———. [Naphtha Synthesis From Water Gas for the Supply of Germany with Fuels.] Oel u. Kohle Erdoel Teer, vol. 11, 1935, pp. 782–785; Chem. Abs., vol. 30, 1936, p. 3968.

Process and the types of products obtained are briefly described.

961. ———. [Synthesis of Fuels and Lubricating Oils From Carbon Monoxide and Hydrogen.] Oel u. Kohle, vol. 11, 1935, pp. 120–123; Jour. Inst. Petrol. Technol., vol. 21, A, 1935, p. 170.

Hydrogenation of CO in the presence of Co, Ni, and Fe catalysts is first discussed. The maximum reaction temperature for the 1st 2 catalysts is 180°–200°, and for Fe 230°–250°; lower temperatures are required when the concentration of H_2 is high. The heat of reaction, unless controlled, favors the production of CH_4. A mixture of CO and H_2 is obtained from the gasification of coke. The proportion of the 2 gases should be 1 : 2. The mixed gases freed from S are brought into contact with the catalyst under suitable conditions, and about 100–120 gm. of liquid hydrocarbons (Kogasin) are formed per $m.^3$ of gas. The fraction up to about 200°, termed Kogasin I, is of low octane number (47); that above 200°, Kogasin II, contains wax and after removal of the latter forms a satisfactory Diesel fuel. The separated wax has a melting point of 50°–60°. Kogasin II may be cracked to give a higher yield of low boiling constituents of high octane value. Alcohols may be obtained indirectly from the unsaturated hydrocarbons. No lubricating oils occur naturally in Kogasin, but they may be synthesized by a number of processes, including condensing the fraction rich in olefins with $AlCl_3$ and chlorinating high-boiling fractions and condensing the product with activated Al or aromatic hydrocarbons. The oils formed are resistant to oxidation, of low C residue, and of low pour point.

962. ———. [Synthesis of Fuels (Kogasin) and Lubricants From Carbon Monoxide and Hydrogen at Ordinary Pressure.] Brennstoff-Chem., vol. 16, 1935, pp. 1–11; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 334–356; Petrol. Refiner, vol. 23, 1944, pp. 70–76; Chem. Abs., vol. 29, 1935, p. 1959; vol. 38, 1944, p. 1621.

Work on the benzine synthesis begun in 1925 is completely reviewed. The conversion of CO or CO_2 by H_2 to liquid hydrocarbons depends upon the nature of the catalysts as well as the composition of the gas and the temperatures. The best catalyzing agents are Fe, Co, and Ni, each of which has the property of forming carbides, the splitting up of which is responsible for the formation of liquid hydrocarbons. With Co the reaction proceeds as follows: $CO+2H_2=(CH_2)+H_2O$ at a temperature of 180°–200°; with Fe $2CO+H_2=(CH_2)=CO_2$ at 250°. The pure metals are not used as catalysts, the conversion being promoted best by mixed catalysts, the composition of several of which is given together with some data as to their efficiency. In general, the yields obtained per $m.^3$ of synthesis gas are 100–120 gm., as compared with the theoretical yield of 180 gm. Considerable is said about the heat of reaction and its disposition, the preparation of synthesis gas from coke and other gases, the primary products of the synthesis, their properties and uses, and their further conversion to alcohols and lubricants.

963. ———. Conversion of Coal Into Liquid Fuels by the Fischer Process. Petrol. Times, vol. 36, 1936, pp. 613–614; Chem. Abs., vol. 31, 1937, p. 1983.

Tropsch and Fischer (abs. **1018**) found that $CO+H_2$ at 400° and 100 atm. with alkaline Fe catalyst produced oxygenated hydrocarbons. At lower pressures less O_2 combines. A catalyst was developed, active at 190° and 1 atm., producing the paraffinic hydrocarbons Kogasin. Steam + CH_4 produces water gas containing 1 part CO to $2H_2$. The gas reacts over the catalyst with dispersion of heat, and the products are recovered by condensation and adsorption. The weight, percent, of products are: Gasol, 8; motor spirit, 62; diesel fuel, 24; paraffin wax, 2; and ceresin, 4, varying with operating conditions. The higher-boiling motor spirit requires treatment to improve antiknock properties; the diesel fuel is of the best type.

964. ———. Conversion of Coal Into Liquid Motor Fuels and Other Products by Way of Carbon Monoxide. Colliery Guard., vol. 153, 1936, pp. 719–721; Chem. Abs., vol. 31, 1937, p. 239.

Review.

965. ———. Motor Fuels From Coke by Way of Carbon Monoxide. Gas Jour., vol. 216, 1936, pp. 278–279; Jour. Inst. Fuel, vol. 10, No. 49, 1936, pp. 10–14; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 568–576; Chem. Ind., vol. 40, 1937, pp. 33–35; Ind. Chemist, vol. 12, 1936, pp. 483–484; Chem. Age, vol. 35, 1936, pp. 353–355; Engineering, vol. 142, 1936, pp. 481–482; Machinery Market, 1936, pp. 921–922, 942; Chem. Abs., vol. 31, 1937, p. 238.

Production of motor fuels from coal or coke by way of CO is described. Monoolefins have been found in the product and can be converted by addition of a few % of $AlCl_3$ into lubricating oils.

966. ———. Conversion of Coal Into Liquid Fuels by the Fischer Process. Chem. Inds., vol. 40, 1937, pp. 33, 35.

Review.

967. ———. [Synthetic Motor Fuels.] Osterr. Chem.-Ztg., vol. 40, 1937, pp. 159–162; Chem. Abs., vol. 32, 1938, p. 3121.

Lecture.

968. ———. [Hydrocarbon Syntheses in the Field of Coal Investigation.] Ber. deut. chem. Gesell., vol. 71A, 1938, pp. 56–67; Chem. Abs., vol. 32, 1938, p. 3329.

Summary of the investigations at the Kaiser-Wilhelm Institut für Kohlenforschung on the synthesis of C_2H_2 and C_6H_6 from CH_4 and of benzine and its homologs from CO and H_2.

969. ———. [Chemistry and Motoring.] Proc. 10th. Internat. Cong. Pure and Applied Chem., Rome, 1938, vol. 1, 1939, pp. 336–340; Brennstoff-Chem., vol 19, 1938, pp. 244–245; Forschungen u. Fortschr., vol. 14, 1938, pp. 239–241; Chem. Abs., vol. 32, 1938, p. 9435.

Lecture in which recent developments in production of motor fuels are briefly reviewed.

970. ———. [Present and Future Possibilities in the Production of Liquid Motor Fuels.] Brennstoff-Chem., vol. 22, 1941, pp. 2–7; Kraftstoff, vol. 16, 1941, pp. 378–9; Acqua e gas, vol. 31, March–April 1942, pp. 25–30; Chem. Zentralb., 1941, I, p. 2203; 1943, I, p. 1540; Chem. Abs., vol. 36, 1942, p. 3653.

Address reviewing briefly the many ways of producing liquid fuels.

971. ———. Middle Pressure Synthesis With Iron Catalysts. TOM Reel 49, July 13, 1943, frames 533–540; Bureau of Mines Transl.T–423, Dec. 1, 1947, 8 pp.

After presenting briefly the work of the Kaiser Wilhelm Institute on the middle-pressure synthesis with Fe catalyst, conditions are discussed that permit carrying out the synthesis at the lowest possible temperatures. Example: A synthesis gas $CO:H_2=1:2$ is converted at temperatures 200°–210° in several stages. The use of higher H_2 synthesis gas is particularly advantageous for the stability of the Fe catalyst. Using the Co middle pressure reactors for synthesis, the requirements may be met by using water gas as the synthesis gas. With a normal throughput (4 l. water gas per 10 gm. of Fe per hr.) the reaction temperature is about 220°, and it can be lowered to 210° with a reduced gas throughput.

972. ———. [Survey of Synthesis From Carbon Monoxide and Hydrogen.] Oel u. Kohle Erdoel Teer, vol. 39, 1943, pp. 517–522; Coke Smokeless-Fuel Age, vol. 5, 1943, pp. 208–210, 215; U. O. P. Co. Lib. Bull., Nos. 4–5, 1944; Chem. Zentralb., 1943, II, p. 1071; Chem. Abs., vol. 38, 1944, p. 949.

Historical survey. CH_4 synthesis, kogasin, isosynthesis (direct synthesis of high octane fuels), production of naphthenes and aromatics, production of MeOH and synthol, and direct production of fatty acids.

———. *See* abs. **1492.**

973. FISCHER, F. AND BAHR, H. [Decomposition of Carbide-Containing Masses of the Iron Group by Acids, Water, or Hydrogen.] Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 269–274.

974. ———. [Decomposition of Methane at Various Temperatures on Various Catalysts.] Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 274–279; Chem. Zentralb., 1930, I, p. 31; Chem. Abs., vol. 25, 1931, pp. 2411–2412.

When a gas mixture rich in CH_4 (natural gas from Altengamme with 92.5% CH_4) was conducted through a heated quartz tube or through a heated porcelain tube, which was empty or filled with porcelain fragments, the decomposition started at 850° with deposition of C on the tube walls and with the formation of H_2, tar mist, and a slight quantity of small $C_{10}H_8$ crystals. When moist CH_4 is used, the quantity of the H_2 formed is almost twice that with dry CH_4 (34.3 : 19.1%). With finely distributed graphite as a catalyst, no tar and only very little $C_{10}H_8$ is formed. With $BaSO_4$ as a catalyst H_2O and H_2S are formed at 630°–650°; in this case also traces of an unsaturated hydrocarbon were noticed. The latter was also obtained when BaO was used. CH_4 is also decomposed when its presence in the gas current amounts to only 15%; in this case traces of C_6H_6 were noticed, which was identified as $PhNO_2$. When ZnO with addition of 1% K_2O in the form of K_2CO_3 was used, the CH_4 decomposition began at 700°; at 850° the increase in volume of the gas was 50.9% and remained the same when the velocity of the current was reduced from 2–5 l. per hr. to 0.5 l. per hr., but it was considerably lessened when the velocity of the current was increased to 6 l. per hr.

975. ———. [High-Carbon Carbides of the Iron Group.] Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 255–269; Chem. Abs., vol. 25, 1931, p. 2932.

When CO is passed at 270° over finely divided Co or CoO, a mass is obtained that appears to contain the carbide Co_3C_2. This substance is decomposed by H_2 at 270°, half the C (presumably derived from the carbide Co_3C) being evolved as CH_4. Similar addition of C to an equimolecular mixture of CuO and Fe_2O_3 affords the carbide Fe_5C_4 in addition to Fe carbonyl. H_2 liberates CH_4 in proportion corresponding with the formula Fe_2C, formed apparently by separation of C from the unstable carbide Fe_5C_4. Small quantities of hydrocarbons are also formed. The Fe, but not the Co, carbide affords, when treated with acids, a mixture of hydrocarbons.

976. ———. [Reaction of Methane and Lower Homologs With Carbon Monoxide and Dioxide on Various Catalysts.] Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 279–281; Chem. Zentralb., 1930, I, p. 31; Chem. Abs., vol. 25, 1931, p. 2411.

Repetition of Berthelot's experiment in which C_3H_6 was formed when 1 vol. CO and 2 vol. CH_4 were conducted through a glowing glass tube filled with pumice, yielded the same phenomenon. It was impossible to identify the hydrocarbon on account of the small quantity obtained. In another experiment, the same mixture of CH_4 and CO was conducted over various catalysts at different temperatures. CO was decomposed with formation of CO_2, CH_4 dissociated partly into C and H_2, but a reaction between CH_4 and CO was scarcely detectable. When the waste gas from a catalyst for the synthesis of mineral oil was conducted over metallic sponge Fe at 900°, the greatest part of the CO_2 was reduced to CO; gasol, heavy hydrocarbons, and a fraction of H_2 disappeared, and a large quantity of H_2O was formed.

977. FISCHER, F., AND BANGERT, F. [Formation of Carbides Decomposable by Water From Manganese Oxide and Methane at Relatively Low Temperatures.] Brennstoff-Chem., vol. 10, 1929, pp. 261–265; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 694–706; Chem. Abs., vol. 24, 1930, p. 3453.

An excess of CH_4 was passed over pulverized oxide (MnO_2 or Mn_3O_4) heated to 800°–1,000°, both with and without admixture of other metallic oxides. Carbides formed were decomposed by H_2O and by HCl, and the hydrocarbons resulting were measured and analyzed. Of the admixed oxides, BaO and Al_2O_3 alone favored formation of carbides decomposable by H_2O. Formation of carbides decomposed by HCl was favored by NiO, Cr_2O_3, and Fe_2O_3. CeO_2, CaO, TiO_2, CuO, V_2O_5, and K_2CO_3 exerted little or no influence. The following are conclusions reached: (1) Carbides are formed by passing CH_4 over the Mn oxides at 800°–1,000°; (2) admixtures of foreign oxides strongly affect the properties of the carbides formed; (3) in the absence of heavy metal oxides, the Mn oxides heated to 800° and above in CH_4 give a carbide that will yield 90% of its C as gaseous hydrocarbons on decomposition with H_2O; (4) existence of a previously unknown Mn carbide (Mn_5C_2) x is indicated.

978. FISCHER, F., AND DILTHEY, P. [Preparation of Pure Carbon at Low Temperatures.] Brennstoff-Chem., vol. 8, 1927, pp. 388–391; vol. 9, 1928, pp. 24–30; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 234–255; Chem. Abs., vol. 22, 1928, p. 2641.

C is prepared by passing CO with H_2 (abs. **3580**) over reduced alkalized Fe_2O_3 at temperatures around 500°. The catalyst is prepared by moistening 10 gm. Fe_2O_3 with 1 cc. water glass +15 cc. H_2O and painting this on an Fe spiral made from a strip of Knepp soft sheet 70 x 4 cm. This was heated in an Al retort similar to that used for low-temperature assay of coal, the preheated supply gas passing in at the bottom and out at the top of the retort chamber. A contact mass of this size, active Fe 6.8 gm. Fe_2O_3, will take gas at about 40 l./hr. and give 47% of the theoretical yield of C. The yield falls off in time, possibly because of conversion of active Fe_3C into higher inactive carbides. S is a contact poison; both the gas and Fe used must be free from S. A used contact mass could be repeatedly regenerated by dipping into 5 *N* KOH. The optimum temperature for CO reduction was 480°–490°, and the optimum ratio $CO : H_2 = 3 : 1$ An apparatus is shown for moderately large-scale work in which the C formed can be renewed continuously. The form of C recovered was investigated by X-ray and chemical methods, but no definite conclusion was reached. Its reactivity was found to be high. This, however, diminished on removal of Fe.

979. ———. [Solubility of Gas Benzines and Gases in Paraffin Oil.] Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 305–306; Chem. Zentralb., 1929, II, p. 3265; Chem. Abs., vol. 24, 1930, p. 5994.

On agitating 2 cc. of paraffin oil with various gases, it was observed that C_5H_{12}, CO_2, and CH_4 were soluble to a remarkable degree, while H_2, CO, air, and water gas were insoluble. Corresponding experiments with the reaction gas of an active benzine catalyst did not succeed in connecting the results with the contraction of the catalyst or with the gas analysis.

980. ———. [Effect of Different Carriers on the Synthesis of Benzine.] Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 501–511; Chem. Abs., vol. 25, 1931, p. 3807.

Satisfactory catalyst was prepared by depositing Fe and Cu (4 : 1) in the form of nitrates upon a suitable support. Fe alone was unsatisfactory, as

were Fe and Ag catalysts. The reaction was carried out in Fe tubes, but unless these were treated with 5 *N* HNO_3 the catalyst lost its activity. The contact materials lose activity by the accumulation of high-boiling substances, but neither extraction nor hydrogenation restored activity, which could only be achieved by combustion in a current of air. Pt and Ru on an asbestos support proved an unsatisfactory catalyst. The formation of unsaturated hydrocarbons was considered doubtful.

981. ———. [Influence of Organic Sulfur Compounds in the Water Gas on the Synthesis of Petroleum.] Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 512–513; Chem. Abs. vol. 25, 1931, p. 3806.

In the synthesis of paraffins from water gas at 270°, using a contact mass prepared from Pb carbonate and Fe oxide, the catalyst takes up S from unpurified gas. The contact material can be regenerated by oxidation with air. The water gas used for the synthesis must be completely freed from S compounds.

982. FISCHER, F., AND JAEGER, A. [Reduction of Carbon Monoxide by Hydrogen in Contact With a Heated Iron Spiral in a Hot-Cold Tube.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 68–74; Chem. Abs., vol. 21, 1927, p. 2550.

When an electrically heated Fe wire spiral was brought to red heat in a mixture of 15% of CO_2, 23% of CO, and 56% of H_2, contained at 120–150 atm. in an Fe autoclave surrounded by cold water, the pressure fell to 70–80 atm. and a gas mixture containing about 9% of CO_2, 40% of CO, 22–29% of H_2, and 15–19% of CH_4 hydrocarbons was formed. H_2O containing a considerable amount of formaldehyde was also produced, and solid C was deposited on the spiral. By heating the spiral more carefully, to about 620°, the H_2 disappeared almost completely, and a larger amount of saturated hydrocarbons was produced, together with much free C and an aqueous liquid of acid reaction containing formaldehyde. The results were practically identical if the Fe spiral was previously treated with alkali, except that the yield of formaldehyde appeared to be less.

983. FISCHER, F., AND KOCH, H. [Chemism of the Benzine Synthesis and the Motor and Other Properties of Products Resulting Therefrom (Gas Oil, Benzine, Diesel Oil, Hard Paraffin).] Brennstoff-Chem., vol. 13, 1932, pp. 428–434; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 516–530; British Chem. Abs., 1933, B, p. 50; Chem. Abs., vol. 27, 1933, p. 2017.

Theories of hydrocarbon formation are discussed critically; the carbide theory of Fischer and Tropsch is believed most satisfactorily confirmed by experimental findings. Hydrocarbons higher than CH_4 are obtainable from CO_2–H_2 mixtures only when the intermediate reduction to CO takes place. These are also obtained when HCOOH and MeOH are passed over Cu–Ni catalyst. Catalytic formation of paraffins of high melting point and molecular weight, composition, and characteristics of synthesis products, and their behavior as motor and diesel fuels have been investigated. Bibliography.

984. ———. [New Developments in the Adaptation of Cobalt Catalysts to the Benzine Synthesis.] Brennstoff-Chem., vol. 13, 1932, pp. 61–68; Ges. Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 556–577; British Chem. Abs., 1932, B, p. 376; Chem. Abs., vol. 26, 1932, p. 2582.

By increasing the activity of Co catalysts, the yield of liquid hydrocarbons has been increased from 100 to 153 cc./m.^{3} of gas mixture or to 71% of the theoretical. As catalysts, Co+18% Th precipitated with K_2CO_3 and Co+15% Mn precipitated with Na_2CO_3 were equally effective when used on kieselguhr as carrier. The influence of various precipitating agents in catalyst preparation and the effect of varying the proportion of carrier to catalyst and to activator in the catalyst at various temperatures have been determined. The use of Cu as activator for the Co resulted in lower reduction temperatures in the preparation of the latter by precipitation from the nitrate. Such catalysts, however, almost completely lost their activity at temperatures >350° and in H_2. Co catalysts have been used more than 2 months without interruption. Complete regeneration is effected simply by extracting the accumulated paraffins. In experiments to determine the reaction mechanism, the extent to which Co catalyst influenced the reaction $CO+H_2O \rightarrow CO_2+H_2$ was found strongly dependent upon reaction temperature. At 200° the effect was the same and at 235° much better than with Fe catalysts.

985. ———. [Synthesis of Lubricating Oils From Kogasin. Preliminary Communication.] Brennstoff-Chem., vol. 14, 1933, pp. 463–468; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 444–454; Petrol. Refiner, vol. 23, 1944, pp. 260–266; British Chem. Abs., 1934, B, p. 133; Chem. Abs., vol. 28, 1934, p. 2513.

Series of chlorination products has been prepared from the olefin-containing gas-oil fraction, Kogasin II, obtained in the benzine synthesis from CO and H_2. They were condensed with a number of aromatic hydrocarbons by using $AlCl_3$. Best yields were obtained with the trichloro and tetrachloro compounds and xylene. The oils resembled napthene-base oils in properties. Catalytic hydrogenation gives a water-white oil of low specific gravity, high stability against oxidation, and small carbon residue, which retains its lubrication value at low temperature. Comparative physical data are given for the various oils prepared. Bibliography.

986. ———. [Catalytic Hydrogenation of Carbon Disulfied at Ordinary and Elevated Pressures.] Brennstoff-Chem., vol. 19, 1938, pp. 245–249; Chem. Abs., vol. 32, 1938, p. 9437.

Analogy to the hydrogenation of CO_2 has been studied. Experiments at atmospheric pressure over Co catalyst at 170°–350° and at 184 atm. pressure at 305° with MoS_3 show complete conversions of a 1 : 3 mixture of CS_2 and H_2. In a 90% contraction with 4 l./hr. passage at 250°, H_2S and MeSH and Me_2S in a 3 : 1 proportion representing 80% of the CS_2 were formed. A maximum of 20% CH_4 was formed at 350° in 16 l./hr. passage of 1 : 5 CS_2–H_2 mixture. Separation of C was not observed nor was the formation of C_2H_4 established, although 1% of unsaturated hydrocarbons was noted in the 300°–320° tests. Strong exothermal fractions began at 190° in the steel autoclave with the 1 : 3 mixture with 30% CH_4 and H_2S. Slower hydrogenation at 200°–225° to 42 atm. was obtained with a 2 : 1 mixture, the balance of the H_2 being added subsequently, whereby no hydrocarbons were formed. The main liquid products then were a mixture of organic S compounds boiling 20°–150°, in which $(CH_2S)_3$ was identified with thioethers and mercaptans.

987. FISCHER, F., AND KÜSTER, H. [Influence of Pressure and Temperature Upon the Synthesis of Benzine and Synthol in Liquid Medium.] Brennstoff-Chem., vol. 14, 1933, pp. 3–8; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 454–465; British Chem. Abs., 1933, B, p. 211; Chem. Abs., vol. 27, 1933, p. 2793.

Temperatures higher than those in the gas phase are necessary in the liquid phase because there can be no local spots of high temperature. Benzine yield is best at pressures near atmospheric. Synthol (alcohols, higher fatty acids, aldehydes, ketones, etc.) is formed at higher pressures. Describes apparatus. Bibliography.

988. FISCHER, F., AND MEYER, K. [Applicability of Nickel Catalysts to the Benzine Synthesis.] Brennstoff-Chem., vol. 12, 1931, pp. 225–232; Ges. Abhandl, Kenntnis Kohle, vol. 12, 1932, pp. 534–555; Chem. Abs., vol. 25, 1931, p. 4685.

Effect upon yields of liquid products of adding various activators to Ni catalyst has been determined and is discussed at length. With Ni catalyst, it is possible to hydrogenate CO at atmospheric pressure and obtain products, of which ⅔ are liquids. As activator, 18% Th is used with the Ni in a 1:1 metal-kieselguhr mixture. The Th and Ni are precipitated by K_2CO_3 and are reduced with H_2 at 450°; addition of Cu does not serve to lower this reducing temperature. Addition of Mn appears, however, to increase the effect of the Th. The stability of the catalyst is such that only a 17% loss in yield was observed after 5 weeks' continuous use.

989. ———. [Activating Action of Ammonia Upon the Reduction and Activity of Nickel Catalysts.] Brennstoff-Chem., vol. 14, 1933, pp. 86–89; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 555–561; Chem. Abs., vol. 27, 1933, p. 3801.

Presence of NH_3 during the preparation of the catalyst increases subsequent yields in the benzine synthesis from CO and H_2. Reduction temperatures for maximum yields of fluid products are lowered from 450° to 300°–350°. Addition of NH_3 during the reduction, however, lowers the yields. Addition of 5% dry K_2CO_3 to the catalyst, prepared in presence of NH_3 to increase alkalinity, decreases its activity slightly. Impregnation with K_2CO_3 by solution almost completely removes activity.

990. ———. [Influence of Conditions of Preparation Upon the Efficiency of a Nickel–Manganese–Aluminum Catalyst.] Brennstoff-Chem., vol. 14, 1933, pp. 47–50; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 542–548; Chem. Abs., vol. 27, 1933, p. 3803.

Best yields in the benzine synthesis are obtained with 4–5 washings of the catalyst preparation. Lime water, instead of $CaCO_3$, as precipitant produces a nonuniform catalyst requiring more washing and giving poor yields. Previously described conditions for preparation still produce the best catalyst. Kieselguhr alone or with starch as supporting medium gave the best yields. Regeneration with H_2 in the presence of NH_3 gave the highest yield. Technical materials can be used in preparing the catalyst.

991. ———. [Reducibility of Standard Nickel Catalyst.] Brennstoff-Chem., vol. 14, 1933, pp. 64–67; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 549–554; Chem. Abs., vol. 27, 1933, p. 4034.

Reduction temperature of Ni–Mn–Al catalyst cannot be lowered by the addition of Cu in preparation or afterward as CuO or $CuCO_3$. Activity is, however, decreased by the former and increased by the latter method. CO–H_2 or 1:3 CO_2–H_2 mixtures cannot be used in place of H_2 for catalyst reduction, whereas 3:7 and 7:3 N_2–H_2 mixtures at 450° give normal activity.

992. ———. [Suitability of Alloy Skeletons as Catalysts for Benzine Synthesis.] Brennstoff-Chem., vol. 15, 1934, pp. 84–93, 107–110; Ber. deut. chem. Gesell., vol. 67B, 1934, pp. 253–261; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 356–382; British Chem. Abs., 1934, A, p. 389; Chem. Abs., vol. 28, 1934, p. 2871.

Catalysts prepared by Raney's method by dissolving Al or Si from alloys with Ni and Co are effective in hydrocarbon synthesis from water gas. The best results are obtained with a Ni–Co–Si alloy, in weight proportions of ½ : ½ : 1, from which the Si is removed as completely as possible with caustic soda. The effect of particle size, depth of catalyst, and depth of technical raw material is investigated. The activity of a mixed Ni–Co catalyst is decreased by Fe. With pure raw materials, the maximum yield of liquid hydrocarbons was 96 cc./m.³ of mischgas (23% CO and 46% H_2) and with technical material 80 cc. The addition of 10% Mn increased the yield with technical material to 88 cc. By increasing the amount of catalyst, the yield of liquid hydrocarbons can be considerably increased without cutting down the space velocity. With a mischgas containing 31.7% CO and 65% H_2, 161 cc. of liquid products could be obtained/m.³ of mischgas. Under special operating conditions, the space velocity can be increased 4-fold without any decrease in the yield. Addition of Cu decreases markedly the efficiency of Ni and Co alloys. By remelting catalysts poisoned by S with Si the original activity of the catalyst can be restored. The advantages and disadvantages of alloy skeletons are presented.

993. ———. [Use of Coke-Oven Gas for the Synthesis of Gasoline.] Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 497–500; Chem. Zentralb., 1934, II, p. 1061; Chem. Abs., vol. 29, 1935, p. 6747.

Coke-oven gas containing 5–6% CO is suitable for this synthesis with a Ni–Mn–Al catalyst. As a result of the ratio of H_2 : CO, which is higher than that of gas mixtures usually used for this synthesis, the reaction temperature must be reduced from 195° to 160°. The process is carried out so that a contraction of 20–25% is obtained, by which all of the CO but none of the CO_2 is used. In this way 20–22 cc. of hydrocarbons is obtained/m.³ of gas, of which 75% is gasoline. The heating value of the end gases is increased from 4,200 to 5,300 cal. Because of the S content of the gas, the reaction temperature must be increased slowly, 25° in 4 weeks, in order to compensate for poisoning of the catalyst. After this time, a complete reconditioning of the catalyst is necessary. The catalyst absorbs all the gaseous S.

994. FISCHER, F., AND PETERS, K. [Decomposition of Methane, and Coke-Oven Gas in Particular, at Low Pressure by Electric Discharge.] Brennstoff-Chem., vol. 10, 1929, pp. 108–113; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 640–654; Chem. Abs., vol. 23, 1929, p. 4326.

Orienting experiments were made at atmospheric pressures and temperatures —185° to 750° wherein CH_4, coke-oven gas, and water gas were passed through a high-frequency-type ozone tube. Very little decomposition of CH_4 resulted, and the method was changed in that the discharge was passed directly through the gas maintained at low pressures, a Geissler-type tube of glass being used. The best conditions for decomposition of CH_4 were: pressure 40 mm. Hg, gas flow 367 l./hr., reaction tube diameter 35–60 mm., voltage drop between electrodes spaced at 40 cm. 5,000–7,000 v. room temperature. By starting with gas analyzing 2.8% CO_2, 1.5% illuminants (C_2H_2-free), 1.2% O_2, 5.4% CO, 52.3% H_2, 23.4% CH_4, and 13.4% N_2, a gas containing 8.5% C_2H_2, 67.7% H_2, and 4.8% CH_4 was obtained by one passage through the tube. The main reaction is considered to be $2CH_4 = C_2H_2 + 3H_2$—4,000 cal. About 15% of the energy supplied does useful work. Tar precipitated in the reaction tube is easily removed by passing water gas or air through the tube, electric discharge being maintained. Experiments in which $C_{10}H_8$ was introduced into the reaction tube with H_2 and N_2 showed the reaction $C_{10}H_8 + H_2 + 5N_2 = 10HCN$ took place.

995. ———. [Influence of Electrical Discharge on Gas Containing Hydrocarbons at Diminished Pressure.] Ztschr. physik. Chem., Abt. A, vol. 141, 1929, pp. 180–194; Chem. Abs., vol. 23, 1929, p. 3861.

Discharge tube with steel electrodes, both cooled by incoming gas, was used. CH_4, both pure and distilled

with H_2, was drawn through the tube. C_2H_2 was condensed with liquid air. Most of the CH_4 was converted to C_2H_2 and H_2. The influence of gas velocity, tube loading, and pressure are shown in tables. A pressure of 50 mm., gas velocity of 370 l./hr., and 1.3 kv.-a. power input gave 8.5% C_2H_2 in the exit gas, at an electric energy consumption of 31 kv.-a./m.^{3} C_2H_2.

996. ———. [Catalytic Gas Reactions in Liquid Medium.] Brennstoff-Chem., vol. 12, 1931, pp. 286–293; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 441–454; Chem. Abs., vol. 26, 1932, p. 24.

Results were similar when the catalyst was suspended in paraffin oil or methylnapthalene and when the catalyst was in contact with one of the liquid phases. Studies were made of hydrogenation and polymerization of C_2H_2 with Ni catalyst, formation of cuprene with Cu catalyst, hydrogenation of C_2H_4, formation of $Ni(CO)_4$, and formation of hydrocarbons from CO in a paraffin-oil medium with catalyst of Ni–Al–Th–kieselguhr (mol. ratio 1 : 1 : 0.4). The results are shown as follows:

Temperature, ° C.	CO, conv. percent	Products obtained, percent			
		CO_2	CH_4	C_2H_6	Higher hydrocarbons
175	7	2	--------	36	62
210	26	11	--------	26	43
250	72	20	32	18	30
270	75	30	44	10	16

Contact of the gas with the oil (about 20 sec.) was not sufficient for a quantitative conversion of the CO. The higher hydrocarbons contained relatively little unsaturated products and consisted chiefly of propane and butane when higher temperature was used, while at lower temperature the proportion of liquid hydrocarbons increased. Use of the catalyst in liquid media is advantageous for both laboratory and technical gas reactions, because it makes possible close control of temperature and eliminates overheating.

997. ———. [Electrical Formation of Hydrocarbons From Water Gas.] Brennstoff-Chem., vol. 12, 1931, pp. 268–273; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 586–597; Chem. Abs., vol. 25, 1931, p. 5853.

Method for quantitative conversion in gas reactions, especially exothermic, which in the glow discharge produce only low concentrations of reaction products. The apparatus consists of a discharge tube, operated with a relatively low charge, a freezing-out vessel and a Hg-vapor pump so connected as to permit recirculation of the reaction gas. It is possible to obtain corresponding electrical discharge equivalents for the concondensable reaction products, which are removed continually. From CO–H_2 mixtures, various hydrocarbons are obtained in addition to CO_2 and H_2O. With liquid air for chilling, C_2H_2 and C_2H_6 predominate. At slightly higher freezing-out temperatures only higher hydrocarbons are recovered. The formation of CH_4 is believed to be the intermediate reaction, while traces of HCHO and MeOH are formed in the side reactions. When using water gas containing N_2, a 80–90% conversion of the N_2 into NH_3 and HCN takes place.

998. Fischer, F., and Philippovich, A. [Production of Formates From Carbon Monoxide and Bases in Presence of Water.] Ges. Abhandl. Kenntnis Kohle, vol. 6, 1921, pp. 366–381; Chem. Abs., vol. 18, 1924, p. 3170.

Percent yields of formate from different bases when 100 cc of a *N* solution, or suspension, of the base was heated, with shaking, with CO (88.7% purity) under 20 atm. for 1 hr. at 160° in an Fe autoclave, were as follows: KOH, 97.8; LiOH, 91.7; NaOH, 96.1; $Ca(OH)_2$, 92.3; $Ba(OH)_2$, 90.2; $Sr(OH)_2$, 84.8; NH_3, 15.3; calcined ZnO, 1.4; precipitated $Zn(OH)_2$, 3.5; $Zn(NH_3)_2(OH)_2$, 12.2; precipitated $Mg(OH)_2$, 4.4; $Fe(OH)_3$, 2.4; aniline, 0.2; low-temperature tar bases (boiling 250°–270°), 0.5; pyradine, 1.90; piperidine, 28.30. The reaction liquor contained Fe in all cases. With the weak bases, the yield of formate was increased by prolonging the time of heating. The rate of formation of HCO_2NH_4 at 100° was increased by the addition of HCO_2Na. From 11.09 *N* NH_3 solution by continued addition of CO under pressure at 160°–180°, 31.6% of formate was obtained, although partial hydrolysis apparently set in. The yield of formate was increased by the addition of $CaCO_3$ to neutralize the HCO_2H set free. Varying yields of formate were also obtained under similar conditions from hydrolyzable salts (Na silicate, borax, CaS, Na_2CO_3 and Li_2CO_3), Ca, Ba, and Mg carbonates, $Ca(HCO_3)_2$, Fe turnings, metallic oxides, and Na_2HPO_4.

999. Fischer, F., and Pichler, H. [Preparation of Hydrocarbons From Brown-Coal Coke at 500°.] Brennstoff-Chem., vol. 8, 1927, pp. 307–309; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 108–114; Chem. Abs., vol. 22, 1928, p. 1458.

These authors repeat the work of Hoffman and Groll (abs. **1453**), which purported to show synthesis of hydrocarbons by passing N_2 and steam over activated coke mixed with various metals and metallic oxides as catalyzers. Hoffman and Groll's results were not confirmed.

1000. ———. [Formation of Liquid Hydrocarbons From Acetylene.] Brennstoff-Chem., vol. 10, 1929, pp. 279–282; Chem. Abs., vol. 24, 1930, p. 483.

Experimental method consisted in passing C_2H_2 over silica gel or active C at 600°–700°, the following results being obtained: With pure C_2H_2 at first CH_4 and C were mainly formed, the latter serving as a contact whereby 70% of the C_2H_2 was converted into liquids (heavy oil : light oil = 1 : 1). With distilled C_2H_2, made by decomposing CH_4 in coke-oven gas, the total conversion was smaller, but the light-oil yield was as high as with pure C_2H_2. Distillation with CO_2 favored light oil formation and increased the life of the contact mass; CO_2 could serve for revivifying the catalyst. With CO_2–C_2H_2 mixtures in an empty tube, 70% of the C_2H_2 was converted into oil; reduced pressure was unfavorable.

1001. ———. [Partial Combustion of Methane at Various Pressures With Particular Consideration of Accompanying Acetylene Formation.] Brennstoff-Chem., vol. 11, 1930, pp. 501–507; Chem. Abs., vol. 25, 1931, p. 796.

By use of CH_4–air, CH_4–O_2 and coal gas–O_2 mixtures in various proportions with various flow-rates, temperatures, and pressures, the decomposition of CH_4 has been determined and is shown in tabulated analyses and graphs. A heated porcelain tube passing the gas-air mixtures is used for the low pressures and a bomb for the high pressures. The arrangement and construction are given in diagrams. The importance of time and temperature is demonstrated. A primary formation of —CH and —OH radicals is followed by a secondary decomposition into CO and H_2, making the prompt removal of the C_2H_2 necessary for recovery. These reactions may be accelerated by large catalytic surfaces. Yields of C_2H_2 as high as 50–60% of the CH_4 used have been obtained over a temperature range of 600°–1,500°. The rest of the CH_4 in burning to CO and H_2O, furnishes the necessary heat of formation for the C_2H_2. The use of diminished pressure does not materially increase C_2H_2 formation but does retard the secondary decomposition. Explosion pressures do not produce

greater yields. Oxidation and decomposition reactions of CH_4 are briefly discussed.

1002. ———. [Influence of Pressure Upon Several Conversions of Water Gas.] Brennstoff-Chem., vol. 12, 1931, pp. 365–372; Von den Kohlen, vol. 4, 1931, pp. 9–34; Chim. et ind., vol. 28, 1933, pp. 62–63; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 368–385; Chem. Abs., vol. 25, 1931, p. 5970; vol. 26, 1932, p. 5195.

Elevated pressures hinder the gasification of carbonaceous material by steam because of the surface layer of inert gases so produced. A secondary formation of hydrocarbons results when this is prevented by using high temperatures or addition of alkali, the H_2 already formed then reacting with C. The higher the partial pressure of H_2, the greater is the hydrocarbon formation. In the catalytic hydrogenation of CO, elevated pressure favors the formation of high-molecular hydrocarbons upon catalyst surfaces, which rapidly lessen catalyst effectiveness. O_2-containing products also are formed in addition to hydrocarbons. Lower pressures require greater contact surfaces for equal conversion to hydrocarbons. Pressure strongly affects the manner and rate of CH_4 decomposition by CO_2 or steam. The equilibrium $CH_4+CO_2 \rightleftharpoons 2CO+2H_2$ is displaced completely to the right at 1 atm. pressure at 900° in the presence of a Ni catalyst. At 0.003 atm. and 400° only 50% conversion occurs, while at 0.003 atm. and 300° only 25% occurs. Reaction rate increases proportionally with pressure decrease. Temperature and pressure dependence of the equilibrium have been determined and calculated. A literature review is appended.

1003. ———. [Thermal Conversion of Ethylene and Ethane Into Other Hydrocarbons With Particular Regard to the Formation of Acetylene.] Brennstoff-Chem., vol. 13, 1932, pp. 406–411, 435; Chem. Abs., vol. 27, 1933, p. 2016.

Influence of time, distillation with H_2, CH_4, or N_2, 2-stage treatment for liquid products, and partial combustion with O_2 have been studied at high and low pressures for C_2H_4. Quantitative pure thermal dehydrogenation to C_2H_2 depends upon high temperature, a controlled brief time, low pressure, and distillation with H_2. The dehydrogenation of C_2H_6 proceeds by stages, and yields of either 86% C_2H_2 or 72% C_2H_4 are obtainable by the control of similar factors as with C_2H_4. Includes brief review and bibliography.

1004. ———. [Thermal Decomposition of Methane. Benzine and Acetylene Synthesis.] Brennstoff-Chem., vol. 13, 1932, pp. 381–383; Chem. Abs., vol. 27, 1933, p. 2016.

Conditions of CH_4 concentration, temperature, pressure, time, etc., from experimental and theoretical standpoints have been determined for maximum yields of C_2H_2 or C_6H_6. Effects are shown with curves. Brief review and bibliography.

1005. ———. [Thermal Fission of Benzine and Petroleum With Particular Consideration for the Formation of Acetylene.] Brennstoff-Chem., vol. 13, 1932, pp. 441–445; Chem. Abs., vol. 27, 1933, p. 2016.

By use of apparatus previously described, yields of decomposition products at low and atmospheric pressure at 900°–1,400° have been determined and are shown graphically to conform to theories previously advanced. Bibliography.

1006. ———. [Simultaneous Effect of Carbon Monoxide and Carbon Dioxide During Hydrogenation, With Particular Regard to Benzine Synthesis.] Brennstoff-Chem., vol. 14, 1933, pp. 306–310; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 393–402; British Chem. Abs., 1933, B, p. 849; Chem. Abs., vol. 27, 1933, p. 5937.

In previously described apparatus, experiments with various catalysts, as Ni, Co, and Fe, indicate that the presence of CO in a CO_2–H_2 mixture retards catalytic hydrogenation while the presence of CO_2 in a CO–H_2 mixture exerts no influence on the yields of benzine obtained in the synthesis. While only H_2O is obtained in addition to higher hydrocarbons in the hydrogenation of CO and H_2 at temperatures <200°, at higher temperatures CO_2 and CH_4 are obtained as in the water-gas equilibrium, and at still higher temperatures C and CO_2 are formed.

1007. ———. [Conversion of Carbon Monoxide and Carbon Dioxide Into Methane at High Pressures.] Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 386–389; Chem. Zentralb., 1934, II, p. 1062; Chem. Abs., vol. 29, 1935, p. 6565.

It has been previously shown (abs. **1005**) that at high pressures the equilibrium $CH_4+CO_2=2CO+2H_2$ is displaced toward the left by increasing the temperature. The reduction of CO at 700° and 70–80 atm., even without a catalyst, was studied experimentally. A Mo catalyst was most satisfactory of those used. With a Ag catalyst considerable C_2H_6 was produced. Even CO_2 was reduced to CH_4 at 600° and 300 atm. without a catalyst. Magnesite thoroughly treated with H_2 yielded C_2H_6 in addition to CH_4.

1008. ———. [Increasing Yields of Fluid Hydrocarbons by Performing the Benzine Synthesis of Franz Fischer and Hans Tropsch in Steps.] Brennstoff-Chem., vol. 17, 1936, pp. 24–29; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 382–393; Chem. Abs., vol. 30, 1936, p. 5764.

Results of laboratory and semi-industrial tests of stepwise synthesis without increasing the amount of catalyst/unit volume of the gases used are described. In the first stage, the 1:2 mixture of $CO:H_2$ is treated at a temperature so low that the conversion is incomplete, but a good degree of liquefaction of the gases is effected. After a more or less complete extraction of the reaction products the residual CO : H_2 mixture is subjected to a second and possibly a third synthesis. Some of the possibilities of the method are discussed. The semi-industrial trials were made with a Co–Cu–Th precipitated catalyst unsuitable for maximum yield owing to its tendency to form CH_4. The largest apparatus used 10 kg. of Co and 10 $m.^3$ of mixed gas/hr. It is concluded that such a stepwise synthesis increases the yield of liquid hydrocarbons by 10–20%. The durability of the catalyst is increased by arranging that the gas flow (allowing for contraction) is the same/unit weight of catalyst in all stages. Using equally active catalyst in all stages, the yield is highest if the temperature in the 1st stage is lower than in the 2d; by this means 76% of the CO is converted to liquid hydrocarbons. The intermediate removal of products is an essential feature of the method. By 3-stage working, up to 141 gm. of gasoline plus oil can be obtained/$m.^3$ of mixed gas, plus another 10 gm. for the gas oil and the synthetic wax. These figures relate to a gas with 29.5% CO and 60% H_2 for which the theoretical maximum yield is 185 gm. By using higher quality gases, yields exceeding 150 gm./$m.^3$ could be obtained.

1009. ———. [Factors in the Synthesis of Kogasin and Paraffin in Water Phase.] Brennstoff-Chem., vol. 20, No. 13, 1939, p. 247; Refiner and Nat. Gasoline Mfr., vol. 19, 1940, pp. 479–481; Chem. Abs., vol. 35, 1941, p. 1599.

CO and H_2 reacted in the presence of Ni, Co, Fe, and Ru catalysts suspended in water or aqueous solutions. Hydrocarbons, mainly solid, were obtained but only when using Co and Ru. The disappearance of gas, indicating the yield, varied from 50 to 80%. The results were not seriously affected by the presence of

3 *N* solutions of H_3PO_4, HCOOH, CH_3COOH, or $(COOH)_2$. The experiments were performed at 170°–200°.

1010. ———. [Synthesis of Paraffin From Carbon Monoxide and Hydrogen.] Ber. deut. chem. Gesell., vol. 72B, 1939, pp. 327–330; Chem. Abs., vol. 33, 1939, p. 3995.

In the catalytic hydrogenation of CO with Co, Ni, or Fe catalysts at atmospheric pressure chiefly aliphatic hydrocarbons (benzine synthesis) are formed. The working temperatures with Co and Ni are 180°–200° and with Fe 230°–250°. With catalysts that are less favorable to the hydrogenation process, such as ZnO, Cr_2O_3, Mn_2O_3, reaction occurs only at higher temperatures (usually above 300°) and pressures (above 100 atm.), and O-containing compounds are formed, especially MeOH or synthol. Aside from the nature of the catalyst, the temperature and pressure have a decisive influence on the course of the process. With a Co catalyst a slightly increased pressure produces a remarkable change. At 5–20 atm., solid paraffin is the chief product, and the yields of solid + liquid hydrocarbons and the life of the catalyst attain a maximum. Any appreciable increase of pressure above these limits results in a rapid decrease in life of the catalyst. At 50–100 atm. or higher O-containing compounds in increasing amounts with increasing pressures are formed, along with the paraffin hydrocarbons, and volatilization of the catalysts as Co carbonyl begins. The use of Ni is restricted to pressures near atmospheric, for at slight overpressures the activity centers are broken down with formation of Ni carbonyl. The new process, which gives solid paraffin as the chief product, is called the medium-pressure synthesis. With a Co–ThO_2 kieselguhr catalyst (1 : 0.18 : 1) (abs. **984**), the following yields were obtained at overpressures of 0, 1.5, 5, 15, 50, and 150 atm., respectively. The yields are expressed in gm./m.^{3} of so-called ideal gas (inert-free CO–H_2 mixture (1 : 2) at 0° and 700 mm.) employed, not that consumed, and represent the average yields during a 4-week run without renewal of the catalyst: Total solid and liquid hydrocarbons, 117, 131, 150, 145, 138, 104; oil-free paraffin, 10, 15, 60, 70, 54, 27; oil boiling above 200°, 38, 43, 51, 36, 37, 34; benzine boiling below 200°, 69, 73, 39, 39, 47, 43; gaseous hydrocarbons including gasol, 38, 50, 33, 33, 21, 31. The effect of pressure on the life of the catalyst is especially characteristic. At atmospheric pressure the yield of total hydrocarbons fell from 120–130 gm. initially to 100 gm. within the 4-week period; at 1.5 atm. overpressure the yields were better; at 5 and 15 atm. overpressures, even after ½ yr. without regeneration of the catalyst, the yields were still 100–110 gm.; at 50 atm. overpressure they again fell more rapidly; at 150 atm. overpressure the activity of the catalyst decreased with extraordinary rapidity, and in the 2d week the yields fell below 100 gm. The solid paraffin separates in a high degree of purity. The oil-containing product softens at about 60° and melts clear at 90°–100°; after being freed from oil, it begins to melt about 80° and the last solid particle disappears at 100°–115°. By stepwise extraction at the boiling point with different high-boiling solvents, fractions melting up to about 130° can be isolated. The portion boiling above 300° of the total products obtained at 50–20 atm. overpressure contained 85.1–85.2% C and 14.7–14.9% H. The crude liquid hydrocarbons are water-clear and are distributed uniformly through the boiling point range 30°–300°. They are aliphatic and contain only a small amount of unsaturated compounds. The total liquid products contained 84.6–84.8% C and 15.2–15.4% H.

1011. ———. [Synthesis of Paraffin From Carbon Monoxide and Hydrogen Upon Cobalt Catalysts, Medium-Pressure Synthesis.] Brennstoff-Chem., vol. 20, 1939, pp. 41–48; Chem. Abs., vol. 33, 1939, p. 9605.

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Laboratory- and semitechnical-scale apparatus is shown schematically and described. The influence of various factors upon the process has been determined. The 1 : 2 CO–H_2 mixture passed over Co–Th catalyst precipitated on kieselguhr at 185°–190° at the rate of 1 l./hr./gm. Co at pressures to 150 atm. gave maximum yields of solid and liquid hydrocarbons at 5 and 15 atm. in test runs over 4 weeks. White solid products were obtained up to 50 atm.; at 150 atm. O-compounds were found together with Co carbonyl. Maximum paraffin formed at 15 atm. in 70 gm./m.^{3} yield; oil boiling above 200° increased to a maximum at 5 atm.; maximum gasoline boiling to 200° was obtained at 1.5 atm. Catalyst stability has been determined; its comparatively longer life at 5–15 atm. is outstanding. Reaction temperature is controlled to give maximum conversion and increases up to 190°–195° at 5–15 atm. after 6 months. Increasing pressure to increase throughput reduces conversion. Repeated passage increases conversion. A catalyst containing Cu gives poorer conversion as does the substitution of U for Th. Alkalinization increased yields only at atmospheric pressure. Experiments using 18, 6, 2, and 0% Th show that (1) paraffin is formed in lower yield without Th, (2) the reaction temperatures increase rapidly with lower Th content, and (3) gaseous products increase at the cost of the solid and liquid. Co–Ni upon alloy skeleton improves yields at higher pressures, but these are lower than those with the precipitated catalysts and decrease with time more rapidly. Almost entirely liquid yields are formed and Ni carbonyl is found beginning at 170° when precipitated Ni is used at medium pressures. Under optimum conditions, 50% of the reaction products are paraffins that, freed of oil, melt at 80°–115°. By extraction, fractions melting at 130° may be obtained from them. Fractions boiling 300°–450° indicate products $C_{17}H_{36}$ to $C_{28}H_{58}$. The use of medium pressure increases the fraction boiling above 300°; at 5–20 atm. 13–25% boils above 450°. Of the 30°–300° fraction, half may be considered gasoline and half as diesel oil. Products are water-clear and contain less unsaturated compounds than the usual pressure-synthesis products, these decreasing with increasing molecular weight. Uses possible because of the high melting point of the paraffin are discussed.

1012. Fischer, F., and Priziza, O. [Electrolytic Reduction of Carbon Oxides Dissolved Under Pressure.] Ber. deut. chem. Gesell., vol. 47, 1914, pp. 256–260; Chem. Abs., vol. 8, 1914, p. 1249.

Experiments were conducted in a steel bomb. CO_2 is reduced quantitatively to HCOOH even with high current densities. No evidence of products other than HCOOH was obtained. Attempts to reduce CO in alkaline, acid, and neutral electrolytes using cathodes of Ni, Fe, Cu, Hg, Pt, Ir, and Zn were without result. With Pb electrodes, small current density, preferably an electrolyte of K_2SO_4, and $(NH_4)_2SO_4$, minimal amounts of MeOH were obtained. No CH_4 could be detected.

1013. Fischer, F., and Tropsch, H. [Direct Combination of Carbon Monoxide With Alcohols.] Ges. Abhandl. Kenntnis Kohle, vol. 6, 1921, pp. 382–390; Chem. Abs., vol. 18, 1924, p. 3170.

CO combines with MeOH and EtOH under pressure to form small quantities of formic esters. The reaction is catalyzed by the addition of HCO_2Na on account of the production of free alkali by the interaction of the alcohol and the salt to form the ester. The ester yields are improved by careful drying of the alcohol and formate. The best yield (7.73 gm. of ester/100 gm. of MeOH) was obtained by heating 100 cc. of the alcohol with 10 gm. of HCO_2K and CO under 60 atm. at 180° for 3 hr. in a Cu-lined autoclave, and the yield was only slightly decreased by reduction of the proportion

of HCO_2K to 2.5 gm. HCO_2Na also promotes the decomposition of HCO_2Me, so that the addition of CO to alcohols must be regarded as a reversible reaction.

1014. ———. [Preparation of Synthetic Oil Mixtures (Synthol) From Carbon Monoxide and Hydrogen. I.] Brennstoff-Chem., vol. 4, 1923, pp. 276–285; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 475–494; Chem. Abs., vol. 18, 1924, p. 459.

Water gas was freed as completely as possible from S compounds and then treated at a temperature of 400°–450° and at 150 atm. pressure in the presence of Fe and K_2CO_3. An oil and a water layer were formed in which the following products were identified. The acids comprised 10% of the mixture HCO_2H; AcOH, propionic, isobutyric, and higher acids to C_8 were identified. 40% water-soluble and partly soluble alcohols, aldehydes, and ketones were found, such as MeOH, EtOH, PrOH, Me_2CO, and MeEtCO. 48% of the oil was volatile with steam and gave such products as EtCHO, Me_2CHCHO, Et_2CO, MePrCO, higher alcohols to C_9, and hydrocarbons. 2% of the oil is nonvolatile with steam. The oil, synthol, which boils 80°–200° is suitable for motor fuel. By heating synthol for 1 hr. at 450° under pressure a mixture of hydrocarbons was obtained that boiled 50°–300°. The hydrocarbons present were saturated. Naphthalene was one of the products identified.

1015. ———. [Preparation of Synthetic Oil (Synthol) From Carbon Monoxide and Hydrogen. II.] Brennstoff-Chem., vol. 5, 1924, pp. 201–208, 217–227; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1927, pp. 495–533; Chem. Abs., vol. 18, 1924, p. 3705.

Theory of the synthesis of hydrocarbons from water gas under pressure in the presence of Fe and alkalies was discussed previously (abs. **1014**). Apparatus is described for the preparation and complete desulfurization of water gas, which is recirculated in a special autoclave containing contact materials for the catalytic production of synthol. Various contact materials are tested, and conditions most favorable to the reactions desired are determined. The following conclusions were reached: (1) For synthol formation the contact material must consist of an H-carrying metal and an alkali; Fe is the best metal, better than Co or Ni, and RbOH or Rb_2CO_3 are the best base. (2) The metal should be in the form of chips, not finely divided. (3) Enough alkali should be used to convert the Fe surface into ferrite; an excess is harmful. (4) For a given amount of contact mass, there is an optimum gas velocity; the optimum temperature is 410° for Fe but higher for Ni. (5) The relative amounts of oily and watery products vary somewhat, even for the same contact material and apparently unchanged experimental conditions; watery products vary most, particularly as regards their alcoholic and ketone content. (6) The Fe catalyst will retain its full activity for a week but gradually becomes reduced to powder; finely divided Fe favors C precipitation from CO, but this is greatly hindered by the alkali. (7) Varying the pressure 70–150 atm. does not affect yields. (8) The richer the gas used is in H_2 the higher the yield of watery products, but the oil obtained is of lower boiling point than that formed when the CO concentration is high; it also contains less hydrocarbons. (9) By a single passage of the gas through the catalyst the yields are low, but by recirculation 27% of the heating value in the gas can be recovered in oil and alcohol formed. Mixtures of CO_2 and H_2 can be used, but they require longer contact than CO and H_2. CH_4 with CO or CO_2 will not yield synthol.

1016. ———. [Reduction of Carbon Monoxide to Methane in the Presence of Iron and Under Pressure.] Brennstoff-Chem., vol. 4, 1923, pp. 193–197; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 463–473; Chem. Abs., vol. 18, 1924, p. 349.

Previous investigators have carried out the reduction of CO to CH_4, using finely divided Ni and Co as a catalyst at 380° in the presence of Fe at 500°–600°. This work was undertaken to study the reduction of CO in contact with Fe under pressure. The apparatus consisted of a heavy iron tube 90 cm. in length by 2.1 cm. inside diameter. The tube was electrically heated. The contact took place over a length of 30 cm. The reduction was studied at 2–100 atm. pressure and at 400°–430°. The gas used consisted essentially of CO and H_2. At 2 atm. pressure only small amounts of CH_4 were formed. At pressures of 45–55 atm. the highest percentage of CH_4 was formed. The reaction may be considered to take place as follows: $CO+3H_2=CH_4+H_2O$. The H_2O formed then reacts with $CO—CO+H_2O=CO_2+H_2$.

1017. ———. [Synthesis of Higher Members of the Aliphatic Series From Carbon Monoxide.] Ber. deut. chem. Gesell., vol. 56B, 1923, pp. 2428–2443; Chem. Abs., vol. 18, 1924, p. 1379.

Having found that formates could be made from CO and bases and that these formates could be converted by thermal decomposition into liquids like MeOH, Me_2CO, etc. (abs. **1013**), Fischer and Tropsch, in an effort to obtain liquid fuels suitable for motors, directly in 1 operation, studied the action on water gas of various bases and salts, which under pressure with CO gave formates, spread on a number of carriers, but only when metals, such as Fe shavings, were used as the carrier were they successful. The bases or the metals alone, German Patents 293,787, 295,208 and 295,202, will not do. The water gas, freed as completely as possible of S compounds, was passed under 150 atm. into the contact chamber, containing, for example, K_2CO_3 on Fe shavings, at 400°–450°, and the product was collected under pressure in a cold receiver. This product generally separated into 2 layers, 1 vol. oil and 2 vol. of an aqueous solution, 20% of which consisted of aliphatic alcohols, aldehydes, ketones, and free fatty acids. Of the oil, 41% boiled below 100°, 73% below 150°, 83% below 180°, and 88% below 200°; 1,450 gm. of the crude product, shaken with 5 *N* NaOH, and washed with H_2O, which dissolved about 10% of nonacid constituents, which on fractional distillaton again gave a distillate only partly miscible with H_2O, yielded 943 gm. oil volatile with steam and 41.6 gm. residue; of the volatile portion, 40, 63, 77, 87, 92 and 96% boiled below 100°, 125°, 150°, 175°, 200° and 225°, respectively. Among the acids in the aqueous and oily layers were identified HCO_2H (by reduction of $HgCl_2$), AcOH (anilide), $EtCO_2H$ (basic Pb salt), and Me_2CHCO_2H (conversion into $Me_2C(OH)CO_2H$); the equivalent weights of the higher fractions indicated the presence of acids up to $C_8H_{16}O_2$. The fraction of volatile oil boiling below 100° contained 7.2% aldehyde (calculated as PrCHO) and the fraction boiling above 100°, 25.9%; in the former were identified, by conversion into the acids, EtCHO, PrCHO, and Me_2CHCHO; no HCHO could be detected. Me_2CO, MeCOEt, Et_2CO, and MeCOPr were isolated, the first as the oxime and semicarbazone, the others as the *p*-nitrophenylhydrazones. MeOH was identified through its oxalate, EtOH through its acetate, and PrOH through its *p*-nitrobenzoate; the Ac number of the oil indicated the presence of about 50% alcohols, calculated as $C_6H_{11}OH$; its saponification value indicated a 4% content of ester, as AcOEt. After treatment with $NaHSO_3$, which dissolved 25%, and repeated distillation from Na, the oil yielded 2.5% hydrocarbons $C_{10}H_8$, still containing 0.22% O. Below are the % yields of products thus far identified: Acids, 10 (HCO_2H 0.1, AcOH 2.3, $EtCO_2H$ 2.1, Me_2CHCO_2H 1.0, higher acids 4.5); H_2O-soluble alcohols; aldehydes and ketones, 29 (MeOH 1.5, EtOH 14.5, Me_2CO 5.2); oil partly miscible

with H_2O, 11; oil volatile with steam 48% (higher alcohols up to C_9 15.0, esters 2.0, hydrocarbons 1.3); oil not volatile with steam, 2%. The HO-soluble product is designated pyrosynthol, the volatile oil, synthol (=synthetic oil). The latter is converted by heating under pressure into synthin (=synthetic benzine); 25 gm. heated in a 250 cc. autoclave filled with N_2 for 1 hr. at 420° gave 2,250 cc. gas (14.5% CO_2, 22.7% hydrocarbons absorbed by fuming H_2SO_4, 0.7% O_2, 14.6% CO, 9.6% H_2, 21.8% CH_4 hydrocarbons, 16.1% N_2), 17.5 cc. of the dark red-brown oil and 3.5 cc. of an aqueous layer. Of the oil, 4, 10, 17, 22, 35, 48, 57, 65, 74, 78, and 84% boiling below 50°, 75°, 100°, 125°, 150°, 175°, 200°, 225°, 275°, and 300°, respectively. The fraction boiling below 100° had a benzinelike odor and only slightly colored concentrated H_2SO_4. Of the fraction boiling above 100°, 50% dissolved in concentrated H_2SO_4. The insoluble portion, washed with H_2O and Na_2CO_3 and distilled with steam, had a pronounced petroleum odor and 24, 44, 27, and 5% boiled at 120°–150°, 150°–200°, 200°–270°, and above 270°, respectively; it consisted of hydrocarbons ranging from C 84.48, H 15.14%, $d.^{20}_4$ 0.762 for the 75°–100° fraction to C 88.43, H 12.05%, $d.^{20}_4$ 0.874 for the 200°–270° fraction. The H_2SO_4 solution on dilution with H_2O gave an oil 33, 54, and 13% of which boiled at 100°–175°, 175°–235°, and above 235°, respectively; the 175°–235° fraction contained 79.05% C and 11.20% H. Outside of Fe, only those of the non-noble metals that are known to be H carriers, Ni, Co, and possibly Mn, will effect the above reaction; a base or salt of a base with a weak acid is also essential, and apparently the oil formation proceeds more satisfactorily the stronger the base. The various possible mechanisms of the reaction are briefly discussed.

1018. ———. [Direct Synthesis of Petroleum Hydrocarbons at Ordinary Pressure. I, II.] Ber. deut. chem. Gesell., vol. 59B, 1926, pp. 830–831, 832–836; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 190–206; Chem. Abs., vol. 20, 1926, p. 2814.

With metals of the 8th group as catalysts, the catalytic hydrogenation of CO at ordinary pressure yields not CH_4 alone but a mixture of CH_4 with its homologs. By following the reaction quantitatively, it was found that the first C derived from the CO is taken up by the catalyst, evidently with carbide formation, and from this carbide, present in the finest state of subdivision, the H_2 regenerates the metal and removes the C as hydrocarbons. The carbides are apparently not the normal, low-C compounds stable at high temperatures but compounds rich in C and stable only at relatively low temperatures, and as a result, the C is removed from them not as CH_4 but as polymembered homologs of CH_4. That in this process the hydrocarbons are not formed through HCHO or MeOH as in the high-pressure catalysis is confirmed by the fact that only hydrocarbons and never O-containing organic compounds are formed. At temperatures such as are used in the high-pressure method, only CH_4 is formed. Finely divided Co is an efficient catalyst, Fe is slower, and Ni is quite weak in the ability to produce hydrocarbons other than CH_4. Better than the metals alone are mixtures of them (1–3 parts) with other substances (oxides of Cr, Zn, Be, the rare-earth metals, U, Si, Al, Mg, and Mn, active charcoal and amorphous C in other forms); faintly alkalinizing the Fe metal increases its catalytic activity. The absence of toxic S compounds must be insured. Commercial mixtures of CO and H_2 (especially water gas) may be used, S compounds being first removed by catalytic conversion into H_2S under conditions that will not change the composition of the gas as regards its other components; such a method of purification will be described elsewhere. With all the gases used (water gas, mixtures poorer and richer in CO, moist CO, etc.), benzine was obtained if they had been sufficiently purified. It is especially important to keep the temperature as low as possible (around 300° with Fe, 270° with Co, and 160° with Ni). The higher the velocity of flow the more can the formation of CH_4 be suppressed but the poorer, of course, is the utilization of the gas mixture. A part of the reaction product condenses in liquid form as soon as the reaction mixture cools, and the rest, remaining in the gas in vapor form, is recovered by the usual methods. The condensed products are, depending on conditions, light oils like illuminating oil but also may contain higher boiling oils and deposit solid paraffin. The benzines are H_2O clear with a pleasant odor, resembling Pennsylvania benzine, and contain only a few % of substances reacting with concentrated H_2SO_4 and do not change at all on standing. The only other products besides hydrocarbons are CO_2 and H_2O. In an experiment with an Fe–Co catalyst, about 100 gm. of liquid and easily liquefiable products were obtained per $m.^3$ of water gas.

1019. ———. [Reduction and Hydrogenation of Carbon Monoxide.] Brennstoff-Chem., vol. 7, 1926, pp. 299–300; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 207–208; Chem. Abs., vol. 21, 1927, p. 642.

Fischer and Tropsch comment on the findings of Elvins and Nash (abs. **817** and **818**). They disagree with their suggestion that at atmospheric pressure hydrocarbons result through preliminary formation of synthol and subsequent dehydration by catalysis. They maintain that formation of hydrocarbons results from the intermediate formation and decomposition of unstable carbides.

1020. ———. [Some Properties of the Synthetic Petroleum Hydrocarbons Prepared From Carbon Monoxide at Ordinary Pressure.] Ber. deut. chem. Gesell., vol. 59B, 1926, pp. 923–925; Chem. Abs., vol. 20, 1926, p. 2815.

The gas-oil fraction contains C_2H_6, C_3H_8, and C_4H_{10}; the corresponding olefins are present in only very subordinate amounts. The benzine, isolated by adsorption with active charcoal and distillation with steam, is H_2O-clear, stable to light, has a pleasant odor, does not turn yellow or resinify on standing for months, $d.^{15}_4$ 0.6718, upper heat value 11,360 cal. per gm., ignition temperature in O_2 335°, b. p. 2.4 vol. % up to 40°, 96.4% up to 180°, d_4^{20} from 0.6367 for the 20°–55° fraction to 0.7264 for the 120°–180° fraction, C and H_2 for the same fractions 84.23, 16.50, and 83.35, 14.96%, respectively, upper heat value of the 75°–120° fraction 11,495 cal. per gm. The petroleum fraction, d_4^{20} 0.7804, b. p. 4.4 vol. % 170°–180°, 83.2% up to 330°, d_4^{20}, C and H_2 for the 170°–270° fraction (58.4 wt. % of the total) 0.7646, 85.04%, 14.94% (heat value 11,225 cal. per gm.), for the 270°–330° fraction (24.1%) 0.7972, 85.36, 14.41. The paraffin fraction freed from adhering paraffin oil with Me_2CO is colorless, odorless, solidifies at 61°, and has a C content of 84.57% and H of 14.57%. The synthetics differ from the natural products in that they require no refining and are wholly free of S compounds.

1021. ———. [Synthesis of Petroleum at Atmospheric Pressures From Gasification Products of Coal.] Brennstoff-Chem., vol. 7, 1926, pp. 97–104; Nat. Petrol. News, vol. 18, No. 41, 1926, pp. 95–96, 99; No. 42, pp. 80C, 80D, 80E, 80F, 80H; Chem. Abs., vol. 20, 1926, p. 2065.

S-free mixture of CO and H_2 (water gas) is passed over finely divided metals of the 8th group, alone or mixed with metallic oxides, such as those of Zn and Cr, at a temperature approximately 270° and atm. pressure. At higher temperatures, CO is reduced to CH_4, but by selecting the catalyst mixture and keeping the temperature down, only saturated higher homologs of CH_4 are formed. These vary in molecular complexity from C_2H_6 to solid paraffin. O appears in the reaction products almost wholly as CO_2 and H_2O. The

process can be so regulated that the molecular complexity of the paraffins formed is to some extent controlled; that is, one can produce mainly casinghead gas or benzine with higher homologs as desired. Boiling ranges of the products are given. The authors believe the catalytic process involves formation of a carbide rich in C as a first stage (Fe_3C_4 or Fe_2C_3), which is afterward reduced to CH_2. This polymerizes in the presence of H_2 to form saturated paraffins. From the reaction $3CO+3H_2=CO_2+H_2O+2CH_2$, 190 gm. of hydrocarbons are obtainable from 1 m.^{3} of water gas. 100 gm. of liquid hydrocarbons of benzine character were obtained by passing 1 m.^{3} of water gas several times over an Fe–Co contact mass. The process may be used primarily for the manufacture of petroleum products, especially motor spirit, or as an adjunct to water-gas plants for gas enrichment.

1022. ———. [Aluminum Oven for Contact Reactions.] Ztschr. angew. Chem., vol. 40, 1927, p. 1204; Brennstoff-Chem., vol. 8, 1927, pp. 323–324; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 308–310; Chem. Abs., vol. 22, 1928, pp. 701, 1253.

The block oven is an Al rod 500 mm. long and 80 mm. diameter with a central longitudinal hole 24 mm. diameter and is insulated with diatomaceous earth and heated with gas burners with automatic temperature control. The segment oven differs in having the tube cut into 10 segments separated by asbestos plates so that each segment may be held at a different constant temperature. An Ostwald thermoregulator keeps the temperature constant. Because of high heat capacity and condition of Al, the temperature can be held uniform (within 1° at 240°) throughout the length of the bore.

1023. ———. [Formation of Synthol on Carrying Out the Petroleum Synthesis Under Pressure and the Synthesis of Hydrocarbons of High Molecular Weight From Water Gas.] Brennstoff-Chem., vol. 8, 1927, pp. 165–167; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 209–214; Chem. Abs., vol. 22, 1928, p. 497.

Results are reported from which it seems clear that products obtained catalytically at pressures of 10–15 atm. are intermediate in character. They were neither exclusively hydrocarbons, as in the atmospheric pressure synthesis, nor mainly oxygenated compounds, as the high-pressure synthol synthesis. A disadvantage of working at 10–15 atm. is that paraffins of high molecular weight are retained by the catalyst, rendering it inactive in time. A paraffin, $C_{70}H_{144}$ was isolated.

1024. ———. [Composition of Products Obtained by the Petroleum Synthesis.] Brennstoff-Chem., vol. 9, 1928, pp. 21–24; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 523–533; British Chem. Abs., 1928, B, p. 324; Chem. Abs., vol. 22, 1928, p. 2657.

Composition of gases (gasols) varied with the catalyst and conditions of the experiment. A gas obtained with a Fe–Cu catalyst showed the following composition by condensation analysis: C_2H_6, 42.5; C_3H_8, 19.5; C_4H_{10}, 2.0; C_2H_4, 6.0; C_3H_6, 21.0; and C_4H_8, 9.0%. Benzine, boiling 60°–185°, recovered by adsorption in active charcoal and steaming out at 250°, contained 30% paraffins, for the most part octane, nonane, and isononane, which were positively identified. The remaining 70% of the benzine were olefins. There were no diolefins present. Heavier products were examined only for unsaturation by the Wijs I method. The degree of saturation could be varied by varying the catalysts or experimental conditions; for example, doubling the gas space velocity increased the unsaturation of the oil 3 times. Water-soluble oxygenated products (aldehyde and acetone) amounted to 2% of total products recovered. There was no trace of compounds of ring structure found. All products could be converted into paraffins by hydrogenation in contact with Ni. The mechanism of the catalytic petroleum synthesis is discussed. In addition to the two previous assumptions of reaction mechanism, the carbide—CH_2, and the molecular complex theories, a third possibility is advanced—the primary formation of high-molecular hydrocarbons and their subsequent catalytic cracking into lower hydrocarbons. In all 3 cases, unsaturated hydrocarbons temporarily occur and then are subjected to a greater or less extent to hydrogenation.

1025. ———. [Conversion of Methane Into Hydrogen and Carbon Monoxide.] Brennstoff-Chem., vol. 9, 1928, pp. 39–46; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 583–602; British Chem. Abs., 1928, B, p. 322; Chem. Abs., vol. 22, 1928, p. 2652.

Mixtures of CH_4 with CO_2 and CH_4 with coke-oven gas and coke-oven gas with water vapor were decomposed by various catalysts (Fe, Co, Ni, Cu, Mo, and W) supported on clay, silica, and $MgCO_3$ or mixed with Al_2O_3. Temperatures 840°–920° were used with various space velocities, throughput in cc. per hr. divided by catalyst volume in cc.; the best space velocity for decomposition of oven gas-steam mixtures was 800. In no case was CH_4 completely decomposed. An example of good conversion of an oven gas-CO_2 mixture at 860° is given by the following analyses of original gas and the products, respectively: CO_2, 18.0, 1.4%; heavy hydrocarbons, 1.0, 0.0; O_2, 1.7, 0.2; CO, 5.1, 33.2; H_2, 41.7, 56.6; CH_4, 19.6, 1.4; N_2, 12.9, 7.2. The catalyst was Ni supported on silica. Fe, Cu, Mo, and W were poor catalysts. Co proved as good as Ni, contrary to literature. Activity of Ni and Co was increased by addition of Al_2O_3. Clay proved best as a carrier for active metals.

1026. ———. [Petroleum Syntheses.] Ges Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 313–501; Chem. Zentralb., 1932, II, p. 2569; Chem. Abs., vol. 27; 1933, p. 5950.

Collection of the experiments of the authors on petroleum synthesis up to 1928 (see abs. **1021**). Gas purification, the question of catalyzers and the operating conditions (temperature, pressure, poisoning of catalyzers) influencing the reaction are treated exhaustively.

1027. Fischer, F., and Wangenheim, F. [Reactions Between Carbon Monoxide, Carbon Dioxide and Hydrogen in a "Cold-Warm" Tube at Atmospheric and High Pressures.] Brennstoff-Chem., vol. 9, 1928, pp. 94–97; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 570–579; British Chem. Abs., 1928, B, p. 355; Chem. Abs., vol. 22, 1928, p. 4323.

Special steel bomb is used in which the contact metals serve as electric resistors. Metals used were: Fe, Ni, W, Mo, and also C, named in order of their catalytic activity. Various mixtures of CO and CO_2 with H_2 were used. C was produced and also CH_4, with traces of higher homologs in some cases. Traces of HCHO were formed but no CH_3OH. Temperatures of 550°–800° were used.

1028. ———. [Some Gas Reactions in a "Cold-Warm" Tube.] Brennstoff-Chem., vol. 9, 1928, pp. 97–98; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 580–582; Chem. Abs., vol. 22, 1928, p. 4323.

Apparatus designed (abs. **1027**) to investigate catalytic reactions of mixtures of CO and H_2 was used with Fe as a catalyst. Mixtures of CO, CO_2, H_2O, and CH_4 were investigated at 600°–700° and up to 6 atm. CH_4 remained practically unchanged. Reactions taking place were: (1) $2CO \rightarrow CO_2+C$ and (2) $CO+H_2O \rightarrow CO+H_2$.

1029. Fischer, F., and Weinrotter, F. [Thermal Cracking of Kogasin to Gaseous Olefinic Hydrocarbons.] Brennstoff-Chem., vol. 21, 1940, pp. 209[217; Chem. Abs., vol. 35, 1941, p. 8253.

Previous work is reviewed briefly. The work of Fischer with Peters and Winzer is continued, and it is shown that at low-glow temperatures, with Pt wire spirals electrically heated, over 50% by weight of Kogasin II can be cracked into higher olefins. Including C_2H_4, the content of the cracked gases is around 90% of unsaturated hydrocarbons. Lowering of the glow-element temperatures does not increase the olefinic yield but increases the proportion of saturated hydrocarbons. At higher temperatures about 70% olefinic yield is obtained but with more C_2H_4 at the expense of the higher members. Similar results were obtained with a Pythagoras tube at 675°–760°, but only part of the Kogasin vapor was cracked in the recirculatory system, thereby interfering with further cracking of the initially formed olefins. Cracking in vacuo gave no different results with the wire spiral. A low-temperature fractionating column for analyzing the gas mixtures is described in detail with operating procedure. The Podbielniak dephlegmator for automatically maintaining desired temperatures with liquid air was employed. Analytical curves are presented of the operation. Sharp separations of the C_2, C_3, C_4 hydrocarbons were obtained. Saturated and unsaturated hydrocarbons were separated by absorption of the latter in $Hg(NO_3)_2$ solution, the H_2 and CH_4 being separated previously and subjected to combustion analysis. 13 refs.

1030. FISCHER, F., BAHR, T., AND MEUSEL, A. [Catalytic Reduction of Carbon Dioxide to Methane and Higher Hydrocarbons at Ordinary Pressure. Preliminary Communication.] Brennstoff-Chem., vol. 16, 1935, pp. 466–469; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 263–270; Chem. Abs., vol. 30, 1936, p. 3967.

When Ru powder or Ru–Th asbestos is used as contact catalyst, CO_2 may be appreciably reduced to CH_4 from 100° upward. Addition of $CaCO_3$ or Rb_2CO_3 results in the formation, from 170° upward, of higher gaseous and fluid hydrocarbons. Weaker alkalies do not have this effect on the catalyst.

1031. ———. [Catalytic Reduction of Carbon Dioxide to Higher Hydrocarbons at Atmospheric Pressure.] Ber. dent. chem. Gesell., vol. 69 B, 1936, pp. 183–186; Chem. Abs., vol. 30, 1936, p. 3401.

Hitherto it was not possible to reduce CO_2 to higher hydrocarbons than CH_4, but it has now been found that this can be accomplished with a Ru catalyst to which have been added small amounts of alkali. It had already been shown that in the active form in which it has recently been employed, Ru catalyzes the reduction of CO_2 even at 100°, but at these low temperatures, only CH_4 is formed. Quite different is its behavior if alkali, for example, 2% K_2CO_3, is added to it. The temperature of incipient CO_2 reduction is thereby raised to 150°, and beginning at 170°–180° there are formed not only CH_4 but also higher gaseous and liquid hydrocarbons. There are deposited at the end of the reaction tube first a colorless, low-boiling oil, later a higher-boiling oil, and finally paraffin-like products. The oil and water formed are at first neutral or faintly acid; later, increasing amounts of acid products with the odor of the lower fatty acids are produced. The gaseous products formed at 180°–225° contain 1.32–1.45 C atoms. The most favorable temperature range for the production of an oil seems to be 200°–225°, although higher hydrocarbons can still be detected at 300°; above this temperature only CH_4 is formed. The reactivity of the catalyst decreases quite rapidly, and the catalyst must be regenerated by passing air at 300°–400° over it. Comparative experiments on the influence of the amount and nature of the alkali on the catalytic behavior of Ru showed that 0.5% K_2CO_3 was not enough to impart an oil-producing power; Li_2CO_3 up to 3% and Na_2CO_3 up to 1.5% were likewise ineffective. Rb_2CO_3 (3.4%) had the same effect as K_2CO_3. Ru with 2.9% $KAlO_2$ at 200° first gave only CH_4, but after about 20 hr. CH_4 homologs and liquid hydrocarbons began to be formed; at lower temperatures (180°) there were no detectable amounts of oil even after 66 hr. and only small amounts of acid products. The formation of higher hydrocarbons by alkalized Ru is believed to proceed through CO, to which the catalyst first reduces the CO_2. From analogy with the metals of the Fe group, it would seem probable that the catalyst is a carbide, although no Ru carbide is as yet known.

1032. FISCHER, F., KOCH, H., AND WIEDEKING, K. [Advances in the Preparation of Lubricating Oils, Starting With Kogasin.] Brennstoff-Chem., vol. 15, 1934, pp. 229–233; Fuel Econ., vol. 10, 1934, pp. 602–604; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 455–465; British Chem. Abs., 1934, B, p. 744; Chem. Abs., vol. 28, 1934, p. 6291.

Relation of viscosity to temperature of lubricants prepared from chlorinated Kogasin condensed with xylene has been improved by increasing the paraffin content. Lubricants possessing properties of paraffin-base oils were obtained in the treatment of Kogasin of Cl content averaging 1–2 atoms with activated Al without the addition of aromatic hydrocarbons. Olefin hydrocarbons in synthetic benzine were polymerized to lubricants by H_2O-free $AlCl_3$, their viscosity depending on the boiling point of the original material. The synthetic lubricants correspond with the best petroleum products in stability toward oxidation, coking residue, and behavior at low temperatures.

1033. ———. Recent Advances in Manufacture of Synthetic Lubricants From Kogasin. Petrol. Refiner, vol. 23, 1944, pp. 312–316; Brennstoff-Chem., vol. 15, 1934, pp. 229–233; U. O. P. Co. Lib. Bull., abs. 34, 1944; Chem. Abs., vol. 38, 1944, p. 5389.

Gasol from the Fischer-Tropsch synthesis, converted into various chloroderivatives, is easily caused to react with aromatic hydrocarbons and an $AlCl_3$ catalyst to produce synthetic lubricants fluid at low temperatures, is very resistant to oxidation, but also susceptible to temperature changes. 3 methods are described for improving the product. The conclusions are that satisfactory high-grade lubricants may be made by gasification of any solid fuel by way of Kogasin synthesis without rejecting any fractions as unsuitable. Products of these improved processes show stability against oxidation, C residue, and pour point and compare favorably with the products of crude petroleum.

1034. FISCHER, F., PETERS, K., AND KOCH, H. [Formation of Liquid Hydrocarbons From Acetylene. II. Catalytic Hydrogenation and Condensation of Acetylene.] Brennstoff-Chem., vol. 10, 1929, pp. 383–385; Chem. Abs., vol. 24, 1930, p. 4918.

C_2H_2 (10%) in water gas was passed over Fe–Cu alkali catalyst prepared from the nitrates heated in O_2 at 250°. The yield of 40–70% of the C_2H_2 consisted of benzine and oil, 2:1, the former being recovered from the activated C in which it was collected by distillation to 300° and condensation with liquid air. The oil separated and was collected in a trap. Since the catalyst was not easily poisoned, the water gas was not purified, pure H_2 giving identical yields but lighter colored oils. In a ratio >10:1 of Cu:Fe, cuprene formed and caused clogging. Adding 1 part Ni lessened this, 50–55% of the C_2H_2 producing benzine:oil=3:1, as against 40% for Cu–Fe alone; the contraction was 22% in both cases. Fe alone gave no results below 340°, then produced 35–40% oil with C also separating. With Co, CH_4 was formed quantitatively. Fe:Ni, 2:1, raised the proportion of benzine in the yield to 85–90%, the total yield at 250° being 30–35% of the C_2H_2 used. Contraction in volume, measured by flowmeters, due to

the formation of C_2H_6 was 26% (90% of the C_2H_2) but fell to 12% at the end with the formation of C_2H_4 and higher unsaturated compounds. Fe : Ni, 10 : 1, was used 2 months at 250° without regeneration, the contraction, however, falling from 22–23% to 14–15% after that time with still no C_2H_2 passing. The products recovered, benzine : oil as 2 : 1, averaged 60% of the C_2H_2 used. Changes in temperature and velocity had little effect on yield or quality, the higher velocities increasing the proportion of benzine to oil. 90% benzine boiled 50°–150° and consisted of 60% unsaturated compounds. The heavy oil obtained contained no paraffin wax. 1 $m.^3$ of coal gas passed first through an electric discharge and then over heated catalyst gave 85 gm. oil, of which 75% was light oil, losing thereby only 10% of its heating value.

1035. FISCHER, F., PETERS, K., AND WINZER, K. [Thermal Splitting of Higher Paraffin Hydrocarbons Upon a Glowing Wire.] Brennstoff-Chem., vol. 16, 1935, pp. 421–429; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 486–503; Chem. Abs., vol. 30, 1936, p. 3991.

Kogasin II and various fractions were passed as vapor over heated wires of various metals at 1–10 atm. With Pt wire, 20% of light benzene and 80% of gaseous products were obtained; the gas contained over 70% of unsaturated hydrocarbons. C did not separate.

1036. FISCHER, F., PICHLER, H., AND DIENST, W. [Approach to Theoretically Possible Yields in the Fischer-Pichler Intermediate-Pressure Synthesis.] Brennstoff-Chem., vol. 20, 1939, pp. 221–228; British Chem. Abs., 1939, B, p. 904; Chem. Abs., vol. 34, 1940, p. 3904.

Synthesis was effected in two stages at 175°–205° under 10 atm., with a Co–ThO_2–kieselguhr catalyst; products condensable at room temperature were removed after the 1st stage. 2 reaction tubes (internal diam. 10 mm. length of catalyst column 50 cm.) were used in parallel in the 1st stage, and a single similar tube was used in the 2d. The reaction tubes, arranged vertically, were heated by circulating hot H_2O, under pressure, through surrounding jackets. With a throughput of 2 l. of gas, $CO+2H_2$ per gm. of Co per hr., the maximum yield was 140–150 gm. of product, wax 14, liquid hydrocarbons 73, gasol 13% per $m.^3$ of inert-free gas: with a throughput of 0.2 l. per gm. of Co per hr. the maximum yield was 190 gm. of product, wax 48, liquid hydrocarbons 44, gasol 8% per $m.^3$ of gas; the latter yield represents 90% of the theoretical. A decrease in the rate of gas throughput necessitates a lowering of the reaction temperature to obtain the maximum yield of hydrocarbons; at the same time there is an increase in the relative proportion of higher-boiling hydrocarbons in the product. The reaction mechanism is discussed.

FISCHER, F., PICHLER, H., AND KÖBEL, *H.* [Mixed Gas for Benzine Synthesis. II. Semitechnical Investigation of the Preparation of Mixed Gas for Benzine Synthesis by Simultaneous Conversion of Coke-Oven Gas and Steam Over Coke in the Generator.] *See* abs. **1040.**

FISCHER, F., PICHLER, H., AND KÖBEL, H. [Mixed Gas for Benzine Synthesis. III. Preparation of Mixed Gas for Benzine Synthesis by Simultaneous Conversion of Coke-Oven Gas and Steam Over Coke in the Generator.] *See* abs. **1041.**

1037. FISCHER, F., PICHLER, H., AND LOHMAR, W. [Synthesis of Kogasin and Paraffin Wax in the Aqueous Phase.] Brennstoff-Chem., vol. 20, 1939, pp. 247–250; British Chem. Abs., 1939, B. p. 904; Chem. Abs., vol. 34, 1940, p. 3904.

By passing $CO+2H_2$ through H_2O containing either a Co–ThO_2 or a Rh catalysts in suspension, at 170°–200° under a total pressure of 50–100 atm., liquid hydrocarbons and wax were obtained similar in yield and composition to the products of the medium-pressure Fischer synthesis (abs. **1036**). A laboratory apparatus of 1 l. capacity was used. Ni was useless as a catalyst, being converted into the carbonyl under the reaction conditions; an Fe catalyst merely brought about the reaction $CO+H_2O=CO_2+H_2$. Although by operating in the aqueous phase the temperature control was very good, the process had disadvantages that precluded its practical development; for example, the results were no better than in the dry phase, a relatively larger reaction space was required, the apparatus had to be lined with acid-resistant material (for example, Cu), owing to the production of small quantities of fatty acids, considerable energy expenditure was necessary to maintain the catalyst in suspension, and the continuous removal of the reaction products presented difficulties.

1038. FISCHER, F., PICHLER, H., AND REDER, R. [Influence of Catalytic Admixtures and Reduced Pressures Upon the Setting-Up of the Producer-Gas Equilibrium for Semicoke.] Brennstoff-Chem., vol. 13, 1932, pp. 346–350; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 358–368; Chem. Abs., vol. 26, 1932, p. 5734.

Equilibrium $C+CO_2 \rightleftharpoons 2CO$ was studied with graphite at pressures <20 mm. Hg, 500°–700°; it shifts almost completely to the right at reduced pressure. With semicoke from brown-coal briquets degasified at temperatures 50° higher, the shift was even more complete. Additions of 5% Fe and Al oxides, Ca, Na, and K carbonates to degasified semicoke greatly increased the rate of reaction with CO_2 at atmospheric pressure, this effect increasing with the basicity of the catalyst.

1039. ———. [Mixed Gas for Benzine Synthesis. I. Survey of the Possibilities of Supply of Suitable Carbon Monoxide–Hydrogen Mixtures for the Benzine Synthesis on Grounds of the Present-Day Position of Science and Technique.] Brennstoff-Chem., vol. 13, 1932, pp. 421–428; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 481–496; British Chem. Abs., 1933, B, p. 49; Chem. Abs., vol. 27, 1933, p. 2017.

Use of various technically available gases and mixtures is examined practically and theoretically. Gas mixtures containing CO and H_2 in approximately the ratio of 1 : 2 may be produced by mixing coke-oven gas with generator gas or with water gas (Mischgas), which may be produced simultaneously in the coke oven by the direct gasification of coal or by the interaction of CH_4 with steam and/or CO_2 or O_2, etc. Heat balances have been drawn up for the more important of these processes. The influence of temperature and pressure upon equilibrium and reaction rate has been determined for the cracking of CH_4 by steam over Ni–Al catalyst at 800° per 1 atm. or at 600° per 0.1 atm. with a contact time of less than 1 sec. The effects of temperature and coke activity upon the conversion of coke-oven gas with steam over coke have been determined. A scheme for using coke-oven gas thus regenerated is proposed.

1040. FISCHER, F., PICHLER, M., AND KÖBEL, H. [Mixed Gas for Benzine Synthesis. II. Semitechnical Investigation of the Preparation of Mixed Gas for Benzine Synthesis by Simultaneous Conversion of Coke-Oven Gas and Steam Over Coke in the Generator.] Brennstoff-Chem., vol. 16, 1935, pp. 331–333; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 322–327; Chem. Abs., vol. 30, 1936, p. 3970.

Apparatus, etc., previously described in abs. **1039** have been improved. Varying the gas : steam ratio gives variation of the $CO : H_2$ ratio from 1 : 2 to 2 : 7 in the product for benzine synthesis.

1041. ———. [Mixed Gas for Benzine Synthesis. III. Preparation of Mixed Gas for Benzine Synthesis by Simultaneous Conversion of Coke-Oven Gas and

Steam Over Coke in the Generator.] Brennstoff-Chem., vol. 16, 1935, pp. 401–404; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 327–333; Chem. Abs., vol. 30, 1936, p. 3970.

In a generator larger than previously used, having a capacity of 100 m.^{3} per hr., it was possible, through the simultaneous conversion of coke-oven gas and coke with steam, to produce a gas containing CO and H_2 in the correct proportion of 1:2 suitable for benzine synthesis. 1 m.^{3} of coke-oven gas in a mixture with water gas produces 3m.^{3} of synthesis gas.

1042. Fischer, F., Roelen, O., and Feisst, W. [Present Technical Position of the Benzine Synthesis.] Brennstoff-Chem., vol. 13, 1932, pp. 461–468; Petrol. Refiner, vol. 22, 1943, pp. 429–436; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 501–516; U. O. P. Co. Lib. Bull., No. 1, 1944; British Chem. Abs., 1933, B, p. 136; Chem. Abs., vol. 27, 1933, p. 2017; vol. 38, 1944, p. 1089.

Recent developments in the production of a suitable initial gas mixture, in the method of gas purification and in the preparation of the catalyst are reviewed. The difficulty of temperature control in large-scale apparatus has been overcome by the design of a narrow, rectangular unit contact apparatus, 20 mm. by 120 cm. in cross-section and 5 m. long, which is packed with the catalyst ($Ni–Mn–Al_2O_3$) and maintained at the reaction temperature, 190°–210°, by the circulation of hot oil around it; the temperature control was made automatic without difficulty, and the apparatus then required little supervision. The yield, 70 gm. of liquid product per m.^{3} of gas, CO 24%, H_2 48%, was equal to that obtained in the laboratory-scale apparatus. After about 1,000 hr. operation the catalyst required regenerating by extraction of the deposited paraffin wax with light petroleum. By using a battery of such units the throughput of the plant could be increased to any desired value.

1043. Fischer, F., Tropsch, H., and Dilthey, P. [Reducation of Carbon Monoxide to Methane in the Presence of Various Metals.] Brennstoff-Chem., vol. 6, 1925, pp. 265–271; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 175–190; Jour. Chem. Soc., 1925, II, p. 982; Chem. Abs., vol. 19, 1925, p. 3367.

Various metals reduced at low temperature from the oxides where possible, (Co, Fe, Mo, W, Ru, Pd, Os, Ir, Pt, Ag, Cu, Rh), were tested with and without admixture of Al_2O_3 at various temperatures, 100°–800°, for conversion of CO and H_2 mixtures to CH_4. Ru gave the best results, that is, 34.4% CH_4 in exit gas at 300° with a mixture $CO_2:H_2=1:5$ at 12 cc. gas flow per min. The use of Al_2O_3 as a carrier of metals proved advantageous particularly in the case of Fe. The order of the catalytic activity of the metals tested was Ru, Ir, Rh, Ni, Co, Os, Pt, Fe, Mo, Pd, Ag.

1044. Fischer, F., Tropsch, H., and Mohr, W. [Reduction of Carbon Monoxide to Methane in the Presence of Iron at Ordinary Pressure.] Brennstoff-Chem., vol. 4, 1923, p. 197; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 473–474; Chem. Abs., vol. 18, 1924, p. 349.

Reduction of CO to CH_4 by means of Fe as a contact substance takes place in small amount at 400° and 2 atm. This investigation was made to discover whether this reduction would take place at atmospheric pressure and at 400°–550°. The amount of CH_4 formed was in all cases less than 1.0%.

1045. Fischer, F., Tropsch, H., and Schellenberg, A. [Decomposition of Barium, Magnesium, and Lithium Formates.] Ges. Abhandl. Kenntnis Kohle, vol. 6, 1921, pp. 355–359; Chem. Abs., vol. 18, 1924, p. 3170.

Ba formate decomposes in the Al distillation apparatus at 350°–375° with considerable frothing; 45.4 gm. gave 2.2 gm. of MeOH and 0.1 gm. of oil, the residue containing some C. On decomposing Ba formate with superheated steam the aqueous distillate contained HCHO and HCO_2H. Contrary to Berthelot's statement, the gas contained no CH_4 and no unsaturated hydrocarbons. Mg formate decomposed at 400°–425°, giving an aqueous distillate; the residue and gas together contained 1.36 gm.-atoms of C per gm.-mol. of formate. Li formate decomposed at 350°, giving an alcoholic liquid but no oil. Heated with H_2O under pressure at 350°, it gave only gaseous products and carbonate.

1046. ———. [Formation and Decomposition of Calcium Formate.] Ges. Abhandl. Kenntnis Kohle, vol. 6, 1921, pp. 330–354; Chem. Abs., vol. 18, 1924, p. 3170.

Ca formate is obtained in practically theoretical yield on shaking 8 *N* milk of lime with CO under 20–50 atm. at 160° for 12–17 hr. At 180° the Fe parts of the autoclave are seriously attacked. When Ca formate was decomposed at 420°–430° (26 gm. in 1–2 hr.) in the Al distillation apparatus, the residue consisted almost completely of $CaCO_3$, with very small quantities of oxalate and undecomposed formate, and traces of carbonaceous products. The primary formation of oxalate (abs. **3561** and **3564**) could not be confirmed. One gm.-mol. of pure Ca formate gave 1.02 gm.-atoms of C in the residue, 0.54 gm.-atom in the gas (which consisted of 47.9% CO, 2.0% CH_4, and 23.8% H_2) 0.20 gm.-atom in the MeOH, and 0.13 gm.-atom in the oil. A mixture of equal parts of Ca formate and CaO gave a rather higher yield of MeOH and less oil, but the addition of more CaO (up to 10 pts.) decreased the yield of MeOH. By carrying out the decomposition of Ca formate in a current of steam, MeOH was obtained in 52% yield. When decomposed in a large Al distillation apparatus 390 gm. of Ca formate gave 15.2 gm. of MeOH containing a small proportion of acetone and 5.5 gm. of oil, of which 2.56 gm. were volatile in steam.

1047. Fischer, F., Tropsch, H., and Ter-Nedden, W. [Synthesis of Paraffin Hydrocarbons of High Molecular Weight From Carbon Monoxide.] Ber. deut. chem. Gesell., vol. 60B, 1927, pp. 1330–1334; Chem. Abs., vol. 21, 1927, p. 2870.

It has already been mentioned that in the preparation of petroleum hydrocarbons from CO solid paraffin hydrocarbons are found in the contact substances (abs. **1020**). In 1 of the usual contact substances, which had been treated for a long time with water gas under 10 atm., there were formed, together with the liquid and solid products, which distilled off with the current of water gas, considerable amounts of nonvolatile compounds, and when the experiment was continued a long time, the contact mass increased greatly in weight, and on opening the contact tube, it was found to contain a mass that was solid at room temperature and became semiliquid on warming; on distillation *in vacuo* large amounts of solid paraffin passed over. A part of the product was so difficultly volatile, however, that it was necessary to extract the contact mass with solvents (C_6H_6, xylene). A partial separation was effected into a less soluble fraction melting 104°–117°, solidifying 109°. Its composition, solidification point, and molecular weight all showed conclusively that it consisted of paraffin hydrocarbons of high molecular weight, around 1,000 or about C_{70}.

1048. Fischer, F., Pichler, H., Meyer, K., and Koch, H. [Synthesis of Aromatic Hydrocarbons From Methane at Atmospheric Pressure and Without Catalysts.] Brennstoff-Chem., vol. 9, 1928, pp. 309–316; Proc. 2d Internat. Conf. Bituminous Coal, vol. 2, 1928, pp. 789–807; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 603–625; Chem. Abs., vol. 23, 1929, p. 2694.

Pure CH_4 from various sources and CH_4 with other gases (coal gas) is decomposed by passage through

porcelain or quartz tubes heated 900°–1,200°. The tar formed is precipitated by a Cottrell precipitator and light oils are absorbed by active charcoal. The time of contact is fully as important as the temperature. For example, 346 l. CH_4 (89% with 8% N_2) passed through the 1-mm. annular space between concentric 14- and 16-mm. tubes 22 cm. long at 63 l. per hr. gave 7 gm. oil, 3 gm. tar, and 0.2 gm. C. Higher temperatures with the same gas flow favor precipitation of C. Tar and oil do not form to an appreciable extent below 900°. The tar is aromatic, naphthalene, anthracene and phenanthrene being isolated. The oils contain mostly benzene with xylene and $C_{10}H_8$. SiO_2, W, Mo, and Sn as catalysts did not favor oil yield; Fe, Cu, and graphite favored C precipitation.

FISCHER, L. E. *See* abs. **1579a.**

FISCHER, W. *See* abs. **868.**

FISCHER, W. A. *See* abs. **1966.**

1049. FISHEL, W. P., AND WOODDELL, J. S. Action of Pure Carbon Monoxide Upon Iron at Elevated Temperatures. Trans. Am. Soc. Steel Treating, vol. 11, 1927, pp. 730–740; Chem. Abs., vol. 21, 1927, p. 3873.

Reaction between CO and Fe to produce Fe_3C and CO_2 has been demonstrated to obey the laws of reversible reactions.

FISHER, P. L. *See* abs. **923, 927, 929.**

FLEMING, H. W. *See* abs. **574.**

1050. FLETCHER, C. J. M., AND ROLLEFSON, G. K. Production of Free Radicals From Ethylene Oxide and the Catalysis of Other Reactions by Them. Jour. Am. Chem. Soc., vol. 58, 1936, pp. 2135–2140; Chem. Abs., vol. 31, 1937, p. 936.

When ethylene oxide is heated to 450° the chief reaction is in isomerization to AcH, but free radicals also are formed to a much greater extent than for most other organic compounds. MeOH at 465° decomposes to the extent of 24.5% in the presence of ethylene oxide, whereas the uncatalyzed reaction is inappreciable at this temperature.

1051. FLEURY, M. [Manufacture of Synthetic Methanol.] Mem. poudres, vol. 24, 1931, pp. 10–48; Chem. Abs. vol. 25, 1931, p. 3310.

Describes mechanical installation and experimental chemical work on the semi-plant-scale production of MeOH from water gas and H_2, in 1922. The best catalyzers were 90% Cu, 10% ZnO, Mn and Zn chromates. High gas speed and high temperatures favored the formation of higher alcohols.

FLOE, C. F. *See* abs. **2562.**

FOEHR, T. *See* abs. **2935.**

1052. FOHLEN, J. [Cracking and Catalysis.] Chim. et ind., Special No., 1932, pp. 273–277; Chem. Abs., vol. 26, 1932, p. 3357.

Decomposition of Saar coal at very high pressures and temperatures is investigated, both in the presence and absence of solvents which are not volatile at the temperatures used, and in the presence and absence of various catalysts. The problem of the industrial synthesis of liquid fuels is also discussed.

FORAN, E. *See* abs. **3038.**

FORESTIER, H. *See* abs. **479.**

1053. FORESTIER, H., AND CHAUDRON, G. [Points of Magnetic Transformation in the System Sesquioxide of Iron–Magnesia.] Compt. rend., vol. 181, 1925, pp. 509–511; Chem. Abs., vol. 20, 1926, p. 698.

Study of system $Fe_2O_3 \cdot MgO$ at various temperatures by dilatometry and also by magnetic susceptibility. The results show the existence of $Fe_2O_3 \cdot MgO$.

1054. ———. [Thermomagnetic Study of Some Ferrites.] Compt. rend., vol. 182, 1926, pp. 777–779; Chem. Abs., vol. 20, 1926, pp. 1939–1940.

Curves showing the change in magnetization with temp. between 0° and 600° to 900° are given for $Fe_2O_3 \cdot CrO$, $Fe_2O_3 \cdot FeO$, $Fe_2O_3 \cdot NiO$, $Fe_2O_3 \cdot MgO$, $Fe_2O_3 \cdot CaO$, $Fe_2O_3 \cdot BaO$, $Fe_2O_3 \cdot PbO$ and $Fe_2O_3 \cdot ZnO$. The mean specific susceptibilities for these ferrites for fields 0–100 gausses are given as 0.102, 0.080, 0.078, 0.054, 0.0425, 0.0099, 0.0012, and 0.00016, respectively.

1055. FORESTIER, H., AND GUIOT-GUILLAN, G. [A New Series of Ferromagnetic Substances; the Ferrites of the Rare Earths.] Compt. rend., vol. 230, 1950, pp. 1844–1845; Chem. Abs., vol. 44, 1950, p. 7700.

Compounds of the type $Fe_2O_3 \cdot M_2O_3$, where M is La, Pr, Nd, Sm, Er, or Y, were prepared by coprecipitation of the oxides followed by heat treatment. They are stable up to 1,000°, although in some cases decomposition occurs after prolonged heating of 1,000°. Magnetization curves were obtained. Ferromagnetic Curie points are: $Fe_2O_3 \cdot La_2O_3$, 465°; $Fe_2O_3 \cdot Pr_2O_3$ 425°; Fe_2O_3 Nd_2O_3, 300°; $Fe_2O_3 \cdot Sm_2O_3$, 300°; $Fe_2O_3 \cdot Er_2O_3$, 255°; $Fe_2O_3 \cdot Y_2O_3$, 275°.

1056. FORESTIER, H., AND KIEHL, J. P. [Effect of Gaseous Adsorption on the Velocity of Reaction of Metallic Oxides.] Compt. rend., vol. 229, 1949, pp. 47–49; Chem. Abs., vol. 44, 1950, p. 403.

Yields of ferrite from powdered Fe_2O_3 and NiO heated in atmospheres of H_2O, CO_2, O_2, air, N_2, Ne, A, and He at 600°, 650°, and 700° plotted as isotherms against absolute temperature of liquefaction of the gases give smooth curves except for N_2, which gives a low yield. Yields decrease with particle size. The explanation advanced is that the gases are most readily adsorbed in the order named, and adsorption swells the particles till they shatter.

1057. ———. [Effect of Adsorbed Gases on the Rate of Reaction Between Metallic Oxides.] Jour. chem. phys., vol. 47, 1950, pp. 165–173; Chem. Abs., vol. 44, 1950, p. 7128.

The rate of formation of ferrite from Fe_2O_3 and NiO increases logarithmically with the partial pressure of H_2O present over the pressure range of 10^{-5}–760 mm. at 500°–700°. Extrapolation indicates 0 reaction rate at 10^{-9} mm. The order of decreasing efficiency of gases in speeding up the reaction in the temperature range 600°–700° is H_2O, CO_2, A and O_2, air, N_2, Ne, and He.

1058. FORESTIER, H., AND LILLE, R. [Variation in Catalytic Power of Ferromagnetic Substances at the Curie Point.] Compt. rend., vol. 23, 1937, pp. 204, 265–267; Brennstoff-Chem., vol. 18, 1937, p. 286; Chem. Abs., vol. 31, 1937, p. 2077.

It has been shown that the speed of inauguration of the equilibrium reaction, $2CO \rightleftharpoons CO_2+C$, in the presence of ferromagnetic metals changes whenever the catalyst Fe or Ni loses its ferromagnetism. A series of ferromagnetic oxides of the type of the ferrites, Fe_3O_4, $Fe_2O_3 \cdot SrO$ and $Fe_2O_3 \cdot NiO$, was investigated for the catalytic power on the inauguration of the water-gas equilibrium $CO_2+H_2 \rightleftharpoons CO+H_2O$ in the temperature range of their Curie points of 350°–700°. A $CO_2 : H_2$ (55 : 45) mixture was used at a velocity of 1 l./hr. The amount of H_2O formed in the reaction plotted against the temperature was used as the criterion for the catalytic efficiency. In the temperature range of the magnetic transition point, for $Fe_2O_3 \cdot SrO$ 480°, for Fe_3O_4 570°, decided maxima occurred in the curves. Three curves for $Fe_2O_3 \cdot NiO$, giving results of 3 successive tests, reveal the progressive reduction of the catalyst. In the first test a maximum in the Curie point of the Ni ferrite occurs at 595°, but in the following tests the $Fe_2O_3 \cdot NiO$ obviously decomposes with formation of Fe_3O_4 as a second maximum point is observed at about 570°. A thermomagnetic analysis confirms this. It is suggested that 3 temporary increases in catalytic power are connected with the changes at the

Curie point and are due to a special mobility of some of the superficial electrons at that point.

1059. FORESTIER, H., AND LONGUET, J. [Formation of Cupric Ferrite at Low Temperature.] Compt. rend., vol. 208, 1939, pp. 1729–1730; Chem. Abs., vol. 33, 1939, p. 5764.

By precipitation of a suitable mixture of ferric and cupric salts with NaOH, a mixture of $Fe(OH)_3$ and $Cu(OH)_2$ in molecular proportions was obtained. On boiling this mixture in H_2O, ferromagnetism began to appear after ½ hr. and gradually increased, the limit being reached after about 24 hr., when it equaled that of $CuO \cdot Fe_2O_3$ heated above 400°. The Curie point was 455°. X-rays indicated that the precipitate was at first amorphous and gradually became crystalline with boiling, developing the spinel structure of $Cu(FeO_2)_2$. This is confirmed by the fact that KCN solution dissolves the Cu from the unboiled precipitate, but is without action on the ferromagnetic product. The production of $Cu(FeO_2)_2$ takes place only in the presence of H_2O and between the anhydrous oxides.

1060. FORESTIER, H., AND NURY, G. [Variation of the Velocity of Cementation of Iron at the Temperature of the Curie Point.] Compt. rend., vol. 227, 1948, pp. 280–282; Chem. Abs., vol. 43, 1949, p. 472.

Velocity of cementation of Fe at temperatures 600°–800° was followed by 2 methods: Variation of electric resistance of wires and hardness of polished faces of cubes. The velocity was a maximum at the Curie point, about 775°.

1061. ———. [Speeds of Reaction in the Vicinity of Magnetic Transformation Points. Application to the Cementation of Iron.] Bull. soc. chim. France, 1949, D, pp. 193–196; Chem. Abs., vol. 43, 1949, p. 6018.

Rate of formation of ferrite from NiO and Fe_2O_3 is studied near the Curie point. Maxima in the % product are observed at 590° and 675°, the Curie points of ferrite and Fe_2O_3, respectively. These maxima are attenuated as the time of heating at 450°–800° is extended from 2 min. to 24 hr. The conclusion is that the magnetic transformation acts essentially on the chemical reaction and not on the speed of diffusion. The cementation of Fe in illuminating gas and in CO is also studied by measuring the variation of electric resistance of an Fe wire and the variation of surface hardness of an Fe cube. Pronounced maxima are observed at the Curie temperature of Fe. Similar results are indicated for the nitridization of Fe.

1062. FORESTIER, H., HAASSER, C., AND LONGUET-ESCARD, J. [Reaction in the Solid State at Low Temperature. Influence of the State of the Surface and of the Water Vapor Adsorbed.] Bull. soc. chim. France, 1949, D, pp. 146–152; Chem. Abs., vol. 43, 1949, p. 6059.

Magnetic detection of ferrites is used to study the rate of reaction between solid Fe_2O_3 and oxides of Ni, Pb, and Mg at temperatures low enough for diffusion to be neglected. For Ni and Pb, reaction can be detected at 200°; for Mg, only above 400°. Starting mixtures are prepared in 3 ways: (*A*) Coprecipitation followed by drying at 100° in vacuo, (*B*) separate precipitation and drying followed by mixing, (*C*) separate precipitation and drying at 750° followed by grinding. The rate and extent of reaction at a given temperature (up to 700°) are $(A) > (B) > (C)$. The presence of water vapor even in trace amounts considerably increases the rate of reaction for (*A*) and (*B*) and has a small effect for (*C*). X-ray analyses indicate that with Ni (*A*) is amorphous but (*C*) is well-crystallized; with Mg (*A*) and (*B*) show $Mg(OH)_2$, but (*C*) shows MgO; with Pb (*A*) is amorphous, but (*B*) and (*C*) show the crystalline structure of PbO. With $NiO–Fe_2O_3$ mixture (*B*) at 500°, grinding during the interval of rising temperature results in a slower reaction during the 1st 1½ hr. at constant temperature, but a faster reaction thereafter. Compression of the initial $NiO–Fe_2O_3$ mixture (*B*) gives a minimum in the % product-pressure curve at about 1,500 kg./cm.^{2} Mixture (*C*) shows no minimum. The data are explained in terms of the number of contact points and the effect of adsorbed water vapor on the surface crystal lattice.

FOROUD, A. K. *See* abs. **162.**

FORRER, R. *See* abs. **3639, 3640, 3641, 3642.**

FORREST, H. O. *See* abs. **1365.**

1063. FORTUNE. Coming: Ersatz Gasoline. Vol. 31, 1945, pp. 200, 203.

Our present crude petroleum reserves have dwindled to about a 14-yr. supply at the present rate of consumption, assuming that no new oil is found and that all of the present reserve can be brought above ground. To supplement that, we have other raw materials from which liquid fuels can be made: Natural gas about equal to the proved petroleum reserves, oil shale sufficient to maintain the normal rate of oil production for 65 yr., tar sands which contain enough oil for gasoline for 100 yr., and, finally, vast coal reserves, enough to supply liquid fuel by the Bergius and Fischer synthetic processes for 1,000 yr. or more. Some conservation-minded experts believe that natural gas should be used as such, since gas loses about half its heat content in being converted into gasoline. Therefore, the Bureau of Mines, in its study of the production of liquid fuels, is turning down natural gas and giving its attention to the production of gasoline and fuel oils from oil shale and from coal by means of the Fischer and Bergius processes. Economically, it is believed that gasoline made by the Fischer process is competitive with gasoline made from crude petroleum, and 2 companies are now ready to construct commercial Fischer plants. However, it is believed that success may not be too rapid, since the transfer of the process from laboratory and pilot-plant stage is sure to be difficult, obsolescence will be rapid, the after-war market for gasoline may be bad, with 7,000,000 cars off the road, and the supply of natural gas is not too secure, with 75% of it already earmarked for other industrial and domestic uses and being consumed at a rate that will exhaust present proved reserves in about 30 yr.

1064. ———. Synthetics: The Great Oil Reserve. Vol. 37, No. 5, 1948, pp. 110–115, 153–154, 156, 158, 160, 162, 164, 166.

Review of developments in setting up a synthetic fuel industry involving the utilization of our natural gas, coal, and shale resources. The economic possibilities of such a program is discussed quite thoroughly. It is concluded that the immediate creation of a huge synthetic fuel industry at enormous cost would disrupt our national economy. The best solution seems to be a combination of vigorous domestic exploration of our energy resources pointing toward a balanced national policy for making the most of them, a stockpiling of national oil products, and the creation of a more manageable synthetic program subsidized by the military, which could supply plans and improvements for quick expansion in an emergency.

1065. FOSTER, A. L. Fischer-Tropsch Synthesis May Prove a Major Oil-Refining Process. I. The Reaction, Its Mechanism and Its Products. Oil Gas Jour., vol. 43, No. 15, 1944, pp. 99, 101, 106, 109; Chem. Abs., vol. 39, 1945, p. 3895.

Synthol theory of Elvin and Nash and the carbide theory of Fischer are discussed. The nature of the products is discussed in general terms, with reference to the influence of operating conditions and of the nature of the catalyst used.

1066. ———. Fischer-Tropsch Synthesis May Prove a Major Oil-Refining Process. II. Methods of Operation. Oil Gas Jour., vol. 43, No. 17, 1944, pp. 46–49; Chem. Abs., vol. 39, 1945, p. 3895.

For a given product to be obtained in satisfactory yield, good temperature control of the reaction is essential, and to avoid poisoning of the catalyst, S should be removed from the reactants. Various methods for the production of high-antiknock hydrocarbons are discussed. The nature of the products varies widely with temperature, pressure, and nature of catalyst used.

1067. ———. Fischer-Tropsch Synthesis May Prove a Major Oil-Refining Process. III. Catalysts and Their Preparation. Oil Gas Jour., vol. 43, No. 18, 1944, pp. 66, 69, 91; Chem. Abs., vol. 39, 1945, p. 3895.

Usual main constituent of the catalyst is 1 or more group VIII metals mixed, if desired, with 1 or more of a wide range of promoters. The catalyst is usually prepared by reduction of a salt or an oxide of the metal, and may be supported on any one of a number of suitable materials—for example, kieselguhr. The precise methods used in preparing the catalyst are critical, since its physical state is as important as its chemical nature.

1068. ———. Chemical Utilization of Natural Gas Limited Only by Commercial Demand. Oil Gas Jour., vol. 44, No. 52, 1946, pp. 83, 84, 91.

Reactions employed to convert natural gases into more useful commercial products include alkylation, polymerization, isomerization, dehydrogenation, condensation, and synthesis. The combination of reactions comprising the Fischer-Tropsch process is referred to as the most versatile synthetic system that has been developed for use on petroleum and natural-gas hydrocarbons. The products range from the lightest oxidation products, such as alcohols, to the heaviest paraffin waxes with molecular weights above 2,000. In addition a long list of aldehydes, ketones, acids, ethers, and other oxygenated products are made. The nature of the hydrocarbons synthesized ranges from the highly paraffinic straight chain products almost entirely free of isomers or olefins into the relatively high octane number products consisting mainly of isomeric hydrocarbons in the gasoline range and heavier, higher-boiling materials of the less paraffinic types. Some 4–6 gal. of gasoline per 1,000 cu. ft. of raw gas can be made. For each bbl. of gasoline produced, there are required 1,360 lb. of coal, or 11,950 cu. ft. of CH_4 (modern designed plants, 10,450 cu. ft.) with a percentage fuel value conversion of 31, 42.5 (48.3), respectively. Comparative yields of products by atmospheric and medium-pressure processes are charted.

1069. ———. Postwar Refinery Operations Capitalize on Skills Developed During Emergency. Fischer-Tropsch Developments. Oil Gas Jour., vol. 45, No. 12, 1946, pp. 165, 216.

Progress in this field has been in developing and perfecting catalysts, equipment, and procedures to improve yields and properties and reduce costs. It is tentatively estimated that gasoline can be produced for $0.0525 per gal., including interest, depreciation and amortization. As regards catalysts, it appears that the sintered Fe type is being favored, with operation by the fluid principle. The technical feasibility of the Fischer process is already demonstrated but its economic practicability is yet to be proved. A crude price ceiling of $2.00 per bbl. has been mentioned as the minimum with which the synthetic process could economically compete.

1070. ———. Hypersorption. Oil Gas Jour., vol. 47, No. 15, 1948, pp. 90, 93, 94, 97, 99, 100.

This process, developed by Union Oil Co. of California, employs the principle of selective adsorption of hydrocarbons by a moving bed of activated C particles, with subsequent removal of the adsorbed hydrocarbons by heat and steam. It has been applied especially to recovery of C_2H_4 and the like from natural gas and cracked gas where high recoveries and high concentrations of the products are desired. The Dow Chemical Co. has a unit at Midland, Mich., designed to process a maximum of 1,800,000 cu. ft. of cracked gases per day. It will circulate up to 32,000 lb. of C per hr. and will strip the C at 500° F. or higher. From a feed containing about 6% C_2H_4, 98–99% was recovered in a CO_2-free purity of about 95%. In separating H_2 from a charge containing 52.2% H_2, 43.5% CH_4, and small amounts of C_2 and C_3, the discharge has showed 100% H_2, with 91% CH_4 and virtually no H_2 in the make gas. Operations to concentrate C_3H_8 show results of 99.2% of C_3H_8 in the make gas from charge containing 28.8% C_3.

1071. ———. Merger of Synthetics Programs. Oil Gas Jour., vol. 46, No. 44, 1948, p. 42.

Cities Service Oil Co. and M. W. Kellogg Co. have merged their synthetic fuel research programs and are prepared to license synthetic fuel plants for operation of the process. Cities Service Co. has been interested for several years in the chemistry and technology of natural gas and is one of the largest producers and controls one of the largest gas reserves in the United States. Research is now being concentrated on the isolation purification of the byproduct chemicals obtained during the process, and the reconversion of the oxygenated products to hydrocarbons. It is stated that the cost of producing a synthetic crude oil is comparable at present to the price of crude oil.

1072. ———. Texaco Now Licensing Process for Synthetic Fuel Production. Oil Gas Jour., vol. 46, No. 41, 1948, p. 68.

Hydrocol process for making synthetic gasoline and other products from natural gas has been tested commercially in a 120-bbl.-per-day pilot plant of the Texas Company at Montebello, Calif., and is being offered for general license. It is estimated that enough natural gas is available in the United States to support 50 Hydrocol plants producing a total of 350,000 bbl. gasoline per day. It is estimated also that the overall cost for present-day American plants will be only about ⅓ that of the German plants. The Fe catalyst used on the fluidized principle has a life of 500 hr. and costs $0.05–$0.10 per lb.

1073. ———. Synthetic Fuels Plant in Shakedown Stage. Petrol. Eng., vol. 23, No. 2, 1951, pp. C29–C30.

Synthetic fuels plant of Carthage Hydrocol and the Stanolind Oil & Gas Co. plant adjacent thereto are being made ready for initial operation. The Hydrocol plant will produce gasoline and oil from natural gas by a modified Fischer-Tropsch process, and the Stanolind plant will work up the dilute, liquid byproducts, such as alcohols, aldehydes, acids, ketones, etc., for delivery to the United States Industrial Chemicals for use as raw materials or intermediates in the manufacture of chemicals. The main steps in the process are pointed out.

1073a. ———. Status of Synthetic Fuels. Petrol. Eng., vol. 24, No. 10, Sept. 1952, pp. C3–C4.

Brief review of economic studies and technological advances.

1074. Foster, J. F. Investigation of a Continuous Process for the Production of Water Gas From Pulverized Coal. Symposium on Production of Synthesis Gas, 112th Meeting American Chemical Society, September 1947, pp. 137–150; Ind. Eng. Chem., vol. 40, 1938, pp. 586–592; Chem. Abs., vol. 42, 1948, p. 4328.

Investigation was made of the feasibility of producing water gas by a continuous method by reacting steam and pulverized coal in a vertical, externally heated alloy tube, 25–12 Cr–Ni, 11 ft. long and 5 in. and 8¼ in. inside diameter, respectively, suspended in and passing through the furnace and heated externally by gas burners to approximately 2,100° and 1,850° F. Only noncoking coals were used successfully at varying feed rates. The rate of production of water gas was found to depend on temperature, rate of fuel feed, rate of stream supply, tube dimension, and chemical reactivity of the fuel. An empirical equation has been developed describing the effect of these variables on gas production. A new constant, called the gasification constant, is shown for measuring the inherent activity of a solid fuel toward reaction with steam. It is useful for comparing on a common basis the gasification characteristics of different fuels at 1 temperature or 1 fuel at different temperatures since it virtually eliminates the effect of different variables on the volume of gas produced. Use of the equation permits an estimate of the capacity of equipment of commercial size for the production of water gas. Estimates of the investment of the larger equipment indicate that these costs are sufficiently higher than those of modern conventional water-gas generators of equivalent capacity to discourage commercial application of the process under present economic conditions.

1075. FOULON, A. How Germany Is Synthesizing Soap Fats. Mfg. Perfumer, vol. 4, 1939, pp. 150–151; Chem. Abs., vol. 33, 1939, p. 9026.

Brief account of fatty acid synthesis by oxidation of paraffin wax and treatment of the oxidation product.

FOX, R. E. *See* abs. **2060.**

1076. FOXWELL, G. E. Fuel Utilization. Jour. Inst. Fuel, Wartime Bull., vol. 19, 1945, pp. 64–71, 81; Engineering, vol. 160, 1945, pp. 502–503.

Paper presented to the Scottish Section of the Institute of Fuel and the National Smoke Abatement Society gives full report of the Nonparty Technical Commission. For the part relating to the chemical derivatives of coal and the Fischer-Tropsch process (*see* abs. **2649**).

1077. FRACASSO, G. [Table for Equilibrium in the Synthetic Preparation of Methanol.] Industria chimica, vol. 9, 1934, pp. 293–299; Chem. Abs., vol. 28, 1934, p. 3972.

Equilibrium of the equations $CO+H_2 \rightleftharpoons H_2CO+H_2 \rightleftharpoons$ MeOH is calculated form the gas law $K=P_M/p_{CO}p^2_{H_2}$, p_M, p_{CO}, p_H being the partial pressures of MeOH, CO and H_2, respectively. Values of K cited in the literature are summarized, and a nomograph of the equilibrium conditions is constructed.

FRANCHETTI, P. *See* abs. **2554, 2555, 2556, 2557.**

1078. FRANCIS, A. W. Free Energies of Some Alcohols. Ind. Eng. Chem., vol. 20, 1928, pp. 283–284.

Equations have been derived for the free energies of formation of 9 alcohols. These have been simplified to linear equations for the range 227°–427°. A general equation for normal alcohols has been derived, and this has been compared with that for olefins to find conditions for dehydration or hydration of the olefins; and with that for CO to find conditions for synthesis.

1079. ———. Free Energies of Some Hydrocarbons. Ind. Eng. Chem., vol. 20, 1928, pp. 277–282; Chem. Abs., vol. 22, 1928, p. 1131.

From equations derived for the free energies of formation of CH_4, C_2H_6, octane, C_2H_4, C_2H_2, C_6H_6, PhMe, $C_{10}H_8$ and cyclohexane as functions of temperature it is shown that production of higher-paraffin hydrocarbons from lower ones is impossible, except with simultaneous production of still lower ones in at least equivalent amounts. The catalytic formation of C_2H_4 in more than traces is impossible. The direct removal of H from a paraffin to form an olefin with the same number of C atoms is possible only at high temperatures and to a very limited extent. Synthesis of gasoline from water gas can take place only below about 450°. Isomerization of olefins to naphthenes require temperatures below about 430°, while the production of aromatics requires 550°–900°. In the Fischer synthesis of gasoline $8CO+17H_2 \rightarrow C_8H_{18}+8H_2O$; $\Delta F=-338740+479.4T$, which is negative up to 700° K. or 427° C. The operating temperature for gasoline is 275°–300°. Higher temperatures give lower hydrocarbons, especially CH_4, as should be expected.

1080. FRANCIS, A. W., AND KLEINSCHMIDT, R. V. Applications of Thermodynamics to Chemical Reactions of Petroleum Products. Proc. Am. Petrol. Inst., 10th Ann. Meeting, vol. 11, sec. III, 1930, pp. 93–99; Chem. Abs., vol. 24, 1930, p. 2369.

It is shown that, per volume of water gas reacted, considering H_2 and CO as equivalent, formation of CO_2 is accompanied by the largest free-energy decrease, and of H_2O by the next-largest decrease. Of the hydrocarbons, CH_4 is formed with the largest free-energy decrease/volume of water gas reacted. MeOH formation is accompanied by the smallest decrease. However, formation of MeOH is accompanied by a larger decrease in volume than the formation of hydrocarbons from water gas, so that pressure may be used to direct the reaction to MeOH, as is done industrially in the presence of mixed oxide type catalysts. Although the most pronounced effect of pressure in changing the character of the product from hydrocarbons to O-containing compounds may be due to a shift in the equilibrium concentrations of the components, changes in specific reaction rates of the various reactions involved may be accountable.

1081. FRANK, F. [Technical and Economic Importance of Liquid Fuels.] Wärme, vol 54, 1931, pp. 438–441; Chem. Abs., vol. 25, 1931, p. 4380.

Application of various liquid fuels for motor and industrial use and for heating purposes is discussed, and reference is made to gaseous fuels and the domestic oil industry. Fuels for light- and heavy-oil motors, natural and synthetic benzine, benzene, spirits and fuel oil are considered.

FRANK, J. C. *See* abs. **1708.**

1081. FRANKENBURG, W. G. Adsorption of Hydrogen on Tungsten. I. Jour. Am. Chem. Soc., vol. 66, 1944, pp. 1827–1828; Chem. Abs., vol. 39, 1945, p. 451.

Data are given for the adsorption of H_2 on metallic W at equilibrium pressures between 1×10^{-5} and 30 mm. and at temperatures from —194° to 750°.

FRANKENBURGER, W. *See* abs. **224a.**

1082. FRANKFURTER ZEITUNG. [New Process for Producing Diesel Oil.] April 1939.

High-class diesel fuel is being made in Germany by blending coal oils from the carbonization of coal with high-boiling fractions of the product of the Fischer synthesis. A new blending plant is being operated at Homberg by the Rheinpreussen Co. The blends now on the market are characterized by a high degree of ignitibility coupled with a smokeless exhaust and are considered to be superior to mineral-oil products.

FRANTZUZ, E. *See* abs. **2774.**

FRANZ, H. *See* abs. **3058, 3060.**

1083. FRAZER, J. C. W. Eighth Report of the Committee on Contact Catalysis. Jour. Phys. Chem., vol. 34, 1930, pp. 2129–2179; Brennstoff-Chem., vol. 12, 1931, pp. 33–34; Chem. Abs., vol. 24, 1930, p. 5584.

General survey of the field, with a review of recent developments is given. Special organic reactions, such

as the synthesis of MeOH and the higher alcohols, the synthesis of petroleum by the Fischer-Tropsch process, and the hydrogenation of coal, as well as general hydrogenation and oxidation reactions, have received extended treatment.

1084. ———. Catalytic Oxidation of Carbon Monoxide. Jour. Phys. Chem. vol. 35, 1931, pp. 405–411; Chem. Abs., vol. 25, 1931, p. 1432.

Carefully purified, finely divided MnO_2, Co_2O_3, and Ni_2O_3 are extremely active catalysts for the union of CO and O_2 at temperatures as low as 0°. Extreme purity, not the presence of promoters, is important for catalytic activity. Impurities may be removed by electrolysis of an aqueous suspension of the oxides. None of 17 other unnamed oxides studied was effective. The 3 active oxides differ from the others in 1 significant particular, namely, their composition is indefinite. By an adsorption apparatus it was shown that the O_2 pressure in equilibrium with a sample of one of these oxides depends on the composition of the oxide. Condensation of water vapor within the pores of these oxides destroys their catalytic activity. Extreme drying does not destroy the activity.

1085. FREI, —. Catalytic Cracking of Products of the Fischer-Tropsch Synthesis Over Silicon–Aluminum Catalysts. TOM Reel 170, July 2, 1941, frames 410–414.

Low-molecular products are obtained on middle-oil fractions, boiling 210°–340°, while no cracking is possible on the heavy gasoline fractions. The yields and composition of end products are compared in charts. The heavy gasoline fraction can be converted into motor gasolines.

FREISS, W. *See* abs. **1991.**

FREMON, G. H. *See* abs. **2178.**

1086. FREUND, M. Properties of Natural and Synthetic Paraffinic Lubricating Oils. Petroleum (London), vol. 33, No. 48, 1937, pp. 1–5; British Chem. Abs., 1938, B, p. 131.

Three groups of products of high-pressure hydrogenation, solvent extraction, chemical synthesis (Fischer process); and conventional acid-earth refining were examined regarding properties dependent on mean molecular weight and H content. Each group consisted of oils of identical refractive index at 50°. The generalization connecting d with these properties holds satisfactorily, except for synthetic oils, which behave somewhat differently from other types.

1086a. ———. [Manufacture of Synthetic Lubricants by the Fischer-Tropsch and Other Processes.] Magyar Kém. Lapja, vol. 5, 1950, pp. 368–371.

Summary.

1087. FRICKE, R., AND ACKERMANN, P. [Heat Content and Lattice Structure of Active Ferric Oxide.] Ztschr. Elektrochem., vol. 40, 1934, pp. 630–640; Chem. Abs., vol. 29, 1935, p. 33.

The lower the temperature of dehydration of synthetic microcrystalline α-FeOOH, the greater is the energy content of the resulting α-Fe_2O_3; the energy differences as shown by heats of solution may reach 5 kcal. per mol. Fe_2O_3. Quantitative photometric measurements of x-ray powder photographs show imperfect lattice formation of the low-temperature Fe_2O_3, rather than differences in particle size or in lattice dimensions relative to the high-temperature Fe_2O_3. Tempering at 220° increases the lattice perfection of low-temperature Fe_2O_3 and restores its energy content to normal.

1088. FRICKE, R., WALTER, K., AND LOHRER, W. [Effect of the Physical State of the Solid Reactants on the Equilibrium Fe/Fe_3O_4 with H_2O/H_2.] Ztschr. Elektrochem., vol. 47, 1941, pp. 487–500; Chem. Abs., vol. 36, 1942, p. 4010.

Below 560°, Fe reacts with steam according to the binary equilibrium, $3Fe+4H_2O \rightleftharpoons Fe_3O_4+4H_2$; above 570°, FeO is first formed, and from this Fe_3O_4. The equilibrium was measured at a constant steam pressure, so that the only variable was the pressure of the H_2. Calorimetric data and specific heats indicate that at 525° the heat of reaction is greater for active Fe than for ordinary Fe by about 22.6 kcal. An x-ray examination of active Fe at 450° indicated an average particle size of 275 Å., and for inactive Fe 470 Å. The increase in the heat of reaction when active Fe is used is due to the increased heat content. Owing to large differences in the surface of the Fe particles, x-ray results are not sufficient to account for the large differences in the heat of reaction. This may be due to the fact that x-ray values are always average values, whereas only the more active particles are involved in equilibria.

1089. ———. [Effect of the Physical State of the Solid Reactants on the Equilibrium Fe/Fe_3O_4 with H_2O/H_2. Addendum.] Ztschr. Elektrochem., vol. 47, 1941, p. 811; Chem. Abs., vol. 36, 1942, p. 4010.

Instead of the value of 265.4 kcal. given in abs. **1088**, the authors propose the later value of 266.76 ± 0.22 kcal. by Roth and Wienert (abs. **2909**) for the heat of reaction.

FRIEDEL, R. A. *See* abs. **43, 43a, 49, 3645, 3646, 3651, 3656b, 3656c.**

1090. FRIEDEL, R. A., AND ANDERSON, R. B. Composition of Synthetic Liquid Fuels. I. Product Distribution and Analysis of C_5–C_8 Paraffin Isomers From Cobalt Catalyst. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 1212–1215, 2307.

Distribution of Fischer-Tropsch synthesis products has been given C_1–C_{20} for precipitated Co catalysts, using $H_2:CO=2:1$ at atmospheric pressure and 190°. Quantitative analysis of C_5–C_8 paraffin isomers by mass spectrometry showed only the presence of monomethyl isomers. The predominant components, the straight-chain isomers, decreased with increasing molecular weight. Approximate analyses of olefins showed that internal doublebond olefins were the major constituents. Preliminary results on Fe-catalyst products also are reported.

1091. FRIEDEL, R. A., AND SHARKEY, A. G. Analysis of Oxygenated Compounds by Mass Spectrometer. Anal. Chem., vol. 23, No. 4, 1951, p. 677.

Abstract of paper presented at the 2d Pittsburgh Conference on Analytical and Applied Spectroscopy. A liquid introduction system has been adapted for rapid vaporization of 0.0005-cc. samples of liquids into a mass-spectrometer vacuum system, with a reproducibility of about 1%. No sealing gaskets are required. Analysis of oxygenated compounds includes determination on dilute aqueous solutions of alcohol, ketone, and acid mixtures. Determinations on gas samples containing alcohols, aldehydes, and ketones from the oxidation of light hydrocarbons have been carried out. These mixtures are complicated by the expected secondary reactions between aldehydes and alcohols to produce acetals.

1091a. ———. Mass Spectrometry in Synthetic Fuels. Consolidated Eng. Corp. Recordings, vol. 5, No. 3, Sept. 1951, pp. 1, 5, and 10.

FRIEDERICHS, H. *See* abs. **167.**

1092. FRIEDWALD, M. [Status of the Synthesis of Hydrocarbons.] Rev. combust. liquides, vol. 12, 1934, pp. 277–281.

Discusses work of Fischer.

1093. ———. [Preparation of Liquid Motor Fuel From Carbon Monoxide and Hydrogen.] Rev. pétrolifère No. 634, 1935, pp. 733–735; Chem. Zentralb., 1935, II, p. 1290; Chem. Abs., vol. 29, 1935, p. 5626.

Results with a semi-large-scale plant are described; factors influencing yields, etc., are discussed as follows: Increase of pressure favors synthol production; of H_2 favors CH_4; decrease of H_2 favors olefins; increase of temperature favors CH_4 and C; catalysts increase the degree of saturation of the product in the order Fe, Co, Ni; presence of CO_2 is without influence; increase of life of catalyst gives an increase of light fraction and a decrease in oil content.

1094. ———. [Problems of Artificial Motor Fuels and Substitutes.] Ann. combust. liquides. vol. 13, 1935, pp. 247–251; Chem. Zentralb, 1936, I, p. 689.

General review of production of fuels by high- and low-temperature carbonization, pressure hydrogenation, and the Fischer-Tropsch process.

1094a. FRITSCHE, W. Water-Gas Equilibrium and Its Relation to Practical Gasification Processes. Brennstoff-Chem., vol. 3, 1950, pp. 337–350. Chem. Abs., vol. 45, 1951, p. 1,749.

1095. FROLICH, P. K. Role of Catalysts in High-Pressure Synthesis From Water Gas. Jour. Soc. Chem. Ind., vol. 47, 1928, pp. 173–179T; Chem. Abs., vol. 22, 1928, p. 3282.

High-pressure synthesis of NH_3 and of synthol is briefly discussed. The latter process is considered to be prohibitive from a commercial standpoint because of the complexity of the products obtained. These 2 applications of high-pressure technic have demonstrated the possibility of synthesizing the entire aliphatic range of compounds from the cheapest grade of coal and have stressed the necessity of bringing the reactions under control so as to obtain (1) 1 compound, (2) a limited number of single compounds or (3) a mixture of related compounds. The synthesis of any aliphatic compound is possible by studying intensively temperature, pressure and specific catalysts. The synthesis of alcohols by oxide catalysts is outlined, and it is shown that there is a very close relation between the decomposition and synthesis of CH_3OH.

1096. ———. Use of Metallic Oxides as Catalysts in Certain Organic Chemical Processes. Trans. Electrochem. Soc., vol. 71, 1937, pp. 313–331; Chem. Abs., vol. 31, 1937, p. 3372.

Specific illustrations indicate their extreme usefulness in the organic field. Their high degree of selectivity and their resistance to the ordinary catalyst poisons are outstanding characteristics. The results obtained in the studies of MeOH and higher alcohols are helpful in throwing light on the catalytic and general physical properties of this class of oxides. It was found that a definite relation exists between the synthesis of the alcohol from CO and H_2 at high pressure and its decomposition over the same catalyst combinations at atmospheric pressure. So close was the agreement between the two sets of observations that the simple and inexpensive decomposition method could be used for evaluating the usefulness of catalysts for the high pressure synthesis. It was also found that in the decomposition of MeOH, any mixture of 2 oxides (ZnO–CuO, ZnO–Cr_2O_3) had a synergistic effect, the addition of 3 mol. % ZnO to CuO increasing the rate approximately 3 times.

FROLICH, P. K. *See* abs. **1101, 1102, 2109, 2485.**

FROLICH, P. K., AND CRYDER, D. S. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. VI. Investigation of the Mechanism of Formation of Alcohols Higher Than Methanol. *See* abs. **1103.**

1097. FROLICH, P. K., AND LEWIS, W. K. Synthesis of Alcohols Higher Than Methanol From Carbon Monoxide and Hydrogen. Ind. Eng. Chem., vol. 20, 1928, pp. 354–359; Chem. Abs., vol. 22, 1928, p. 1755.

Steel or Cr-steel turnings impregnated with KOH was unsatisfactory, the loss as gaseous products varying from 30–70%. A low-Cr steel with a minimum of added alkali appeared the most effective. The highest oil yield obtained was 13.4%, and increase of oil yield was associated with increase of gas losses. In combination with a MeOH catalyst, gas losses were less, but only traces of oil were obtained, the product being a mixture of MeOH and higher alcohols. Metallic oxide catalysts, such as a mixture of ZnO, Cr_2O_3, and $Ba(OH)_2$ on Cu, which yield MeOH at 300°–350°, produced higher alcohols at 450°–500°. The best yield recorded, however, was 13.9%, chiefly PrOH. The loss was somewhat less than with Fe-alkali catalysts and the product was largely alcoholic in place of the complex mixture of alcohols, aldehydes, etc. obtained in the other case.

FROLICH, P. K., DAVIDSON, R. L., AND FENSKE, M. R. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. III. X-Ray Examination of Methyl Alcohol Catalysts Composed of Copper and Zinc. *See* abs. **1100.**

1098. FROLICH, P. K., FENSKE, M. R., AND QUIGGLE, D. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. I. Decomposition of Methanol by Catalysts Composed of Copper and Zinc. Ind. Eng. Chem., vol. 20, 1928, pp. 694–698; Chem. Abs., vol. 22, 1928, p. 3338.

Study of the catalytic decomposition of CH_3OH at 360° and 1 atm., with mixtures of ZnO and CuO in varying proportions, indicates that the maximum decomposition and formation of CO occur when the ZnO is present in excess. At 40–50 mol. % ZnO, the molecules CO formed per mol. CH_3OH increase about 350%. The addition of a small amount of ZnO to CuO very markedly increases the decomposition of CH_3OH. A catalyst consisting of 3 mols. % ZnO and 97% CuO decomposes 26% of the CH_3OH, while pure Cu decomposes only 9% under similar experimental conditions. A mixture containing 98.6 mols. % ZnO and 1.4 mols. % CuO decomposes 41% of the CH_3OH, whereas pure ZnO decomposes 33% under similar experimental conditions. Cu promoted with ZnO favors formation of $HCOOCH_3$, and CO formation is favored by ZnO promoted with Cu.

1099. FROLICH, P. K., FENSKE, M. R., TAYLOR, P. S., AND SOUTHWICK, C. A. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. II. Synthesis of Methanol With Catalysts Composed of Copper and Zinc. Ind. Eng. Chem., vol. 20, 1928, pp. 1327–1330; British Chem. Abs., 1929, A, p. 153; Chem. Abs., vol. 23, 1929, p. 816.

Data on the decomposition of MeOH by CuO–ZnO catalysts at atmospheric pressure have been correlated with experiments on MeOH synthesis at 204 atm., the same catalysts being used. The curves for "% of decomposed MeOH appearing as CO" vs. "composition of catalyst" are of the same shape as those representing "% of CO converted to MeOH" plotted against the same abscissas. Conclusion: The atmospheric pressure decomposition method of testing is eminently fitted for studies of the activity of catalysts for the MeOH synthesis from water gas at high pressure.

1100. FROLICH, P. K., DAVIDSON, R. L., AND FENSKE, M. R. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. III. X-Ray Examination of Methyl Alcohol Catalysts Composed of Copper and Zinc. Ind. Eng. Chem., vol. 21, 1929, pp. 109–111; Chem. Age, vol. 20, 1929, p. 187; British Chem. Abs., 1929, A, p. 406; Chem. Abs., vol. 23, 1929, p. 1342.

Zn oxide is partly reducible at 200°–220° in a stream of MeOH vapor, particularly when in admixture with Cu oxide. The exothermic reduction of the latter

oxide may furnish the necessary energy for the partial reduction of the Zn oxide. An attempt has been made to ascertain by X-ray examination if the Zn oxide is reduced to the metallic state. It has not been possible to prove the presence of metallic Zn, although there are indications that it is present. The complete series of Zn oxide—Cu catalysts studied (from pure oxide to pure Cu) all possess the characteristic crystal structure of the 2 components. The cell-unit sizes of both Cu and Zn oxide are markedly influenced by the presence of the other constituent. The selective activity of these catalysts appears to be related in some way to the distances separating the atoms of their constituents.

1101. CRYDER, D. S., AND FROLICH, P. K. Catalyst for the Formation of Alcohols From Carbon Monoxide and Hydrogen. IV. Decomposition and Synthesis of Methanol by Catalysts Composed of Zinc and Chromium Oxides. Ind. Eng. Chem., vol. 21, 1929, pp. 867–871; British Chem. Abs., 1929, B, p. 934; Chem. Abs., vol. 23, 1929, p. 5157.

Excess of Cr_2O_3 results in the formation of appreciable amounts of CO_2 and unsaturated hydrocarbons, while with an excess of ZnO in the catalyst, CO and H_2 are the main products formed, a sharp maximum occurring at a catalyst composition of approximately $Zn_{78}Cr_{22}$. The relatively constant % of HCHO formed indicates its intermediate formation in the decomposition of MeOH. Reversing the reaction, it is found that the production of MeOH from CO and H_2 parallels the formation of CO and H_2 in the decomposition experiments. The results demonstrate the suitability of the decomposition method as a criterion in the selection of catalysts for the high-pressure synthesis of MeOH. 7 graphs are shown.

1102. FENSKE, M. R., AND FROLICH, P. K. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. V. Decomposition and Synthesis of Methanol With a Zinc-Copper-Chromium Oxide Catalyst. Ind. Eng. Chem. vol. 21, 1929, pp. 1052–1055; British Chem. Abs. 1930, B, p. 49; Chem. Abs., vol. 24, 1930, p. 334.

Catalyst composed of the oxides of Cu, Zn, and Cr in the molal ratio of 49 : 43 : 8 has considerably higher activity for both the decomposition and the synthesis of MeOH than any of the binary systems Cu–Zn and Cr–Zn discussed in previous papers. With a space velocity of 25 cc. of gaseous MeOH per hr. per cc. of catalyst the catalyst showed marked activity even at 220° while at 285°, 90% of the MeOH was decomposed. At temperatures above 250° the decomposition was almost entirely into CO (33%) and H_2 (67%). Activity of the catalyst decreases gradually, but it can be restored by oxidation and subsequent reduction with MeOH vapor. The reduction of the catalyst with MeOH vapor is apparently preceded by decomposition of the MeOH into CO and H_2, and the reduction of the catalyst is due to the CO. In the synthesis of MeOH from CO and H_2 under high pressures, the conversions are high for this catalyst, and it is active at low temperatures.

1103. FROLICH, P. K., AND CRYDER, D. S. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. VI. Investigation of the Mechanism of Formation of Alcohols Higher Than Methanol. Ind. Eng. Chem., vol. 22, 1930, pp. 1051–1057; Chem. Abs., vol. 24, 1930, p. 5717.

Frolich and Cryder continue their study of the high-pressure synthesis of alcohols from mixtures of CO and H_2 (abs. **1100**). The mechanism of formation of alcohols higher than MeOH has been determined by studying the behavior of the individual compounds that might form as intermediates. With MeOH as an intermediate product the higher alcohols are formed by successive condensation of lower ones. The initial condensation of MeOH to EtOH controls the overall rate of this stepwise process: $2MeOH \rightarrow EtOH + H_2O$. The ease with which further condensation takes place accounts for the small amount of EtOH in the product. CO in excess aids in the formation of higher alcohols because it acts on the water vapor and removes it from the surface of the catalyst: $H_2O + CO \rightarrow CO_2 + H_2$. This reaction explains the presence of large amounts of CO_2 in the higher alcohol synthesis. Any acids formed are found as esters and these appear to be produced directly by polymerization of aldehydes rather than by the intermediate production of acids by addition of CO to MeOH.

1103a. NUSSBAUM, JR., R., AND FROLICH, P. K. Catalysts for Formation of Alcohol From Carbon Monoxide and Hydrogen. VII. Studies of Reduction of Methanol Catalyst. Ind. Eng. Chem., vol. 23, 1931, pp. 1386–1389; Chem. Abs., vol. 26, 1932, p. 1503.

Samples of a MeOH catalyst containing 58.3 mol. % ZnO and 41.7 mol. % CuO were reduced at progressively higher temperatures. The activity as measured by the decomposition of MeOH slowly increased as the temperature of reduction rose until a certain point was reached after which any rise in temperature caused a rapid decline in the effectiveness of the catalyst. The percentage of CO in the decomposition products followed the catalytic activity, whereas the percentage of HCHO followed a curve which was the reverse of the activity of the catalyst. The catalyst was found by X-ray examination to be crystalline for all temperatures of reduction. The CuO was found to be reduced to Cu having a unit cell size of 3.634 Å. U. This corresponds to α-brass containing 13% Zn. A shorter period of reduction was found partly to offset the lessened catalytic activity due to sintering. Reoxidation of the catalyst stimulated its activity temporarily, but the increased activity rapidly fell. O_2 added along with MeOH stabilized the rate of decomposition, the O_2 reacting with the CO to form CO_2.

1104. FROLICH, P. K., FENSKE, M. R., AND QUIGGLE, D. Studies of Copper Catalysts Prepared From Precipitated Hydroxides. I. Activity as a Function of the Temperature of Precipitation. Jour. Am. Chem. Soc., vol. 51, 1929, pp. 61–65; Chem. Abs., vol. 23, 1929, p. 1342.

Activity for the decomposition of CH_3OH of Cu catalysts prepared from the NH_3 precipitated hydrates varied markedly with the temperature of precipitation. A maximum in activity was observed with catalysts precipitated at about 22°. X-ray examination of the dried gels before reduction indicated that the activity was associated with small particle size. The maximum of the activity curve may have been the result of 2 opposing factors: (1) the tendency for the initial particle size to decrease with decreasing temperature of precipitation; and (2) the tendency for the initially formed particles to grow while drying at 110°.

1105. FROLICH, P. K., FENSKE, M. R., PERRY, L. R., AND HURD, N. L. Studies of Copper Catalysts Prepared From Precipitated Hydroxides. II. Comparison of Sodium Hydroxide and Ammonia as Precipitating Agent. Jour. Am. Chem. Soc., vol. 51, 1929, pp. 187–193; Chem. Abs., vol. 23, 1929, p. 1342.

Cu catalysts prepared by precipitation with NaOH are more active in the decomposition of CH_3OH than those precipitated with NH_3. The difference is due to promoter action of the occluded Na salts. The NaOH-precipitated catalysts, like other promoted Cu catalysts, favor $HCOOCH_3$ rather than HCOOH production from CH_3OH.

FROLICH, P. K., FENSKE, M. R., TAYLOR, P. S., AND SOUTHWICK, C. A. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. II. Synthesis of Methanol With Catalysts Composed of Copper and Zinc. *See* abs. **1099.**

1106. FROST, A. V. [Thermodynamics of the Synthesis of Methanol From Water Gas.] Jour. Gen. Chem. (U. S. S. R.), vol. 1, 1931, pp. 367–376; Chem. Abs., vol. 26, 1932, p. 3987.

Free energy of the reaction $CO+2H_2 \rightleftarrows MeOH$ is $-\Delta F/4.573T=\log K(RT)^2=3925/T-9.840 \log T+0.00347T+14.8$. The value calculated on the basis of Nernst's heat theorem differs from the experimental value by $+1.04=0.4$, while for other reactions the discrepancy is, according to Eucken and Fried's figures, +0.9.

———. *See* abs. **1584, 2169.**

1107. FROST, A. V., IVANNIKOV, P. Y., SHAPIRO, M. I., AND ZOLOTOV, M. N. [Structure and Genesis of Methanol Catalysts.] Acta physicochim. U. R. S. S., vol. 1, 1934, pp. 511–520; Chem. Abs., vol. 29, 1935, p. 6711.

With various Zn–Cu catalysts under the experimental conditions of Frolich and others (abs. **1100**), the composition of the reaction products changed at 369° as observed by them. At 305° and 337° the composition of the products was quite different. The activity of the catalysts decreased only very slowly. Lattice dimensions did not change with the composition of the catalyst, $c=5.198\pm0.004$ A. and $c/a=1.602\pm0.002$. Microscopic and x-ray determination of various preparations of ZnO showed that the crystal size changed from 0.8×10^{-4} to 4.5×10^{-4} cm. on changing the 3-hr. annealing temperature from 110° to 1,300°, and that the adsorptive capacity toward methylene blue was approximately inversely proportional to the crystal size, while the catalytic activity fell still more rapidly. A study of $ZnO\cdot Cr_2O_3$ catalysts in the ratios 3.2 : 1 and 1 : 1 obtained, respectively, by joint precipitation and by simple mixing, showed that the size of the crystal of the 1st was always about ¼ that of pure ZnO crystals, while the latter always gave the same size, 0.9 μ, as for pure Cr_2O_3 on annealing at any temperature above 110°. X-ray analysis showed spinel formation. The catalytic activity decreased rapidly as the annealing temperature was raised with ZnO, 3.2 $ZnO\cdot CrO_3$ and $ZnO\cdot Cr_2O_3$ but was constant for pure Cr_2O_3, except above 900°. For a given treatment 3.2 $ZnO\cdot Cr_2O_3$ was always more active catalytically, as measured by MeOH decomposition, than pure ZnO. The greatest difference was obtained about 100° below the temperature of rapid spinel formation and was attributed to the production of distortions or "Lockerstellen" later stabilized into the crystal.

1108. FRY, A. [Steels for Oil-Cracking Tubes and Hydrogenation Vessels.] Oel u. Kohle, vol. 1, 1933, pp. 184–188; British Chem. Abs., 1934, B, p. 763.

In the production of steels for hydrogenating vessels, methods are used, that is, addition of 6% of Cr or V, followed preferably by special annealing, which bind the C so that it resists reduction by the H_2 under the operating conditions; the further addition of Mo to the steel improves its durability.

1109. FRYDLENDER, J. H. [Manufacture of Synthetic Methanol From Methane.] Rev. prod. chim., vol. 28, 1925, pp. 433–440, 469–476; Chem. Abs., vol. 19, 1925, p. 2928.

Review.

FRYE, C. G. *See* abs. **3642a.**

1110. FUCHS, W., AND DAUR, R. [Synthesis of Higher Hydrocarbons From Methane and Carbon Monoxide.] Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 327–329; Chem. Zentralb., 1934, II, p. 1062; Chem. Abs., vol. 29, 1935, p. 6566.

A 2 : 1 mixture of CH_4 and CO at 1 atm. when passed over glowing pumice yields some propylene. Experiments at 500°–550° under a pressure of 240 atm. yielded propylene and also liquid hydrocarbons, but the yield was slight.

1111. FUCHS, W. M. When the Oil Wells Run Dry. Ind. Research Service, Dover, N. H., 1946, 447 pp.; Man-Made Petroleum, chap. VI, pp. 324–392.

Integrated picture of the subject of oil, written for the average citizen in an easily readable and generally understandable manner. Gives a short account of the Bergius and Fischer-Tropsch processes, and the entrance of the United States Government into synthetic fuel production.

1112. FUEL. Catalysts for the Fischer-Tropsch Synthesis. Vol. 25, 1946, p. 123.

Brief notes from CIOS Reports XXV–1, PB 284; XXV–27, PB 289, 890; XXVII–69, PB 415. (*See* abs. **1302, 701, 1327.**)

1113. ———. Synthetic Liquid Fuels in the United States. Vol. 25, 1946, pp. 134–137.

Comprehensive summary of the Report of the United States Secretary of the Interior on the Synthetic Liquid Fuels Act covering 1945. A progress report covers investigations already made in coal hydrogenation, liquid fuels from water gas by the Fischer-Tropsch synthesis, synthesis-gas production, oil-shale research, and the production of fuels from agricultural residues.

1114. FUEL ECONOMIST. Hydrocarbons From Water Gas. Vol. 9, 1934, p. 303.

It is stated that a plant of semicommercial dimensions is to be erected at Sterkrade-Holten in the Ruhr district at a cost of several million marks, for producing liquid hydrocarbons by the Fischer-Tropsch process. It is expected that erection of the plant will be financed by the Ruhrchemie A.-G., which has already carried out some preliminary work on the process. The plant will have a capacity for producing about 1,000 tons of synthetic motor fuel/yr., as well as lubricating oils and rich hydrocarbon gases which it is proposed to utilize as motor fuel in compressed form in cylinders. The process is based entirely on coal, for the gas used as raw material will be generated from coke. It is suggested that this process will successfully compete with that of the I. G. Farbenindustrie A.-G., whose production costs are said to be about 20 pf./l. of motor fuel produced.

1115. ———. Synthetic Lubricating Oil. Vol. 12, 1936, pp. 113–114.

Summary of status of the research work being conducted at the Fuel Research Station, England. The production of hydrocarbons from water gas by the Fischer synthesis is mentioned.

1116. FUJIMOTO, H. Catalytic Action of Reduced Nickel on the Methane-Water Reaction. Jour. Soc. Chem. Ind., Japan, vol. 36, Suppl., 1933, pp. 147–148; Chem. Abs., vol. 27, 1933, p. 3661.

Study of the reactions $CH_4+H_2O=CO+3H_2$; $CH_4+2H_2O=CO_2+4H_2$ (1) and $CH_4=C+2H_2$ (2) at temperatures 400°–1,000° in the presence of reduced Ni reveals that (1) and (2) begin at about 400° and 700°, respectively, with the reaction velocity of (2) increasing with temperature, while that of (1) passes a maximum at 600° and a minimum at 800°, probably because of the effect of CO on the catalyst. Reaction (2) is accelerated at lower temperatures by adding 10% Al to the catalyst, and reaction (1) is not accelerated but the maximum and minimum are avoided. With 6 times as much H_2O as CH_4, the CO_2 : CO ratio is 2 : 1, while with 2.5 times as much H_2O it is 8 : 1 (700°), and the life of the catalyst is prolonged (250 hr. at 700°).

FUJIMURA, K. Catalytic Reduction of Carbon Monoxide at Ordinary Pressure. VIII. Iron–Copper Catalyst. *See* abs. **1846.**

———. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. IX. Additional Tests With a Co–Cu–MgO Catalyst. *See* abs. **1847.**

———. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. X. Influence of Certain Materials on the Catalytic Action of Cobalt-Copper-Magnesium Oxide Catalysts. *See* abs. **1848.**

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressures. XI. *See* abs. **1849.**

———. *See* abs. **1845.**

FUJIMURA, K., AND TSUNEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressures. XII. *See* abs. **1850.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressures. XIII, XIV. Nickel Catalysts. *See* abs. **1851.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressures. XV, XVI. Nickel catalysts. *See* abs. **1852.**

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen Under Ordinary Pressure. XVII. General Properties and Chemical Composition of the Reaction Products. *See* abs. **1853.**

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen Under Ordinary Pressure. XIX. Composition of the Initial Gas Mixture (1). *See* abs. **1855.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen Under Ordinary Pressure. XX. Composition of the Initial Gas Mixture (2). *See* abs. **1856.**

FUJIMURA, K., TSUNEOKA, S., AND KAWAMICHI, K. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XVIII. Effect of Sulfur Compounds on the Nickel Catalyzers. *See* abs. **1854.**

FUJISAKI, T. *See* abs. **3177, 3178.**

FUJITA, H. *See* abs. **1913.**

FUJITA, K. *See* abs. **1892, 1915, 1916, 1917, 1918, 1919, 1920, 1921, 1922, 1923, 1924, 1925, 1926.**

FUJITA, T. *See* abs. **1908.**

FUKUSHIMA, I. *See* abs. **1927, 1928, 1929.**

FUKUSHIMA, R. *See* abs. **1118, 1119, 1120.**

FUNABASHI, W. *See* abs. **1930.**

1117. FUNASAKA, W. [Removal of Sulfur From Gases to Be Used for Synthetic Gasoline.] Chem. Rev., Japan, vol. 3, 1937, pp. 368–386; Chem. Abs., vol. 32, 1938, p. 9464.

Review with 86 refs.

———. Benzine Synthesis From Carbon Monoxide and Hydrogen. L. Removal of Organic Sulful Compounds From Water Gas. *See* abs. **1886.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen. LI. Highly Active Sulfur-Fixation Agent Which Purifies Water Gas to the Highest Degree of Comparatively Low Temperatures Such as 200°–250°. *See* abs. **1887.**

———. *See* abs. **1878, 1879, 3466, 3467, 3468.**

1118. FUNASAKA, W., AND FUKUSHIMA, R. Removal of Organic Sulfur Compounds From Gas Mixtures for Synthesis. X. Influence of Impurities on the Purification of Industrial Gases. Jour. Soc. Chem. Ind. (Japan), vol. 50, 1947, pp. 122–124; Chem. Abs., vol. 44, 1950, p. 9136.

Studies were made on the influence of various gases on the removal of organic S compounds from industrial gases. C_2H_4 had a deleterious effect on Fe and Al catalysts but not on Ni and Cu at 250°. At 400° no effect was detectable. C_6H_6 had no effect, while C_2H_2 had a deleterious effect. Acidic gases, such as CO_2 or HCN, transformed CS_2 to H_2S, especially at high temperature. A high CO_2 content had a deleterious effect at high temperatures. HCN also had a deleterious effect. Air, N_2, and water vapor gave good results. Superimposed effects of various impurities were complicated.

1119. FUNASAKA, W., FUKUSHIMA, R., JINTA, T., MATSUBARA, I., AND YUGUCHI, M. Removal of Organic Sulfur Compounds From Gas Mixtures for Synthesis. XI. Removal of Carbon Disulfide and Thiophene From Water Gas and Natural Gas. Jour. Soc. Chem. Ind. (Japan), vol. 50, 1947, pp. 124–125; Chem. Abs., vol. 44, 1950, p. 9136.

CS_2 could be removed by Ni, Cu, and Sn catalysts and thiophene by Fe, Ni, Cu, Mn, Cr, Al, and Mg. With Cr as a catalyst, H_2 was formed.

1120. FUNASAKA, W., FUKUSHIMA, R., JINTA, T., INABA, T., MATSUBARA, I., AND YUGUCHI, M. Removal of Organic Sulfur Compounds From Gas Mixtures for Synthesis. XII. Removal of Ethyl Mercaptan and Ethyl Sulfide From Hydrogen, Natural Gas and Cracking Gas. Jour. Soc. Chem. Ind. (Japan), vol. 50, 1947, pp. 125–126; Chem. Abs., vol. 44, 1950, p. 9136.

EtSH could be removed easily, Et_2S with difficulty. Fe, Ni, Cu, Mn, Cr, Al, and Mg catalysts were suitable for EtSH and Cu and Ni for Et_2S. Et_2S gave H_2S with Cr and Al catalysts.

FUNASAKA, W., AND KATAYAMA, I. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLIV. Purification of the Gaseous Raw Material Used for Benzine Synthesis. 3. Removal of Organic Sulfur by Means of Luxmasse and Admixtures. *See* abs. **1880.**

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLV. Purification of the Gaseous Raw Material Used for Benzine Synthesis. 4. Removal of Organic Sulfur by Means of Synthetic Agents. *See* abs. **1881.**

FUNASAKA, W., AND TOJO, T. Synthesis of Gasoline From Carbon Monoxide and Hydrogen. LXVII. Desulfurizing Ability of Various Metal Hydroxides. *See* abs. **1903.**

FUNASAKA, W., FUKUSHIMA, R., JINTA, T., MATSUBARA, I., AND YUGUCHI, M. Removal of Organic Sulfur Compounds From Gas Mixtures for Synthesis. XI. Removal of Carbon Disulfide and Thiophene From Water Gas and Natural Gas. *See* abs. **1119.**

FUNASAKA, W., FUKUSHIMA, R., JINTA, T., INABA, T., MATSUBARA, I., AND YUGUCHI, H. Removal of Organic Sulfur Compounds From Gas Mixtures for Synthesis. XII. Removal of Ethyl Mercaptan and Ethyl Sulfide From Hydrogen, Natural Gas, and Cracking Gas. *See* abs. **1120.**

1121. FURNAS, C. C., AND BROWN, G. G. Equilibria in the Reduction of Ferric Oxide. Ind. Eng. Chem., vol. 20, 1928, pp. 507–510; Chem. Abs., vol. 22, 1928, p. 2099.

New thermal data on Fe_2O_3 have been used with other data in the literature to compute, by means of the 3d law of thermodynamics the equilibrium constants of 7 reactions involved in the reduction of Fe_2O_3 by CO, C and H_2, and one for the decomposition of Fe_2O_3 into Fe_3O_4 and O_2. Such values of K (equilibrium constant) are given for 100°, 250°, 500°, and 750° based upon actual measurable data, and for 1,000° and 1,500° upon extrapolation data. It is shown that (*a*) reduction of Fe_2O_3 by CO and Fe_2O_3 to Fe_3O_4 by H_2 takes place readily at lower temperatures; (*b*) reduction of Fe_2O_3 by C will not occur to any great extent at low temperatures, but the possibility of such reduction with higher temperatures becomes increasingly greater, a conclusion in harmony with experimental evidence but contrary to popular

belief (if the gaseous phase is absent no reduction occurs except at high temperatures); (*c*) reduction of Fe_2O_3 by H_2 shows that the power of superheated steam to oxidize metallic Fe decreases with temperature, while its ability to oxidize Fe_3O_4 increases with the temperature; (*d*) data for the decomposition of Fe_2O_3 to Fe_3O_4 and O_2 are not conclusive, but in general the *K* are lower for 1,000° and 1,500° than the experimental work justifies. Inconsistencies are ascribed to the variations in solid phases used. The existence of solid solutions rather than intermediate compounds in the series FeO, Fe_3O_4, Fe_2O_3 may be assumed. Graphs and tables give much condensed information on the matter treated above.

1122. FURNESS, R. Synthetic Motor Fuels. Ind. Chemist, vol. 1, 1925, pp. 475–480; Chem. Abs., vol. 20, 1926, p. 653.

From the point of view of cost of production in competition with gasoline as motor fuel, the author discusses at some length the following processes: (1) Alcohol by fermentation, (2) synthetic CH_3OH, (3) CH_3OH from CH_4, (4) synthol, (5) synthetic C_6H_6, (6) synthetic C_2H_5OH from C_2H_4, (7) the same from carbide. Much information regarding conditions, yields, and costs for each of the above is given. Gasoline will continue to dominate the liquid-motor-fuel market for such time as its present price is maintained. Synthetic CH_3OH and liquid fuels produced by some simple, catalytic gas reactions are its most likely competitors. Fermentation alcohol, synthetic C_2H_5OH (either from C_2H_2 or C_2H_4), and synthetic C_6H_6 cannot hope to compete with gasoline.

1123. ———. Oils, Fats, and Soaps Industries in 1938. Ind. Chemist, vol. 15, 1939, pp. 37–39, 83–84.

Refers to the German work on the production of fatty acids from hydrocarbons by the Fischer-Tropsch method and their subsequent oxidation to soaps and fats. These processes have little practical significance to the British manufacturer. They are too costly and too complicated to be commercially attractive.

1124. FURTH, A. AND MUNDERLOH, H. Braunkohle und ihre Chemische Verwendung. Theodor Steinkopff, Dresden; Iron and Coal Trades Rev., vol. 163, Aug. 10, 1951, p. 310.

Statistical data and a summary of the theories concerning the origin of brown coal and the structure of the derivatives are first presented followed by a description of low-temperature carbonization of brown coal. The most significant recent development is the introduction of the Lurgi furnace with forced gas circulation and electrostatic tar precipitation. All pertinent patent specifications are reviewed. Gas scrubbing methods for the production of light fractions of oils are presented together with methods for the utilization of brown coal coke. Gas producers are unable to utilize raw brown coal, the moisture content of which is 50–55%, but several types of producers fed with brown-coal briquets are included. Distillation of the tar for production of benzol, diesel fuel, lubricating oil, fuel oil, paraffin wax and pitch, and the solvent extraction and cracking of tar are described. The various processes for the production of synthetic fuel, including the Fischer-Tropsch hydrogenation process, as applied to brown coal are considered. A summary of the patent literature and a description of the drying and briquetting processes complete the book.

1125. FUSSTEIG, R. [Gasoline From Coal.] Mat. grasses, vol. 25, 1933, pp. 9810–9811; Chem. Zentralb., 1933, II, p. 1951.

Review of development of coal liquefaction, Bergius process, Fischer-Tropsch process, and hydrogenation according to Sabatier, with special reference to the problem of catalysts.

1126. ———. [New Methods for the Production of Automobile Gasoline With Coal as the Raw Material.] Mat. grasses, vol. 25, 1933, pp. 9863–9868; Chem. Zentralb., 1934, I, p. 980.

Discusses Bergius process and conversion of water gas.

1127. ———. Synthesis of Lubricating Oil by Polymerization of Gaseous Hydrocarbons. Petrol. Eng., vol. 9, Feb. 1938, pp. 120, 123, 124, 127.

1128. ———. Synthesis of Petroleumlike Hydrocarbons From Carbonaceous Material. Petrol. Eng., vol. 11, No. 8, 1940, pp. 95–96, 98, 100; Chem. Abs., vol. 34, 1940, p. 7086.

Discusses fundamental principles of the Fischer synthesis and the allied processes with emphasis on the production of the starting material, water gas. The efficiency of the Fischer synthesis centers upon the control of reaction conditions, especially the ratio of $CO:H_2$, pressure, and temperature. Mentions effects of changes in reaction conditions, especially on quality of product. A flowsheet is given of the Fischer process combined with true vapor-phase cracking, and typical yields are tabulated. The necessity for the desulfurization of the starting gases is stressed, the maximum permissible S content being given as 2 mg. per $m.^3$ Catalytic desulfurization with alkali-activated Fe oxide is briefly outlined. Paraffin wax can also be synthesized by the Fischer process. A 2-stage synthesis in which the catalyst temperature is kept 5°–10° higher in the 2d stage than in the 1st is claimed to increase the yield of hydrocarbons from 110 to 125–130 gm. per $m.^3$ gases.

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1129. GALL, D. Production of Lubricating Oils From the Olefins Produced in the Fischer-Tropsch Synthesis. Jour. Soc. Chem. Ind., vol. 65, 1946, pp. 185–189; Chem. Abs., vol. 40, 1946, p. 7582.

Preparation of lubricating oils by polymerization with $AlCl_3$ of the olefins present in the primary product obtained by synthesis from CO and H_2 (1:2) over a Co catalyst at atmospheric pressure has been carried out in 2-gal. batches. The effect of varying the temperature, catalyst, and boiling range of the starting material on the reaction and its products is described. Two fractions b. 40°–140° and 140°–210°, with 8.6 and 28% by weight, respectively, of olefins were polymerized at the reflux point to a material apparently above the original boiling range. The yield of lubricating oil of similar viscosity is much lower from the higher-boiling fraction; this is due partly to the relatively higher proportion of olefins which are lost as $AlCl_3$ complex and partly to a tendency of the olefins of higher molecular weight to give oils of lower viscosity, so that these have to be topped to a higher initial boiling point to give the same viscosity as the polymers from the lower olefins. The use of higher olefins gives a lubricating-oil fraction of higher viscosity index, but there appears to be little difference in the other properties tested. Investigations on the effect of varying the reaction temperature and the proportion of catalyst with the 40°–140° fraction were made. It was found that increasing the proportion of catalyst increases the reaction velocity and the viscosity of the product but lowers the yield, whereas increasing the temperature increases the rate of reaction but decreases both the yield and the viscosity of the lubricating-oil fraction but has little effect on the viscosity index. The oils obtained possess properties which approximate the requirements of Air Ministry Spec. D. T. D. 109 for aircraft lubricants in

all respects except the increase in viscosity on oxidation. It was found possible to overcome this disability by subjecting the oils to a carefully controlled hydrogenation in the presence of MoS_2 at 200° and 200 atm. H_2 pressure, using 20% by weight of catalyst calculated on the oil charged.

1130. ———. Characteristics of Fischer-Tropsch Waxes. Inst. Petrol. Rev., vol. 1, Oct. 1947, pp. 336–337.

The mixture of aliphatic hydrocarbons produced by the Fischer-Tropsch process ranges from CH_4 to solid waxes. The boiling range of the individual products varies with the reaction conditions and the catalyst. Wax production is favored by increase in pressure and by catalysts in the order of Co, Fe, Ru. The Ruhrchemie prepared soft, block, and hard waxes from the medium-pressure synthesis product, the fraction boiling above 320° being divided by distillation in vacuo into a residue boiling above 460° at 760 mm., which constituted the hard wax, and two distillates, from which the soft and block waxes were obtained by sweating. Similar low-melting waxes can be prepared from the atmospheric pressure product. No data are available for comparison of the Fischer-Tropsch waxes with natural hydrocarbon waxes in respect of properties such as solvent retentivity, tensile strength, solubility, viscosity, etc. It is known, however, that the soft and block waxes are closely similar to the corresponding petroleum paraffin waxes. The value of the high-melting waxes is not so readily assessed, and from what is known of their structure it is doubtful if they are adequate substitutes for natural waxes of high-melting point and hardness.

———. *See* abs. **671, 675, 1334, 1335, 1335a, 1336.**

1131. Gall, D., and Hall, C. C. Production of Fatty Acids by the Oxidation of Fischer-Tropsch Waxes. Fuel, vol. 27, No. 5, 1948, pp. 155–167.

A study has been made of the effects of temperature, time, rate and distribution of air stream, nature and amount of catalyst, composition of raw material, and recirculation of nonacidic products, on the reaction rate and the yield and properties of the fatty acids obtained by the liquid-phase oxidation of the high-boiling fractions of Fischer-Tropsch primary products. The rate of air flow has a comparatively small effect on the reaction velocity although an optimum rate can be found. It is desirable to distribute the air stream over the whole cross-sectional area of the reaction tube, but increase in the fineness of subdivision over that afforded by coarse, sintered glass has no favorable effect. The velocity of oxidation increases with increase in the reaction temperature over the range 100°–140°, but at the lower temperatures acids of higher quality are obtained. Optimum results were obtained by oxidizing a mixture of approximately equal proportions of the saturated fraction of boiling range 300°–375° and unsaponifiable material from a previous oxidation to a final saponification number of 150, by passing 16.5 l of air per 100 gm. raw material at 110°, in the presence of an oil-soluble Mn catalyst. Compounds of Mn are preferable to those of Co, giving a higher reaction velocity and products of good quality. The efficiency of the catalyst depends upon its solubility in the reaction mixture. By returning the unsaponifiable material formed to a subsequent oxidation, it is possible to obtain over 90% conversion of wax to fatty acids, with the advantages of a higher reaction velocity and a better quality C_{10}–C_{20} acids than are obtained when wax is oxidized alone. Using this technique a 50–70% conversion is possible. The maximum space-time output of these acids is obtained by oxidizing a mixture of approximately equal proportions of wax and recovered unsaponifiable material. The acids in the range C_{10}–C_{20} give good soaps, which, however, are unsuitable for toilet purposes because of the unpleasant odor left on the skin.

1131a. Gall, D., Gibson, E. J., and Hall, C. C. Distribution of Alcohols in the Products of the Fischer-Tropsch Synthesis. Proc. Pure Applied Chem., 12th Internat. Cong., Sept. 1951; Jour. Appl. Chem. (U. S. S. R.), vol. 2, 1952, pp. 371–380.

Alcohol-rich product obtained by Fischer-Tropsch synthesis at 160°–175° and 150 p. s. i. g. in the presence of a Co catalyst has been examined. It was found that *n*-primary alcohols constituted 40 wt. % of the organic liquid products and 92.4% of the total oxygenated products. The proportions of acids and carbonyl compounds were, therefore, markedly lower than those reported to be present in an Fe-catalyst product of the hydrocol type. The proportion of MeOH present was very low, EtOH was present in the largest proportion and the proportions of alcohols higher than PrOH decreased with increasing C number. The proportion of PrOH was less than that of BuOH or AmOH so that the C-number distribution curve for the alcohols showed a marked inflexion in the C_3–C_4 region, which is not shown by the published distribution curve for the alcohols in the hydrocol product. From a study of the relative rates of decomposition of a series of *n*-primary alcohols at 150° in the presence of H_2 and a Co catalyst, it was possible to plot a curve relating alcohol stability and C number. This curve resembled the distribution curve in showing a low value for C_1, a maximum at C_2 and a marked inflexion in the C_3–C_4 region, suggesting that the individual alcohols are present in the synthesis products in proportions which are determined, at least in part, by their relative stabilities under the synthesis conditions. It is considered that the alcohol distribution curve is of a form which would be predicted if the mechanism of alcohol formation involved stepwise addition of methylene radicals to 1 end of a growing chain terminated by a hydroxymethylene radical, and if the survival of the alcohols was controlled by their relative stabilities. It is concluded that there is a balance of evidence in favor of the view that alcohols are the precursors of hydrocarbons in the synthesis.

1132. Galle, E. [Motor Fuel From Czechoslovak Coal.] Montan. Rundschau, vol. 29, No. 6, 1937, pp. 1–7; Petrol. Ztschr. vol. 33, No. 10, 1937, p. 4; Chem. Zentralb., I, 1937, p. 3902.

Reviews the various processes for the production of motor fuels and the possibilities of their use in Czechoslovakia. Economically, the facts appear to favor the Bergius process over the Fischer process.

1133. ———. [Chemical Possibilities for the Production of Motor Fuels.] Montan. Rundschau, vol. 30, 1938, No. 15, pp. 1–8; No. 16, pp. 1–4; Chem. Abs., vol. 32, 1938, p. 8739.

After a description of production of oil and gasoline from coal by the Fischer process, the Bergius hydrogenation process and the synthesis of MeOH from coke, details are given of high-pressure hydrogenation and of the Fischer-Tropsch gasoline synthesis. Gasoline obtained by high-pressure hydrogenation has octane numbers of 70–75, and by special treatment octane values of 80–90 can be obtained. The Fischer-Tropsch process yields gasolines with 45–50 octane values, and by special treatment this can be raised to 60–62.

1134. ———. [Production of Liquid Fuels by Chemical Methods.] Petrol. Ztschr., vol. 34, No. 19, 1938, pp. 1–12.

Reviews development of the coal-hydrogenation and Fischer-Tropsch processes.

Gallissot, M. *See* abs. **2273.**

1135. Gallo, G. and Correlli, R. [Synthetic Production of Liquid Fuels.] Atti cong. nazl. chim. pura applicata, 1923, p. 257; Chem. Abs., vol. 18, 1924, p. 2594.

Preliminary work is described on the cracking of vegetable oils by a method similar to that used by Mailhe for obtaining petroleum products from such oils. The vegetable oil is decomposed by superheated steam in the presence of an alkaline earth, the products are led in the vapor state over pumice stone containing FeO at 550°–560° and the new products passed over pumice stone containing Ni at 200°–250° where hydrogenation is carried out. The FeO remains unaltered on account of the oxidizing action of the H_2O and simultaneous reducing action of the oil vapor. A gaseous product of the following percentage composition was obtained: CO_2 4.2, heavy hydrocarbons 33.5, CO 3.7, saturated hydrocarbons 43.4, H_2 15.2. A yellowish brown, slightly fluorescent, mobile liquid was also recovered with a yield of 60.65% of the original oil, an aromatic odor, 0.5% acidity, calculated as oleic acid, saponifiable 0.46%, giving in large part nitro derivatives with HNO_3–H_2SO_4 mixture and yielding in percentage on fractional distillation: 45°–200°, 24.5; 200°–300°, 41; 300°–350°, 29.5; tar residue 5%.

GALLOWAY, A. E. *See* abs. **373, 374, 375.**

1136. GALT, J. K., MATTHIAS, B. T., AND REMEIKA, J. P. Properties of Single Crystals of Nickel Ferrite. Physiol. Rev., vol. 79, 1950, pp. 391–392; Chem. Abs., vol. 44, 1950, p. 8712.

Mixture of 16–17 gm. borax glass, 6.4 gm. Fe_2O_3, and 3.0 gm. NiO was heated in Pt to 1,330°, held there 10–12 hr., and cooled $\approx$ 2°/hr. for 25–40 hr.; the furnace was then turned off completely. Crystals of $NiFe_2O_4$ up to 2 mm. on a side, with impurities $<0.5\%$, were obtained. The dielectric constant, the saturation magnetization, the magnetic anisotropy constant K_1, and the complex initial permeability were measured.

1137. GANDINI, A. [Analytical Examination of Two New Methods for the Reduction of Iron Ores by Carbon Monoxide and Their Relation to the Iron-Ore and Fuel Resources of Italy.] Atti cong. nazl. chim. ind., 1924, pp. 311–329; Chem. Abs., vol. 19, 1925, p. 1394.

Most promising methods for the reduction of Fe ore are those involving the production of CO and direct reduction by the latter, particularly that of Bourcoud and the newly developed process of Gandini. The Bourcoud process is described in detail, with a general discussion of the physical chemistry involved in the reduction of Fe oxides by CO. The velocity of this reduction and the yield of Fe at a given temperature are shown to be functions of the pressure and concentration of the CO, of the square root of its kinetic energy at the moment of impact with the oxides, of the absolute number of CO molecules, and of the degree of subdivision of the Fe ore.

1138. GANSWINDT, A. [Commercial Benzines.] Neueste Erfin. u. Erfahr., vol. 37, 1920, pp. 74–79; Chim. et ind., vol. 5, 1921, p. 416; Chem. Abs., vol. 15, 1921, p. 3203.

Brief review of the different grades of benzine, their origin, and methods of preparation, including the catalytic reaction of H_2 on CO or on CO_2 in the presence of Co oxide or of osmic acid.

1139. GANZ, S. N. [Obtaining Synthetic Methanol From Waste Gases.] Jour. Chem. Ind. (U. S. S. R.), vol. 17, No. 9, 1940, pp. 45–46; Chem. Abs., vol. 35, 1941, p. 1758.

Discusses apparatus.

1140. GARCIA Y LASTRES, N. [Manufacture of Synthetic Petroleum Products.] Cuerpo de Ingenieros de Minas, Bull. 126, Peru, 1940, 347 pp.

Review of production of fuels in Germany, Scotland, and England by various treatments of coal, lignite, tars, and oil shale. Discusses carbonization, hydrogenation, distillation, and synthesis.

GARCIN, M. *See* abs. **2329.**

GARDNER, J. B. *See* abs. **295, 2444.**

1141. GARFINKEL, I. M. [Carbon Monoxide the Main Factor in Crude-Oil Synthesis.] Neftyanoe Khoz., vol. 15, 1928, pp. 556–558; Chem. Abs., vol. 23, 1929, p. 4807.

Reviews various synthetic crude-oil processes.

1142. GARNER, F. H. Liquid Fuels and Other Products From Petroleum and Coal. Internat. Cong. Pure Appl. Chem., 11th Cong., London, July 1947; Jour. Inst. Petrol., vol. 33, 1947, pp. 678–686; Fuel Abs., vol. 2, No. 2, August 1947, p. 61.

Development of hydrogenation and Fischer-Tropsch processes has made all natural sources of hydrocarbons—natural gas, petroleum, coal, shale—available for the production of liquid fuels, of all types of hydrocarbons, C_2H_2, olefins, paraffins and aromatics, and of synthetic chemicals. Application of the Fischer-Tropsch process may lead, as in the case of petroleum, to production of synthetic chemicals. The most important products, such as plastics, synthetic fibers and detergents, made from synthetic chemicals, are being derived to an increasing extent from hydrocarbon sources.

1143. ———. Extractive Distillation. Ind. Chemist, vol. 25, 1949, pp. 238–242.

Discusses process in detail. It may be used in separating alcohols, aldehydes, ketones, and acid present in Fischer-Tropsch products. Gives list of 15 refs.

1144. GARNER, W. E., AND KINGMAN, F. E. T. Adsorption of Hydrogen and Carbon Monoxide on Oxide Catalysts. Nature, vol. 126, 1930, p. 352; Chem. Abs., vol. 24, 1930, p. 5567.

H_2 or CO adsorbed at room temperature on ZnO–Cr_2O_3 catalysts was given off at 100°–120° but after 20–30 min. was readsorbed on the surface of the catalysts. On raising the temperature further, no gas was given off up to 350°, when H_2O or CO_2 was liberated. Physically adsorbed gas must leave the surface before it can chemically combine with metallic oxides.

1145. ———. Heat of Adsorption of Hydrogen and Carbon Monoxide on Zinc and Chromium Oxide Catalysts. Trans. Faraday Soc. vol. 27, 1931, pp. 322–333; Chem. Abs. vol. 25, 1931, p. 4758.

Heats of adsorption and adsorptive capacity of H_2 and CO on ZnO, Cr_2O_3, and ZnO–Cr_2O_3 catalysts were measured by means of a vacuum calorimeter previously described. The heats of adsorption ranged from 25–10 cal. per gm. mol., the maximum value being obtained for the first small quantities adsorbed. The heat of adsorption of CO on ZnO is the same as that of ZnO–Cr_2O_3, although the adsorptive capacity is much greater in the latter case. This indicates that the greater efficiency of the mixed catalyst is due to an enlargement of the internal area of the catalyst. Cr_2O_3 and ZnO did not adsorb H_2 as strongly as the mixed catalyst, but the Cr_2O_3 adsorbed CO very readily. At low temperatures H_2 and CO are mainly adsorbed without disruption of the molecules, but at 100° and over the adsorption was irreversible, and the gas could only be removed as water and CO_2, respectively, by heating to high temperatures. In the case of the mixed catalyst, the rate of evolution from 1 type of adsorbed film was greater than the rate of condensation to a second type of film, so that on heating to about 100° of a catalyst that had adsorbed H_2 at 20°, there occurred an evolution of H_2 which was followed by slow readsorption.

1146. GARRAN, R. R. Equilibria at High Temperatures in the System Iron–Oxygen–Carbon. Trans. Faraday Soc. vol. 24, 1928, pp. 201–207; Chem. Abs. vol. 22, 1928, p. 2099.

Most of the experimental results dealing with this system given in the literature were made below 1,000°. Extrapolation to temperatures above 1,000° is very uncertain. Experimental results are given covering the temperature range 600°–1,300°.

GARRISON, W. *See* abs. **2891.**

1147. GAS AGE. Gasoline From Natural Gas. Vol. 97, No. 3, 1946, p. 50.

Carthage Hydrocol, Inc., is proposing to build a plant near Brownsville, Texas at a cost of approximately $14,000,000 to manufacture gasoline from natural gas by the Hydrocol process. The plant is being designed for a capacity of processing approximately 60,000,000 cu. ft. of gas per day with a calculated production of 5,900 bbl. of gasoline and 1,100 bbl. of Diesel and other oils. The participators are named. (*See* abs. **2777**).

1148. ———. Carthage Hydrocol to Use Hidalgo County Natural Gas. Vol. 98, No. 8, 1946, pp. 44, 46.

Most of the natural gas to be used in gasoline conversion at the Carthage Hydrocol plant will be supplied by fields in Hidalgo County, Texas. Both the La Gloria Corp. and the Gulf States Oil Co., stockholders in the Hydrocol plant, own production in these fields. Hydrocol is now negotiating a contract with the Brownsville Navigation District for construction of the gasoline-conversion plant. An estimated 55 miles of gas line will transport the gas from the fields to the plant.

1149. ———. Synthetic Research. Vol. 98, No. 8, 1946, p. 52.

It is announced by J. A. Glen, Minister of Resources, that Canada is giving serious attention to development of synthetic fuel processes. A sum of $50,000 has been voted for a small-scale pilot plant in Ottawa to experiment with synthetic liquid fuel. An official has been sent to Germany to investigate plants, and research will extend to all forms of hydrogenation. A fuel-research board will be set up to direct an overall program of fuel research.

1150. GAS JOURNAL. Indirect Hydrogenation. Vol. 215, 1936, p. 482; Colliery Guard., vol. 153, 1936, p. 419.

Koppers Co. is closely identified with the Fischer-Tropsch process. In 1935, the Koppers Co. of Essen received an order to supply the plant to produce the mixture of CO and H_2 (the "synthesis gas") necessary for this process. This order comprised the whole of the plant to produce in a sufficiently pure condition the gases for the Fischer Tropsch installation at Braunkohle-Benzin A.-G., Ruhland, for the Braunkohle-Benzin A.-G., Berlin. The first section of the plant has a capacity of 900,000 cu. ft. of synthesis gas per hr., which corresponds to a yearly production of 25,000 tons of primary products. The Koppers plant at Braunkohle-Benzin A.-G., was put into operation in April, 1936. Since then Koppers has received a further order for the extension of this installation to produce an additional 4,500,000 cu. ft. of synthesis gas per hr., for the production of which 5 new units will be needed. All the Braunkohle-Benzin A.-G. units manufacture the synthesis gases from brown-coal briquets. At another plant ordered in 1935 by the Rheinpreussen Company,. Homberg, identification of the Koppers Co. with the Fischer-Tropsch process has been carried a stage farther. Originally the Koppers Co. had to provide the synthesis gases only, but now the arrangement has been extended so that Firma Heinrich Koppers G.m.b.H., as general contractors, have charge of the designing, and the supervision of the erection and starting of the whole of the plant for the production of liquid power fuels. This plant is to produce 30,000 tons of primary product per year, the raw materials being blast furnace coke and coke oven gas. The products will consist of motor spirit (benzine), diesel oil, soft and hard paraffin wax, and oils for the production of domestic fats, and other chemical uses.

1151. ———. Queensland's Coal Resources. Vol. 261, 1950, p. 103.

As a result of a preliminary survey, it is concluded that Queensland has cheap, abundant supplies of coal of a wide range of types. Many high-class coking coals are available. There is a prima facia case for a thorough investigation of the potentialities in developing an oil-from-coal industry, using one of the modern variants of the Fischer-Tropsch process.

1152. GAS- UND WASSERFACH. [Hydrocarbon Synthesis From Water Gas.] Vol. 77, 1934, p. 798; Fuel Economist, vol. 10, 1935, p. 759.

Ruhrchemie at Oberhausen-Holten is operating the Fischer process in a plant of 1,000-ton per yr. capacity. The process works at atmospheric pressure and at a temperature of 190°–210° C. The gases used for the synthesis are water gas or cracked coke oven gas, both of which are carefully purified, particularly from organic S, in order to prevent the rapid deterioration of the catalyst (Ni-Al-Mn precipitated on kieselguhr). The hydrocarbons formed range from petrol to solid paraffin wax, the respective quantity being about ⅔ of petrol and ⅓ of fuel and heavy oils. No detailed information is as yet available with regard to the yield obtained on the large-scale plant and the cost of operation. If the process should prove economical, the Ruhrchemie will erect an installation of some magnitude. Likewise, the Colliery Victor at Rauxel contemplates erection of a plant with an annual capacity of 25,000 tons of petrol. The primary object of this plant is to find an outlet for the gas (presumably H_2) not required in the synthetic NH_3 works attached to the colliery. The synthetic NH_3 works at Scholven, belonging to the Prussian State Colliery, Rocklinghausen, has the same object in view but intends to employ the hydrogenation process of the I. G. Farbenindustrie, if the experiments with hydrogenation of coal now carried out at Oppau yield satisfactory results.

1153. GAS WORLD. Synthetic Methyl Alcohol. Vol. 82, 1925, p. 416.

Synthetic production of MeOH is now successful on a commercial scale. In 1921 Patart and in 1922 the Badische Anilin Co. patented the catalysis of CO and H_2 at high pressures and moderate temperatures in the presence of catalysts. The reactions are:

$$(a)\ CO+2H_2 \rightleftarrows CH_3OH.$$
$$(b)\ CH_3OH+H_2 \rightleftarrows CH_4+H_2O.$$
$$(c)\ CH_3OH+CO \rightleftarrows CH_4+CO_2.$$

Reaction (*a*) is favored by high pressures, since it is accompanied by a diminution in volume. Reactions (*b*) and (*c*) are unaffected by pressure, since there is no change in volume, but since they are endothermic from left to right, they are favored by high temperatures. By keeping the temperature low the production of CH_3OH is favored. With a special saline catalyzer 1 $m.^3$ of CO and 2 of H_2 at 250 atm. and 220°–300° C. will yield 1.36 kg. of CH_3OH of remarkable purity, free from aldehydes and acetone in an apparatus similar to that used for synthesis of NH_3. By raising the temperature higher, alcohols and CH_4 are produced. The economic importance of this reaction is evident.

1154. ———. Liquid Fuels and the Gas Industry. Vol. 83, 1925, pp. 8–9 (Suppl.); Chem. Abs., vol. 20, 1926, p. 980.

Liquid-fuel production should be taken over by the gas industry and not allowed to become a competitor in other hands. Synthetic NH_3 is cited as a commercial undertaking lost to the gas industry. The production of liquid fuels from coal and water gas is discussed.

1155. ———. Petrol Synthesis. Vol. 103, 1935, p. 253.

2 more Fischer plants for the production of motor fuel from water gas have been installed in Germany—1 by the Ruhrchemie A.-G. at Oberhausen-Holten, the other by the Klöckner combine at Castrop-Rauxel. The combined capacity is estimated at 25,000 tons of gasoline per year.

1156. ———. Progress in Coal Processing and Byproduct Treatment. Vol. 105, Coking Sec., Sept. 5, 1936, p. 22.

Discusses recent Koppers activities in constructing the plants at Brabag and Homberg (Rheinpreussen Co.) for producing the synthesis gases for the Fischer-Tropsch process.

1157. ———. Oil and Petrol From Coal. Vol. 120, 1944, pp. 487–489.

An editorial urging greater British development and utilization of the Fischer-Tropsch process for the production of liquid fuels from British coal. The point is emphasized, based on the recent lecture by J. G. King before the Junior Institution of Engineers, that the logical development is toward combining coal carbonization with the Fischer-Tropsch synthesis, whereby only 3.45 tons of coal would be required to produce 1 ton of primary product at a thermal efficiency of 42% instead of the 25% usually quoted.

1158. ———. Reconstructed Ruhrchemie Co. Vol. 127, 1947, p. 174.

Nearly 5,000 workers are now employed in the Ruhrchemie works; only rarely has it employed as many workers in the past. The N_2 plant is working with 3 8-hr. shifts daily, and as soon as permission is granted for the processing of coal–H_2 the works will extend its activities to produce synthetic gasoline and other products such as alcohol, lubricating oil, fatty acids, and detergents.

1159. ———. Gas-Synthesis Demonstration Plant. Vol. 132, 1950, p. 654.

General, brief description of the United States Bureau of Mines synthetic liquid fuels demonstration plant.

1159a. ———. American Gas-Synthesis Experiment. Vol. 135, 1952, pp. 423–424.

Summary of a report of the second integrated plant test at the Bureau of Mines Fischer-Tropsch demonstration plant at Louisiana, Mo., at the end of a 25-day run.

GAUDECHON, H. *See* abs. **250.**

1160. GAUGER, A. W. Gasification of Solid and Liquid Fuels. Physical Chemistry and Technology of Fuels. 21st Ann. Priestley Lectures, Pennsylvania State College, State College, Pa., 1947, pp. 65–84; Fuel, vol. 26, No. 5, 1947, pp. 138–144.

Describes gas-making processes that depend upon heat and those which involve reactions of hot C with steam and CO_2, such as water gas, producer gas, oil, and synthesis gas. Discusses the thermodynamic data connected with these reactions and the physical chemistry thereof. Some results of commercial plant tests at Trail, B. C., on an O_2-blown gas producer utilizing anthracite coal are presented. Two new gasification processes of major interest, the Lurgi and the Winkler, are given detailed consideration.

1161. ———. Interconversion of Solid, Liquid, and Gaseous Fuels. Physical Chemistry and Technology of Fuels. 21st Ann. Priestley Lectures, Pennsylvania State College, State College, Pa., 1947, pp. 43–63.

General procedure in the commercial hydrogenation of coal is described. Whereas in Europe it required from 4–4.5 tons of coal to produce 1 ton of gasoline at an overall thermal efficiency of about 42%, the Bureau of Mines has recently demonstrated that 1 ton of gasoline can be produced on an improved plant from 3.14 tons of coal at an overall thermal efficiency of 56.4% compared to 28.9% for a typical German plant. The chemistry of coal hydrogenation and the effect of various factors, such as coal composition, turbulence, liquefaction, H adsorption, catalysts, etc., on the hydrogenation process are briefly reviewed. It has previously been indicated that the primary process in hydrogenation is the formation of heavy oil, which is later converted into lighter products and hydrocarbon gases, but it is recently reported that the primary product is asphalt. As to the character of the products formed, the subject is still exceedingly complex, but current studies of the middle oil are developing considerable interest and probably will lead to products of commercial value. The isolation of several polynuclear aromatic compounds of high molecular weight has already been reported. The synthesis of MeOH and other hydrocarbons from CO and H_2 is discussed at some length and the thermodynamics and the mechanism of the processes set forth in detail. Considers commercial development of the synthetic oil processes and their economic possibilities.

———. *See* abs. **930.**

1162. GAUGER, A. W., AND TAYLOR, H. S. Influence of Temperature Pressure and Supporting Material for the Catalyst on the Adsorption of Gases by Nickel. Jour. Am. Chem. Soc., vol. 45, 1923, pp. 920–928; Chem. Abs. vol. 17, 1923, p. 1913.

Isotherms of the absorption of H_2 on Ni, using N_2 as a reference gas, show that there exists a definite saturation capaicity of Ni for H_2 which depends on the temperature. A value of approximately 2,500 cal. per gm. mol. has been deduced from variation of the saturation pressure with temperature for the heat of adsorption of H_2 on Ni, whereas by a different method Rideal obtained a value of 12,000 cal. The use of an inert material for catalyst support increases greatly the adsorptive capacity per gm. of Ni and yields a catalyst capable of standing more severe heat treatment.

1163. GAUGER, A. W., AND WRIGHT, C. C. Coal as Related to the Liquid-Fuel Industry. Min. Cong. Jour., vol. 30, No. 4, 1944, pp. 27–30; Chem. Abs., vol. 38, 1944, p. 3446.

Brief descriptions of the Bergius, Fischer-Tropsch, and Pott-Broche processes.

GAUKHMAN, S. S. *See* abs. **2888, 2889, 2890.**

1164. GAUKHMAN, S. S., AND ROITER, V. A. [Role of Sorption of Nitrogen in the Mechanism of Ammonia Synthesis in the Presence of Technical Iron Catalyst.] Jour. Phys. Chem. (U. S. S. R.), vol. 11, 1938, pp. 569–577; Chem. Abs. vol. 33, 1939, p. 4386.

Adsorption of N_2 and H_2 on technical catalyst 340 (composition is not disclosed) was investigated at −184°–425° and −184°–250°, respectively, at a constant pressure of 435 mm. With H_2, a definite sorption process was observed in the region below 250° K. and another up to 500° K. The energy of activation of the low-temperature process increased from 7,200 to 10,680 cal. per mol., with increase of surface from 0.5 to 3.5 $cm.^2$ One type of N_2 sorption was observed. The energy of activation of low-temperature adsorption of N_2 was calculated to be equal to 1,500 cal. per mol. The difference in the catalytic activity of the previously described Fe–Mo catalyst cannot be explained by difference in the magnitude of total surface, since the variation of the latter was inverse to the variation in the catalytic activity. The velocity of sorption process in the presence of this catalyst increased with the increase of the catalytic activity. The velocity of formation of NH_3 at 375° was near that of sorption of N_2 under the same conditions. The energy of activation of the synthesis was considerably lower than that of the sorption of N_2.

1165. ———. [Comparative Characteristics of the Adsorptive and Catalytic Properties of Variously Prepared Synthetic Ammonia Iron Catalysts.] Jour. Phys. Chem. (U. S. S. R.), vol. 13, 1939, pp. 593–599; Chem. Abs. vol. 34, 1940, p. 1543.

Adsorption isotherms for H_2 and N_2 on 2 Fe catalysts promoted by 2% Al_2O_3 are given for temperatures 184°–425°. Physical adsorption was found at 184°, 2 types of activated adsorption at 250°–425° on the sintered catalyst only. For the NH_3 synthesis at 360°–385° the catalytic activity of the sintered catalyst was proportional to the activated adsorption.

1166. GAUTIER, A. [Action of Carbon Monoxide on Steam at Red Heat, and Action of Hydrogen on Carbon Dioxide.] Bull. soc. chim., vol. 35, 1906, pp. 929–934; Compt. rend., vol. 142, 1906, pp. 1382–1387; Jour. Soc. Chem. Ind. (London), vol. 25, 1906, p. 1145; Chem. Abs., vol. 1, 1906, p. 274.

Boudouard (*see* abs. **321**) determined the ratio, CO : CO_2, in the equilibrium between CO, steam, CO_2, and H_2 at different temperatures; and Hahn (*see* abs. **1310**) determined the coefficient, $K=\frac{CO\times H_2O}{CO_2\times H_2}$, at different temperatures. The author shows that, when a current of CO, mixed with a varying excess of steam, is passed through a porcelain tube heated to 1,200°–1,250° C. at the rate of about 1 liter of the mixed gases per hr., or when a dry mixture of equal volumes of CO_2 and H_2 is similarly treated at 1,300,° the reaction proceeds until the volume of H_2 is about double that of CO. The reactions correspond with the equations: $3CO+3\ H_2O=CO+H_2O+2\ H_2+2CO_2$. $3CO_2+3\ H_2=CO+H_2O+2\ H_2+2\ CO_2$. Under these conditions, any mixture of CO, steam, H_2, and CO_2 tends toward the composition, $CO+H_2O+2H_2+2\ CO_2$ Small quantities of formic acid, but no formaldehyde, are produced. These results are discussed with reference to the composition of volcanic gases, and attention is directed to the occurrence of formic acid in certain hot mineral springs.

1167. ———. [Reactions Between Hydrogen and Carbon Monoxide and the Effect of Steam on Carbon Monoxide at Elevated Temperature.] Compt. rend., vol. 150, 1910, pp. 1564–1568; Bull. soc. chim., vol. 7, 1910, pp. 765–768; Chem. Zentralb., 1910, II, p. 292; Chem. Abs., vol. 6, 1912, p. 287; vol. 4, 1910, pp. 2251, 3048.

Reduction of CO by H_2 begins approximately at 400°, resulting in the formation of H_2O, C, and some CH_4. The mutual reactions are limited and equilibrium is reached at approximately 1,000°. The formation of CH_4 is favored by a higher % CH_4 and by a greater velocity to prevent its splitting off at red heat. Between 450° and 650° traces of formol are formed but disappear again at 950°. On passing a mixture of 1 vol. CO and 6 vol. H_2 at a speed of 1 l. per hr. through a porcelain tube heated to 1,200°, there was obtained, after removal of the CO and CO_2 from the end gas, a mixture of 99.8% H_2 and 0.2% CH_4. At 1,300° and a 3 times greater gas velocity, 98.65% H_2 and 1.35% CH_4 were obtained. The higher velocity thus appears to prevent decomposition of the CH_4 formed.

1168. GAUTIER, A., AND CLAUSMANN, P. [Action of Iron and Its Oxides at Red Heat on Carbon Monoxide.] Compt. rend., vol. 151, 1910, pp. 16–22; Chem. Zentralb., 1910, II, p. 729; Chem. Abs., vol. 5, 1911, p. 53.

Action of CO on Fe yields C, carbides, and CO_2. If the oxides are mixed with Fe, CO_2, free C and several carbides of which the most probable are $Fe_{12}C$ and Fe_3C—the former more easily attacked by H_2SO_4—are formed. The action of acids upon the carbides thus formed gave CH_4, H_2, and a small amount of petroleum compounds. The action of steam at red heat upon the carbides formed as above was studied for its bearing on geological problems. There were formed at 500°–600° and at 800°–900°: H_2, 98.23 and 23.17; CH_4, 1.77 and 3.44; CO, 0.00 and 65.10; and CO_2, 0.00 and 8.33. It is believed that the high pressures within the earth's crust would also produce the cyclic hydrocarbons of petroleum.

1169. ———. [Action of Mixtures of Carbon Monoxide and Hydrogen or of Carbon Dioxide and Hydrogen on the Oxides of Iron.] Compt. rend., vol. 151, 1910, pp. 355–359; Chem. Abs., vol. 5, 1911, p. 2605.

Finely divided Fe_3O_4 was heated for 11 hr. at 500° in a mixture of 3 vol. of CO and 1 of H_2. The product is a mixture of C, FeO, and $Fe_{12}C$. Boiled with dilute H_2SO_4, it yields a mixture of CH_4 and H_2. With steam at 100° it also yields CH_4 and H_2, but at 650° the CH_4 disappears almost entirely, and CO_2 takes its place. Fe (coated on pumice) was heated to 1,250° in a stream of $2H_2+CO_2$; and the resulting gases, after washing with KOH, contained CO, 23.26%; H_2, 75.93%; CH_4, 0.15%; and N_2 (probably from the air), 1.27%. Fe_2O_3, heated in a mixture of equal volumes of CO and H_2 for 2 hr., yielded a product having properties similar to those of vaseline and the simple solid hydrocarbons. It is suggested that CO in the depths of the earth (either with or without H_2) has reacted with reducible oxides, forming carbides, which later, at temperatures below red heat, reacted with steam and formed the hydrocarbons issuing from the earth in volcanic regions or deposited as petroleum.

1170. GEBHARD, K., HANEMANN, H., AND SCHRADER, A. [Martensite System.] Arch. Eisenhüttenw., vol. 2, 1929, pp. 763–771; Chem. Abs., vol. 23, 1929, p. 3648.

Thermal and photomicrographic investigation of martensite, using electrolytic Fe and steels with C content ranging 0.06–1.75%. The heterogeneity of martensite is established, as well as the existence of a 2d metastable system of Fe–C alloys. Photomicrographs and a phase diagram of the martensite system are included. In the metastable martensite equilibrium only ϵ-Fe occurs up to about 0.1% C. 0.1–0.37% C, martensite consists of ϵ-Fe and heynite (θ-phase), while 0.37–0.9% C, heynite and hardenite (η-phase) are the constituents of martensite. With more than 0.9% C, a quenched steel contains hardenite and austenite, the austenite increasing as C increases. If the steel contains more than 1.1% C, the η-phase crystallizes from the γ-Fe immediately. If the equilibrium is not completely established, hardened steel contains austenite even with less than 0.9% C, and heynite even with more than 0.9% C.

1171. GEHRKE, —, AND SCHUFF, —. [Catalyst Plant and Synthesis Installation at Harnes.] FIAT Reel K–29, frames 7005–7028, 1938; PB 70,218.

Report on inspection of the catalyst plant and synthesis installation at Harnes. Proposals are made for the increase of the output and for eliminating certain existing deficiencies.

1172. GEISELER, —. Separation of Alcohols From Their Mixtures With Hydrocarbons. Scientific Contrib. 11, Laboratory, Merseburg Ammonia Plant, April 1943; Office Publication Board Rept., PB 870, 2 pp.

Following the work of H. P. Kaufmann on the separation of fatty acids by adsorption on silica gel, attempts were made to separate the mixture of alcohols and hydrocarbons arising from the Fischer-Tropsch medium-pressure synthesis. The method has for a basis the difference in the heats of wetting of alcohols and hydrocarbons. The process is covered by German Patent Applications I 72,811, IVd/12o, O.Z. 13570, and I 73,795, IV–d/12o, O.Z. 13,831. The alcohol-hydrocarbon mixture is mixed thoroughly with the active gel, which is then washed with a low-boiling hydrocarbon (petroleum ether, benzine, ligroin, benzol) to remove the adsorbed hydrocarbon, leaving the alcohol

adsorbed on the gel. The alcohol is then recovered by being displaced by a highly polar liquid such as MeOH, EtOH, acetone, diethylether, etc., which likewise preferably remains attached to the gel. The gel is then regenerated by being treated with an excess (1:1,000) of hot gas (N_2, CO_2) at 150°. The process works best at room temperature and with a highly porous granular gel of 0.5–1 mm. size. The adsorption of the gel for alcohols embraces the whole range from C_1 to C_{20} and higher and becomes somewhat selective as the chains lengthen.

1173. GEMASSMER, —. Semiworks Experiments on the Oxo Process. Office Publication Board Rept., PB 853, 1942, 5 pp.

Oxo process was developed on pilot-plant scale according to the Maische procedure aided by the Fischer-synthesis catalyst. Describes plant, olefin product, catalyst, and gases.

1174. ———. Application of the Oxo Reaction to Olefinic Mineral Oil Products. Scientific Contrib. 8, Laboratory, Merseburg Ammonia Plant, April 1943; Office Publication Board Rept., PB 867, 1 p.

Possibility of using olefin products from various sources in the Oxo-reaction was investigated. Most of the materials used required no preliminary refining. Somewhat higher temperature was required than with olefins from the Fischer synthesis and conversion was also somewhat less (about 50%) than was to be expected from analysis of the samples. Hydrogenation was influenced by the S content and the boiling range of the oils; the higher boiling fractions hydrogenating the most satisfactorily. In those products, with which hydrogenation of the intermediate aldehydes did not occur smoothly, the Co_2C formed was still capable of reduction without difficulty to metallic Co, so that the incompletely hydrogenated products after separation of the catalyst were entirely free of metal. The complete hydrogenation to alcohol could then be carried out smoothly and without loss with the sulfide catalyst at remarkably low temperatures. The alcohols, recovered either by distillation or by esterification with boric acid, are water clear or pale yellow liquids of a pleasing, weakly aromatic odor having a low melting point and a remarkably high density due apparently to the cyclic structure. Chemically they behave similarly to other alcohols. The alcohol sulfates are good detergents, and their high solubility makes possible the use of members as high as C_{20} for the above purpose.

1175. GÉNIE CIVIL. [Underground Gasification of Coals in the U. S. S. R.] Vol. 122, No. 9, 1945, pp. 66–68.

Gives general review of the methods followed in Russia. (*See* abs. **1**, **1628**, **3698**). The operation may be so varied that different types of gases for different specific uses can be produced as, for example, for the synthesis of NH_3 or hydrocarbons by the Fischer-Tropsch process. The average cost of gas produced in this way is about ⅓ that of the producer gas, and the cost of plant therefore about 60–70% of the cost of water-gas plant.

1176. GENIN, G. [Fluidization.] L'Industrie chimique, vol. 38, June and July 1951, pp. 157–163, 185–191.

History, theory and applications of fluidization are discussed. Its application to the petroleum industry, to the Fischer-Tropsch synthesis process, the catalytic manufacture of phthalic anhydride, the calcination of limestone, the reduction of minerals, the carbonization and gasification of coal, the manufacture of active C, and the classifying and drying of solid particles are reviewed. 34 refs. are given.

1177. GEORGES, P. [Substitute Liquid Fuels.] Jour. usines gaz, vol. 62, 1938, pp. 103–112; Chem. Abs., vol. 32, 1938, p. 7241.

Survey of the production of synthetic fuels according to Bergius and Fischer-Tropsch syntheses, and their development in important countries.

GERARD, F. W. *See* abs. **2769.**

1178. GERASIMOV, Y. [Activities of Components of Austenite.] Acta physicochim. U. S. S. R., vol. 18, 1943, pp. 275–299; Chem. Abs., vol. 38, 1944, p. 5717.

Thermodynamic method is given for the calculation of the activities and free energies of a binary solution from the gas-solution equilibrium constants. The activities of the components Fe–C and Fe–Fe_3C at 800°–1,100° are calculated on the basis of the equilibrium constants between austenite and CO_2+CO. The values of K_g at 800°, 850°, and 900° K. are, respectively, 268.8 N_2, 510 N_2 and 962 N_2, where N_2 is the mole fraction of C in austenite. Since this means that the activity coefficient is practically unity, austenite can be considered a regular solution of a regular modification of carbide $Fe_3C(r)$ in γ-ferrite at 800°–1,100°. The free energy of formation of cementite is small and positive. The integral heats of solution of carbide and the solubilities of a "regular" carbide modification in Fe are given as: $Fe_3C(\beta)$ in $Fe(\gamma)$, 10,243 cal.; $Fe_3C(\beta)$ in a saturated solution, 5,000–7,000 cal. This latter modification is found to be less stable than cementite. The results indicate that the data of Bramley and Lord (*see* abs. **330**) are probably vitiated by some sort of systematic error.

1179. GERDES, —. [Preparation of Water Gas From Brown Coal in the Pintsch-Hillebrand Generator.] Braunkohle, vol. 34, 1935, pp. 193–197, 216–219; Chem. Abs., vol. 30, 1936, p. 5762.

Describes new process using briquets and operating continuously without O_2. The process is particularly suitable for producing synthesis gas for the Fischer-Tropsch benzine synthesis. By utilizing the end gas from the benzine synthesis for heating the generator and with a briquet cost of 8 RM per ton the benzine can be produced for 8.3 pf. per kg.

1180. GERLACH, W., AND VON RENNENKAMPFF, J. [Magnetic Properties of Nickel Supersaturated With Carbon.] Naturwissenschaften, vol. 31, 1943, p. 96; Chem. Abs., vol. 37, 1943, p. 4999.

Anomalous decrease of saturation magnetization with increasing temperature in Ni supersaturated with C is restricted to the temperature range of room temperature <300°. The coercive force decreases normally between —200° and +50°, and remains constant from 50° up to 300°. In this range no saturation is reached, even at 3,000 oersteds. Numerous Curie points are in this range. The % remanence increases under 0°. This behavior is attributed to the facts that the alloy is a definite ferromagnetic substance of a Curie temperature about 50° plus a number of ferromagnetic Ni–C alloys of decreasing or indefinite C content, and that C separates and the alloy gradually approaches pure Ni with gradual rise of the Curie temperature and hardening. After separation of all the C the normal character reappears. After annealing at 600°, the temperature curve of magnetic saturation is normal.

1181. ———. [Magnetic Studies With Nickel–Carbon Alloys.] Ztschr. Elektrochem., vol. 49, 1943, pp. 200–203; Chem. Abs., vol. 37, 1943, p. 6507.

Curves are given for magnetization in low and in high fields, remanence, and coercive force as functions of temperature from —196° to 400° for Ni supersaturated with C. C in Ni is precipitated by heating at 600° leaving a material having the normal characteristics of Ni (abs. **1180**).

GERNES, A. C. *See* abs. **2577.**

GERSTEN, E. *See* abs. **2924**, **2925**, **2926.**

GHOSH, J. C. *See* abs. **460**, **461**, **462.**

1182. GHOSH, J. C., AND BASAK, N. G. Chromium Oxide as Catalyst Promoter for Fischer-Tropsch Synthesis at Medium Pressures. Petroleum, vol. 11, June 1948, pp. 131–132, 146; Chem. Abs., vol. 42, 1948, p. 5643.

Incorporation of Cr_2O_3 and Ce_2O_3 with a Co–Cu–ThO_2–kieselguhr catalyst, which has been claimed to have good activity, improves its quality in various respects. The catalyst, besides being reducible at lower temperature (237°–240°), functions steadily and yields, with cheap water gas at a pressure of 5 atm. and 205°, 160 gm. of hydrocarbons per $m.^3$ of normal water gas. The space velocity is 570–600 cc. per hr. per cc. of catalyst in a 1-stage operation. Therefore, the synthesis of hydrocarbons by the Fischer-Tropsch process may be economically improved by the use of this catalyst.

1183. GHOSH, J. C., AND CHAKRAVARTY, J. N. Dehydrogenation of Methanol and Formaldehyde With Copper as Catalyst. A Study of the Conditions of the Equilibrium in the System: $HCHO \rightleftharpoons CO+H_2$. Quart. Jour. Indian Chem. Soc., vol. 2, 1925, pp. 142–149; Chem. Abs., vol. 20, 1926, p. 860.

Equilibrium of the rection $CH_3OH \rightleftharpoons HCHO+H_2$ (I) and $HCHO \rightleftharpoons CO+H_2$ (II) were determined by a static method with Cu-pumice catalyst. For (I) the value found for K_p at 155° was 0.37 and at 205°, 0.65; these values differ widely from those calculated by a Nernst-type equation. For (II) the values of K_p from 155° to 340° (ranging from 0.032–2.20) were represented fairly well by the equation: $\log_{10}K_p = -(11{,}800/4.571T) + 1.75 \log_{10}T - 0.001T + 0.3$.

1184. GHOSH, J. C., AND CHAKRAVARTY, K. M. Catalytic Preparation of a Gas Rich in Methane From a Mixture of Water Gas and Steam. Proc. Indian Sci. Cong., 15th Cong., 1928, pp. 148–149; Chem. Abs., vol. 25, 1931, p. 2835.

The authors have previously shown that a gas mixture containing CO and H_2 1 : 1 by vol. can be made to yield a fuel gas containing over 25% CH_4 if passed over suitable catalysts at temperatures 350°–450°. The efficiency and life of certain catalysts have now been increased very considerably by introducing steam in suitable proportions in the reacting gas mixture. The following reactions take place simultaneously on the catalyst surface: (1) $2CO \rightarrow CO_2+C$; (2) $C+H_2O \rightarrow CO+H_2$; (3) $CO+3H_2 \rightarrow CH_4+H_2O$; (4) $2CO+2H_2 \rightarrow CH_4+CO_2$. It is seen from (1) and (2) that CO reacts with steam, giving CO_2 and H_2. The H_2 so produced increases the ratio of H_2 to CO in the reacting gases and prolongs the life of the catalyst by preventing deposition of C. Catalysts (not mentioned) have been found which so regulate the rates of the reaction given above that the resulting fuel gases, after removal of CO_2, contain more than 50% CH_4.

1185. GHOSH, J. C., AND SASTRY, S. L. Chromium Oxide as Promoter in Catalysts for the Fischer-Tropsch Synthesis. Nature, vol. 156, 1945, p. 506; Fuel Abs., No. 5107, November 1945; Chem. Abs., vol. 40, 1946, p. 1083.

Economics of synthesis of hydrocarbons by the Fischer-Tropsch process may be improved by using (1) cheaper catalytic material, (2) water gas as such in place of enriched synthesis gas, and (3) medium pressures instead of atmospheric pressures. A cheap Fe-Cu catalyst prepared by Ghosh and Sen gave 86 gm. of hydrocarbons/$m.^3$ of gas and has since been developed by Japanese investigators. The fact that Cr_2O_3 possesses very high adsorption for H at 200° has been taken advantage of in preparing a catalyst (Co 34%, Cu 4, ThO_2 2.3, Ce_2O_3 0.24, Cr_2O_3 4.6, remainder kieselguhr) which has been found to be remarkably steady, and yields, with water gas at a pressure of 5 atm. and 205°, 160 gm. of liquid hydrocarbons/$m.^3$ with a space velocity of 600 cc./hr./cc. of catalyst.

1186. GHOSH, J. C., AND SEN, S. Synthesis of Higher Paraffins From Water Gas. Use of Promoters for Activating Iron–Copper Catalyst. Jour. Indian Chem. Soc., vol. 12, 1935, pp. 53–62; Brennstoff-Chem., vol. 18, 1937, p. 161; Chem. Zentralb., 1935, I, p. 3496; Chem. Abs., vol. 29, 1935, p. 3903.

Investigation of possibility of activating an Fe–Cu catalyst by addition of Ni alone or by the simultaneous addition of Ni, Ce and Th. The catalyst was prepared from the nitrate and deposited on asbestos at as low a temperature as possible and subsequently impregnating with 0.5% K_2CO_3. The asbestos was one-half the amount of Fe and Cu. The effect of 1 and 2% of Ni and Ni, Ce and Th in the ratio of 8.03 : 0.13 : 0.95 on the Fe–Cu (4 : 1) catalyst was determined over a 14-hr. reaction period at 265° and a velocity of 0.65 l./hr. The yields of liquid hydrocarbons/$m.^3$ of water gas were respectively 30, 45, and 80 gm.

1187. GHOSH, J. C., BASAK, N. G., AND BADAMI, G. N. Nickel-Thoria–Kieselguhr Catalyst for the Fischer-Tropsch Reaction. I. Current Sci., vol. 16, 1947, pp. 318–319, 353; British Abs., 1948, B, I, p. 190; 1949, B, II, p. 141.

Catalyst prepared by precipitation of Ni and Th carbonates on kieselguhr by addition of NH_4HCO_3 to a solution of the nitrates in presence of excess of CO_2, and subsequent reduction in H_2, first at 500° and then at 300°–350° (for 6 hr. in each case), gave 147.5 gm. hydrocarbons other than CH_4/$m.^3$ of synthesis gas with a space velocity of 0.90 l./hr./gm. of Ni.

1188. ———. Nickel–Thoria–Kieselguhr (100 : 18 : 100) Catalyst for the Fischer-Tropsch Reaction. II. Current Sci., vol. 16, 1947, p. 353; British Abs., 1949, B, II, p. 141; Chem. Abs., vol. 43, 1949, p. 3167.

By the use of water gas (CO : H_2=1 : 1) instead of H_2-enriched synthesis gas (CO : H_2=1 : 2), it has been found that this catalyst gives (*a*) yields of hydrocarbons comparable with those produced from synthesis gas, (*b*) gaseous preponderating over liquid hydrocarbons, and (*c*) lower yields of CH_4 which remain almost constant with increasing space velocity. The experiments were carried out at 195° and 1 atm., and a maximum yield (125 gm./$m.^3$ of gas) was obtained with a space velocity of 0.9 l./gm. of Ni. The catalyst used is described in abs. **1187**.

1189. GHOSH, J. C., BASAK, N. G., AND VENKATESAN, C. Nickel-Thoria-Kieselguhr (100 : 18 : 100) Catalyst for the Fischer-Tropsch Synthesis at Medium Pressure. III. Current Sci., vol. 16, 1947, p. 377; Chem. Abs., vol. 43, 1949, p. 3167.

At 70 p. s. i. with synthesis gas, as well as water gas, the best reaction takes place at 205°. When synthesis gas is used, the yield of CH_4 is high. With water gas the yield of CH_4 goes down with a corresponding increase of gaseous and liquid hydrocarbons.

1190. GHOSH, J. C., CHAKRAVARTY, K. M., AND BAKSHI, J. B. [Catalytic Formation of Methane From Carbon Dioxide and Hydrogen: Simultaneous Acceleration of the Water Gas and Armstrong-Hilditch Reactions.] Ztschr. Elektrochem., vol. 37, 1931, pp. 775–779; Chem. Abs., vol. 26, 1932, p. 648.

Catalysts I, II and III were prepared respectively by impregnating pumice with nitrate solutions, drying in air at 110°, then heating for 16 hr. at 300° in pure H_2. The weights of catalyst used were 0.6440, 0.7100, 0.6565 gm., the densities after reduction 0.4155, 0.4438, 0.4646, % Ni 8.882, 8.433, 8.030, % Ce —, 0.0687, 0.1308, % Th —, 4.978, 9.479, and % pumice 91.11, 86.52, 82.37, respectively for I, II, and III. The reaction tube was maintained at 405° and the catalyst at 471°. Equal volumes of H_2 and CO, saturated with water vapor,

were admitted at constant velocity. With catalyst I, reactions (1) $CO+H_2=C+H_2O$ and (2) $CO_2+2H_2=C+2H_2O$ did not take part because no free C was deposited in disagreement with Randall and Gerhard (*see* abs. **2769**). Catalyst I lost its CH_4-forming properties with use but was still capable of promoting the water-gas reaction. Catalysts II and III showed no loss of CH_4-forming properties. After 180 l. had passed, II gave 32.02% CO_2, 9.65% CO, 25.58% CH_4, 22.52% H_2, 10.23% H_2O from 44.48% CO, 44.48% H_2, and 11.03% H_2O. II gave after 190 l., 36.19% CO_2 5.43% CO, 30.12% CH_4, 17.38%. H_2, 10.78% H_2O from 44.78% CO, 44.78% H_2 and 10.46% H_2O.

1191. ———. [Simultaneous Determination of the Equilibrium Constants of the Reactions $CO+H_2O \rightleftarrows CO_2+H_2$; $2CO+2H_2 \rightleftarrows CO_2+CH_4$; $CO+3H_2 \rightleftarrows CH_4+H_2O$; $CO_2+4H_2 \rightleftarrows CH_4+2H_2O$ by Using Activated Nickel Catalysts.] Ztschr. anorg. Chem., vol. 217, 1934, pp. 277–283; Chem. Abs., vol. 28, 1934, p. 6613.

Experimental arrangement was similar to that previously described (*see* abs. **1190**) but the gas mixture was passed much more slowly over the $Ni–ThO_2–CeO_2$ catalyst to insure that the temperature of the gases should be the same as that of the furnace. The required equilibrium constants were determined at temperatures 400°–490°.

1192. GHOSH, J. C., SASTRI, M. V. C., AND KINI, K. A. Adsorption of Hydrogen and Carbon Monoxide and Their Mixtures on Fischer-Tropsch Catalysts. I and II. Current Sci., vol. 15, 1946, pp. 282–283; Chem. Abs., vol. 41, 1947, p. 1907.

Adsorption of H_2 and CO, both as pure gases and as mixtures, was studied on a catalyst of the following composition: Co 34.2, Cu 4.08, ThO_2 2.33, Ce_2O_3 0.24% on kieselguhr. In mixtures the presence of 1 gas promoted the adsorption of the other, even at temperatures considerably below those where the velocity of reaction becomes perceptible. The increase of adsorption with H_2 was conspicuous, even at 25°. The adsorption was measured volumetrically and is tabulated in terms of the volume adsorbed by 9.41 gm. of catalyst from the pure gas from 1:1, 1:2, and 2:1 mixtures of H_2 and CO at temperatures up to 178°. The logs of the values for the rate of adsorption at constant pressure when plotted against the logs of the corresponding volumes adsorbed, gave straight lines that were parallel for different pressures at a given temperature. The results suggested $u=kP/V^n$ as the empirical relation between the rate of adsorption, the pressure and the amount of adsorption, where $u=$ rate of adsorption in cc./min., $P=$pressure, $V=$volume adsorbed, and n and k are constants.

1193. ———. Mixed Adsorption of Hydrogen and Carbon Monoxide on Fischer-Tropsch Catalysts. Research, vol. 3, 1950, p. 584.

Previously (*see* abs. **1192**) it was found that on a Fischer-Tropsch catalyst (A) containing 34% Co, 4% Cu, 2.33% ThO_2, 0.24% Ce_2O_3 and the rest kieselguhr, the adsorption of H_2 from 1 CO : 1 H_2 and 1 CO : 2 H_2 mixtures, at temperatures 25°–97° and mixed pressures below 76 cm., was greater than from pure gas at equivalent pressures. At the same time, there was a suppression of CO adsorption from the mixtures. The addition of 4% Cr_2O_3 to (A) (*see* abs. **1182**) caused marked improvement in the yield of gasoline and facilitated the use of water gas (1 CO : 1 H_2) without the usual enrichment of H_2. It also increased the adsorption of pure CO at all the temperatures studied (25°–97°) but suppressed that of pure H_2 up to 76° and increased it at higher temperatures. The adsorption of CO at higher partial pressures was found to be greater from the 1 CO : 2 H_2 than from the 1:1 mixture, while the reverse was true of H_2 adsorption. That is, adsorption of either gas was greater from that mixture in which its concentration was lower. On both catalysts it was observed that the adsorption of each constituent began to increase at much lower temperatures in presence of the other gas than in its absence. These facts point to the possibility of progressive formation of a CO–H complex on the surface of the catalyst. If the simultaneous adsorptions of the constituent gases were plotted against each other the "isotherms" so obtained tended to become linear at the higher temperatures, and for every 2 cc. increase in CO adsorption that of H_2 increased by nearly 1 cc. This again supports CO–H complex formation. It therefore appears that the chemisorbed CO–H complex, rather than the Co carbide, may be the intermediate in Fischer-Tropsch synthesis by catalyst (B) Cr_2O_3+(A).

1193a. ———. Adsorption of Hydrogen and Carbon Monoxide and Their Mixtures by Cobalt Fischer-Tropsch Catalysts. Ind. Eng. Chem., vol. 44, 1952, pp. 2,463–2,470.

In order to gain an insight into the nature of the reactive substrate in Fischer-Tropsch synthesis, the adsorption of H_2 and CO was studied at various temperatures from the pure gases as well as from their mixtures on 2 Co catalysts, 1 of which contained Cr_2O_3 as a promoter. Both gases underwent activated adsorption at fairly low temperatures. Cr_2O_3 enhanced the amounts and rates of adsorption of both, lowered their activation energies of adsorption, and thus acted as a promoter. Experiments were conducted with $1CO+1H_2$ and $1CO+2H_2$ mixtures, using a thermal conductivity meter for analysis. The adsorption of each constituent was found to be markedly influenced by the presence of the other. Kinetic studies revealed that the high initial adsorption of H_2 was followed by a partial replacement of adsorbed H_2 by CO. Near the minimum temperature of appreciable reaction, the concurrent adsorptions of CO and H_2 increased with the partial pressures in the ratio of $2CO:1H_2$. The observations reported in this paper point to the formation of chemisorbed $CO–H_2$ complexes as 1 of the 1st steps in the transformation of the substrate. The results are also in correlation with reaction-performance data previously reported on these catalysts.

1194. GHOSH, J. C., SASTRI, M. V. C., AND VEDARAMAN, S. Adsorption Studies on Methanol-Synthesis Catalysts. I. Adsorption of Carbon Monoxide and Hydrogen on Zinc Oxide–Chromium Oxide Mixture. Current Sci., vol. 19, 1950, p. 342. Chem. Abs., vol. 45, 1951, p. 7406.

Temperature range studied was 50°–200° for CO and up to 250° for H_2. The adsorption isobars of CO at pressures below 1 atm. show 2 maxima, at 52° and at 178°. The activation energy is 5–8.5 kcal., and the heat is 6 kcal. for 0.9 cc. adsorption/gm. For H_2, activated adsorption is observed at the lowest temperature; the heat is 10 kcal. for 1.30 cc. adsorption/gm. and the energy of activation is 8.5 kcal. for 1.19 cc. adsorption/gm. at 37 cm. pressure. The maximum adsorption is at 204°.

GIBSON, E. J. *See* abs. **1131a.**

GIESEN, —. *See* abs. **3703, 3704.**

GIESSEN, A. *See* abs. **407.**

1195. GIFFORD, A. P., ROCK, S. M., AND COMAFORD, D. J. Mass-Spectrometer Analysis of Alcohols and Other Oxygenated Derivatives. Anal. Chem., vol. 21, No. 9, 1949, pp. 1026–1032.

Mass-spectrometer analysis of alcohols or mixtures of oxygenated compounds containing them has been difficult because of strong sorption tendencies of these materials. In an examination of the erratic behavior of the alcohol spectra, it was found possible to minimize the effect of these difficulties by minor changes in the mass-spectrometer sample inlet system sufficient to permit analysis of synthetic mixtures of oxygenated

compounds. It is shown by alternate analyses of known mixtures widely varying in concentration of light and heavy alcohols that the different materials can be separated in the mixture spectra and that any effect of 1 sample upon a succeeding one is insignificant. Analysis of a synthetic mixture of the 4 butanol isomers shows that alcohol isomers are also readily resolved. That the errors in the analyses are relatively small demonstrates that sufficient accuracy can be obtained in the separation of alcohols to meet normal analytical needs. Analysis of the 4 butanol isomers mixed with water demonstrates that the presence of water does not prevent precise results and that water can be determined accurately. Analyses of complex mixtures show that other oxygenated compounds can be determined with adequate precision in the presence of alcohols and water.

GILFERT, W. *See* abs. **1820, 1821, 1822.**

1196. GILLET, A. [Synthesis of Fuel Oils and Lubricating Oils From Carbon Monoxide and Hydrogen at Ordinary Pressure.] Rev. univ. mines, vol. 11, 1935, pp. 180–184; Chem. Abs. vol. 29, 1935, p. 4561.

Two principal methods of industrial transformation of coal into oil are the Fischer and the Bergius processes. The former seems to be the more advantageous because it operates at ordinary pressure with simple apparatus made of sheet Fe and because it permits the manufacture, at the same time, of high-grade lubricating oils. The yield depends to a high degree on the catalysts used. The most effective are Fe with additions of Ni, Mn, Al, Th, Co, singly or several together. A table shows the yield in gm. of oil per m^3 of $CO+2H_2$ and time required for an efficiency of 80%. The reasons for the deterioration of catalysts are discussed. As the transformation into fuel oil sets free about 600 cal. per $m.^3$, means must be provided to carry away this heat quickly enough to maintain reasonably constant temperature. The products with a Co catalyst are usually 100–120 gm. of liquid hydrocarbons (180 gm. theoretically). The process and products are described.

1197. GILLILAND, E. R. Techniques of Contacting Fluids and Solids. 5th Westman Memorial Lecture; Canadian Chem. Process Ind., vol. 34, 1950, pp. 632–640.

Discusses techniques of fixed, moving, and fluidized beds in industrial operations. The greatly improved heat-transfer characteristics in the fluidized bed are emphasized; it merits consideration for any reaction in which (1) temperature control within the reaction or (2) heat transfer to and from the reaction vessel, or (3) frequent, alternate cycles with the catalyst are necessary.

——. *See* abs. **2110.**

GILMONT, P. *See* abs. **262a.**

1198. GILMORE, R. E. Carbonization of Canadian Fuels. Canadian Chem. and Met., vol. 10, 1926, pp. 31–34, 51–54, 85–87, 140–144.

Application of high- and low-temperature carbonization to wood, peat and other classes of Canadian fuels; gasoline and substitute fuels in Canada, with special reference to synthetic MeOH and synthol.

1199. GINSBERG, I. Wood Alcohol From Water Gas. Am. Gas. Jour. vol. 122, 1925, pp. 461–462.

Review of process developed by Patart and Badische, with a sketch of the apparatus and a description of the catalyst. It generally consists of a mixture of Zn and ZnO, with traces of Cd and CdO in admixture with a commercial Cu powder. Best results are obtained at a temperature of 220°–300° and 150–250 atm. The yield per hr. reaches as high as 100 cc. of MeOH per vol. of catalyst of 200 cc. This product is relatively very pure.

1200. GIORDANI, C. [Gasoline Substitutes.] Jour. usines gaz, vol. 61, 1937, pp. 170–175, 196–202, 229–233; Chem. Abs., vol. 31, 1937, p. 5537.

Present state of development of the coal hydrogenation and Fischer-Tropsch processes is comprehensively summarized. Yields and cost figures are included.

1201. ———. [Liquid Substitute Fuels.] Acqua e gas, vol. 27, Feb. 16, 1938, pp. 37–46; Chem. Zentralb., II, 1938, p. 1164.

Fischer and Bergius processes are discussed in relation to the production of high-octane fuel and high-grade lubricants under war demands.

GIORDANO, I. *See* abs. **2558.**

GIRARD, J. *See* abs. **553.**

1202. GITTIG, M. Exothermic Reaction Techniques. Petrol. Processing, vol. 5, No. 10, 1950, pp. 1080–1082.

Exothermic reaction techniques are classified and their application for heat-removal and control purposes in commercial chemical processes reviewed. The use of fluidized solids reactors in the Fischer-Tropsch process has served to greatly reduce the total volume of cooling surface required. Since a rocket motor is essentially an exorthermic reactor, the application of the same principle in chemical-process reactor design is considered a possibility. The injection of various fluids as temperature-control mediums in exorthermic gas reactions has been patented.

1203. GIVAUDON, —. [Industrial Reactions of Methane.] Assoc. franç. techn, pétrole, Conf. 1945, pp. 22–50; Chaleur et ind., vol. 26, 1945, p. 43D.

Sources of CH_4 and its conversion into CO and H_2 are discussed. Various processes are outlined: Harnes, Grande-Paroisse, Padovani, Soc. belge. de l'azote. The possibility of introducing CH_4 directly into the Fischer hydrogenation is considered. The decomposition of CH_4 into C and H_2 and carbon black, the production of C_2H_2, and its use in the plastics industry are treated.

GIVAUDON, J. *See* abs. **1604.**

GIVEN, P. H. *See* abs. **3397.**

GIVENS, J. W. *See* abs. **180.**

GLAESSNER, A. *See* abs. **168.**

GLENN, R. D. *See* abs. **2178.**

1204. GLOOR, W. E. Notes on the Development of Protective Coatings in Germany. Am. Paint Jour., vol. 30, No. 12, 1945, pp. 95, 98, 100, 102, 104, 106; Chem. Abs., vol. 40, 1946, p. 1047.

New placticizer used with cellulose acetate was the triethylene glycol ester of long-chain fatty acids from Fischer-Tropsch synthesis.

1205. GLUUD, W., AND SCHÖNFELDER, R. [Increasing the Activity of Iron (Ammonia) Catalysts.] Ber. Gesell. Kohlentech., vol. 3, 1930, pp. 96–99; Chem. Abs. vol. 25, 1931, p. 3779.

Catalyst containing Fe is treated with CO to form Fe_2C, which is then reduced by H_2.

1206. GLUUD, W., OTTO, K. V., AND RITTER, H. [Iron Carbide by Reduction of Iron Oxide With Carbon Monoxide at Low Temperature.] Ber. Gesell. Kohlentech., vol. 3, No. 1, 1929, pp. 40–51; Ber. deut. chem. Gesell., vol. 62B, 1929, pp. 2483–2485; Chem. Abs., vol. 24, 1930, p. 561.

CO is passed over Fe_3O_4 at 275° and the C content determined periodically. Graphic treatment of the data gives values for dissolved C which, when subtracted from the totals, give values which become constant after 20 hr. This value corresponds to Fe_2C. Removal of C by H_2 gives the same values. The data of Fischer and Bahr (*see* abs. **973**), similarly interpreted, give the same results.

GODDIN, C. S. *See* abs. **810.**

1207. GODDIN, C. S., AND THORNTON, D. P. Low-Temperature Carbonization of Coal Produced Most of Japs' Synthetic Oil. Petrol. Processing, vol. 3, 1948, pp. 121–122, 124–125, 127, 130–131; Chem. Abs., vol. 42, 1948, p. 9112.

This article reviewing Japanese efforts to synthesize liquid fuels from coal is based on the report of the U. S. Naval Technical Mission to Japan. Report X–38 (N)–7, Japanese Fuels and Lubricants, Progress in the Synthesis of Liquid Fuels from Coal, PB 58,701.

GOECKE, O. *See* abs. **2927.**

1208. GOEPFERT, O. [Deterioration of Fischer-Synthesis Catalysts and Participation of Methane in This Synthesis.] Compt. rend., vol. 224, 1947, pp. 340–341; Chem. Abs., vol. 41, 1947, p. 3739.

Experimentally it is observed that mixtures of C_2H_6 and H_2 react on a Ni-kieselguhr catalyst at 150°–160° C. to form CH_4. The reaction does not proceed simply according to the equation: (1) $C_2H_6+H_2 \rightarrow 2\ CH_4$. Instead, more C_2H_6 than H_2 is used. The results can be explained by means of an additional reaction: (2) $2\ C_2H_6 \rightarrow 3\ CH_4+C$ taking place simultaneously with (1). It is claimed that reaction (2) indicates the capacity of the catalyst to dissociate CH_4 according to the mechanism: (3) CH_4 (ads) $\rightleftharpoons CH_3$(ads) $+H$(ads) $\rightleftharpoons CH_2$(ads) $+2$ H(ads) $\rightleftharpoons$ CH(ads) $+3$ H(ads) $\rightleftharpoons$ C(ads) $+4$ H(ads). These results indicate merely that carbides (possibly bulk carbides) can be formed by the action of C_2H_6 on Ni.

1209. GOERING, —. Synthesis in the Liquid Phase. High-Pressure Experiments, Ludwigshafen 558, Mar. 11, 1943. Bureau of Mines Transl. T–433, Jan. 1948, 7 pp.

Patent history of the process beginning with Pier's German Patent 630,824, and covering a number of I. G. Farbenindustrie applications and patents under the names of Michael, Duftschmidt, Linckh, and others.

1210. GOESCHEL, H. [High-Tension Technic in the Field of Motor-Fuel Recovery Plants.] Elektrotech. Ztschr., vol. 58, 1937, pp. 1282–1287, 1317–1320; Coal Carbonisation, vol. 4, 1938, p. 63; Chem. Abs., vol. 32, 1938, p. 3575.

Relative situations of petroleum and synthetic motor fuels (the major processes for liquid fuel production from coal) are described and discussed from an electrical engineering point of view for plant equipment and operation. The nature of the problems imposed upon the electrical industry is discussed, particularly as regards making maximum use of standard equipment in the interests of economy and rapid construction. Security of supply and safety against explosion risk are primary requirements, and the necessary arrangements in networks, distribution circuits, motors, switchgear, lighting and other equipment are explained. Pressure and vacuum pumps and compressors are required in sizes up to several thousand kw. Available types of motors are discussed. Application of electricity to process control is exemplified and illustrated in the case of the catalytic chambers of the Fischer-Tropsch process.

GOFMAN, E. *See* abs. **1664.**

GOHR, E. J. *See* abs. **2347.**

GOLDEN, P. L. *See* abs. **1370, 3215, 3294.**

1211. GOLDSTEIN, R. F. Petroleum Chemicals Reviewed. III. The Fischer-Tropsch Reaction. Petrol. Times, vol. 51, 1947, pp. 892–893.

Review with particular emphasis on the Hydrocol process and its economic significance. As regards the production of chemicals, it is remarked that this new source of aliphatic chemicals is going to have a serious effect upon the plants already producing aliphatics from petroleum.

1212. ———. Petroleum Chemicals Reviewed. Petrol. Times, vol. 52, Nov. 19, 1948, p. 1016.

Probable future development and expansion of petroleum chemicals are reviewed. Present trends indicate that the period of cheap chemical raw materials has passed. Propane and butane are more valuable as domestic fuels than as raw materials for aliphatics. Byproducts of synthetic plants such as Fischer-Tropsch may prove an important source. NH_3 is made from H_2 with natural gas as the source. For MeOH the natural gas is converted to a synthesis gas $CO+2H_2$, which is converted to MeOH by catalytic reaction at high temperature and pressure. Under the head of new products the manufacture of acrolein from petroleum and the Oxo reaction are discussed. The latter gives normal or branch-chain aldehydes by addition of CO and H_2 to an olefinic double bond. Acids and alcohols can be obtained from the aldehydes.

1213. ———. The Petroleum Chemicals Industry. John Wiley & Sons, New York, 1950, 449 pp.

Survey of literature dealing with initiation and development of the petroleum-chemicals industry. Chapters 2–5 deal with the chemistry of the paraffins (chapter 2 treats particularly of the synthesis and reactions of CO–H_2 mixtures as exemplified by the Fischer-Tropsch, the Hydrocol, and the Synol processes). Chapters 6–10 treat of the manufacture of olefins and the chemical developments based on them (chapter 10 discusses briefly the reaction of CO and H_2 with olefins, the so-called Oxo process). The manufacture of diolefins, naphthenes, aromatics and acetylene is discussed in chapters 11–14.

1214. GOLDSTEIN, R. F., AND SNOWDEN, F. F. Oxo Synthesis. Interrogation of Dr. Roelen. BIOS Interrogation Rept. 736, May 1946, 6 pp., PB 81,967.

1215. GOLUMBIC, N. Review of Fischer-Tropsch and Related Processes for Synthetic Liquid Fuel Production. Bureau of Mines Inf. Circ. 7366, 1946, 24 pp.

Review with emphasis on the more recent developments, covering historical, industrial, and process development, mechanism of the Fischer-Tropsch process, production of synthesis gas, manufacture of catalysts (Ni, Co, Fe, and Ru), properties of the primary synthesis products, and their treatment.

1216. ———. Some Chemicals From Synthetic Liquid Fuels Processes. Bureau of Mines Rept. of Investigations 4467, 1949, 58 pp.

Review of some available literature and experimental results of 2 synthetic liquid fuels processes now under investigation; presents summary of information regarding relative amounts of various industrially valuable chemical products thus produced. Gives brief description of the Fischer-Tropsch and related processes with emphasis on the effect of the important variables, catalyst, pressure, temperature and H_2: CO ratio upon the composition of the product. Enumerates byproducts and chemicals obtainable from hydrogenation of CO. Also reviews the work accomplished on the hydrogenation of typical United States coals, including a description of the liquid-phase hydrogenation assay procedure and summarized results of characterization of the oils produced during the hydrogenation of Pittsburgh-seam (Bruceton) coal under various conditions in the Bureau of Mines experimental plant. Important byproducts from the Fischer-Tropsch synthesis are water-soluble organic chemicals, such as EtOH, acetic acid, and acetone. These products will be available in large enough quantities to have a tremendous economic effect upon established sources and uses. They may become the principal source of many basic, organic chemicals, particularly those used in cellulose plastics and fibers, acetate rayon, pharma-

ceutical, and aliphatic solvent industries. Another potential source of important organic chemicals is the production of high-boiling alcohols from the Oxo and Synol processes. Oil from the liquid-phase hydrogenation of coal is an important source of organic chemicals of commercial value, such as tar acids for plastics, tar bases for pharmaceuticals, and benzene, toluene, and xylene for explosives manufacture and solvents.

———. *See* abs. **3296, 3297.**

1217. GOLUMBIC, N., ANDERSON, H. C., AND GRASS, R. C. Revised Bibliography of Bureau of Mines Investigations on the Production of Liquid Fuels From Oil Shale, Coal, Lignite, and Natural Gas to 1949. Bureau of Mines Inf. Circ. 7534, 1949, 53 pp.

Includes Government publications written by the Bureau of Mines staff for the technical press and reports of work done jointly with States, colleges, and industries. (*See* abs. **923.**)

GONDZIK, J. *See* abs. **1972.**

1218. GOODEVE, C., AND JACK, K. H. Kinetics of Nitrogen Evolution From an Iron–Nitrogen Interstitial Alloy. Disc., Faraday Soc., No. 4, 1948, pp. 82–91; Chem. Abs., vol. 43, 1949, p. 4933.

Rate of N evolution from ϵ–Fe nitride at 350°–500° is given by a 2d-order equation with respect to interstitial N concentration and is associated with an activation energy of 42,100±1,400 cal. per gm. mol. The evolution rate of N atoms per 100 Fe atoms per sec. is given as $r=2\,z\,(10^2/A)=(10^2\,Ncwn/A)\,e^{-E/RT}$, where A is the number of Fe atoms in the nitride particle. The approximate value for the successful collisions w is taken as 3 A. From the known structure of ϵ–nitride and the observed particle diameter N, n and A are known. At 450°, the values are $c=1.05\times10^5$ cm. per sec.; $N=1.9\times10^8$; $n=3.8\times10^{14}$; $A=2.3\times10^{12}$. Thus, at 450°, r ranges from $0.7–4.3\times10^{-3}$ with a most probable value of 1.8×10^{-3} N atoms per 100 Fe atoms per sec. The velocity of diffusion of N atoms to the surface is at least 10^4 times as rapid as the rate-determining process. The rate-determining stage of the reaction is considered the combination of N atom pairs at the solid surface. By calculation of the collision frequency on the assumption that this surface reaction behaves as in a 2-dimensional gas, the correct order of magnitude for the absolute reaction rate is predicted.

GOODMAN, J. B. *See* abs. **2576, 2577.**

1219. GORDON, A. S. Uncatalyzed Reaction of Natural Gas and Steam. Ind. Eng. Chem., vol. 38, 1946, pp. 718–720: Chem. Abs., vol. 40, 1946, p. 5545.

Uncatalyzed reaction of natural gas with steam has been studied 1,225°–1,516° with steam : natural-gas ratios of 1.5 : 5, and time of contact 0.21–4.6 sec. Even at high temperatures, long contact times, and steam : natural gas ratio of 5 there is some carbonization of the natural gas. The extent of carbonization is shown to be a function of the ratio of steam to natural gas, and to vary erratically with temperature and time of contact. As the temperature is increased, the % of natural gas undecomposed in a single pass through the furnace becomes less dependent on contact time (in the range of contact times studied), until at about 1500° there is little or no effect. At any temperature the % of undecomposed gas shows little if any dependence on the ratio of steam to natural gas. The application of this reaction to the production of a mixture of H_2 and CO for synthesis gas is pointed out.

1220. ———. Mechanism and Kinetics of the Thermal Decomposition of Methane in a Flowing System in the Region 1,000°–1,075° C. Jour. Am. Chem. Soc., vol. 70, 1948, pp. 395–401.

Mechanism and kinetics of the thermal decomposition of CH_4 have been studied in a porcelain reaction vessel using a flow system at 1,000°–1,075°. The data were treated in accordance with the assumption that the reaction was unimolecular and homogeneous as had been reported previously for a static system up to 850°. The reaction constants were found to increase with increasing decomposition which indicates a reaction less than first order or autocatalytic. The latter hypothesis was tested by adding separately small % of the various product gases to the original CH_4. It was shown that 0.72% C_2H_2 increased the reaction rate 2 to 2½ times its original value. The catalysis may be a homogeneous direct attack on CH_4. The addition of 1% of C_2H_4 likewise increased the reaction to about the same extent, but this is probably due to the C_2H_2 which is rapidly formed from the C_2H_4. Addition of 2% H_2 to the reactant CH_4 also gives a 20–30% increase in reaction rate with a concurrent increase in C_2H_2 content, which accounts for at least part of the effect on the reaction rates. Larger concentrates of H_2 had previously been shown markedly to slow the rate of decomposition. By increasing the surface : volume ratio about fourfold, the rate of decomposition is about 2½ times as great, part of the effect arising from an increased % of C_2H_2.

1220a. ———. Reaction Between Methane and Steam in the Temperature Region 1,000°–1,100°. Ind. Eng. Chem., vol. 44, 1952, pp. 1857–1859; Chem. Abs., vol. 46, 1952, p. 11,637.

The present work is an outgrowth of a study of the uncatalyzed steam-natural gas reaction at temperatures 1,200°–1,500° and a total pressure of 1 atmosphere. Between 1,000°–1,100° and 1 atmosphere the results of this work show that the reaction between CH_4 and steam is probably a combination of the decomposition of CH_4 followed by the steam-carbon reaction. Until C is formed as a result of the decomposition, steam behaves as an inert gas. Production of synthesis gas from CH_4 and steam for the Fischer-Tropsch process proceeds smoothly at about 900° on a Ni catalyst. Without an efficient catalyst, at considerably higher temperatures, there is no problem of decomposing CH_4, but gasification of the resulting C is so slow that an efficient catalyst for this reaction would be required to make the reaction economically feasible.

1221. GORDON, K. Development of Hydrogenation and Fischer-Tropsch Processes in Germany. Jour. Inst. Petrol., vol. 33, 1947, pp. 469–490; Chem. Abs., vol 42, 1948, p. 2417.

This paper, presented at a meeting of the Institute of Petroleum in May 1947, summarizes what has been done in Germany on the hydrogenation and Fischer-Tropsch processes and compares briefly the techniques adopted in both Britain and Germany.

1222. ———. Hydrogenation in the Fuel and Chemical Industries. Jour. Inst. Fuel, vol. 21, Dec. 1947, pp. 53–61; Petroleum (London), vol. 10, 1947, pp. 244–246, 262; vol. 11, 1948, pp. 16–17, 35–38; Gas World, vol. 127, 1947, pp. 556–558; Chem. Abs., vol. 42, 1948, p. 2077.

Melchett lecture for 1947 first deals with the manufacture of H_2 and of mixtures with N_2 required for making synthetic NH_3, and with CO for making synthetic MeOH. Refers to the manufacture of synthetic fuels by the Fischer-Tropsch process and to the reactions between olefins, CO, and H_2, according to the work of Roelen and Reppe. Considers a number of different types of reaction involving hydrogenation and describes analogous operations as carried out in the petroleum, fuel, and chemical industries. Gives account of the manufacture of aviation fuel.

1223. ———. Production of Petroleum by Synthetic Methods. Gas World, vol. 127, 1947, p. 78; Chem. Age, vol. 57, 1947, pp. 221–222, 269–270.

Paper presented at St. Andrew's symposium. Discusses 2 main methods for the production of gasoline—

coal hydrogenation and Fischer-Tropsch synthesis. Coal has been used at Billingham as the raw material; it has now been superseded by creosote oil and tar, as the coal caused great abrasion of the plant and during the war the plant could be more easily and safely shut down in case of air attack. When coal is used, it is first washed by flotation, then powdered and mixed with oil to give a paste from which the oil may be recovered by recycling. Owing to the nature of coal, about 5% avoids hydrogenation, a figure that may be increased if the coal is alkaline. To obtain more complete hydrogenation it is customary to add to the charge a small excess of HCl in the form of NH_4Cl. The ideal method of hydrogenating coal is to use 4 stages, although a satisfactory product may be obtained using 2, while at Billingham 3 stages are employed. In the initial stages the catalysts employed are Sn oxide and Fe sulfide, and in the final stage WS_2. The product from coal or tar hydrogenation is purely hydrocarbon in character in the fraction boiling up to 180°; above this temperature phenols and basic substances are obtained. The average yield of gasoline from bituminous coal is about 50%, although this figure will be slightly increased if the gasoline is for motor fuel and decreased if for aviation fuel. German annual output during the was was about 4,000,000 tons, while that at Billingham and Heysham was 500,000 tons. Gasoline obtained by this method has an octane number of 80, which can be increased to 95 by addition of Pb, and to 100 by addition of iso-octane. The economic prospects for this process are less favorable than they were 20 yr. ago mainly due to the increased costs of coal and labor, coupled with the fact that the gasoline sold today is of a higher quality than formerly.

1224. ———. Report on the Petroleum and Synthetic Oil Industry of Germany. BIOS Overall Rept. 1, 1947, 134 pp., PB 88,981s.

Divided under the following headings: Carbonization and gasification of coal; hydrogenation processes; Fischer-Tropsch process; crude-oil production; petroleum refining; lubricating-oil production; and testing and evaluation of products. The report comprehensively reviews the oil situation during the war, the sources of liquid fuels, and the contribution thereto made by coal-oil processes. Oil from various sources reached a maximum output of 6,930,000 tons in April 1944, but fell rapidly by the end of August to 120,000 tons. Hydrogenation was the largest oil producer (up to 3,250,000 tons); Fischer-Tropsch was less important (up to 585,000 tons); while petroleum, coal-tar distillation, and benzol showed, respectively, 1,770,000, 945,000, and 380,000 tons. Costs of synthetic fuels were entirely uneconomic compared with natural petroleum. Translated to present-day costs in Great Britain, the production costs of hydrogasoline from coal and tar respectively were 27.5 d. and 21.9 d. per gal., and for Fischer-Tropsch primary product 27.1 d. The processes for refining petroleum and for producing high-octane motor and aviation fuels were similar to those in general use but had not reached as high a state of development as in the allied countries.

1225. Gordon, W. R. South African Coal Industry. Canadian Min. Jour., vol. 70, No. 5, 1949, pp. 76–79.

Summary of report of the Coal Commission and of annual report for the Fuel Research Board for 1947 and a review of the coal trade are presented. Some discussion of proposed oil-from-coal plant now licensed to be erected at Vereeniging. The Hydrocol process is to be employed. One of the major improvements in this new plant is the use of "fluidized" Fe as the catalyst. The plant will have a capacity of 76,000,000 gal. of liquid fuel per year, including 10,000,000 gal. of diesel oil. The coals to be utilized are for the most part low-grade. It has not yet been definitely ascertained whether or not such coals will be satisfactory for making synthesis gas by gasification to be converted into liquid fuel.

Goss, W. H. *See* abs. **2176, 2177.**

1226. Göthel, —. Grenzflachen-Katalyse. Kröger, editor, Hirzel, Leipzig, 1933, p. 67.

It was found that the electrical conductivity of various powdered catalysts varied during the Fischer synthesis in such a way as to indicate the progressive formation of carbide.

1227. Gotoh, Y. [Reduction of Ferric Oxide by Hydrogen and Oxidation of Metallic Iron Reduced From Ferric Oxide.] Mem. Ryojun Coll. Eng., Inouye Commemoration, vol. 1934, pp. 393–413; Chem. Abs., vol. 29, 1935, p. 2124.

Describes apparatus for following changes of weight continuously by measuring the current required by a solenoid to counteract the displacement of a magnet attached to a silica spring, which is connected to a Pt bucket containing the sample. The material used was pure Fe_2O_3 and Anshan hematite, containing Fe_2O_3 93.89, Fe_3O_4 2.61, SiO_2 2.42 and Al_2O_3 1.08%. The reduction takes place in the stages $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe$. The reduction to Fe_3O_4 is rapid at all gas velocities; further reduction increases with increasing gas velocity up to 120 cc. per min. At constant gas velocity, the rate of reduction of Fe_3O_4 increases with the temperature, being rather slow up to 450°. The curves showed no breaks coresponding to FeO, and its absence was proved by X-ray photographs of samples at varying stages of reduction.

Gottlieb, S. *See* abs. **924, 925.**

1228. Goubeau, J. [Investigation of the Optical Analysis of Gasolines.] Brennstoff-Chem., vol. 23, 1942, pp. 1–7; Chem. Abs., vol. 36, 1942, p. 3033.

Data obtained by the Raman spectral analysis are discussed. Comparative tables show good checks with analytical results obtained by other methods. Particular stress is placed on the anlysis of Kogasin.

1229. Goutal, E. [Preparation of Synthetic Petroleum by the Andry-Bourgeois and Olivier Process.] Chaleur et ind., vol. 5, 1924, Special No., pp. 90–96; Chem. Abs., vol. 19, 1925, p. 1194.

Process consists essentially in making water gas, hydrogenating catalytically at 230° at atmospheric pressure to produce CH_4, decomposing into C_2H_2 and H_2 in an electric furnace at 2,000°, and hydrogenating the C_2H_2 catalytically at 150°–300° under a pressure of ½ atm. Products having a calorific value of 2,850 cal. are obtained by expenditure of 12,100 cal.; but raw materials having little or no commercial value (wood waste, high-ash coal, etc.) can be utilized. Discusses economic importance of process.

Goutel, F. *See* abs. **2720, 2721.**

1230. Graefe, E. [Ceresin From Coke.] Öle, Fette, Wachse, Seife, Kosmetik, vol. 43, No. 13, 1936, pp. 1–4; Jour. Inst. Petrol. Technol., vol. 23, 1936, p. 78A; Chem. Abs., vol. 31, 1937, p. 241.

Discusses production of hydrocarbons by catalytic reduction of CO and CO_2 of water gas. Comparatively lower working temperatures yield wax products of high melting point, called synthetic ceresin. The product melting at 96° is capable of taking up more solvent and remain a paste than natural ceresin, paraffin, montan wax, etc.

1231. ———. [Ceresin From Coke.] Petrol. Ztschr., vol. 32, No. 37, 1936, pp. 5–8; Refiner and Nat. Gasoline Mfr., vol. 16, 1937, pp. 335–337; Chem. Abs., vol. 31, 1937, p. 5137.

Properties of the wax produced in the Fischer benzine synthesis are briefly discussed (*see* abs. **1828**). Its high oil-binding properties make it suitable for the preparation of polishes, etc. It may also prove a use-

ful source of fatty acids, into which it can be converted by oxidation.

GRAETZ, A. *See* abs. **410.**

GRAF, E. *See* abs. **2339.**

GRAFINS, M. A. *See* abs. **3025.**

GRAGES, E. *See* abs. **1504.**

GRASS, R. C. *See* abs. **1217.**

1232. GRASS, R. C., AND STORCH, H. H. Coal-to-Oil Research at Bruceton, Pa. Chem. and Eng. News, vol. 28, No. 9, 1950, pp. 646–648.

Progress report on the conversion of coal to liquid fuels by the 2 basic processes and their variations: The Bergius process of direct hydrogenation of coal and the Fischer-Tropsch process of indirect hydrogenation of coal by way of synthesis gas. Some of the reseach activities that have not been described in the literature are touched upon.

1233. GRAUE, G., AND KOCH, H. W. [Diffusion of Gases in Solids, Studies on Iron Oxide and Iron Aluminum Oxide.] Ber. deut. chem. Gesell., vol. 73, B, 1940, pp. 984–995; Chem. Abs., vol. 35, 1941, p. 3151.

Atomic pores of highly dispersed materials remain accessible by the addition of certain substances. Effect of Al_2O_3 (A) was studied on increasing the accessibility to gases of the inner surface of röntgenographically amorphous Al_2O_3–Fe_2O_3 (AF) catalysts obtained by precipitation at 20°. The porosity was determined by the Hahn built-in radioactive-substance emanation method. On heating (AF) the atomic diffusion pores decrease to nearly zero at 600°; for pure Fe_2O_3 (F) corresponding parts of the curve lie about 100° lower. The density of Fe_2O_3 increases on heat treatement from 3.7 and 3.3 at 250° and 4.9 and 4.4 at 450° to 5.1 and 5.1 above 600° as measured by the emanation and the xylene-20°-pycnometric methods, respectively. Although pure (F) rapidly ages to a maximum density of 5.1 when heated at 450°, the (AF) catalysts age only slowly and still show differences in density as measured by the 2 methods. The absolute rate of diffusion of gases in (AF) as measured by the emanation method is greater than in (F), and increases again at high temperatures, but the Tammann position-exchange temperature is about 820° for the (AF) and only 620° for (F) catalysts. Above 600° for (F) and 700° for (AF) diffusion into the lattice leads to abnormally high values of the density which are not observed by the xylene method. Debye-Scherrer X-ray photographs give the same maximum for both, but the observed intensities of the maximum are greater for (F) than for (AF). It is concluded that (A) is dissolved in the (F) lattice and that its addition in some way hinders the mobility of the lattice constituents until higher temperatures are reached.

1234. GRAUE, G., AND RIEHL, N. [Size of the Pores and Inner Volumes of Amorphous and Crystalline Materials.] Ztschr. anorg. Chem., vol. 233, 1937, pp. 365–375; Chem. Abs., vol. 32, 1938, p. 18.

Specific tests show that gases do not penetrate into catalysts through the large pores alone. Where there is random distribution or where the arrangement of the lattice lacks regularity, the irregular spacing of the atoms allows penetration, even through openings of atomic dimensions.

1235. GRAVES, G. D. Higher Alcohols Formed From Carbon Monoxide and Hydrogen. Ind. Eng. Chem., vol. 23, 1931, pp. 1381–1385; Chem. Abs., vol. 26, 1932, p. 1235.

Several higher alcohols have been identified as by-products of the industrial high-pressure MeOH synthesis: 1–propanol, isobutanol, 2–methyl–1–butanol, 2–methyl–1–pentanol, 2, 4–dimethyl–1–pentanol, 4–methyl–1–hexanol, isopropanol, 3–methyl–2–butanol and 2, 4–dimethyl–3–pentanol. Strong evidence for the presence of the following was obtained: 2, 4–dimethyl–1–hexanol, 4– or 5–methyl–1–heptanol, 3–pentanol, 2–pentanol and 2–methyl–3–pentanol. Acids, esters, ketones, olefins, and tertiary alcohols were absent. The presence of all the products identified can be accounted for by assuming that the mechanism of synthesis is intermolecular dehydration of 2 lower alcohols involving H_2 either from the hydroxylated C atom or the adjacent C atom. H separates most readily from a CH_2 group, more difficultly from a Me group, and not at all from a CH group.

GRAYSON-SMITH, H. *See* abs. **1624.**

1236. GREAT BRITAIN COMMITTEE OF IMPERIAL DEFENCE, SUBCOMMITTEE OF OIL FROM COAL. Falmouth Report on the Production of Oil From Coal. H. M. Sta. Office, London, 1938, 71 pp.; Coal Carbonisation, vol. 4, 1938, pp. 46–48.

Committee's report on the Fischer-Tropsch process has little value, as the evidence obtained is conflicting. The general, though indefinite, conclusion to be drawn therefrom is that the capital cost and economics of a Fischer-Tropsch plant would be similar to that of a coal-hydrogenation plant. The committee recommends "the establishment of a plant to work the Fischer process, and designed for the production of not less than 20,000–30,000 tons of primary products per annum." This is the commercially economic size of plant for the operation of this process.

1237. GREAT BRITAIN FUEL RESEARCH BOARD. Lubricating Oil. Fischer Process. Rept. for the Year Ended Mar. 31, 1935, pp. 122–123.

In working on the synthesis of liquid hydrocarbons from mixtures of CO and H_2, products have been obtained that embrace the entire series of paraffins from CH_4 to hard paraffin wax with the related olefins, but contain no fraction corresponding to a lubricating oil. Recently, however, products are reported, the specifications of which are those of excellent lubricants. These are formed by the polymerization with $AlCl_3$ of the fractions that are rich in unsaturated hydrocarbons. Some investigation has been made sufficient to confirm the nature and conditions of the synthesis reaction.

1238. ———. Production of Hydrocarbons From Water Gas by the Fischer Synthesis. Rept. for the Year Ended Mar. 31, 1936, p. 148.

Laboratory-scale apparatus capable of treating 10–15 l. of gas per hr. has been designed and operated. The results fully confirm those of Fischer. The catalyst used is Co promoted with Th supported on kieselguhr. Pelleting the catalyst considerably increases the volume of gas that can be treated in a unit of time in a given volume of catalyst space. Examination of the absorption spectra of the oils produced show these to have a definite though small content of aromatic hydrocarbons; the presence of benzene, toluene, and naphthalene was detected in amounts of from 0.1–1.0%. Small samples of lubricating-oil fractions have been produced from the primary products by treatment with anhydrous $AlCl_3$. On the basis of the experience gained with the laboratory-scale apparatus, a plant of sufficient capacity to give 1 l. of lubricating oil per day will be constructed.

1239. ———. Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. Rept. for the Year Ended Mar. 31, 1937, pp. 141–147.

Laboratory investigation on the synthesis of hydrocarbons from CO and H_2 has been directed mainly to determine the influence of the % of ThO_2 promoter on the activity of the Co catalyst, and the effect on the yield of hydrocarbons of changing the ratio $CO:H_2$. No conclusions have been reached. As to the mecha-

nism of the synthesis reaction, the evidence points toward the Fischer carbide theory, although an alternative theory is postulated that the CO molecules are first linked to the catalyst surface, forming a bond similar to that existing in a Co carbonyl molecule, except that the metal atom is not detached from the lattice. The H_2 absorbed on adjacent Co atoms may then react with the absorbed CO, attacking either the O_2 or the C atom. In the latter case, HCHO would be formed as an intermediate product. Neither of the above hypotheses explains how the methylene or other radicals first formed link up to give the long hydrocarbon chains. A plant, large enough to convert 100–150 cu. ft. of a mixture of H_2 and CO per hr. into hydrocarbons has been designed and constructed. A flow diagram of the plant is shown. Catalyst cooling is accomplished by circulating hot water under pressure through horizontal tubes in the catalyst bed. Details of catalyst preparation are presented, and the importance of washing the precipitated catalyst with boiling H_2O is emphasized. With the unwashed catalyst no contraction took place, even at a temperature of 238°, whereas with the washed catalyst a contraction of 65% at 198° took place and was maintained for 24 hr. At an equivalent gas rate per gm. of catalyst, the catalyst that had been washed and electrodialyzed brought about a contraction of 71% at 193°. Some difficulty was found in transferring the catalyst preparation from the laboratory to the larger scale, the causative variables have not been determined.

1240. ———. Production of Synthesis Gas. Rept. for the Year Ended March 1938. H. M. Sta. Office, London, pp. 134–135.

In connection with water-gas experiments, a process has been adapted for producing synthesis gas for the Fischer-Tropsch process by combining the Lane process of H_2 production with the normal water-gas process. The Lane process consists of the alternate reduction and oxidation at 700°–800° C. of calcined spathic Fe ore, the reduction being effected by water gas and the oxidation with production of H_2 by steam. The Research Board process involves removing the checker brickwork from the tar cracking chamber and its replacement by spathic Fe ore. The temperature of the ore is raised to 700°–800° by the flow gases and is then reduced by passing through it the water gas produced during the up-run. The spent gas from this reduction (calorific value 200 B. t. u. per cu. ft.) is collected in a separate gas holder. H_2 is produced by passing the back-run steam through the reduced ore, a part of the steam being decomposed by the reduced Fe ore with the production of H_2 and the excess steam passed to the generator containing coke, where normal water gas is made. The finished gas contains 32.3% of CO and 61.9% of H_2.

1241. ———. Synthesis of Hydrocarbons and the Production of Lubricating Oils. Rept. for the Year Ended March 1938. H. M. Sta. Office, London, pp. 186–206.

Investigations have extended from a study of the mechanism of the synthesis, through laboratory-scale and semi-technical-scale plant work, to an examination of the quality of the products under practical conditions. Investigation of the mechanism leads to the conclusions that carbide formation proceeds much more rapidly when CO reacts at 200° with an active Fischer catalyst than with ordinary reduced Co; that the carbide formed reacts very readily with H_2 to give a gas consisting mainly of CH_4 and a small % of higher hydrocarbons; that the rate of reaction of the carbide with H_2 is very much greater than its rate of formation from CO and the catalyst. By studying the *o–p*-H_2 conversion on the catalyst during the synthesis reaction, it is found in general that, if the conversion is being catalyzed by a metal, adsorbed H atoms are present on the metal surface; and, if on the other hand, conditions are such that no absorbed H atoms can be formed on the surface, the metal will not catalyze the *o–p* conversion. The results of experiments show that when the product is higher hydrocarbons, no H atoms are detectable on the surface, but when the product is CH_4, H atoms are there. Thus it seems reasonable to conclude that, if the chemisorbed CO is attacked by adsorbed H atoms, the product will be CH_4, but attack by molecular H_2 leads ultimately to higher hydrocarbons. Previous difficulties in catalyst preparation have been largely removed and a satisfactory composition has been found in Co : ThO_2 : kieselguhr=100 : 18 : 100. Before the semi-technical-scale plant runs, described in detail, the catalysts was reduced in H_2 at 350°, compared with the operating synthesis temperature of 180°–230°. The highest yield of recovered oil product was 77.0 gm. per *N* m.^{3} of synthesis gas (exclusive of lighter constituents). This yield has later been improved to 90–100 gm. per m.^{3} The crude product consists almost entirely of straight-chain paraffins and olefins, from the lightest member of the series up to wax having a melting point above 100°. Appropriate fractions may be used as motor fuel and diesel oil, the former of very low antiknock value (30 by the Cooperative Fuel Research Committee method), the latter with a high cetene number (93). Important possibilities of the process lie in the polymerization with $AlCl_3$ of the unsaturated constituents of the product to form lubricating oil, considerable details of which are presented. Some experiments have been carried out on the oxidation of the wax for the production of fatty acids, and it has been shown possible to produce a soap by this means. The procedure is to oxidize the wax at 100°–130° with 0.25–0.5% Mn resinate as catalyst. The only point in which the synthetic lubricating oils fall short of high-grade natural products is that they failed to pass the test with respect to increase of viscosity on oxidation associated with formation of acidic and saponifiable substances.

1242. ———. Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. Rept. for the year Ended March 1939. H. M. Sta. Office, London, pp. 151–176.

Continuation of the investigations begun in 1937–38 gives further account of the operation of the plant and of the yields obtained during a run lasting more than 2 mo. An important aspect of the process is the possibility of using certain fractions of the crude product for the preparation of lubricating oils. During the most favorable stage of the run, the yield of recovered liquid hydrocarbons was over 90 gm. per *N* m.^{3} of synthesis gas and, in addition, about 10 gm. per m.^{3} of easily condensible hydrocarbons and 3 gm. per m.^{3} of hard wax. The rate of input of synthesis gas was standardized at 120 cu. ft. per hr. The normal synthesis was started at 186° and progressively raised to 215° as the activity of the catalyst diminished. It was found necessary, at least at the end of each 24-hr. period and sometimes oftener, to revivify the catalyst by passing H_2 over it for 1 or 2 hr., after which a spurt in the activity occurred accompanied by the production of excessive amounts of CO_2. To obtain the best results, a special "running-in" technique of the catalyst had to be observed. Further data regarding the synthesis mechanism indicate that carbide is not formed on the catalyst in the usual way $2Co+CO \rightarrow Co_2C+CO_2$ but rather by $2Co+CO+H_2 \rightarrow Co_2C+H_2O$. These conclusions are confirmed and put on a quantitative basis by measuring the rates of the various reactions at a series of temperatures and so obtaining the corresponding energies of activation; that of (1) is 18,000 cal., that of (2) 9,500 cal., and that of the reduction of carbide $Co_2C+2H_2 \rightarrow 2Co+CH_4$, 11,500 cal. The results indicate that reaction (1) wil not occur during the Fischer synthesis, and that the formation of carbide by reaction

(2) will occur, followed by its reduction to CH_2 groups. Previous work on the *o–p*–H_2 conversion has proved that in the presence of large amounts of chemisorbed H_2 these CH_2 groups are reduced further to give CH_4; when, however, the amounts of chemisorbed H_2 is small, they polymerize and give higher hydrocarbons. It is reasonable to suppose that the larger numbers of CH_2 groups produced on the surface during the synthesis are equivalent to a macro-molecule from which fragments can be broken off to form the Fischer products. If so, cracking of paraffin hydrocarbons should occur on the catalyst at 200° by interaction of the paraffin hydrocarbon with chemisorbed H_2, and hence in the Fischer synthesis the products actually obtained are hydrogenation-cracking products of the macro-molecules of CH_2 groups, caused by the presence of quite small amounts of chemisorbed H_2. In the presence of larger amounts the hydrogenation-cracking is carried so far that CH_4 only is produced.

1243. ———. Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. Summary Report for the Period 1940–45, based on information from Dr. C. C. Hall, 1947, 12 pp.

Work is summarized in 2 parts: Study of the synthesis process, particularly the production of lubricating oils and the working-up of the primary products. The apparatus was the same as previously described, except that the oil jacket used as the heating and temperature-regulating means was replaced by a vertical steel tube embedded in an electrically heated Al block. The most active catalyst at the reaction temperature of 185° and at atmospheric pressure, was found to be Co : ThO_2 : MgO : kieselguhr= 100 : 5–6 : 2–8 : 200–300, reduced by H_2 at a high velocity (5,000–6,000 vol. per vol. of catalyst per hr.) for 2 hr. at 380°–420° C. It could be dewaxed by passing H_2 at 185°–200° and entirely regenerated by repeating the original high-temperature reduction in H_2. It was found that the initial life (the period up to the first H_2 dewaxing treatment) of this catalyst was appreciably increased by operating at a temp. of 185° from the start, instead of raising it from 175° to 185° gradually. The maximum converter life (the period between the original reduction and the re-reduction) is obtained when the H_2 dewaxing treatment is carried out at short intervals (7–10 days) and the temperature raised as slowly as possible. The conditions necessary for maximum total life (the period up to re-manufacture) are not fully known, although evidence has been obtained that restricting the maximum synthesis temperature to 195° during each converter life is beneficial. One of the most important factors affecting the performance of the Co–ThO_2–MgO catalyst is the nature of the kieselguhr used as carrier. The best one yet tested was of Portuguese origin. It gave a robust catalyst of high activity and long life and, as a result of the high density, a high space-time yield. It was thought possible to avert deterioration of the catalyst by wax deposition by maintaining a higher partial pressure of H_2 during the synthesis, but such improvement was nullified by an undesirable increase in CH_4 formation. Neither did a decrease in the reaction temperature help the situation since any reduction in CH_4 by this means was offset by the formation of wax. Dilution of the synthesis gas with N_2 at a constant gas rate of 1 l. $CO+2H_2$ per gm. Co per hr. causes a marked fall in total conversion and a serious reduction in liquid hydrocarbons. When CH_4 is used as a diluent it enters into the reaction, giving a 10–20% higher yield of liquid hydrocarbons per $m.^3$ of CO and H_2 than when N_2 is used and at the same time a greatly enhanced yield of C_3 and C_4 hydrocarbons. It has not yet been established whether this reaction persists or is merely confined to the initial phase of high catalyst activity. Use of gas rates 1½ times and 2 times normal causes a sharp fall in conversion and, initially, a more rapid deterioration, which later, however, becomes no greater and may be even less than at normal rate. Catalysts with a high Co density (12 or more gm. Co per 100 ml.), which operate satisfactorily at atmospheric pressure with a high space-time yield, have been found unsatisfactory for synthesis at medium pressure. Excessive CH_4 production occurs and lower yields of liquid and solid hydrocarbons. When water gas is used instead of normal synthesis gas, however, excessive formation of CH_4 is suppressed, and yields of liquid and solid hydrocarbons as high as those for catalysts of normal density (7–9 gm. Co per 100 ml.) are obtained. Only slight work has been performed on Fe catalysts and of those tested, none has given the consistently good yields (130–140 gm. per N $m.^3$) obtainable with Co catalysts at 10 atm. pressure. Addition of C_2H_2 to the synthesis gas was tried to determine if branched-chain hydrocarbons might be formed. An increase in the octane number of the gasoline fraction from 30 to 78 was obtained but it was found that this increase was due to the olefins and aromatic hydrocarbons formed by the reaction between C_2H_2 and H_2 independently of the reaction between CO and H_2. The formation of rubberlike polymers also caused rapid deterioration of the catalyst. The carbide mechanism of the Fischer–Tropsch process is supported and further extended through experimental studies. The production of lubricating oils by polymerization of the primary, olefin-containing Fischer–Tropsch products has received further detailed study with emphasis on the use of water gas rather than synthesis gas as the raw material. An extensive study has also been made, and the results have been summarized of the production of fatty acids for the preparation of soap or edible fats by the controlled oxidation of Fischer–Tropsch wax of initial b. p. 300° and average molecular weight 315 prepared in the semi-technical-scale plant.

1243a. ———. Oils and Chemicals From Coal. Report of the Fuel Research Board for 1949–50; Chem. Age, vol. 66, 1952, pp. 371–374.

Study of the Fischer–Tropsch synthesis had been continued. The work based on Co catalysts was concluded as Fe catalysts were found to be cheaper and more flexible in operation in the fluidized and liquid-phase processes. Operation of a 30–50 gal. daily capacity pilot plant was begun. Work was carried out with Fe catalysts at 20 atm. and 300°–320° temperature. Formation of CO_2 was suppressed and the linear gas velocity necessary for fluidization was maintained by recirculation of 3–10 vol. residual gas with each volume of fresh synthesis gas. Yields of C_5 and higher hydrocarbons increased at the expense of the C_2–H_4 hydrocarbons. However, formation of free C and of CH_4 was increased and the degree of unsaturation of the products was reduced. The fused NH_3–synthesis catalyst gave lower yields of liquid hydrocarbons and H_2O–soluble compounds containing O and higher yields of CH_4 than the sintered mill-scale catalyst. Best operating results were obtained when using a mill-scale catalyst diluted and expanded by C formation so as to contain about 200 gm. Fe per liter as compared with 1,800 gm. Fe per liter for freshly reduced catalyst. Depth of the slurry through which the synthesis gas passed was not a significant factor. Proportion of gas that reacted and the yield of products appeared to be controlled by the gas throughput per volume of slurry rather than that per volume of catalyst. Best performance was obtained with a slurry containing about 300 gm. reduced catalyst per liter. The maximum gas rate consistent with satisfactory conversion was about 500 vol. fresh gas per vol. slurry per hr. Effect of reaction conditions on the proportion of alcohols in the products was investigated. Temperature and pres-

sure had the greater influence, the proportion of alcohols increasing with fall of reaction temperature and increase in pressure. An increase in the rate of gas flow, and a decrease in the ratio H_2 : CO in the gas both favored production of alcohols.

1244. ———. Synthesis of Methane. 5th Annual Rept., 1943–44, pp. 13–25; Gas Abs., vol. 1, No. 7, 1945, p. 10.

Problem of the synthesis of CH_4 from CO and H_2 by means of promoted Ni catalysts at 350°–800° C. and at pressures 1–50 atm. has been investigated separately by the Gas Research Board Laboratories and the Fuel Research Station in Britain. Both laboratories have studied methods to prevent (*a*) the loss of activity of the catalyst due to overheating, which causes a diminution of active surface (sintering) and (*b*) deposition of C at higher temperatures. Their suggested means of overcoming these difficulties are in fairly close agreement: (1) Catalysts prepared by the precipitation of nitrates with alkali as carbonate in the presence of kieselguhr support, followed by a very thorough washing, are more resistant to heat treatment and give a much lower C deposition than those obtained by impregnation, that is, ignition of the absorbed nitrates on the support. (2) Overheating, or sintering, as well as the rate of C deposition, depends on the effective removal of the exothermic heat of reaction and increases with increasing working temperatures. At 700° C. the life of the catalyst becomes relatively short. However, at 800° C. an extremely long life was observed in spite of sintering, probably because at such high temperature the reaction is no longer dependent upon specially active atoms in the catalyst. (3) The rate of C deposition depends upon the nature of the support. Catalysts of identical composition supported on kieselguhr from 1 source gave 10 times more C deposition than those on kieselguhr from another source. (4) C deposition decreases as the size of the catalyst granules increases. Heat dissipation is also favored by the use of a narrow catalyst space surrounded by a jacket containing a high-boiling liquid. (5) The admixture of steam with the process gas decreases C deposition, and 15% steam (by volume) entirely prevents it. (6) The higher the H_2 : CO ratio the less the tendency to deposition of C. The amount of steam required by gases of various H_2 : CO ratio in preventing C deposition is shown by curves for various temperatures 350°–600° C.

1245. ———. Synthesis of Methane. 6th Annual Rept., 1944–45, pp. 18–32.

Since the 5th report (*see* abs. **1244**) a medium-scale plant has been designed to allow purification from S compounds of the synthesis gas, the modification of the proportions of H_2 and CO in the gas, and the division of the gas into streams for evaluation of a number of variables including pressure, each stream carrying about 250 cu. ft. of gas per hr. Methods were recorded in the 5th report for controlling the heat of reaction by (1) recirculation of gas, (2) the use of rod-shaped catalysts over which streamline conditions of flow were maintained, so that the rate of diffusion of gas to the surface of the catalyst controlled the rate of reaction by giving a natural distribution over a wide surface, and (3) the use of forced distribution by means of a perforated feed pipe extending over a length of catalyst surface. Using methods (2) and (3), life periods of over 2,000 hr. were maintained at gas velocities of 2,000 vol. per vol. of catalyst per hr., and with method (3) it was possible to use a synthesis gas as low as 1.0 in H_2: CO ratio, and to avoid C deposition for 2,700 hr. Some study of the reactions involved in C deposition were made. Variations have been made with some success in the composition of the standard Ni catalyst, with the object of preventing deposition of C. Further studies have also been made of the increases in temperature over the catalyst surface and of the connection between this temperature and loss of activity due to sintering. Little success has been obtained in employing MoS as a CH_4-forming catalyst resistant to poisoning by S, but the potentialities are so great that the work will be continued. Experimental details are given in tabular and graphic form on the effect of additions to the catalyst of S, Mn, and Al on C deposition; S up to 0.2% of the Ni and Al in excess were favorable in their effect. Mn favored C deposition. The S-containing catalyst resists sintering less effectively than does the Al-containing catalyst. Other experiments studied the influence of space velocity, control temperature, and size of catalyst granule upon the maximum temperature developed in a column of granulated catalyst at atmospheric pressure with dissipation of reaction heat. The mechanism of C deposition on the Ni catalyst involves the formation of NiC by the reaction between CO and Ni at 200° and the subsequent breakdown of this into Ni and C. The Fuel Research Station has studied the effect of the carrier on C deposition on catalysts of Ni–ThO_2–MgO–kieselguhr and has concluded that a kieselguhr with low specific surface area promotes the most rapid C deposition. Calcination of the kieselguhr is best carried out at 700°–800°. It was also found that the effect of heating the catalyst in H_2 was to decrease the activity for CH_4 synthesis and to increase the tendency to deposit C. The addition of small proportions of P and S reduces its tendency to C deposition but increases the rate of deterioration; the addition of 0.2% S as $NiSO_4$ reduced the rate of C deposition with process gas H_2: CO=1.5 : 1 from 0.462% to 0.157%, but reduced the active life with gas of H_2: CO=3.0 : 1 and space velocity 3,700 vol. per vol. per hr. from 1,700–910 hr.

1246. ———. Synthesis of Methane. 7th Annual Rept., Commun. 24, November 1946, pp. 20–38; Gas Times, vol. 54, Feb. 27, 1948, p. 295; Fuel Abs., No. 3536, June 1948.

Research work has been continued by both the Gas Research Board and the Fuel Research Board on the catalytic synthesis of CH_4 as a means of gas making or gas enrichment, and progress is reported in the study of the reactions involved in the development of simpler and more effective catalysts and in the methods of purification of the synthesis gas from organic S compounds. The study of the mechanism of the reactions leading to the deposition of C on catalysts has been continued, but so far none of the findings has been applicable to the general problem of controlling the CH_4 synthesis reaction on an increased scale. Laboratory-tested variations of known methods of control of catalyst temperatures will be studied, including (1) recirculation of gas, (2) the use of rod-shaped catalysts over which streamlined conditions of flow are maintained so that the rate of diffusion of gas to the surface of the catalyst controls the rate of reaction by natural distribution, and (3) the use of perforated inlet pipe extending along or through the catalyst column and providing mechanically controlled distribution. Some success has been found in the use of an annular layer of granulated catalyst with which the reaction gases make contact progressively along its length through perforations in an inner tube. At a rate of 120 cu. ft. of synthesis gas per hr., the extent of C deposition has been greatly reduced. Modified Ni–Mg catalysts have been developed which are active enough to be operative at temperatures down to 186°, not only with synthesis gas but also with town gas. Studies have also been made of the effects of the conditions of preparation of the catalysts, and of their activity at stages during progressive poisoning by S.

1247. ———. Report of the Director for 1947. Commun. 37, 1948, 55 pp.; British Abs., 1948, B, I, p. 370.

Some of the subjects dealt with are: (*a*) Direct hydrogenation of coal. Difficulties in temperature control and in dissipating the heat of reaction in a static bed of coal have turned attention to the hydrogenation of fluidized coal, for which a high-pressure apparatus has been constructed. (*b*) Synthesis of CH_4. The pilot plant with temperature control by circulation of the gases has operated satisfactorily, the catalyst keeping its full activity for 3,500 hr. at 20 atm. A life test is to be made at 1 atm. While the surface area of the $Ni–Al_2O_3$ catalysts is not a measure of their activity, its retention without diminution when heated is an indication that activity will be maintained in use. (*c*) Water-gas process. (*d*) Removal of organic S compounds from gas. (*e*) Removal of H_2S by Fe_2O_3.

1248. GREAT BRITAIN HYDROCARBON OIL DUTIES COMMITTEE (SIR AMOS L. AYRE, Chairman). Report of Hydrocarbon Oils. Coke Smokeless-Fuel Age, vol. 7, 1945, pp. 88–90; Chem. Trade Jour., vol. 116, 1945, pp. 423–426; Chem. Age, vol. 52, 1945, pp. 343–345; Petrol. Times, vol. 49, 1945, pp. 304–309.

Report, with comments indicating the importance of developing chemical manufactures based on coal by products. It is recommended by the committee that imported hydrocarbon oil used for chemical synthesis should be free of duty and for indigenous oil similarly used, allowances should be paid equal to the respective duties. An interesting feature of the Fischer-Tropsch process is that the products are aliphatic, not aromatic, in character and thus resemble petroleum rather than coal oils produced by other processes. Many of the more important chemicals which can be produced from petroleum could therefore be derived with equal and, in some cases, greater facility from the primary products of hydrocarbon synthesis.

1249. GREAT BRITAIN. NORTHERN INDUSTRIAL GROUP. COAL PROCESSING INDUSTRIES PANEL (H. L. Riley, chairman). Coal-Processing Industries Report. Chemicals From Coal in the North. Chem. Age, vol. 53, 1945, pp. 565–568.

Objectives to be considered are development of the tar-distillation industry and extraction of C_2H_4 from coke-oven gas. The statment is made that the northeast provides one of the most suitable areas in the country for large-scale trials of the Fischer-Tropsch process. The County of Durham, with its large coke-producing units and potential reservoirs of surplus gas, is eminently well placed for this research work, and the products made by the Fischer-Tropsch process may be linked with those from the C_2H_4 extraction plan.

1250. GREBEL, A. [Practical Substitute Fuels, Particularly Synthetic Fuels.] Chaleur et ind., vol. 6, 1925, pp. 273–282; Chem. Abs., vol. 19, 1925, p. 3007.

From a detailed discussion of the problem, Grebel concludes that a successful gasoline substitute should fulfill at least the following conditions: O less than 25%, H 7–16%, calorific value over 7,000 cal. per l., thermal potential (cal. per $m.^3$ of perfect explosive mixture) over 750, flash point as little below 20° as possible, price per 1,000 cal. between that of petroleum and of gasoline.

1251. ———. [Coal as a Source of Liquid Fuels.] Mat. grasses, vol. 19, 1927, pp. 7958–7961, 7984–7987, 9011–9013; Chem. Abs., vol. 22, 1928, p. 1226.

Address.

1252. ———. [Processes for the Manufacture of Liquid Hydrocarbons as Fuels for Explosion and Internal-Combustion Engines, Starting From Mineral Fuels.] Chaleur et ind., vol. 8, 1927, pp. 324–332; Chem. Abs., vol. 21, 1927, p. 2779.

Critical review of recent processes, particularly the Bergius, Fischer-Tropsch and Prudhomme-Houdry.

1253. GREENFIELD, G. J. Coal Gas as a Raw Material. Coke Smokeless-Fuel Age, vol. 2, 1940, pp. 201–202, 204; Chem. Abs., vol. 35, 1941, p. 1206.

Typical coke-oven gases are classified according to analysis: Valueless: CO_2 4, N_2 5, H_2S+HCN 1; low-calorific-value gases: H_2 54, CO 4; high calorific-value gases: CH_4 29, illuminants 3%. A possible treatment is to pass this gas with steam over heated catalysts, converting the CH_4 into CO and H_2. This resulting mixture opens up a vast field to the synthetic chemical industry.

GREENFIELD, H. *See* abs. **3655, 3655b.**

1254. GREENWOOD, H. D. Technical Developments During 1936 in the Gas and Allied Industries. Fuel Econ. Rev., 1937, pp. 49–54; British Chem. Abs., 1938, B, p. 12.

Carbonization of cannel coal, the Fischer-Tropsch process, and the removal of S compounds from town gas are discussed.

1255. GREGG, S. J., AND JACOBS, J. Examination of the Adsorption Theory of Brunauer, Emmett, and Teller, and Brunauer, Deming, Deming, and Teller. Trans. Faraday Soc., vol. 44, 1948, pp. 574–588; Chem Abs., vol. 43, 1949, p. 2065.

Brunauer-Emmett-Teller and Brunauer-Deming-Deming-Teller theories have been examined, and the following points are discussed: The heat of adsorption E_1 calculated via the parameter c of the theory, is shown to be compatible with thermo-dynamic requirements as expressed in the Clausius-Clapeyron equation, but the latter are equally compatible with a value E_1+RT in C, where C=any constant. E_1 shows a moderate qualitative correspondence with the calorimetric or isosteric value, but close quantitative agreement is lacking. The relationship, which the theory implies between I_L and Ix, the integration constants of the vapor equation and the adsorption isostere, respectively, is not found to hold in practice. Arguments are adduced against the assumption made by the theory that the evaporation-condensation conditions of the adsorbed multilayer differ inappreciably from those of the bulk liquid. The implicit assumption that the adsorption isotherms above and below the critical temperature of the adsorbate are markedly different is shown to be improbable. The values of the monolayer capacity derived from the theory and from the "phase-change" method of Gregg and Maggs are compared; only for isotherms of types I and II of the BDDT classification is agreement to be found. According to the phase-change method, the adsorption isotherm cannot invariably be represented by a single equation as assumed by the BET-BDDT theory; where phase changes occur, the isotherm is split up into separate parts each following its own equation. The BET-BDDT theory does not account for hysteresis, but the phase-change conception includes it as a natural consequence.

1256. GRIFFIN, C. W. Adsorption of Hydrogen by Supported Nickel Poisoned With Carbon Monoxide. Jour. Am. Chem. Soc., vol. 59, 1937, pp. 2431–2434; Chem. Abs. vol. 32, 1938, p. 1158.

Adsorption was measured at 0° for H_2 on a supported Ni catalyst poisoned with CO. A small quantity of poison causes an increase of H_2 adsorption at all pressures up to 1 atm. A large amount of poison gives a slight low-pressure increase and a high-pressure decrease of adsorption. Larger amounts of poison decrease the rate of adsorption.

1257. ———. Sorption of Hydrogen by Poisoned Copper. Temperature Variation Experiments. Jour. Am. Chem. Soc., vol. 67, 1945, pp. 62–64; Chem. Abs., vol. 39, 1945, p. 1342.

The sorption of H_2 with temperature variation on pure massive Cu was determined and compared with

that of H_2 on the same Cu poisoned with a small quantity of CO. The effect of the poison is to prevent largely solution of H_2 in Cu.

1258. GRIFFITH, R. H. Catalytic Removal of Sulfur Compounds. Inst. Gas Eng., Copyright Pub. 175/64, 1937, pp. 45–64; Gas Jour., vol. 220, 1937, pp. 475–476, 479–485, 667; Gas World, vol. 107, 1937, pp. 379–383, 471–476, 563; Chem. Abs., vol. 32, 1938, p. 6438.

An active $Ni(OH)_2$ catalyst is deposited on porous china clay by soaking in a boiling solution of $NiCl_2$, drying, plunging the pellets into excess alkali, washing, and activating with coal gas at 350° for 2 hr. Purified coal gas was passed through the catalyst bed at about 1,500 vol. per hr. per unit vol. of catalyst space at an inlet temperature 160°–180°. In an experimental run of 40 weeks, 10,000,000 cu. ft. of gas were treated without renewal or alteration of the catalyst. CS_2 was converted to CO_2 and SO_2 with small porportions of SO_3. If temperature rose too high, a back reaction occurred, and H_2S was produced by hydrogenation of SO_2. Temperature can be controlled by adjustment of O_2 in gas; the normal amount is 0.6–0.7%. Combustion of H_2 and complete elimination of O_2 increase calorific value, permitting extraction of more benzene. Heat requirements are met by exchange between outgoing and incoming gas. Gas treated by the catalytic process and then by active charcoal for recovery of benzene should contain less than 1 gr. S per 100 cu. ft. of gas, no O_2, no NO, and a considerably lowered % of diolefin hydrocarbons. It should be free from formation of gummy deposits and produce only traces of SO_2 on combustion.

1259. ———. Geometrical Factor in Catalysis. Advances in Catalysis. Academic Press, Inc., New York, 1948, vol. I, pp. 91–114.

Reaction kinetics and mechanism of catalysis are studied from the viewpoint of 2-point adsorption on an active catalyst surface. The reactions of unsaturated organic molecules and of C_2H_2 are discussed. The synthesis of hydrocarbons from CO, and related reactions, are argued, and evidence is brought forward to support the chain-growth hypothesis.

———. *See* abs. **1465.**

1260. GRIGUARD, V., DUPONT, G., AND LOCQUIN, R. Traité de chimie organique. Maison & Cie, Paris, 1937, vol. 5, p. 826.

Discusses MeOH synthesis.

1261. GRIMME, W. [Recovery of Liquefied Gases From Coke Ovens, Synthesis and Other Gases.] Ztschr. Ver. deut. Ing. Beih. Verfahrenstech., 1940, pp. 12–16; British Chem. Abs., 1941, B, p. 271.

Light hydrocarbons in coke-oven gas, hydrocarbon-synthesis waste gases, etc., owing to their low concentration, are usually recovered by means of active C. The technique is described and details are given of the working of an active-C plant at a Fischer-Tropsch hydrocarbon-synthesis works.

1262. ———. [Gasoline Products by Direct Synthesis. German Developments in the Fischer-Tropsch Process.] Oel u. Kohle u. Brennstoff-Chem., June 1, 1944; Chem. Trade Jour., vol. 117, 1945, pp. 289–290.

Recovery of the lower-boiling products produced in the Fischer-Tropsch process is discussed. The activated C process is employed. The Fischer-Tropsch feed gas generally contains 15–20% of inert constituents such as CH_4, CO_2 and N_2. From such a gas about ⅓ leaves the catalyst chamber in gaseous form, the hydrocarbons in this exit-gas mixture containing 40–50% of the total hydrocarbons produced in the conversion. Even after cooling, it still contains 200 gm. of gasoline and gas oil per $m.^3$ The activated C, arranged in a tower, has a selective adsorptive action on the gas constituents, the gasoline and gas oil being taken up first. The lower portions of the C become saturated first with gasoline, this gradually displacing upward the lighter hydrocarbons and other products until, at the end of the operation, the C has adsorbed about 5% of its weight of gasoline, which is recovered by steaming. The operation is effected on a large scale in groups of 4 adsorbing columns, 1 of these being cut out automatically in series for regeneration. The lower hydrocarbons recovered may be used for the synthesis of high-octane fuels.

1263. ———. [Fischer-Tropsch Synthesis.] Bergbau Archiv, vol. 9, 1949, pp. 114–121; Coke and Gas, 1949, p. 331.

Reviews process.

GRIMNES, F. B. *See* abs. **3108.**

1264. GRINEVICH, V. M. [Carbon Catalyst for Carbon Monoxide Conversion.] Jour. Appl. Chem. (U. S. S. R.), vol. 13, 1940, pp. 831–840 (in French, p. 840); Chem. Zentralb., 1941, I, p. 1209; Chem. Abs., vol. 35, 1941, p. 2286.

Activity of catalysts prepared by impregnating charcoal with K_2S, K_2CO_3, and calcining in the absence of NH_3–CO or CO_2 was low. The catalysts prepared by impregnation of activated fir charcoal with KCNS, or better with K_2S, K_2CO_3, or K_2SiO_3, and calcining in an NH_3–CO or CO_2 stream were nearly as active as the Fe–Mg catalyst. Removal of K from the C catalyst virtually destroyed its activity. Therefore, the action of C catalysts is due to the presence of K compounds distributed on the surface of the carrier (active C). The flash point of C catalysts decreased with an increase in their activity. The presence of Pt in the C catalyst containing K considerably increased its activity. All experiments were carried out at 400° and 500° at a volume velocity of 100 and 600 and steam: gas ratio=3.

1265. ———. Selection of New Raw Materials for Ammonia Catalyst. Jour. Appl. Chem. (U. S. S. R.), vol. 18, 1945, pp. 313–321 (English summary); Chem. Abs. vol. 40, 1946, p. 3576.

Study of Vysokogorsk, Magnitogorsk, and Pokrovsk ores, after magnetic separation from SiO_2, showed the possibility of preparation of an NH_3 catalyst, since the presence of SiO_2 up to 2% does not show a negative effect on the catalyst activity, provided that enough K_2O is present. This effect is explained by separation of much SiO_2 with K_2O in the process of catalyst formation, with consequent formation of essentially pure magnetite crystals. The ore is subjected to double magnetic separation and alkaline fusion and followed by a double separation to yield 23% of finished product. The catalyst can be regenerated by oxidation of KNO_3.

1266. ———. [Zinc-Chrome Catalyst for Methanol Synthesis.] Jour. Appl. Chem. (U. S. S. R.), vol. 18, 1945, pp. 90–96; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 580, 1946; Chem. Abs., vol. 39, 1945, p. 5247.

It was shown that substitution of Cr_2O_3 by CrO_3 in ZnO–Cr oxide catalysts increases catalyst efficiency by 40% in MeOH synthesis. Catalysts 8 $ZnO \cdot 3CrO_3$ and 2 $ZnO \cdot CrO_3$ have the same activity. Increase of Cr to the limit of $ZnO \cdot CrO_3$ lowers the efficiency by 60%. Compression of the catalyst, after a brief working period, improves its efficiency and the mechanical strength.

1267. GRINEVICH, V. M. and KLAPCHUK, S. V. [Utilization of the Krivoi-Rog Hematite as a Raw Material for the Ammonia Catalyst.] Jour. Appl. Chem. (U. S. S. R.), vol. 10, 1937, pp. 1868–1870; Chem. Abs., vol. 32, 1938, p. 2298.

Hematite described contains Fe_2O_3 96.70, FeO 0.53, Al_2O_3 0.90, Mn_3O_4 traces, SiO_2 1.60, CaO 0.09, MgO 0.05, S (sulfide) 0.004, S (sulfate) 0.02, and P_2O_5 0.04%. The preparation of catalyst is schematically described. 3 refs.

1268. GRISWOLD, J., AND BUFORD, C. B. Separation of Synthesis Mixtures. Vapor-Liquid Equilibria of Acetone–Methanol-Water. Ind. Eng. Chem., vol. 41, No. 10, 1949, pp. 2347–2351; Chem. Abs., vol. 44, 1950, p. 1788.

Acetone and MeOH are major components of the water product obtained from hydrocarbon synthesis by the Fischer-Tropsch-type process. Vapor-liquid equilibria of the binaries and the ternary are needed in fractionation calculations for separation and recovery of the organic compounds. This ternary and the 3 binary boundary systems were studied completely at 760 mm. Hg pressure. Tabular and graphic data are presented for: d^{25}_4, $n^{25}D$, boiling point, and vapor-liquid equilibria for all of the systems and actvity coefficients for the 3 binaries only. No ternary azeotropes were found.

1269. GRISWOLD, J., CHU, P. L., AND WINSAUER, W. O. Separation of Synthesis Mixtures. Phase Equilibria in Ethyl Alcohol–Ethyl Acetate–Water System. Ind. Eng. Chem., vol. 41, No. 10, 1949, pp. 2352–2358; Chem. Abs., vol. 44, 1950, p. 1788.

Above compounds occur in the water product of Fischer-Tropsch type hydrocarbon synthesis processes and in the manufacture of ethyl acetate by esterification. Vapor-liquid equilibria are reported for the AcOEt–EtOH and AcOEt–H_2O binaries as well as for the ternary system. In additon d^{25}_4 and boiling point (760 mm. Hg) are given. The 2-phase liquid region is explored for the AcOEt–H_2O binary and for the ternary with tie-lines and isothermal boundaries reported. No well-defined ternary azeotrope was found, but a low-boiling zone at 70.3° covering a sizable range in ternary composition was reported along the ester-rich side of the 2-phase liquid region.

GRODDE, K. H. *See* abs. **1270.**

GROH, E. *See* abs. **3101, 3102.**

GROLL, E. *See* abs. **1457.**

GROLL, H. *See* abs.**1453.**

GROSS, —. *See* abs. **1504.**

1270. GROSS, H., AND GRODDE, K. H. [Structure of Solid Hydrocarbons as Basis for Classification.] Oel u. Kohle, Erdoel, Teer, vol. 38, 1942, pp. 419–431; Chem. Abs. vol. 37, 1943, p. 5693.

This study of the physical constants of the solid-paraffin hydrocarbons shows that, for a given moleuclar weight, branching of the chain causes lowering of the solidification point, and that presence of rings causes, in addition, an increase in density. In this way a "ring val." (indicating presence of ring paraffins) and an "asymmetry val." (indicating branching of the chains) can be deduced. Heterogeneous mixtures of solid hydrocarbons were examined by separating them acording to molecular weight by fractional distillation and according to their asymmetry by fractional crystallization from solutions in $(CH_2Cl)_2$. Of the products examined, the Fischer-Tropsch synthesis product was a mixture of normal and isoparaffins, that is, of aliphatic nature, while the solid hydrocarbons from petroleum and brown-coal tars contained varying quantities of ring paraffins with different numbers of rings per molecule. The result suggests a classification of solid hydrocarbons on the basis of their composition, solidification points, and ceresin character.

1271. GROSS, H. W. [Production of Detoxified City Gas by Pressure Gasification and Synthesis With Iron Catalysts.] Erdöl u. Kohle, vol. 3, No. 1, 1950, p. 11; No. 5, 1950, pp. 218–222; Chem. Abs., vol. 40, 1950, p. 7513.

Abstract of paper presented at the 1949 meeting of the Deutsche Gesellschaft Mineraloelwissenschaft u. Kohlechemie. Previous processes for the detoxification of city gas, such as the conversion of CO with steam to H_2 and CO_2 or the washing out of CO with Cu salts, have only occassionally been used since they, in general, raise the cost of the gas too greatly. Since 1938 the Lurgi Ges. für Wärmetechnik m. b. H. has been working on a process that changes the poisonous CO with a small amount of the H_2 in the gas into a more valuable Fischer-Tropsch product. In most cases the detoxified gas is cheaper, since the net excess for the production of hydrocarbons, in general, exceeds the cost of the used gas. This method, therefore, is of great interest, since it places gas detoxification on an economical basis. Especially favorable is the relation in the working up of city gas from the Lurgi pressure gasification plants since this gas possesses a relatively high CO content of 15–20% and a favorable pressure of 20 atm. for the catalytic conversion to hydrocarbons. Special Fe catalysts are used which need for the reaction, beside CO, only a little H_2. Because of the equalizing effect in the gas contraction associated with the reaction the H_2 content in the detoxified gas remains virtually the same, and the end gas still corresponds to a normal city gas. In 1942 the process was experimentally tested at Bohlen near Leipzig on a large scale processing 1,600 *N* $m.^3$ of gas per hr. Several months operation showed that, depending on the catalyst compostion and the operating conditions, mainly paraffin or low-boiling hydrocarbons could be obtained. Since CH_4 formation in the synthesis is favorable to the city gas, the yield per *N* $m.^3$ of gas used, is far above 200 gm.

1272. GROUNDS, A. Review of Work on the Production of Oils—the Fischer-Tropsch Process. Chem. Age, vol. 38, 1938, p. 164.

Reviews development of synthesis of liquid fuels from the early discoveries of Sabatier in 1902. Fischer and Tropsch, working together since 1922–23, first established that, in the presence of an alkaline Fe catalyst at 400° C., and at a pressure of 100 atm., alcohols, aldehydes, ketones, and fatty acids could be produced. 17 different compounds were isolated in this early work, and the mixture of these compounds was called Synthol. With Zerbe, Fischer found that, as lower pressures were used, compounds containing less O were formed and that the rate of the reaction decreased. Eventually, it was found that, at 7 atm. pressure, an oil was produced consisting principally of hydrocarbons of a paraffinoid nature. In 1905, Fischer and Tropsch found that the reaction could be carried on at atmospheric pressure; they also discovered that, if the catalyst was to have a long life, it would be necessary to work at temperatures of 200°–300° C. With a reduction in temperature the reaction was slowed still further, so that new and more highly active catalysts had to be found. Tropsch left Fischer in 1928 to found the new Institute for Coal Research at Prague, and it took Fischer and his co-workers (Koch and Meyer) 6 yr. to produce catalysts that were active enough at 200° C. and at atmospheric pressure and yet had a reasonably long life. It was found that the presence of a strong alkali brought about polymerization, until eventually solid paraffin instead of liquid oils was obtained as an end product. Eventually a Co–Th catalyst was produced, which was found not only to give high yields of liquid products, but which also had a long life in actual practice. The theoretical yield of liquid products was actually 185 gm. per $m.^3$ of gas, containing 29.5% of CO and 60% H_2. The latest reports showed that 151 gm. per $m.^3$ could be obtained, corresponding to a conversion of 81.6% of the total material. This result was brought about with the use of a 2-stage operation at 190° C. and 184° C.,

respectively, using a Co–Cu–Th–kieselguhr catalyst. One of the essentials for satisfactory operation of the Fischer-Tropsch synthesis was purification of the synthesis gas from organic S compounds. A method had been elaborated by Fischer and his collaborator Roelen, which was found to be perfectly satisfactory in industrial practice and which was capable of reducing the organic S in the gas to the abnormally low figure of 0.2 gm. per 100 $m.^3$ or 0.087 grain per 100 cu. ft. The synthesis of liquid products from $CO–H_2$ was an exothermic reaction. The heat generated raised the temperature of the gases several hundred degrees. The conversion vessels were surrounded by a circulating oil system, so that the oil picked up the heat evolved and transmitted it to H_2O for the generating of steam in a special-type boiler. The products formed by the synthesis were water-white. Before use they were freed from traces of organic acids by a light soda wash. The products were free from S. The remarkable flexibility of the Fischer-Tropsch process from the point of view of the raw material available was stressed, and the yield of finished products from the primary oils obtained was given as: Gasol (consisting mainly of C_4H_{10} and C_3H_8), 8%; petrol, 50%; diesel oil, 39%; and soft paraffin wax, 3%. In addition, a hard paraffin wax was recovered from the catalyst mass during regeneration. This wax almost paid for the cost of regeneration of the catalyst. It was shown how the octane number of the petrol produced could be improved by cracking and by blending with benzol and/or alcohol, together with the addition of $PbEt_4$.

GRUMMER, M. *See* abs. **2098, 2099, 2100, 2101, 2102, 2103, 2103a.**

1273. GRUNDMANN, C. [Nitration of Higher-Molecular Paraffin Hydrocarbons.] Die Chemie, vol. 56, 1943, pp. 159–163; Great Britain Fuel Research Intel., No. 5, July 1944; Oel u. Kohle, Erdoel, Teer, vol. 40, 1944, p. 227.

Charging stocks employed included mixtures of liquid hydrocarbons from the Fischer-Tropsch synthesis.

1274. GRUNER, L. O. [Motor Fuels.] Tek. Ukeblad, vol. 85, 1938, pp. 383–389, 400–403, 411–413.

Surveys the motor-fuel problem and the possibilities of synthetic fuel production as they affect Norway, with special reference to the use of the cheap electric power available. Petroleum refining, hydrogenation, the Fischer-Tropsch synthesis, and the use of NH_3 as fuel are discussed.

1275. GUELPÉRINE, N. L., AND NAIDITCH, I. M. ["*I–S*" Diagrams for H_2, CO, N_2, N_2+3H_2 and $CO+2H_2$.] Chim. et ind. vol. 34, 1935, pp. 1011–1020, 1279–1288; Chem. Abs., vol. 30, 1936, p. 2064.

Diagrams are presented for pressures up to 1,000 atm. and temperatures <600°. They were constructed from experimental data on compression and thermal capacities found in the literature, including the low-temperature and relatively low pressure curves of Keesom and Houthoff for H_2 and N_2. The diagrams are not absolutely accurate but are sufficiently so for use in synthetic-NH_3, synthetic-MeOH, and oil-cracking industries.

1276. GUERTLER, W. [Investigations of Vittorf and Hanemann Relative to the Carbides of Iron.] Internat. Ztschr. Metallog., vol. 5, 1913, pp. 239–277; Chem. Abs., vol. 8, 1914, p. 1407.

Discusses status of the Fe–C system.

1277. ———. [Law Governing the Transformations of the Carbide System Into the Graphite System.] Stahl u. Eisen, vol. 34, 1914, pp. 520–525, 751–754; Chem. Abs., vol. 8, 1914, p. 3002.

Discusses Fe–C diagram in detail. Fe_3C is unstable at all ordinary temperatures, but the transformation energy is so weak that it must be heated for hours at 800° before it breaks down. With increases in temperature, the time required for decomposition is shorter. In spite of the instability of Fe_3C, it is possible, under certain conditions, to cause the reaction $Fe_3C=3Fe+C$ to reverse. If the tendency to form graphite is stronger than the force tending to decompose Fe_3C, the speed of the reaction is governed by the former force. There is some doubt as to which of these forces is influenced by the presence of Si. The separation of graphite is accompanied by increase in volume; consequently, its formation is retarded by pressure. The main factor is, however, temperature, and it is by varying this that foundries obtain the various results they desire. Gives diagram that shows graphically the relative amounts of free and combined C with different temperatures; by means of it the changes during cooling are discussed.

GUEST, P. G. *See* abs. **1449.**

1278. GUILLAUD, C. [Ferromagnetic Properties of the Compounds Manganese-Nickel Alloy and Cementite.] Compt. rend., vol. 219, 1944, pp. 614–616; Chem. Abs., vol. 40, 1946, p. 1711.

Alloys of Mn with Ni containing 57–85 atomic % of Ni are paramagnetic when tempered and ferromagnetic when annealed. The most strongly ferromagnetic alloy corresponds to the composition $MnNi_3$. This was prepared by fusing pure Mn (99.98%) and pure Ni (99.76%) in an Al_2O_3 crucible in a high-frequency furnace. To obtain the maximum magnetization the specimens were annealed for 3 wk. at approximately 470°. At 480°, $MnNi_3$ is no longer ferromagnetic. The change is not completely reversible, and the alloy is paramagnetic or weakly ferromagnetic depending on the speed of cooling to a temperature below 480°. In the case of ferromagnetism the spontaneous magnetization reappears at 480°. This indicates probably the simultaneous existence of a Curie point and a point of transformation. Curves are given showing the specific magnetization as a function of T^2 and the law of approach to saturation at 290° K. and 0° K. as a function of the reciprocal of the internal field. For 0° *K.*, $\sigma_\infty=98.16$. Curves are also given showing the results obtained on an exceptionally pure specimen of Fe_3C from which the value $\sigma_\infty=169.3$ at 0° K, is deduced.

1279. GUILLAUD, C., MICHEL, A., BÉNARD, J. AND FALLOT, M. [Ferromagnetic Properties of Chromium Dioxide.] Compt, rend., vol. 219, 1944, pp. 58–60; Chem. Abs., vol. 40, 1946, p. 2365.

Ferromagnetic CrO_2 was prepared by heating CrO_2Cl_2. This gave a mixture of approximately equal parts of CrO_2 and a solid solution of O_2 in Cr_2O_3 corresponding to $(8\ Cr_2O_3+O)$. The exact proportions of the 2 constituents in a particular specimen were deduced from its loss in weight when the whole was converted into Cr_2O_3 by calcining at 900°. Magnetic studies made on 2 specimens with different CrO_2 contents, prepared independently, are reported as giving concordant results, although no experimental details are given.

1280. GUILLAUMERON, P. [Chemical Applications of Natural Gas in the United States.] Génie civil, vol. 124, 1947, pp. 125–130.

Review in which the Fischer-Tropsch process is mentioned.

1281. GUILLEMIN, A. [Corrosion of Metals by Methanol.] Ann. chim. vol. 19, 1944, pp. 145–201; Chem. Abs. vol. 40, 1946, p. 1437–1438.

Corrosion of metals by MeOH was studied at room temperature. Al, Cu, Sn, Pb, Zn, Cd, Sb, Bi, Cr, Fe, Ni, Co were subjected during 4 months to anhydrous MeOH, MeOH containing 20% H_2O, MeOH containing 2% CH_2O, MeOH containing 1% HCOOH, and 1%

aqueous HCOOH. Most of the metals were of 99.9+% purity, Ni 99.8%, Cd 99.5+%, Bi 99–100%, Co 98–99%. Pure MeOH attacked only Pb, Sb, Al, and Sn. In the presence of 20% water Al and Sn are protected by an oxide layer and are not attacked; the corrosion of Pb is reduced; Zn, Cd, Fe, and Co are attacked. Only Pb and Sb are attacked by MeOH containing 2% $CH_2O \cdot MeOH$ containing 1% HCOOH corrodes most metals, particularly Pb, Zn, Cd, Fe, Ni, Co, Cu, and Sb. Al is barely attacked, and Cr, Sn, Bi are not attacked. In 1% aqueous HCOOH solution Cu is not attacked; Pb is attacked much less than in MeOH solution; the corrosion of Al is much stronger; and Sn and Bi are slightly attacked. The results are tabulated and expressed in weight loss per 100 gm., and weight loss per 100 cm.[2] The experiments were carried out in the dark. The apparent importance of the presence of HCOOH led to the study of the mechanism of the corrosion of Fe, Zn, and Cu by MeOH containing traces of that acid. In the presence of air MeOH containing HCOOH reacts with Fe with formation of dimethoxyferric formate, $HCOOFe(OMe)_2$ (I). In an anhydrous solution Zn forms a basic formate, $4(HCOOZnOH) \cdot -ZnO$, and in the presence of water a neutral hydrate, $(HCOO)_2Zn \cdot 2H_2O$. Cu forms a mixture of basic formates. In the absence of air Fe dissolves with formation of neutral ferrous formate; Zn is not attacked; Cu is protected by the formation of an insoluble cuprous formate. Zn and Cu undergo surface oxidation. The formation of $Pb(OMe)_2$ is attributed to an initial surface oxidation; in the absence of air Pb is not attacked by MeOH. (I) was successively hydrolyzed to ferric dihydroxyformate, $HCOOFe(OH)_2$, and to the neutral formate and $Fe(OH)_3$. Calcination at 250° of (I) gave pure, pyrophoric Fe. The complete hydrolysis of the basic Zn formate gave neutral Zn formate and $Zn(OH)_2$. In the presence of sunlight or ultraviolet radiation, Fe is attacked by pure MeOH with formation of (I); this proves that MeOH is partly oxidized to HCOOH. In MeOH containing HCOOH bronzes and Al bronzes were etched (this can serve for micrographic studies); steel containing 13% Cr was not attacked; steel containing 12% Ni was attacked less than steels containing 2%, 3%, 5% Ni; the latter were attacked as repidly as pure Fe.

GUIOT-GUILLAN, G. *See* abs. **1055.**

1282. GUISELIN, A. [From the Theory to the Realization of Synthetic Fuels. VI. The Fischer Process.] Chaleur et ind., vol. 5, Special No., December 1924, pp. 97, 133–134, 162.

Brief statement, within a long discourse, of the production of synthol and synthine by passing water gas through a catalyst of Fe turnings and K_2CO_2 at a temperature 390°–430° and a pressure 100–150 atm.

1283. GULBRANSEN, E. A. Transition-State Theory of the Formation of Thin Oxide Films on Metals. Trans. Electrochem. Soc., vol. 83, 1943, 13 pp.; Chem. Abs., vol. 37, 1943, p. 2251.

Transition-state theory of diffusion was applied to the rate of oxidation of metals as a function of temperature. The expression involves an entropy of activation as well as the energy of activation. Experimental results indicate that the oxidation of Fe, stainless steel, and Cu follows the parabolic law for certain temperature ranges and pressure ranges after a certain initial period. The parabolic-rate-law constants are shown to follow a straight line when log K is plotted against $1/T$. Energies of activation of 22,600, 29,600 and 24,900 are found for Fe, stainless steel, and Cu, respectively. Entropies of activation are calculated to be −31, −35, and −6.8 for Fe, stainless steel, and Cu, respectively. The importance of entropy factor is briefly considered.

1284. GULBRANSEN, E. A., AND RUKA, R. Kinetics of Solid-Phase Reactions in Oxide Films on Iron. Reversible Transformation at or Near 570°. Jour. Metals, vol. 188, Trans., 1950, pp. 1500–1508; Chem. Abs., vol. 45, 1951, p. 426.

Forward and reverse reactions, $Fe_3O_4 + Fe \rightleftharpoons 4\ FeO$, were studied by electron-diffraction methods. In thin films the forward reaction occurs at temperatures 170° below the equilibrium value. The mechanism of the forward reaction is governed by the diffusion of Fe. Studies of the reverse reaction as a function of time, temperature, and oxide composition indicate that a process of nucleation and growth is rate controlling.

1285. GULF RESEARCH & DEVELOPMENT COMPANY. General Summary of Economic Data. Synthetic Liquid Fuels Hearings Before a Subcommitte of the Committee on Public Lands and Surveys, U. S. Senate. 78th Cong., 1st sess., on S. 1243, 1944.

This summary of data is taken from a "Literature Survey on the Fischer-Tropsch Synthesis of Hydrocarbons," January 1940–December 1943, of the Gulf Research & Development Co. Chemistry Division Rept. 260, April 15, 1944.

General summary of cost data for synthetic liquid fuels process [1]

Investment	From coal hydrogenation	From Fischer-Tropsch synthesis, using coal	From Fischer-Tropsch synthesis, using natural gas	From oil shales	From petroleum
($/day bbl.)	7,500–14,300	6,180[2]–16,667	2,200–4,767	375–3,000	700.
Operating costs [3] (¢/gal.)	15.5 [2]–25	18.2 [2]–24.4	4.8 [2]–17.4	([1])–10.7	5–6.
Total raw materials required (ton/bbl.).	Coal: 0.5 [2]–1.25	Coal: 0.7	Natural gas: 0.22–0.25	Oil shale: 0.9–2.7	Crude oil: 0.328.
Steel requirements (ton/bbl.).	8.3–14.1	8.9–14	2.8–6.5	1.3–([1])	0.7.
U. S. reserves of raw material.	Coal: 3.2 trillion ton (3,000 yr.).	Coal: 3.2 trillion ton (3,000 yr.).	Natural gas: 85–170 [2] trillion cu. ft. (30 yr.).	Shale oil: 92 billion bbl. (65 yr.).	Oil: 20–21 billion bbl. (14 yr.).

[1] Data presented represent testimony extremes. In 2 cases, it appears that truly representative ranges were not given.
[2] Trend of testimony indicated that the most probable figure was of this order, although perhaps somewhat higher or lower. For operating costs by the first 2 methods, eventual estimates are somewhat lower.
[3] Including depreciation. Figures are presumably for 70–75 octane-number gasolines.

1286 ———. Literature Survey on the Synthine Process, January 1944–January 1945. Chemistry Division Rept. 295, 1945, 70 pp.

Annotated bibliography.

1286a. GUMZ, W. [Present Status and Future Possibilities in Gasification Processes.] Gas- u. Wasserfach, vol. 88, 1947, pp. 129–136; Chem. Abs., vol. 42. 1948, p. 4,729.

Trend of gas production is in the direction of complete gasification with the use of noncoking coals. Water-gas generators are commonly used for synthesis-gas production; the use of O_2 is advantageous when this

can be generated at a low price. A greatly expanded use of producer gas is seen particularly in steel works owing to the tendency to sell coke-oven gas to super-gas schemes. The Flesch-Winkler gas producer serves as a transition stage between the grate-type producer and the powdered-coal gas producers. In this generator a 1-m. layer of fine fuel is held on a grate by an air pressure of about 4 mm. H_2O column. This is gasified for 10–15 min. until a slag layer is formed, which is caused to sink to the grate by introducing steam; this slag is then removed by means of a H_2O-cooled stirring arm. The slag removal period requires 1–3 min., which is followed by a purge of 1 min. after which fresh fuel is introduced and gasification continued. Low-grade high-ash fuels are used. The slagging-type producer offers considerable promise for low-grade fuels, especially when combined with metal recovery. A dry air blast is ordinarily used, but this producer can be operated with 2 stages, the upper using saturated air and the lower dry air.

1286b. ———. Gasification of Solid Fuels at Elevated Pressures. Ind. Eng. Chem., vol. 44, 1952, pp. 1071–1074.

Effect of pressure on the gasification of solid fuels is investigated by calculation and by evaluation of experimental data. A method of calculation is presented based on the C, H_2, O_2, N_2 and S balances, and on the equilibrium constants of the gasification reactions. Previously published methods have been extended to apply to the behavior of S during gasification. An increase in pressure shifts the Boudouard reaction, the heterogeneous water-gas reaction, and CH_4 formation toward increased CO_2, H_2O, CH_4 content and higher equilibrium temperature. S appears mainly as H_2S in the product gas. Other forms of S such as organic S and S vapor can occur only at extremely high pressures and in the absence of moisture. This fact permits a simplified method of calculation, assuming that S occurs only as H_2S. The increase in equilibrium temperature keeps gas quality nearly constant up to 10 atm. and allows higher steam and lower O_2 content in the blast at higher pressures. Effect of absolute pressure on pressure drop through the fuel bed is calculated and the calculations are supported by experimental results. Pressure drop is a simple function of pressure and is inversely proportional to the absolute mean pressure in the reactor. Elevated pressure has no effect on the terminal velocity of fuel particles in suspension in the range of validity of Stokes' law, but the terminal velocity decreases proportionately to $1/\sqrt{P}$ in the Newton range (constant resistance factor). Formulas are given for the terminal velocity within the transition range of Reynolds numbers; they can be used to estimate carryover losses and the effect on reaction rates of pulverized-coal gasification. Pressurizing is applicable to various coal-gasification processes; it has been applied to the manufacture of high-B. t. u. gas, and it has good prospects for playing a major role in synthesis-gas production and power gas for steam boilers and gas turbines.

1287. GUMZ, W., AND LESSING, R. [Processes for the Manufacture of Synthetic Gas.] Ztschr. Ver. deut. Ing., Beih. Folge No. 2, 1940, pp. 36–42; Chem. Abs., vol. 34, 1940, p. 6794.

Comprehensive summary, with diagrams, data, and 46 refs.

1287a. GUNDERMANN, E. [Residues From Distillation of Synthetic Fatty Acids (Oxide Pitches).] Bitumen, Terre, Asphalte, Peche, vol. 5, 1951, pp. 114–117; British Abs., 1951, B, I, p. 1202.

In Germany fatty acids are produced by oxidation of Fischer-Tropsch slack wax (b. p. >350°) containing the maximum amount of C_{25}–C_{35} paraffins. The oxidized product contains 30–35% of mixed fatty acids and aldehydes, alcohols, dicarboxylic acids, ketones. The complex mixture of acids is separated by conventional methods and fractionally distilled in a vacuum into C_4–C_9 fatty acids and C_{10}–C_{20} (soap) fatty acids. The residue of oxide pitch (7–15% of the original mixture) resembles tar or pitch; extensive distillation does not produce a hard pitch. The material reacts with S to form materials of high molecular weight, the rise in softening point depending on the amount of S, reaction time and temperature; the maximum reaction temperature is 190°–200°. With 10% of S, polymerization mainly occurs; with 20% of S, crosslinking with combination of S takes place and infusible products are formed. Addition of 5% of 62% HNO_3 to oxide pitch has a pronounced polymerizing effect. The S and HNO_3 products of the pitch are gummy and tough but are not hard.

1288. GUNNESS, R. C. Future Liquid Fuels. Chem. and Eng. News, vol. 26, 1947, pp. 2123–2127, 2171; Chem. Abs., vol. 42, 1948, p. 6509.

During 1947 the United States used about 5.8 million bbl. of petroleum/day. 25 yr. ago about 27% of each bbl. of crude oil was made into gasoline, last year over 40%, while a 75% yield could be produced if this were the only product required. The gasoline demand has increased 20% over 1941 and 7% over 1946 but is believed to be slowing up. Most of the increase in fuel consumption in recent years has been oil. Petroleum demands in 1970 are established at 7,130 bbl. per day, of which 3,160 bbl. will be motor fuel. Diesel fuel will also be used more widely by the railroads and for heavy motor vehicles; changes in the fuel may be required, which must be tested in service engines rather than in the laboratory. Present known crude petroleum reserves are equal to about 12 yr. consumption, at the present rate, but more reserves were found last year than were used. Imports, especially from the middle east, will be required to maintain reasonable reserves. The immediate production of large quantities of synthetic fuels from coal would be very expensive; much more research is required. A modified Fischer-Tropsch process, with natural gas as the raw material, will soon be in production in several plants. The hydrocarbons produced in this synthesis consist principally of straight-chain compounds ranging from CH_4 to solid waxes. The major portion of this product is unsaturated in structure (in contrast to results obtained with the German Co catalyst) and can be refined to give a gasoline with an octane number of about 80, and heavier refined products comparing favorably with those from petroleum. In a plant producing 6,000 bbl. per day of synthetic hydrocarbons, the established yield of other organic chemicals is about 420,000 lb. per day. This will be a major source for these compounds, which will be separated and purified at plants near the hydrocarbon-synthesis plants. Gasoline quality requirements will improve, and cars having octane requirements of 95 or even higher are planned for the future. Even with decreasing demands per car, the increased number of cars will require more gasoline. The cost of this improved fuel will be greater. The gas turbine probably will require a clean distillate oil for fuel. The fraction of the motor fuel produced by synthesis will be small for some time but will increase with demand. Residual fuel-oil supply can be expected gradually to decrease, so that coal will be called on to handle an increasing share of the expanding industrial fuel load. Enough high-quality liquid fuels will be available to meet all demands most efficiently served by petroleum fuels.

———. *See* abs. **372.**

1289. GUNTERMANN, W. [Gasification of Solid Fuels.] Wärme, vol. 59, May 9, 1936, pp. 321–323.

Discusses matters of interest in relation to the production of NH_3, alcohol, oil, and gasoline from sub-

stances derived wholly or partially by the gasification of fuels. The Bubiag-Didier, the Drawe, the Winkler, the Lurgi, and the Pintsch-Hillebrand processes are characterized and the gasification prospects in relation to general gas supply, heating gas for industrial purposes, gas for synthetic processes, and for power applications are discussed. Activity is especially pronounced in the field of syntheses, particularly as regards meeting German requirements for motor fuels. The Bergius hydrogenation process and the Fischer synthesis of gasoline require very large quantities of gas, which can be supplied conveniently by the gasification of solid fuels.

1290. GUNTHER, I. Thesis, Bonn University, 1935, 22 pp.

Contribution to the study of the high-boiling liquid and solid hydrocarbons formed by synthesis from CO and H_2 by the process of F. Fischer and H. Tropsch.

GUSEV, V. I. *See* abs. **1586.**

GUSEVA, I. V. *See* abs. **791.**

GUSTAVSON, E. *See* abs. **1384.**

1291. GUTHRIE, V. B. Nazis Dropped Fischer-Tropsch Process for Coal Hydrogenation. Nat. Petrol. News, vol. 37, No. 44, 1945, pp. 4, 44, 46.

According to a report of the U. S. Technical Oil Mission, indications are that the Fischer-Tropsch process, as a means for making synthetic liquid fuels and lubricants, was discarded in favor of coal hydrogenation. It appears, however, that the decision to do this was of political rather than scientific nature. The authorities considered that operation of the Fischer-Tropsch process was important from the point of view of the production of chemicals but not of light fuels. Neither was there any evidence of any development that would make the process more attractive economically. It was learned, too, that the German Government had discontinued erection of new Fischer-Tropsch plants early in the war and that the viewpoint existed that the process had not been as successful as anticipated in meeting wartime needs. Development work on the coal-hydrogenation process had been instituted with the prospect of increasing the aromatic content of aviation gasoline, although it did mean some sacrifice in volume yield. Methods were found to operate at 700 atm. pressure in both liquid and vapor phase. The process, known as the D. H. D. process (Dehydrogenation High-Pressure), provides for dehydrogenation of the inferior gasoline from the direct hydrogenation step in an intermittent manner in a series of converters containing a single bed of catalyst consisting of active alumina, on which is deposited 10% of Mo oxide. The final D. H. D. naphtha is said to contain 65–68% of aromatics and is blended back with a corresponding light gasoline fraction to give a finished aviation gasoline with an aromatic content of 40–45% and a minimum octane number of 78 or 87 with 0.09 vol. % of tetraethyl lead. Another interesting point was the manufacture of synthetic lubricating oil from the gas oil or naphtha obtained by the Fischer-Tropsch process. Gas oil is chlorinated, treated with benzol-dichlorethane in the presence of $AlCl_3$, the benzol removed, and the various grades of lubricating oil extracted and processed by conventional methods. In the second process, Fischer-Tropsch gasoline is treated with $AlCl_3$ in special equipment. Another utilization of the Fischer-Tropsch process has to do with the manufacture of higher alcohols by the named Oxo process from olefins; the alcohols were to be used in making soaps and edible fats.

1292. ———. Bureau of Mines Reports. Meager Test Data From Five Years of Synthetic Fuels Research. Petrol. Processing, vol. 5, No. 5, 1950, pp. 505–508, 510.

Critical analysis of the annual 1949 report of the Secretary of the Interior.

1293. GUYER, A. [Gasoline Synthesis.] Bull. Schweiz. electrotech. Ver., vol. 29, 1938, pp. 564–567; Chem. Zentralb., 1939, I, p. 298.

Describes Bergius and Fischer-Tropsch processes and discusses their possibilities for operation in Switzerland.

GVALIYA, T. M. *See* abs. **2890.**

GWATHMEY, A. T. *See* abs. **2090.**

1294. GWOSDZ, J. [Theory of Water-Gas Formation.] Ztschr. angew, Chem., vol. 31, I, 1918, pp. 137–140; Jour. Soc. Chem. Ind., vol. 37, 1918, p. 538A; Chem. Abs., vol. 13, 1919, p. 1009.

Experiments were made to ascertain the parts played in water-gas formation by the supposed primary reactions (1) $C+H_2O=CO+H_2$, and (2) $C+2H_2O=CO_2+2H_2$, and the secondary reactions (3) $C+CO_2=2CO$, and (4) $CO+H_2O=CO_2+H_2$. Superheated steam was passed over various forms of heated C and the composition of the issuing gases determined. The temperatures varied from 855° down to 560°, and the speed of the current of steam was also varied. Natural forms of C containing ash in appreciable quantities behaved in a markedly different manner from purified C almost free from ash. With gas coke (8.5% ash) and wood charcoal (1.4% ash), a considerable proportion of CO_2 was always formed (up to 29%). On the other hand, lamp C (0.1% ash) at temperatures down to 600° gave mixtures closely resembling water gas as manufactured. Even at 500° the mixture: CO_2 8.6%, CO 39.5%, H_2 40.0%, residue 11.9% was obtained. It is concluded that reaction (2) cannot be a primary reaction, because reaction (3) is known to be too sluggish to account for the formation of the % of CO found at these low temperatures. It is also concluded that reaction (1) is the primary reaction of water-gas formation, and that the CO formed reacts with the excess of steam tending to establish the water-gas equilibrium and that this reaction is catalytically influenced by the finely divided ash in the C.

1295. ———. [Gasification of Fuels and the Synthesis of Oils.] Erdöl und Teer, vol. 3, 1927, pp. 171–173; Chem. Abs.; vol. 21, p. 1532.

Review and discussion of recent developments.

1296. ———. [Water Gas and the Oil Industry.] Petrol. Ztschr., vol. 24, 1928, pp. 859–870; Chem. Abs., vol. 23, 1929, p. 956.

Reviews methods in use for manufacturing water gas and its uses and relationships to the modern processes for producing synthetic hydrocarbons.

1297. ———. [Production of Hydrogen-Rich Gases for Synthetic Purposes by the Water-Gas Process.] Brennstoff-u. Wärmewirt., vol. 18, 1936, pp. 59–64, 82–85, 96–99; British Chem. Abs., 1936, p. 1187.

Comprehensive review.

H

1298. HAASE, —. [Analysis of the Fatty Acids for Soaps, From Tief-Temperatur Hydrierung Paraffin.] FIAT Reel R–19, frames 6668–6685, Aug. 8, 1940; PB 73,594; TOM Reel 261.

Describes extensive analysis of fatty acids obtained from Tief Temperatur Hydrierung paraffin by oxidation. Investigation consists of the following steps: Conversion of the mixed acids into methyl esters;

separation of the hydroxy-, keto-, and dicarboxylic esters and their derivatives by adsorption on silica gel; hydrogenation of the olefin carboxylic esters to saturated esters; preliminary and final fractionation of the methyl esters and their saponification. The results show that the fatty acid mixture consists of 15.4% constituents adsorbable on silica gel, 8.1% unsaturated fatty acids, 75.5% straight-chain fatty acids, and 1% branched-chain acids. The C number ranges C_9–C_{25}, includes 2 tables and 9 graphs.

———. *See* abs. **3637.**

HAASSER, C. *See* abs. **1062.**

1299. HABER, F., AND RICHARDT, F. [Equilibrium of Gases in the Bunsen Flame.] Ztschr. anorg. Chem., vol. 38, 1904, pp. 5–64; Jour. Chem. Soc., vol. 86, (2), 1904, p. 166A.

In the inner combustion zone, the equilibrium $CO_2+H_2 \rightleftharpoons CO+H_2O$ is very quickly attained and is not appreciably altered when the gases are cooled. From the products of combustion in the inner zone, the temperature of the latter may be directly estimated using the reaction isochores of the equilibrium.

HABESHAW, J. *See* abs. **259.**

1300. HACKSPILL, L. [Industrial Progress in the Use of High Pressures.] Chim. et ind., vol. 53, 1945, pp. 387–392; Chem. Abs., vol. 40, 1946, p. 5856.

Discusses the synthesis of NH_3 by the Haber, Claude, and Casale processes; the superpressures of Basset and their application in the synthesis of NH_3 without a catalyst; and the synthesis of MeOH, of Synthol, and the Bergius hydrogenation process.

1301. HAEHNEL, G. [Hydrogenation—a Further Development of High-Pressure Technique of the Ammonia and Methanol Syntheses.] Chem. Tech., vol. 2, 1950, pp. 83–87; Chem. Abs., vol. 44, 1950, p. 7040.

Discusses technology of the hydrogenation of coal to gasoline and diesel oil with the high-pressure techniques developed for the syntheses of NH_3 and MeOH.

1302. HAENSEL, V. Kaiser Wilhelm Institut für Kohlenforschung, Mülheim. CIOS Rept. XXV–1, 1945, 16 pp.; PB 284; TOM Rept. 9; TOM Reel 197; TAC Rept. SnMC–3.

Contains information obtained in interviews with Drs. Pichler and Koch. The subject matter on Ru catalyst, medium pressure catalysts, synthesis with Fe catalysts, isosynthesis, and aromatization has already been reported in abs. **1303,** and **701.** The magnetic-chemical investigation of the Fe catalyst showed that higher carbides, such as Fe_2C, can be formed during the synthesis at 220°, but that they decompose between 300°–400°, leaving Fe_3C as the only stable component. It was found that the most active catalysts were those containing the most Fe_3C. When the catalyst is pretreated at about $^1/_{10}$ atm. absolute pressure, more Fe_3C is obtained than at atmospheric pressure. During the synthesis, the amount of Fe_3C decreases at the catalyst deteriorates, while the concentration of Fe_3O_4 increases. When an equilibrium mixture of Fe_3C and Fe_3O_4 appears to exist in the catalyst, there is no rapid drop in activity, but with a higher concentration of Fe_3C an initial decrease in activity is observed. An attempt was made to prepare the Fe_2C by reducing Fe oxide with H_2 and then passing CO over it and measuring the CO_2 formed. Then H_2 again was passed over the catalyst at higher temperatures, and the amount of CH_4 was determined. From the data it was concluded that Fe_2C was formed. However, magnetic measurements showed that Fe_3C also was present, thus indicating that, along with Fe_2C and Fe_3C, a third carbide must be present richer in C than Fe_2C. In other words, the Fe_3C crystallites must be embedded in a phase with C:Fe ratio exceeding 2:1. Additional Curie points were observed but not identified. At higher temperatures, Fe_3C becomes sintered, and care must be taken to maintain the temperature low enough to prevent it. Formation of Fe_3C does not occur if the fresh untreated catalyst is impregnated with water gas under pressure at 220°. Some Fe_3C can be obtained at 280° under such conditions, but the catalyst produced is not good.

1303. ———. New Version of Fischer-Tropsch Reaction Gives 90% Yields of Isoparaffins. Nat. Petrol. News, Tech. Sec., vol. 37, 1945, pp. R955–R956.

Report of the U. S. Technical Oil Mission giving details of a laboratory-scale investigation of a 1-step synthesis carried out at the Kaiser Wilhelm Institut für Kohlenforschung, Mulheim. The 1-step synthesis of isoparaffins by the Fischer-Tropsch process can be performed by first producing higher alcohols (primarily isobutanol), then dehydrating the alcohols, and finally hydrogenating the olefins to the corresponding isoparaffins. Synthesis gas for the reaction is preferably in the ratio of $1.2CO:1H_2$ instead of $1CO:2H_2$. The reaction is carried out at 450° and 300 atm. It does not take place at atmospheric pressure, but as the pressure is increased yields improve. Above 300 atm. O_2-containing compounds begin to be formed and in increasing quantities. The throughput is about 5–10 times higher than in the regular Fischer-Tropsch process. Over 90% of the C_4 and C_5 fractions in the products are iso-compounds, as compared to 10–15% in the normal reaction using Co or Fe catalyst. The yield of product varies 60–120 gm. of C_4 fraction and higher; depending upon the catalyst, the yield of C_4 and higher fraction is 80 gm. per $m.^3$ of gas; that of C_3H_8, 10 gm. The products are as follows: C_4H_{10} (90% isobutane), 60–70% by weight; C_5H_{12} (96–98% isopentane), 20–30%; C_6C_7 and C_8, small amounts. The C_6 fraction contains no neohexane, but primarily 2 and 3 methyl pentanes and no n-hexane. Some naphthenes have been found in the higher-boiling fraction. The yield of C_6–C_8 fraction is higher at the lower temperature. Some alcohols, amounting to less than 10% of the hydrocarbons, a small amount of MeOH, and a large amount of isobutanol also are formed. The end gas from the synthesis consists of: CO_2, 30; N_2, 20; CH_4, 10%; and the rest CO and H_2. Catalysts found suitable are mainly oxides of Zn, Al, and Th used alone or in combination. Details are given on the preparation of the catalysts.

1303a. ———. Catalytic Cracking of Pure Hydrocarbons. Advances in Catalysis, Academic Press, Inc., New York, vol. 3, 1951, pp. 179–197.

The discussion covers the cracking of compounds representative of different hydrocarbon classes, the mechanism of catalytic cracking and the nature of cracking catalysts. 20 refs. are listed.

———. *See* abs. **1327.**

HAENSEL, V., AND JONES, J. P. I. G. Farbenindustrie A.-G. Works at Leuna. XIV. Oxo Process. *See* abs. **1478.**

HAENSEL, V., JONES, J. P., AND HORNE, W. A. I. G. Farbenindustrie A.-G. Works at Leuna. XV. Synol Process. *See* abs. **1479.**

HAFFNER, A. E. *See* abs. **2445.**

1304. HAGEMANN, A. Catalytic Hydrogenation by the Fischer-Tropsch Process. Engineering, vol. 146, 1938, p. 517.

Digest of paper appearing in the Frankfurter Zeitung, June 1938.

HAGEN, H. *See* abs. **3185.**

HAGER, K. F. *See* abs. **2260.**

1305. HÄGG, G. X-Ray Studies on the "Nitrides" of Iron. Nature, vol. 121, 1928, pp. 826–827; Chem. Abs., vol. 22, 1928, p. 4056.

X-ray examinations by the powder method have been made of Fe nitrides prepared by passing NH_3 over pure Fe, which was prepared by reducing Fe oxides with H_2. The structure is dependent only on the N content and not on the method or conditions of preparation. The maximum N content is 11.3%. The nitrides are really solid solutions of N in Fe. At 0.2% N, faint lines of a face-centered cubic lattice begin to appear; all α-Fe lines have disappeared at 5.7% N. The new lines remain fixed as N increases and indicate a unit cube of edge 3.789 Å. U. somewhat larger than that of γ-Fe. However this is called γ-phase and is considered to be a solid solution of N in γ-Fe. The Fe atoms are in a close-packed cubic array, with N atoms in the interstices. No evidence that the N atoms are regularly arranged appears. A new phase, ϵ, appears at 5.7–6.1% N. It is hexagonal and close-packed, the unit cell remaining fixed in size at first, but beginning to increase at 7.3–8.6% N. The phase is estimated to become homogeneous at 7.5–8% N. The ϵ parameters are the a=2.695 Å. U., c=4.362 Å. U. Increase in N increases the parameters, c increasing relatively less than a. The ϵ phase is a solid solution of N in hexagonal close-packed Fe. A thin Fe sheet nitrided at 450° for 4 hr. showed strong γ and weak ϵ lines.

1306. ———. [Metallic Nitrides, Carbides, Borides, and Hydrides.] Metallwirtschaft, vol. 10, 1931, pp. 387–390; Chem. Abs., vol. 25, 1931, p. 4192.

Discussion of the chemical and physical properties of the nitrides, carbides, borides, and hydrides of the metallic elements, particularly as related to the lattice structure of these compounds. Special attention is given to the compounds of these elements with such transitional metals as V, Cr. Ti, Mn, Fe, Co, Ni, Mo, W, Os, Ir, Pt, U. The nitrides, borides, carbides, and hydrides of these metals exhibit strongly metallic properties, while analogous compounds with the other metals are nonmetallic in nature. The lattice structure of these transitional elements seems to be characterized by an electron defect, and this together with the small atomic radii of the metalloids in question seem to be a factor in the metallic nature of these compounds.

1307. ———. [Regularity in Crystal Structure in Hydrides, Borides, Carbides and Nitrides of Transition Elements.] Ztschr. physik. Chem., vol. 12, B, 1931, pp. 33–56; Chem. Abs., vol. 25, 1931, p. 2615.

Structure of crystals of binary compounds containing a so-called "transition element" and H, B, C, or N is critically examined with respect to the ratio of atomic radii. If this ratio $r_m : r_x > 1.7$ the structure is simple, while if the ratio is smaller, the structure becomes more complex the smaller the radius of metal ion. Only these combinations show a typical metallic character in crystal structure, which is termed an infiltration structure. The latter shows a combination M_4X, M_2X, MX, and MX_2, each of which is described. The face-centered cubic or close-packing hexagonal lattice, both of coordination number 12 are most often observed. 1 case each of body-centered cubic and simple hexagonal, both of coordination number 8, was found. Careful discussion follows of the packing arrangement of atoms and the relation to coordination numbers.

1308. ———. [Powder Photographs of a New Iron Carbide.] Ztschr. Krist., vol. 89, 1934, pp. 92–94. Chem. Abs., vol. 28, 1934, p. 7100.

X-ray patterns of Fe that had been in contact with CO for 430 hr. at 225° show weak lines of Fe_3O_4 and Fe_3C, with stronger lines of a new carbide, which is probably Fe_2C. At higher temperatures the Fe_3C grows at the expense of the Fe_2C. After heating *in vacuo* at 500°, only lines of Fe_3C remain. It was not found possible to index the lines of the pattern for Fe_2C.

1309. ———. [Crystal Structure of Magnetic Ferric Oxide, γ-Fe_2O_3.] Ztschr. physik. Chem., vol. 29, B, 1935, pp. 95–103; Chem. Abs., vol. 29, 1935, p. 6122.

When Fe_3O_4 is oxidized at low temperature, the spinel structure is retained to form γ-Fe_2O_3 with a steady decrease in the dimension of the elementary cell from 8.380 to 8.322 Å. Change in intensity of the X-ray patterns and the density indicates that the increase in the O concentration produces empty spaces in the spinel lattice so that in γ-Fe_2O_3, where the O concentration reaches a maximum, 1/9 of the original Fe atomic positions are unoccupied, and the elementary cell contains an average of 21⅓ Fe and 32 O.

HAHN, D. A. *See* abs. **2173.**

HAHN, H., AND MÜHLBERG, H. [Metal Amides and Metal Nitrides. XX. System Iron–Nickel–Nitrogen.] *See* abs. **1650.**

1310. HAHN, O. [Contribution to the Thermodynamics of Water Gas.] Ztschr, physik. Chem., vol. 44, 1903, pp. 513–547; Chem. Zentralb., 1903, 2, p. 540; Jour. Soc. Chem. Ind. (London), vol. 22, 1903, p. 1038.

From the results of experiments, at a constant temperature with mixtures containing varying proportions of CO_2 and H_2 the author finds that the law of mass action can be applied for the reaction:

$$CO_2+H_2=CO+H_2O.$$

The value of equilibrium-constant K $(=\frac{CO.H_2O}{CO_2.H_2})$ is 0·534 at 686°C., 0·840 at 786°, 1·197 at 886°, 1·571 at 986°, 1·62 at 1,005°, 1·96 at 1,086°, 2·12 at 1,205°, and 2·49 at 1,405°. Up to 1,100° C. the constant may be expressed by the formula: $\log K=-\frac{2232}{T}-0{\cdot}08463 \log T-0{\cdot}0002203\ T+2{\cdot}5084$.

1311. ———. [Equilibrium $CO+H_2O=CO_2+H_2$.] Ztschr. physik. Chem., vol. 48, 1904, pp. 735–738; Jour. Chem. Soc., vol. 86, 1904, (2), p. 643A.

1312. HAKANSON, H. [Production of Motor Fuels.] Tek. Tid. Uppl. D. Mekanik, Skeppsbyggnadskonst Flygtek., Automobil Motortek., vol. 70, 1940, No. 8, pp. 74–76; No. 42, pp. 77–84; No. 46, pp. 85–89; No. 51, pp. 98–100.

Discussion on the production of motor fuels from petroleum and from coal by carbonization, distillation, hydrogenation, gasification, and the Fischer-Tropsch synthesis.

1313. HALE, C. H. Rapid Analysis of Fischer Synthesis Catalyst. Petrol Refiner, vol. 25, No. 6, 1946, pp. 117–120.

Describes methods that have been found most satisfactory for the determining Co and Th in Fischer synthesis catalyst. The procedure for Co involves titration in an ammoniacal solution with $K_3Fe(CN)_6$. The end point is detected by means of the dead-stop technic. The method is very rapid and accurate and is not subject to interference by any of the other materials commonly associated with Co. Th is precipitated as the iodate. The $Th(IO_3)_4$ is dissolved, reacted with iodide, and the liberated iodine titrated with thiosulfate ($Na_2S_2O_3$). The method is more rapid and equally as accurate as the gravimetric method involving precipitation of thorium oxalate.

1314. HALL, C. C. Chemische Werke Essener Steinkohle A.-G. Bergkamen Near Kamen-Dortmund, Germany. Inspection of Fischer-Tropsch Plant. CIOS Rept. XXVII–54, 1945, 5 pp. PB 413; TOM Rept. 10; TAC Rept.SnMC–4; TOM Reel 197.

This plant contained 124 standard-type atmospheric-pressure ovens, divided into 2 stages; the exact distribution between them depended on catalyst life, plant operation, etc. Each oven contained 1 ton of Co catalyst, the life of which was about 8.5 mo. The synthesis

gas was prepared from coke and coke-oven gas in 12 Demag water-gas sets and contained CO, 29% and H_2, 59%. A freshly charged oven was treated 1st at 185°–190° for 24–48 hr. with residual gas from stage 2 and then put on stream in stage 2 at 180° where it remained for 2–3 mo. It was then transferred to stage 1 when the operating temperature had risen to about 190°. The gas contraction in stage 1 was 45–50% and the over-all contraction 72–75%. The average annual yield of products was 156–157 gm. per $m.^3$ of gas. After 2–3 mo. in stage 2 and 3 weeks in stage 1, reactivation of the catalyst took place by means of H_2 treatment at 195° for 24 hr. alternated with solvent extraction with benzine at 120°–150°. The products of the process were: 14.7% gasol, 47.9 gasoline, 17.3 diesel oil, 10.7 heavy oil, 7.7 gatsch, and 1.7 hard wax from catalyst. The annual output was 80,000 ton. The composition of residual gas from the process (500,000 $m.^3$ per day) was : CO_2, 20.3%; C_nH_m, 1.6; O_2, 0.1; CO, 10.5; H_2, 18.0; CH_4, 30.9; N_2, 18.5%.

1315. ———. Fischer-Tropsch Catalyst Ovens and General Information on the Fischer-Tropsch Process Obtained at Offices of Gutehoffnungshütte A.-G., Sterkrade, Ruhr. CIOS Sept. XXVII–70, 1945, 5 pp.; PB 975; TOM Rept. 37; TOM Reel 197; TAC Rept. SnMC–10.

3 firms controlled the manufacture of Fischer-Tropsch ovens: Mannesmanne Rohrwerke, Krupps, and Gutehoffnungshütte, the former being the largest manufacturer. There were 3 types: (1) The normal Lammellanofen for use at atmospheric pressure; (2) the double-tube oven for medium pressure, Co-catalyst synthesis; and (3) the double-tube oven designed for use at 20 atm. pressure for the Fe-catalyst synthesis and of the same size and catalyst capacity as (2). Each oven contained 2,100 double tubes. The construction is shown in sketch.

1316. ———. The Fischer-Tropsch Process. Jour. Imp. Coll. Chem. Eng. Soc., vol. 1, 1945, pp. 15–20; Fuel Abs. 5105, November 1945.

Briefly discusses historical background and characteristics of process. Production of synthesis gas and its purification are outlined. The synthesis reaction is described, with various suggested improvements, which have appeared in the literature. Discusses condensation, recovery, and utilization of products. A section is devoted to the efficiency and economics of the process.

1317. ———. Oils and Waxes From Coal—Recent German Work on Catalysts. Chem. Age, vol. 55, 1946, pp. 569–570; Colliery Guard., vol. 173, 1946, pp. 698–700; Chem. Trade Jour., vol. 119, 1946, pp. 729–730; Ind. Chemist, 1946, pp. 761–763; Jour. Inst. Fuel, vol. 20, 1947, pp. 65–76, 95.

Lecture presented before a joint meeting of the Society of Chemical Industry and the Institute of Fuel. The Fischer-Tropsch process was operated in 9 plants in Germany having an annual capacity of 740,000 ton of hydrocarbon products but a maximum output of only 570,000 ton. The catalyst used throughout the plants was of the standard type Co 100 : ThO_2 5 : MgO 8 : kieselguhr 200; research during the last years was concerned with development of the Fe catalyst, and the general trend was toward the production of olefins, waxes, and alcohols for chemical use rather than products for fuel use. The general efficiency of the process and plants was low; not more than 30% of the total heat input was recovered as primary products, with an additional 25% as steam and residual gas. The net heat consumed in producing 1 ton of primary products was equivalent to 4.5 tons of coal. On the basis of 10 RM per £, the capital cost of the German plants varied from 450 to 850 RM per ton annual production and the operating cost, including capital charges, from 240 to 390 RM per ton of primary products. The manufacture of synthesis gas was the major item of cost; to improve the economic prospects of the process 2 possibilities exist: The utilization of a high proportion of the products as high-priced chemical products and a reduction in the cost of synthesis gas. It is estimated that the production of the primary products under present-day British conditions would cost between 2s. and 2s. 6d/gal.

1318. ———. Summary of Information on Fischer-Tropsch Waxes. BIOS Rept. 1831, 1946, pp. 284–303. *See* abs. **444.**

1319. ———. Chemical Products From the Fischer-Tropsch Process. Chem. and Ind., 1947, p. 722; Chem. Age, vol. 57, 1947, p. 701.

Abstract of paper read before the Glasgow Section, Society of Chemical Industry. With Co catalysts, the formation of straight-chain aliphatic hydrocarbons is favored, whereas Fe catalysts promote the production of alcohols. The general range of products was discussed under the heads of fuels, waxes, lubricating oils, alcohols, fatty acids, detergents, etc. The most interesting chemicals are the primary alcohols and the fatty acids. The prospects for operating the Fischer-Tropsch process in Britain are not bright for the production of fuels, but there is some hope of operation for the production of chemicals in competition with similar products from petroleum.

1320. ———. Fischer-Tropsch Process as a Source of Synthetic Products. Gas World, vol. 57, 1947, p. 47.

Paper presented at the St. Andrews symposium. This process may be used for converting coal into liquid fuels or into a variety of aliphatic products. Only the latter application is of immediate economic interest to Great Britain. It is believed possible to operate the process so as to produce materials of the type of hydrocarbon waxes, lubricating oils, long-chain alcohols, fatty acids, and detergents as a major proportion of the entire output with liquid fuels as relatively minor products.

1321. ———. Fischer-Tropsch Process—Present Position and Future Possibilities. Gas World, vol. 126, 1947, pp. 58–64; Iron and Coal Trades Rev., vol. 154, 1947, p. 62; Gas Times, vol. 50, 1947, pp. 37–38, 40–42; Engineering, vol. 163, 1947, pp. 30, 54–55, 79; Inst. Fuel (London) Bull., April 1947, pp. 97–99, 113; Ind. chim., vol. 34, 1947, pp. 127–129.

Abridged version of paper presented before the Yorkshire Section of the Institute of Fuel. The major part of the paper is taken up with a discussion of the operation of the process in Germany, including performance data, composition of the reaction products for both the normal- and medium-pressure processes, and the thermal efficiency. Mentions experimental departures from the orthodox method of carrying out the process with the viewpoint of improving its efficiency or increasing the range of the products. Makes an attempt to compare German costs with British conditions. Taking the cost of coke for synthesis-gas manufacture at 3£ per ton and converting the other costs on the basis of 10RM=1£, the total production cost for the medium-pressure process as operated in Germany would be 32£ per ton or 2s.1.5d. per gal. of primary product. Assuming a production of and a revenue from a ton of primary product to be as follows: 0.10 ton liquefied gas at 10£ per ton; 0.50 ton gasoline and diesel oil at 18£ per ton; 0.13 ton Kogasin at 30£ per ton; 0.17 ton soft wax (Gatsch) at 28£ per ton; and 0.10 ton hard wax at 60£ per ton the income would be 24.7£, or a loss of 7.3£ per ton of primary products. The conclusion is therefore made that the operation of the process in England would not be economical or profitable. To make it attractive, certain improvements would have to be made: The cost of synthesis gas must be reduced, the synthesis process must be improved either in the direction of in-

creased space-time yield or by the production of more valuable products as raw material for the chemical industry, and further applications must be found for the products.

1322. ———. Production of Oil From Coal by the Fischer-Tropsch Process. Jour. Junior Inst. Eng. (London), vol. 57, 1947, pp. 309–334; Chem. Abs., vol. 42, 1948, p. 2743.

Discussion of the history and the main steps of the process, reaction products, and costs.

1323. ———. Recent Research on the Fischer-Tropsch Synthesis. Ind. Chemist, 1949, pp. 163–173; Chim. et ind., vol. 60, No. 3, 1948, p. 69; Fuel Abs. 1949, No. 1080.

Paper presented to Congres de chimie industrielle, 21st Congress, Brussels, September 1948. The Co catalyst process, hitherto used commercially, gives a low space-time yield of products, unsuitable as a source of motor fuel. By using an Fe synthetic NH_3 catalyst at high space velocities and temperatures, it has been shown, in confirmation of American claims, that the space-time yield can be increased 15 times and primary products suitable for the production of good-quality motor fuel can be obtained as the major final product. The use of residual gas recirculation is an essential requirement for achieving the desired results. The Fe catalyst is shown to be particularly active when used as a fluidized powder, and this system would be applicable for large-scale operation. The normal type of Co catalyst is unsuitable for operation under conditions of high conversion at high gas-space velocities. The results of experiments with a Co catalyst at temperatures below the normal synthesis range and of a study of the behavior of alcohols in the presence of Co and Fe catalyst give a strong indication that formation of alcohols is an intermediate step in the synthesis of hydrocarbons by the Fischer-Tropsch process.

1324. ———. Hydrogenation and Fischer-Tropsch Processes. Jour. Inst. Fuel, vol. 23, 1950, pp. 148–151; Chem. Abs., vol. 44, 1950, p. 6101.

General review of the development of the 2 processes for the synthetic production of liquid fuels from coal. The review covers the commercial development, process technique, chemistry, reaction mechanism, and present economic status. It is pointed out that most of the more recent advances in the technique of the 2 processes are the result of American work. Most of the investigations being made by both Government and industry have greater efficiency of method and increased economy of operation in view.

1324a. ———. Fischer-Tropsch Process. Birmingham Univ. Chem. Eng., vol. 2, 1951, pp. 84–92.

Review of the process since its early days.

1325. ———. Synthetic Liquid Fuel. Chem. Age, vol. 64, 1951, pp. 385–386.

Summary of a paper presented at a meeting of the Royal Institute of Chemistry. Brief review of research work in British and American laboratories on the synthesis of liquid fuels.

———. *See* abs. **446, 447, 672, 673, 674, 675, 1131, 1131a, 1417.**

1326. HALL, C. C., AND CRAXFORD, S. R. Additional Information Concerning the Fischer-Tropsch Process and Its Products. BIOS Final Rept. 1722, 1946, 178 pp.; PB 93,498.

Acount of further investigations into the operation and development of the Fischer-Tropsch process in Germany including, specifically, a considerable amount of cost information at the more efficient plants and many important details of plant operation and research developments. The important subjects discussed are: Production of synthesis gas and its purification; Co catalysts, their composition, preparation, costs, reduction, and regeneration; design of reaction vessels; synthesis at atmospheric and medium pressures, recovery of products and general costs; synthesis with Fe catalysts, its mechanism, gas recycle, liquid phase, and oil recirculation processes; primary products, fatty acids and alcohols, Diesel oil, waxes, refining of primary products, analysis; Oxo synthesis; synthetic fatty acids and detergents, wax oxidation, synthetic soap and edible fats.

1326a. HALL, C. C., AND CRUMLEY, P. Observations on Fluidization as Applied to Fischer-Tropsch Process. Conf. Fluidization Technol., June, 1952; Jour. Appl. Chem. (U. S. S. R.), vol. 2, 1952, Suppl. 1, pp. S47–S55; Fuel Abs., vol. 12, No. 3, 1952, abs. 2,600.

Fischer-Tropsch process has been studied in beds of fluidized Fe catalyst in baffled tubes of small diameter; various fluidization phenomena peculiar to such a system and/or to the Fischer-Tropsch process are reported. The presence of baffles does not affect the validity of the normally acceptable criteria of fluidization but tends to promote segregation of the particles by hindering solids circulation. By use of a mechanical stirrer, a turbulent fluid condition can be obtained at about ½ the linear gas velocity otherwise necessary. Fischer-Tropsch Fe catalysts suffer little mechanical attrition as a direct result of fluidization but C formation within the particles causes rapid disintegration and reduction in particle size. In the presence of small amounts of wax formed in the synthesis the resulting small particles form fragile agglomerates approximating in shape to true spheres and greater in size than the largest particles in the original catalyst. Under conditions which favor C formation, the catalyst in a synthesis reactor is composed of particles of a wide range of densities and sizes. In narrow baffled beds the particles become distributed at various levels in the bed such that the height of a particle above the gas inlet is proportional to the product of the particle density and the square of its effective diameter. The largest particles, therefore, are not necessarily found at the bottom of the bed, nor those of lowest density at the top. The advantages and limitations of the use of fluidized catalysts in the Fischer-Tropsch process are reviewed.

1327. HALL, C. C., AND HAENSEL, V. Combined Intelligence Objectives Subcommittee. Fischer-Tropsch Plant of Ruhrchemie A.-G., Sterkrade-Holten. British Coal Utilisation and Research Assoc., Monthly Bull., vol. 10, 1946, Abs. 1155; CIOS Rept. XXVII–69, 97 pp., PB 415, 1945; TOM Rept. 44; TOM Reel 197; TAC Rept. SnMC–11.

During the war the Fischer-Tropsch process was developed as the starting point for numerous processes yielding chemicals rather than fuels. Besides giving a detailed description of the synthesis-gas manufacture and the catalyst chambers used in the normal and medium-pressure processes, this report deals with: (1) The manufacture and recovery of the Co catalyst; and (2) the chemical and economic aspects of the Oxo process in which C_{12}–C_{18} alcohols are formed by hydrogenation of aldehydes produced by the reaction of olefins and synthesis gas over a Co catalyst. Reaction (2) also was studied in relation to a wide variety of other compounds, for example, cyclic olefins, styrene, butadiene, oleic alcohol, rubber, and vinyl ether. Costs are quoted as pf. 77 per kg. of alcohol. Much information was obtained on the manufacture of synthetic lubricating oils, the oxidation and chlorination of waxes, and the direct synthesis of higher alcohols and fatty acids.

1328. HALL, C. C., AND JOLLEY, L. J. Fluidized-Solids Technique and Its Industrial Applications. Petroleum (London), vol. 13, 1950, pp. 217–223.

Summary of characteristics of fluidized-solid systems to indicate their advantages and limitations and to review their application to industrial processes, such as the refining of petroleum, Fischer-Tropsch process, manufacture of phthalic anhydride, burning of lime, carbonization and gasification of solid fuels, retorting of oil shale, hydrogenation of coal, and gas purification. Includes bibliography of 26 refs. and 8 flowsheets.

1329. HALL, C. C., AND POWELL, A. R. Krupp-Lurgi Low-Temperature Carbonization Plant. CIOS Rept. XXV–25, 1945, 8 pp., PB 288; TOM Reel 197; Iron and Coal Trades Rev., vol. 152, 1946, pp. 249–250.

Krupp works at Wanne-Eickel was primarily a Fischer-Tropsch plant for producing synthetic oil. In connection with it was a low-temperature carbonizing plant using high-volatile Ruhr coking coal to make a coke suitable for synthesis-gas production. The ovens were heated by the Fischer-Tropsch tail gas. The large coke was used in water-gas generators giving a water gas with a 1.35 ratio of H_2 : CO, which is considerably higher than obtained from high-temperature coke. It was claimed that the process as carried out gave 30–35% more total oil than would be obtained from a high-temperature coking plant plus a Fischer-Tropsch plant.

1330. ———. Plant of Klocknerwerke A.-G., Castrop-Rauxel. CIOS Rept. XXV–7, 1945, 12 pp., PB 286; TOM Rept. 25; TAC Rept. SnMC–9; TOM Reel 197; British Coal Utilisation and Research Assoc., Monthly Bull., vol. 10, 1946, abs. 1046.

Synthesis gas consists of a 2 : 1 mixture of water gas and high-H_2-content coke-oven gas produced by thermal cracking. Operation of the cracking plant is described as well as the purification of the synthesis gas (0.25% O_2 is added for S removal). In the synthesis process the usual Co catalyst is regenerated with H_2 and by solvent extraction with Fischer-Tropsch benzine. Coke-oven gas also is separated into H_2, C_2H_4, etc. by partial liquefaction in 4 Claude plants and 1 Messer plant.

1331. HALL, C. C., AND SMITH, S. L. Life of a Cobalt Catalyst for the Synthesis of Hydrocarbons at Atmospheric Pressure. Jour. Soc. Chem. Ind., vol. 65, 1946, pp. 128–136. Chem. Abs., vol. 40, 1946, p. 5895.

Detailed account of the experimental operation of a Co–ThO_2–MgO–kieselguhr catalyst for the synthesis of hydrocarbons from CO and H_2 and the nature of the reaction products. The catalyst employed (Co 100, ThO_2 6, MgO 12, kieselguhr 200) was prepared by mixing simultaneously boiling solutions of Co and Th nitrates (40 gm. Co and 2.4 gm. ThO_2 per 1. and Na_2CO_3 (88 gm. Na_2CO_3 per l.) and a warm, aqueous suspension of MgO and kieselguhr. After filtering, precipitating, washing, and drying, the catalyst was reduced by passing dry electrolytic H_2 downwards through it at a rate of approximately 560 l. per hr. for 2 hr. at 390°–405° and then cooling to 150°. Synthesis gas of composition CO_2, 2.5; CO, 31.4; H_2, 63.1; and N_2, 3.0% was passed through the catalyst at 150°, raised to 175° during 12 hr. and maintained for 24 hr., then raised to 180° for a second 24-hr. period and then to 185°, which was maintained constant. The synthesis gas rate was maintained at 1 l. per gm. Co per hr. throughout. Over a period of 14 months at atmospheric pressure an average yield of 122 gm. of liquid hydrocarbons per N m.^{3} of inert-free synthesis gas was obtained. The composition of the liquid products remained unchanged throughout the period for a given reaction temperature. Increase in temperature caused an increase in the proportion of the gasoline fraction and a decrease in that of the wax fraction. Various methods of maintaining and restoring catalyst activity were examined, and it was concluded that maximum catalyst life is obtained by intermittent treatment with H_2 at temperatures in the synthesis range and by repetition of the original reduction process when a reaction temperature of 195° becomes necessary to maintain activity. By adhering to such a procedure it is estimated that with an active catalyst and a S-free gas (not more than 0.1 gm. S per 100 N m.^{3}) it should be possible to maintain in a single-stage synthesis an output of 115–120 gm. of liquid hydrocarbons per N m.^{3} inert-free gas for 5–6 mo. without repetition of the reduction process and for at least 18 mo. before remanufacture of the catalyst becomes necessary. The experiments indicated the existence of 3 processes leading to the deterioration of the catalyst apart from S poisoning; the relatively rapid deposition on the catalyst of hydrocarbons readily removeable by the H_2 treatment; a change, possibly oxidation of the Co, which takes place more slowly and can be reversed by repetition of the original reduction procedure; and a still more gradual but more fundamental change, probably a physical alteration of the active surface of the catalyst or of the presence of some substance strongly absorbed on the active centers.

1332. ———. Hydrocarbon Synthesis in the Presence of Cobalt Catalysts at Medium Pressures. Jour. Inst. Petrol., vol. 33, 1947, pp. 439–459; Chem. Abs., vol. 42, 1948, p. 735.

Effect of a pressure of 150 p.s.i. on the synthesis of hydrocarbons from H_2 and CO with a Co : ThO_2 : MgO : kieselguhr catalyst was studied. Conversion with synthesis gas (H_2 : CO=2 : 1) was about 10% greater, and the rate of catalyst deterioration was 30–50% less than at atmospheric pressure. Improvement in performance over that at atmospheric pressure was not as marked as Fischer and Pichler obtained with their Co : ThO_2 : kieselguhr catalyst, abs. **1011.** Treatment with H_2 at synthesis temperatures did not lengthen the life of the catalyst; rereduction treatment at higher temperatures did not bring improvement under medium-pressure conditions. Catalyst with a high Co content per unit of volume produced an excessive amount of gaseous hydrocarbons at 150 p.s.i. This was corrected by using water gas (H_2 : CO=1.2 : 1) instead of the synthesis gas. Gas production was reduced from 45 to 17 gm. per m.^{3} of inert free charge, and at the same time, the production of nongaseous hydrocarbons was reduced only from 134 to 130 gm. per m.^{3} of charge. The olefin content of the fraction b. 30°–150° was increased by the reduction of H_2 in the charge 8–53%. The highest conversion to liquid and solid hydrocarbons was obtained with a H_2 : CO ratio of 1.5 : 1. In the first few weeks of the catalyst's life the conversion was 85% of the charge.

1333. HALL, C. C., AND TAYLOR, A. H. Chemical Engineering Aspects of the Fischer-Tropsch Process. Trans. Inst. Chem. Eng. (London), Advance Copy, Jan. 7, 1947, 15 pp.; Ind. Chemist, 1947, pp. 231–239; Chem. Abs., vol. 41, 1947, p. 1827.

Summary of chemical engineering data on the Fischer-Tropsch process as collected in Germany by Allied investigators. Synthesis gas was produced from coke in standard water-gas generators, the ratio of H_2 : CO being boosted from approximately 1.25 : 1 to the desired 2 : 1 with additional H_2 from coke-oven gas or by bringing a portion of the water gas into contact with a promoted Fe oxide shift catalyst. H_2S was removed from the gas by the ordinary Fe oxide process. Organic S compounds were removed by a novel hot-purification process in which the gas at 300° passed through towers containing granules of 70% Luxmasse and 30% Na_2CO_3. The O_2 (0.2%) in the inlet gas combined with the decomposition products of the organic S to deposit Na_2SO_4 on the granules. A drawing of the

arrangement of equipment is shown. Synthesis was carried out at either atmospheric pressure or medium pressure (10 atm.). Separate systems were used for the 2 processes, and figures and tables are presented to give details of design, operation, efficiency, and costs of plants operating each process. Synthesis catalyst was granular (1–3 mm. in diameter), containing in parts, by weight: Co 100, ThO_2 5, MgO 8, kieselguhr 200. The reaction was exothermic (80 B. t. u. per cu. ft. CO and H_2 converted) and was carried out at a temperature of 170°–220°, depending on catalyst age. Approximately 80% of the reaction heat was recovered as steam generated in the cooling-water tubes running through the reaction zone. 2 reaction stages were used in the atmospheric-pressure process and 3 in the medium-pressure process. Catalyst in the 1st stage became coated with wax in 1–4 wk. and was solvent extracted with the 165°–320° cut of product to remove the wax. Primary products condensed and recovered included: (1) Liquefied C_3–C_4 gas, separated from other products by adsorption in active C and containing not more than 2% CO_2; (2) gasoline, b. 30°–165°, sp. gr. 0.68, Reid vapor point 0.5–0.8 atm., octane No. (motor) 45–52; (3) light Diesel oil, b. 165°–230°, sp. gr. 0.75, f. p. —40°, flash point 30°, cetane number 76, (4) gas gas oil, b. 230°–320°, used as raw material for detergent manufacture; (5) soft wax, b. 320°–460°, raw material for fatty acid synthesis; (6) hard wax, b. over 460°, m. 80°–90°, formed in the medium-pressure process only; and (7) catalyst wax, m. 80°–90°, recovered by solvent extraction of the catalyst. The chief obstruction to cost reductions in the German processes is the low space-time yield (maximum 0.2 ton primary product per cu. ft. reaction space per month, which is due to the necessity of having a large cooling surface for removing the heat of reaction. Alternate methods of cooling, which were in experimental stages, included gas recirculation or oil circulation, both through the catalyst space, with the heat being removed from the coolant outside the reaction zone. Mention is made of the recently developed American practice in which the use of the fluid catalyst technique has permitted a substantial increase in space-time yield.

1334. HALL, C. C., CRAXFORD, S. R., AND GALL, D. Interrogation of Dr. Otto Roelen of Ruhrchemie A.-G. BIOS Final Rept. 447, 1945, 50 pp.; PB 77,705; TOM Reel 226.

Discussion of Co catalyst, normal and medium-pressure synthesis, primary and secondary products, Fe catalyst, liquid-phase synthesis, incorporation of C_2H_2 in the synthesis gas, reaction mechanism in Fischer synthesis, the Oxo synthesis, and development of Co–ThO_2–MgO catalyst.

1335. ———. Interrogation of Dr. Otto Roelen of Ruhrchemie A.-G. The Catalyst. BIOS Final Report 447, 1945, pp. 2–9; An Account of the Development of Co–ThO_2–MgO Catalyst, by Dr. O. Roelen. Appendix III, pp. 48–52; PB 77,705; TOM Reel 226.

Original Fischer-Tropsch catalyst, Co 100 : ThO_2 18 : kieselguhr 100, was found to be slightly less active than one of composition Co 100 : ThO_2 15 : kieselguhr 100. This latter, however, had a short life (probably because of its high wax production) and a high CH_4 production owing to its high Co density. Therefore, the kieselguhr content was increased to about 200 parts, and a constant Co density of about 80 gm. per l. of catalyst was established. This appeared to be the minimum Co density allowable, since it is one of the main factors controlling the reducibility of the catalyst. In the search for a catalyst promoter, ThO_2 had been chosen as having satisfactory properties. It increased the activity, directed the synthesis to the production of the higher molecular-weight hydrocarbons, was easy to regenerate, was not sensitive to the influence of impurities, and reduced the thixothropic tendency of the wet catalyst filter cake to liquefy and destroy the essential colloidal structure. Cu was tested as an additive because of the possibility of reducing the catalyst at a low temperature but was at once ruled out owing to its favoring sintering of the finely divided Co and thus reducing the active life of the catalyst; it also favors the rapid saturation of the catalyst with wax. Mn was then tried and showed an effect similar to ThO_2, but its use was avoided because of the difficulties involved in the regeneration of the Co solutions. Systematic investigation of MgO showed that it was one of the best activators available for Co catalysts and combined with ThO_2 produced a synergistic effect, which made the mixed Co–ThO_2–MgO–kieselguhr catalyst the best thus far produced. Although Co–MgO catalysts are in themselves very sensitive to temperature and difficult to control, those containing both ThO_2 and MgO have the advantages of easier running, higher activity, easier regeneration, cheaper production, less subject to disintegration, and a well-balanced product. MgO directs the synthesis toward the formation of lighter products, and ThO_2 directs it toward higher molecular hydrocarbons and waxes, thus giving a product having a boiling range intermediate between the 2. The amount of ThO_2 can be reduced to as low as 5 parts giving a composition 100 Co : 5 ThO_2 : 8 MgO : 180–200 kieselguhr. The limits defining the best ratios of the 4 constituents are not narrow, so that variations in composition of catalysts prepared on a large scale are virtually of no importance. Kieselguhr as catalyst support was found to be the most suitable material investigated. In reducing the catalyst with H_2 it was found that the most active catalysts were obtained by stopping the reduction before all the Co was reduced to metal; the most active catalysts had reduction values of 65–70%. It was thought that the unreduced CoO may have a very important role in preventing sintering and, alternatively, that it may be a promoter for the synthesis itself. It was the opinion that further improvements in Co catalysts would not be from the standpoint of yield but rather in the direction of catalysts favoring the production of special types of products. Further investigations of CO–Mn–kieselguhr catalysts, which had a high activity at low temperatures (165°), with or without ThO_2, might be profitable.

1335a. HALL, C. C., GALL, D., AND SMITH, S. L. Alternative Techniques in the Fischer-Tropsch Synthesis. Fuel Abs., 1952, abs. 488; Fuel, vol. 31, 1952, p. 370.

Compares the fixed bed, the liquid phase (slurry) and the fluidized bed techniques. In the work carried out by the British Fuel Research Station on the 3 different techniques identical conditions of catalyst, temperature, pressure, gas composition and throughput, and recycle ratio have been maintained. The limitations of the fluidized bed system imposed a restriction as regards operating conditions with the other 2 techniques. For example the use of H_2–rich gas and temperatures of at least 300° was essential, as well as high fresh feed-gas rate. Experiments were made at both 300 and 600 p. s. i. g. Allowing for increase in activity with reduction in particle size of fused and sintered catalysts, activity of the catalyst is the same in the fixed- and fluid-bed systems, but appreciably lower in the liquid phase system. The space-time yield, which is dependent on catalyst concentration, is greatest in the fixed bed and lowest in the liquid phase. Fluidization itself does not increase the rate of reaction, but the presence of the liquid medium in the slurry process retards the reaction rate. Selectivity as judged by CH_4 formation expressed as a % of the total CO converted, is approximately the same in the fixed and fluid beds but appreciably higher in the slurry system. This is attributed to the prevention of

localized high temperatures because of the direct contact between catalyst particles and liquid medium. The boiling range and olefin contents of the liquid products are independent of the nature of the process technique, as also is the formation of C with a given catalyst.

1336. HALL, C. C., CRAXFORD, S. R., GALL, D., AND SMITH, S. L. Medium-Pressure Synthesis With Iron Fixed-Bed Catalysts and Operation of the Fischer-Tropsch Synthesis in the Liquid Phase—Interrogation of Dr. H. Kölbel, Rheinpreussen. BIOS Final Rept. 1712 (Interrogation Rept. 679), December 1947, 7 pp.; PB 91,925.

Good catalyst composition was found to be, in parts by weight: Al_2O_3, 3.4; Fe_2O_3, 46.3; CaO, 40.7; MgO, 6.5; CuO, 3.1; K_2O, 0.5; CO_2, 40.1; the main constituents being Fe and dolomite. The catalyst was prepared by precipitation from the nitrates by Na_2CO_3 solution. The critical step was the pretreatment in synthesis gas at 240°–280°at atm. pressure for 3–24 hr. The gas was recirculated in the proportion of 9 parts of recycle gas to 1 of fresh gas at a minimum space velocity of 1,000 vol. per vol. catalyst per hr. After cooling the catalyst, synthesis is started at 10 atm. and the full space velocity (100–150), the temperature varying from catalyst to catalyst. Multistage operation is preferred, with recirculation of the residual gas. With 3 stages, a Co-conversion of 90–95% can be obtained at an overall space velocity of 150. Investigation of operation in the liquid phase with the catalyst suspended in oil of Diesel oil composition was carried out over several years with favorable results. The usual catalyst composition was Fe, 100; Cu, 0.2; K_2CO_3, 1.0. Some performance data are given. Using a benzine-forming catalyst at 8–10 atm., 230°, and a space velocity of 75 vol. gas per vol. reaction space per hr., the synthesis gas has a H_2 : CO ratio of 0.5 : 1, and a total yield of 168 gm. per $m.^3$ was obtained with a utilization ratio of H_2 : CO=0.5 : 1. No CH_4 was detected, and the amount of C_2H_6 was very small. Distribution of the product was: C_3–C_4, 19.6%; 35°–200°, 55%; 200°–320°, 20.8%; 320°, 5.6%. The fraction 35°–150° contained 60% olefins. Using catalysts that tended to produce wax, as much as 67% of the total product was obtained as such. It was observed that the Diesel oil used as the liquid medium took part in the reaction and was converted to wax.

1337. HALL, C. C., and others. Coal, Shale, Peat, and Their Products. I. Fuels Produced by Hydrogenation and Synthetic Processes. Rev. Petrol. Technol., vol. 10, 1948, pp. 244–263.

1338. HALL, G. H. Labour's Plan for Oil From Coal. Labour's Pub. Dept., London, 1938, 79 pp.

See Egloff, abs. **771.**

HALL, W. K. *See* abs. **41, 45, 47, 48, 50, 54, 2073a, 2228.**

HALL, W. K., TARN, W. H., AND ANDERSON, R. B. Studies of the Fischer-Tropsch Synthesis. VIII. Surface-Area and Pore-Volume Studies of Iron Catalysts. *See* abs. **51.**

HALL, W. K., TARN, W. H., AND ANDERSON, R. B. Studies of the Fischer-Tropsch Synthesis. XIII. Structural Changes of a Reduced Iron Catalyst on Reoxidation and on Formation of Interstitial Phases. *See* abs. **53c.**

1339. HALLS, E. E. Synthetic Waxes. Food, vol. 19, 1950, pp. 27–28, 68–70, 108–110; Chem. Zentralb., 1950, II, p. 595.

Survey of synthetic waxes, including those from the Fischer-Tropsch process, their production, properties, and uses.

1339a. HALSEY, G., AND TAYLOR, H. S. Adsorption of Hydrogen on Tungsten Powders. Jour. Chem. Phys., vol. 15, 1947, pp. 624–630; Chem. Abs., vol. 41, 1947, p. 7,200.

Frankenburg's data (abs. **1081a**) on the adsorption of H_2 by W powder from −194°–750° are analyzed by the Fowler-Guggenheim treatment.

1340. HALSEY, G. D. Physical adsorption on Nonuniform Surfaces. Jour. Chem. Phys., vol. 16, 1948, pp. 931–937; Chem. Abs., vol. 42, 1948, p. 8,573.

Analysis of adsorption on a uniform surface by using the quasichemical theory of interaction shows that the hypotheses of the Brunauer-Emmett-Teller theory lead to substantially no adsorption beyond the first layer if $E_2=E_L$, and stepwise isotherms if $E_1>E_2>E_3 \cdots >E_L$. For the monolayer adsorption of gases on Ag, Pt, and steel, the heterogeneous nature of the adsorbing surface is clearly indicated. Cooperative adsorption on the nonuniform surface is treated and the cooperative analog of the Freundlich equation derived. The typical multilayer isotherm is shown to be composed of 3 regions: Noncooperative adsorption on a strongly heterogeneous surface; cooperative adsorption on a still heterogeneous surface; and cooperative multilayer adsorption induced by small van der Waals perturbations some distance from the surface. The isotherm p/p_0=experiment $(-a/O^r)$ is derived and shown to be a good representation of adsorption data that conform to the Brunauer-Emmett-Teller type I, II, or III shapes.

1341. ———. Rate of Adsorption on a Nonuniform Surface. Jour. Phys. Colloid Chem., vol. 55, 1951, pp. 21–26; Chem. Abs., vol. 45, 1951, p. 3,220.

On the assumption that the activation energy for the adsorption process is proportional to the zero-point energy between the gas and the solid, an expression is derived for the rate of adsorption of a gas on a nonuniform surface, and it is shown that it is in qualitative agreement with earlier observations of the adsorption of H_2 on ZnO.

1342. HAMAI, S. Physicochemical Investigations of Catalytic Mechanisms. I. Fischer-Tropsch Synthesis of Hydrocarbons With Special Reference to Its Mechanisms. Jour. Chem. Soc. Japan, vol. 62, 1941, pp. 516–518; Chem. Abs., vol. 37, 1943, p. 4681.

In the Fischer-Tropsch synthesis of hydrocarbons the catalyst acts as a carrier, as ascertained in 350 experiments. With Co the catalytic mechanism is as follows: Co adsorbs CO on its surface, and the CO is hydrogenated to CHOH. CoCHOH by catalytic reduction is changed into $CoCH_2$ and H_2O. In the beginning when the amount of $CoCH_2$ is small as compared with that of H_2, CH_4 is formed by the reaction $CO+3\ H_2 \rightleftharpoons CH_4+H_2O$ (particularly when CO : H_2 is greater than 1 : 3) or at 300° CH_4 results from the reaction $CoCH_2+H_2 \rightleftharpoons CH_4+Co$. However, at the later stage of the reaction or at 200° CH_4 is not formed. The $CoCH_2$ then polymerizes into $Co(CH_2)_n$, which further separates into Co and $(CH_2)_n$, the hydrogenation of the latter resulting in a high hydrocarbon (liquid). This catalytic mechanism was found with Fe and Ni. In the case of Fe (synthesis carried out at 250°), however, CO_2, instead of H_2O, was obtained after the catalytic reduction owing to the presence of the rapid reaction $CO+H_2O \rightleftharpoons H_2+CO_2$.

1343. ———. Physicochemical investigations of Catalytic Mechanism. II. Fischer-Tropsch Synthesis of Hydrocarbons With Special Reference to Its Reaction Mechanisms. Bull. Chem. Soc. Japan, vol. 16, 1941, pp. 213–228; Chem. Abs., vol. 36, 1942, p. 739.

Following mechanism of the Fischer-Tropsch synthesis over a Co catalyst is proposed and discussed from the standpoint of energetics and thermodynamics: CO is adsorbed or displaces H_2 adsorbed on the Co surface, forming Co—Co(—C=O)Co, which is reduced first by adsorbed H_2 to Co—Co(—HCOH)Co, then to Co—Co(—CH_2)Co. The (CH_2) mol. adsorbed on the Co surface migrate freely over the surface to interact

with one another to form Co—Co(—$CH_2CH_2CH_2CH_2$ . . . . . .)Co, which, upon desorption, yields $(CH_2)_n$ and finally liquid products by hydrogenation. At 200°, Co—Co(—C=O)Co does not form CH_4 by hydrogenation, but at 300° CH_4 is formed; CH_4 formation probably results from reaction of CO and H_2 in the gas phase. Maximum adsorption does not necessarily coincide with maximum catalytic activity. The same mechanism applies to Fe- and Ni-type catalysts. If the catalyst is pretreated with CO at 350°, it suffers a loss of activity, possibly owing to prevention of adsorption of H_2 by the adsorbed CO.

1344. HAMAI, S., HAYASHI, S., AND SHIMAMURA, K. Physicochemical Investigation of Catalytic Mechanisms. III. Desorption of Various Gases From the Catalyst Used in the Fischer-Tropsch Synthesis. Jour. Soc. Chem. Ind. Japan, vol. 45, 1942, pp. 313–318; Chem. Abs., vol. 43, 1949, p. 2401.

To study the mechanism of catalysis in the synthesis of hydrocarbons from CO and H_2, a Co catalyst with certain promoters was heated 190°–200° and saturated with H_2, CO, or N_2. Another 1 of the 3 gases was then passed over the catalyst, and the velocity of desorption of the original gas was measured by analysis of the exhaust gas. H_2 was more quickly desorbed than CO. A comparison of the desorption of CO by H_2 and of H_2 by CO indicates that CH_4 formation predominates when there is an excess of H_2. The mechanism of the Fischer-Tropsch reaction is proposed to be $Co_nCO \rightarrow Co_nCHOH \rightarrow Co_nCH_2$.

1345. HAMAI, S., HAYASHI, S., SHIMAMURA, K., AND IGARASHI, H. Physicochemical Investigations of Catalytic Mechanisms. IV. Fischer-Tropsch Synthesis of Hydrocarbons. Experiment Series 1. Bull. Chem. Soc. Japan, vol. 17, 1942, pp. 166–171; Chem. Abs., vol. 41, 1947, p. 4366.

Experiments substantiated the authors' proposed mechanism for Fischer-Tropsch synthesis. The reaction vessel of Terex glass was made double walled so that the gas mixture, $CO+2H_2$, led in could be heated before entering the catalyst zone. The catalyst used was made of Co, CeO_2, ThO_2, B_2O_3, and diatomaceous earth. The reaction was run at 200° at the rate of flow 4 l. per hr. The reaction products were collected in 2 traps, condensed by water and solids CO_2—C_2H_5OH mixture, respectively. The gas contraction and oil yield were not parallel unless the reaction was normalized. In the initial stage CH_4 formation predominated, cutting down the oil formation, but as time proceeded side reactions other than oil formation were inhibited. Physicochemical properties of the reaction products are tabulated. The catalyst used proved to be very durable.

1346. HAMAI, S., HAYASHI, S., AND SHIMAMURA, K. Physicochemical Investigations of Catalytic Mechanisms. V. Fischer-Tropsch Synthesis of Hydrocarbons. Bull. Chem. Soc. Japan, vol. 17, 1942, pp. 252–259; Chem. Abs., vol. 41, 1947, p. 4367.

Co with kieselguhr was used as catalyst with various amounts of ThO_2, CeO_2, and Cu as promoters. Gas contraction and oil formation from CO and H_2 are recorded. The gas contraction % is higher for 15–10% CeO_2 and for 20–30% ThO_2. When CeO_2% is low, the addition to the ThO_2 lowers the activity, but if CeO_2 is high, the addition of ThO_2 does not improve the gas contraction. CeO_2 gives a relatively high yield of oil and low yield of CH_4, whereas ThO_2 gives a relatively high yield of CH_4 and low yield of oil.

1347. HAMAI, S. Physicochemical Investigations of Catalytic Mechanisms. VI. Fischer-Tropsch Synthesis of Hydrocarbons. Bull. Chem. Soc. Japan, vol. 17, 1942, pp. 339–344; Chem. Abs., vol. 41, 1947, p. 4367.

Effects of B_2O_3 in the Co-type catalysts are reported. When CH_4 formation predominates the contraction % is enormously high, and the oil yield is inappreciable.

1348. ———. Physicochemical Investigations of Catalytic Mechanisms. VII. Durability and Pretreatment of the Catalyst Used for the Fischer-Tropsch Synthesis of Hydrocarbons. Jour. Chem. Soc. Japan, vol. 63, 1942, pp. 1606–1615; Chem. Abs., vol. 41, 1947, p. 3273.

Catalyst used in the Fischer-Tropsch synthesis of hydrocarbons can be revivified by reducing with H_2.

1349. HAMAI, S., HAYASHI, S., AND SHIMAMURA, K. Physicochemical Investigations of Catalytic Mechanisms. VIII. Fischer-Tropsch Synthesis of Hydrocarbons With Special Reference to the Durability of Catalyst. Bull. Chem. Soc. Japan, vol. 17, 1942, pp. 451–461; Chem. Abs., vol. 41, 1947, p. 4367.

Reaction (I), $CH_2 \rightarrow C_2H_4$, is faster than (II), $CH_2 \rightarrow CH_4$. In the normalized reaction (I) is predominant under various conditions of stage of reaction, temperature, etc., whereas (II) is predominant at the initial stage and as the reaction becomes normalized. (II) must be prohibited when the reaction mixture, $CO+H_2=(1:2)$, is passed through the catalysts, Co+15% ThO_2+100% kieselguhr or Co+12% U_3O_8+2.8% Cu+100% kieselguhr, each separately at 190°–250°.

1350. ———. Physicochemical Investigations of Catalytic Mechanisms. IX. Fischer-Tropsch Synthesis of Hydrocarbons, With Special Reference to Factors Essential to the Particular Catalysts. Bull. Chem. Soc. Japan, vol. 17, 1942, pp. 463–477; Chem. Abs., vol. 41, 1947, p. 4367.

Effects of the factors are tabulated, including the composition of the catalysts (Co, U_3O_8, Cu, Mn, and kieselguhr), preactivation temperature, and reaction temperature for the reaction mixture of $CO+H_2$. The presence of kieselguhr contributes to the oil formation, but not the CH_4 formation. Generally higher temperature promotes the formation of gaseous products, such as CH_4 and CO_2, and a very small amount of oil formation.

1351. HAMAI, S. Physicochemical Investigations of Catalytic Mechanisms. X. Reaction Products in the Fischer-Tropsch Synthesis. Experiment Series 2. Bull. Chem. Soc. Japan, vol. 18, 1943, pp. 369–375; Chem. Abs., vol. 41, 1947, p. 4367.

Results of the distillation analysis of the products show that the first trap oil contains C_{12}–C_{13} and the second trap oil contains C_7–C_9 predominantly, as compared with other fractions.

HAMAI, S. Physicochemical Investigations of Catalytic Mechanisms. VI. Fischer-Tropsch Synthesis of Hydrocarbons. *See* abs. **1347.**

———. Physicochemical Investigations of Catalytic Mechanisms. VII. Durability and Pretreatment of the Catalyst Used for the Fisher-Tropsch Synthesis of Hydrocarbons. *See* abs. **1348.**

———. Physicochemical Investigations of Catalytic Mechanisms. X. Reaction Products in the Fischer-Tropsch Synthesis. Experiment Series 2. *See* abs. **1351.**

HAMAI, S., HAYASHI, S., AND SHIMAMURA, K. Physicochemical Investigation of Catalytic Mechanisms. III. Desorption of Various Gases From the Catalyst Used in the Fischer-Tropsch Synthesis. *See* abs. **1344.**

———. Physicochemical Investigations of Catalytic Mechanisms. V. Fischer-Tropsch Synthesis of Hydrocarbons. *See* abs. **1346.**

———. Physicochemical Investigations of Catalytic Mechanics. VIII. Fischer-Tropsch Synthesis

of Hydrocarbons With Special Reference to the Durability of Catalyst. *See* abs. **1349.**

———. Physicochemical Investigations of Catalytic Mechanisms. IX. Fischer-Tropsch Synthesis of Hydrocarbons With Special Reference to Factors Essential to the Particular Catalysts. *See* abs. **1350.**

HAMAI, S., HAYASHI, S., SHIMAMURA, K., AND IGARASHI, H. Physicochemical Investigations of Catalytic Mechanisms. IV. Fischer-Tropsch Synthesis of Hydrocarbons. *See* abs. **1345.**

1352. HAMMERICH, T. Analytical-Arithmetical Way of Finding the Research Octane Number in Gasoline of the Fischer-Tropsch Synthesis. FIAT Reel K–25, 1940, frames 3,853–3,889; PB 70,216; TOM Reel 292.

Gasolines of the Fischer synthesis were selected since they contain only straight chains of aliphatic hydrocarbons. From these gasolines the C_3 and C_4 hydrocarbons were separated. Density at 15° C., I number after the Rosenmund and Kuhnhenn method, and the distillation curve were determined for each gasoline. From a comparison of the olefin contents, I number, and boiling range, certain relations could be established, which were reproduced in a graph. By adding the gasifying property of gasoline new graphs could be drawn for direct octane-number reading.

1353. ———. [Analytical-Arithmetical Determination of the Research Octane Number of Gasolines From the Fischer-Tropsch Synthesis.] Oel u. Kohle, vol. 37, 1941, pp. 148–155; Brennstoff-Chem., vol. 22, 1941, p. 154; British Abs., 1948, B, I, p. 281; Chem. Abs., vol. 35, 1941, p. 8268.

For degasified Fischer-Tropsch gasolines, octane No.$=0.7\times0.4\times$(olefin index)$+0.69\times$(vaporizability), the olefin index being equal to (I number$\times$boiling index)/100, and vaporizability the mean of the constituents going over at 60° and at 100°. For 115 gasoline samples covering production of nearly all German plants, 60% showed 0 to ±1 deviation from the Cooperative Fuel Research octane No.; 20% showed ±1.5 deviation; 15% up to ±3 units; and the remaining 5% from ±3.5 to ±5. Mixed octane numbers in 1:1 mixture with Stanavo aviation gasoline, however, showed considerable deviation. The relationship is not valid if the synthesis conditions are changed or if the gasoline has been treated. Diagrams are given from which octane No. may be read directly.

1254. HÄNDLER, H. [Synthesis of Petroleum.] Allgem. österr. chem.- u. tech. Ztg., vol. 42, 1924, pp. 89–91; Chem. Abs., vol. 18, 1924, p. 2955.

General discussion of the possibility of making synthetic petroleum by hydrogenation of CO, CO_2, or coal.

1355. HANEMANN, H. [Higher Eutectics in the Iron-Carbon Alloys.] Ztschr. anorg. Chem., vol. 84, 1914, pp. 1–23; Chem. Abs., vol. 8, 1914, p. 2142.

To check the results of Vittorf, pure Fe–C alloys were melted at temperatures observed with an optical pyrometer and poured into Fe chills. The cementite contents of the samples gave points on a curve agreeing with the results obtained by Vittorf and Ruff, but the accuracy of this determination decreases at high temperatures. Graphite always separates as a primary product from melts poured from above 1,400°. Vittorf's method of analyzing the crystals separating from the melts is criticized, owing to the difficulty of getting a good separation because of the high viscosity of melts made between 1,700° and 2,500°. At 2,500°, quenched specimens gave an analysis 14% of C, mostly as enmeshed graphite. Ruff's conclusion that the solubility of C decreases at very high temperatures was not confirmed. Vittorf's Fe_4C is believed to be austenite, as it goes over to martensite upon quenching in liquid air, and his FeC and FeC_2 are believed to be graphite.

———. *See* abs. **1170.**

1356. HANEMANN, H., HERRMANN, K., HOFMANN, U., AND SCHRADER, A. [Processes in the Formation of the Martensite Structure.] Arch. Eisenhüttenw., vol. 4, 1931, pp. 479–484; Chem. Abs., vol. 25, 1931, p. 4833.

Martensite system was studied by the most recent röntgenographic methods, and a correlation of the conclusion from recent Röntgen investigations with the facts of micrographs was attempted. The tetragonal, space-centered lattice of hardened steels with 0.91% C as determined by röntgenographs primarily is due to the η–phase. The röntgenographs of steel samples with higher C contents (1.64% C) contain, besides the interferences of the tetragonal lattice, those of cubic face-centered Fe (austenite). A distorted α–Fe lattice with the embedded and adsorbed C atoms exists between the first and second martensite transformations. The röntgenographs show the disappearance of the η–phase on annealing, hardened, high–C steels at 110°, while the photomicrographs show that the needle-formed η–structure is unchanged (a case of pseudomorphism). In photomicrographs the θ–phase is crystalline in form, while in the röntgenographs it shows a primary structure different from that of α–Fe (another case of pseudomorphism). On quenching steels with 0.91% C from 1,100° and 900° in ice–H_2O and from 900° in oil, the tetragonal structure remains unchanged within wide limits of quenching velocity.

HARA, I. *See* abs. **1905, 1906b.**

1357. HARDY, D. V. N. Interaction of Olefins, Carbon Monoxide, and Steam. Jour. Chem. Soc., 1936, pp. 364–365; Chem. Abs., vol. 30, 1936, p. 3771.

Passage of a mixture of 1 volume C_2H_4 and 4 volumes CO under a pressure of 150 atm. at a rate of 40 l. compressed gas/hr. through 350 gm. 87% H_3PO_4 at 290°–300° gives 500 gm. product containing 16.5 gm. high-boiling hydrocarbons, 37 gm. EtOH, and a solution of Na salts containing $EtCO_2H$. For every molecule C_2H_4 converted into acid, approximately 3 were hydrated and 2 polymerized. C_3H_6 and CO at 200° and 200 atm. (850 gm. C_3H_6 during 6 hr.) give 546 gm. of an upper layer (41% free acid) and 284 gm. of a lower layer (6.2% free acid). After refluxing 2 hr. with NaOH there were isolated 88.4 gm. volatile and 61.3 gm. nonvolatile hydrocarbons, 3 gm. Me_2CHOH, 10.5 gm. acids, boiling 150°–159°, and 173 gm. residue. Me_2CHCO_2H was identified. Iso–C_4H_8 (640 gm.) gave 10.6 gm. hydrocarbons, 32.5 gm. acid, boiling 160°–168°, 23.1 gm. acid, boiling 168°–190°, and 24.2 gm. residue. Esterification gave 32.8% of Me pivalate and 22.6% $MeEtCHCO_2Me$. Homologs also were present but not identified.

———. *See* abs. **2318.**

HARDY, R. L. *See* abs. **2459.**

HARKNESS, R. W. *See* abs. **829, 830.**

1358. HARKNESS, R. W., AND EMMETT, P. H. Conversion of Ortho to Para Hydrogen Over Promoted Iron Synthetic Ammonia Catalysts at —190°. Jour. Am. Chem. Soc., vol. 55, 1933, pp. 3496–3497; Chem. Abs., vol. 27, 1933, p. 4730.

Adsorption of H_2 by a promoted Fe synthetic NH_3 catalyst inhibits markedly the activity of the latter toward the *o–p*-conversion at —190°; the results indicate definitely that the activated adsorption of H_2 at the higher temperatures is primarily a surface adsorption and not a solution within the Fe sample. Permitting the promoted catalyst to take up O_2 between room temperature and 450° almost eliminates its high-temperature activity toward the *o–p*-conversion but only slightly impairs the activity toward the conversion at —190°.

1359. ———. Two Types of Activated Adsorption of Hydrogen on the Surface of a Promoted Iron Synthetic Ammonia Catalyst. Jour. Am. Chem. Soc., vol. 56, 1934, pp. 490–491; Chem. Abs., vol. 28, 1934, p. 1588.

There are 3 types of adsorption of H on a promoted Fe catalyst (1.3% Al_2O_3 and 1.59% K_2O): *Physical*, at —196°, —183°, and —144°, at which temperatures 10 cc. of catalyst adsorbs 5, 2.8, and 0.25 cc. H, respectively; *type A activated*, between —78° and 0°, the isobar at 760 mm. showing a gradual decrease from an adsorption of 7–8 to 5–6 cc.; *type B activated*, at 100° or higher, an additional but much slower adsorption, the total adsorption of both types reaching 8–9 cc. at 100° in 2 hr.; at 212° and 450° the adsorption reached an apparent equilibrium in less than 1 hr., the adsorption being 5.5 and 3.5 cc., respectively.

1360. HARMAN, R. W. Substitute Motor Fuels in Australia. Jour. Proc. Australian Chem. Inst., vol. 8, 1941, pp. 270–284; British Chem. Abs., 1943, B, I, p. 54.

Shale oil, benzol, and power alcohol can at present supply about ⅓ of Australia's consumption. Any large extension of power alcohol would have to use wheat as raw material. Cost of production is about 2 s. per gal. Greater possibilities are seen in the Fischer–Tropsch synthesis, which, however, is not yet in operation in Australia.

HARNISCH, C. *See* abs. **2998.**

1361. HARRIS, C. P. Liquid Fuels From Gas—Synthetic Gasoline From Water Gas. Oil Weekly, vol. 45, No. 8, 1927, pp. 31–32, 48; Am. Gas Jour., vol. 126, 1927, p. 566, Progress in Gas Tech., pp. 18, 20; Chem. Abs., vol. 21, 1927, p. 2785.

Brief review of research on the production of synthetic fuels from gases and coal.

HARTLEY, H. *See* abs. **1421**, **1423.**

1362. HARTNER-SEBERICH, R., AND KOCH, H. [High-Boiling Oils (Kogasin II) Obtained in the Benzine Synthesis of Fischer-Tropsch as Fuel for Diesel Motor Operation.] Brennstoff-Chem., vol. 13, 1932, pp. 308–310; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 537–541; Chem. Abs., vol. 26, 1932, p. 5733.

Constitution, physical, and fuel properties of Kogasin II were investigated. Distillation curves and behavior in motor tests are similar and equal to those obtained with a gas oil.

1363. HASCHE, R. L., AND BOUNDY, R. H. Inspection of the Oxo Plant at Ruhrchemie A.-G., Oberhausen-Holten. CIOS Rept. XXVII–18, 1945, 4 pp.; PB 390; TOM Reel 197.

This plant is owned jointly by the Ruhrchemie A.-G., the I. G. Farbenindustrie A.-G., and Henkel & Co. It is damaged very little and could produce 10,000 tons per year of products within 3 mo. Olefins of the C_{11}–C_{17} fraction, obtained by cracking in a Dubbs-type furnace of a C_{20}–C_{40} Fischer-Tropsch fraction, are treated with water gas in the liquid phase at approximately 150 atm. to produce a mixture of straight-chain aliphatic aldehydes and ketones, the former of which are reduced to the corresponding alcohols. Yields of olefins of approximately 50% are obtained in the cracking unit at 400°–450°. The converter is charged with a 50% suspension of the catalyst (90% Co, 7% ThO_2, 3% MgO, deposited as carbonates on kieselguhr) in the liquid olefins, and water gas is admitted at the bottom at 150 atm. pressure. Temperatures range 150°–180°, the higher temperature favoring aldehyde production but reducing the yield owing to polymerization. The yield of alcohols is approximately 1 lb. per lb. of olefins. The process may be carried out with C_2H_4 for production of lower aldehydes, particularly propionaldehyde, at temperatures of 85° and 70% yield. The catalyst can be used 50–100 times without regeneration. The oxygenated compounds are separated from the unreacted olefins by fractional distillation.

HASHIMOTO, G. *See* abs. **1930.**

1364. HASKELL, G. Research Plans in Synthesis Process of the United States Industrial Chemicals, Inc. Oil Gas Jour., vol. 46, No. 37, 1948, p. 111.

U. S. Industrial Chemicals, Inc., is cooperating with Stanolind Oil & Gas Co. in investigating the separation and use of chemical products from the hydrocarbon synthesis process. The processing materials will be obtained from the 2 hydrocarbon-synthesis plants now under construction by the Carthage Hydrocol, Inc., at Brownsville, Tex., and for the Stanolind Oil & Gas Co. at Hugoton, Kans.; and from the 2 auxiliary chemical plants projected by the latter. In a plant of its own the U. S. Industrial Chemicals, Inc., will process the primary chemicals from the auxiliary chemical plants. The process will involve the breaking down of the water-soluble chemicals to yield initially upwards of 300 million lb. per yr. of chemicals including solvents, plasticizers, pharmaceuticals, plastics, etc., at prices competitive with those from other sources.

1365. HASLAM, R. T., AND FORREST, H. O. Methane by Catalysis From Carbon Monoxide in Blue Water Gas. Gas Age-Record, vol. 52, 1923, pp. 615–618, 620; Chem. Abs., vol. 18, 1924, p. 321.

When the H_2 and CO of blue water gas in the approximate ratio of 1 : 1 interact at a temperature of 290°–340° with Ni as a catalyst the main reaction is: $2\ CO+2\ H_2=CH_4+CO_2+59{,}300$ calories. Approximately ⅕ of the CO present reacts according to $CO+3\ H_2=CH_4+H_2O+48{,}900$ calories. With reduced Ni as a catalyst the optimum conditions for the conversion of blue gas to CH_4 at atmospheric pressure is a time of contact of 10 sec. at a temperature 300°–330°. Under these conditions, the gas with a gross heating value of 520 B. t. u. per cu. ft. at 0° has the composition: CH_4, 47%; H_2, 5; CO_2, 44; N_2, 4. Increasing the pressure up to 35 p. s. i. has little effect on the ultimate composition of the gas except to require a slightly higher temperature for a given product. At the above temperature range, the energy lost in the conversion amounts to 20% of the total input. At this temperature there appears to be no C deposition on the catalyst. The impurities present in the cooled water gas have little effect on the vigor of the catalyst. This process has an efficiency of carburetion when producing 520 B. t. u. gas of 61.8%; this can be increased to 80% by washing out the CO_2 under pressure, thus raising the heating value to 834 B. t. u. With coke at $9.00 per ton the material cost of the process will be equal to the material cost of oil carburetion when gas oil costs $0.07 per gal.

1366. HASLAM, R. T., AND THIELE, E. W. Progress in Fuels and Fuel Technology. Ind. Eng. Chem., vol. 16, 1924, pp. 749–753; Chem. Abs., vol. 18, 1924, p. 2591.

Brief review of research and development in the field of fuels and combustion. Mentions Bergius and the Synthol processes.

HASSID, N. *See* abs. **2213b.**

1367. HATZFELD, K. Coal processing in Germany. Bergbau, Jan. 7, 1937, pp. 2–10; Coal Carbonisation, vol. 3, 1937, p. 46.

Processing of coal as related to the 4-Year Plan is discussed. Low-, medium- and high-temperature carbonization, coal gasification, high-pressure hydrogenation, Fischer-Tropsch synthesis, coal dust engines, and colloidal fuel are reviewed. The manufacture of gasoline by coal hydrogenation will provide employment for 8,000 miners per million ton of gasoline produced, each

ton needing 3.5 tons of coal. About 650,000 tons of gasoline by the I. G. Farbenindustrie A.-G. process and 150,000 tons by the Fischer-Tropsch process are already being produced in German plants. The capital cost of the Fischer-Tropsch plant is about one-half that of the I. G. Farbenindustrie A.-G. plant and has the advantage of using coke, 6–7 tons being required per ton of kogasin. The Pott-Broche extraction process is in use at the Mathias Stinnes mine. More than 85% of the coal substance is brought into solution. The Uhde process is under development in the Ruhr district. By these various means Germany will soon be independent of imported gasoline and light oils.

1368. HAUL, R., AND SCHOON, T. [Elementary Range of Ferromagnetism.] Ztschr. Elektrochem., vol. 45, 1939, pp. 663–671; Chem. Abs., vol. 34, 1940, p. 298.

γ–Fe_2O_3 was prepared by oxidation of Fe pentacarbonyl. The magnitude of the primary crystals decreases with decreasing reaction temperature until finally preparations are obtained amorphous to X-ray. When crystal identification by means of X-ray is no longer possible, electron rays are used. The magnetic susceptibility is measured by the cylinder method with different field strengths. Up to a range of lattice magnitudes of about 30–40 Å., there is a slight increase in susceptibility, which then rises about 10% to the amount characteristic of ferromagnetic substances. This experimentally determined value marks the lowest elementary particle at which spontaneous magnetization occurs.

1369. ———. [Structure of Ferromagnetic Ferric Oxides; γ–Fe_2O_3.] Ztschr. physik. Chem., vol. B–44, 1939, pp. 216–226; Chem. Abs., vol. 34, 1940, p. 666.

X-ray studies of γ–Fe_2O_3 prepared from Fe_3O_4, from an Fe arc, and from $Fe(CO)_5$ resulted in the values, $a_w = 8.316 \pm 0.004$, 8.333 ± 0.004 and 8.3Å., respectively. No essential difference was found in lattice constant or intensity distribution in the 3 samples. Both X-ray and electron-diffraction powder diagrams showed new interference patterns. They can be explained on the assumption of lower symmetry or a larger elementary cell. Similar results were found in Al_2O_3.

HAWK, C. O. *See* abs. **3210, 3214, 3215, 3297.**

1370. HAWK, C. O., GOLDEN, P. L., STORCH, H. H., AND FIELDNER, A. C. Conversion of Methane to Carbon Monoxide and Hydrogen. Ind. Eng. Chem., vol. 24, 1932, pp. 23–27; Chem. Abs., vol. 26, 1932, p. 1717.

Small-scale process has been developed for the conversion of CH_4 and steam or CO_2 into CO and H_2. The process is intermittent, 1st blasting the catalyst with a gas-air mixture followed by injecting the reaction mixture into the catalyst bed. Catalysts of Ni deposited on refractory proved most satisfactory for activity and durability. Optimum temperatures for reaction are 900°–1,000°, in which range nearly theoretical conversions were obtained.

HAYASHI, S. *See* abs. **1344, 1345, 1346, 1349, 1350.**

HAYES, A. *See* abs. **368, 854, 2214.**

1371. HAYNES, W. Wood Chemicals Meet Synthetic Competition. Jour. Chem. Education, vol. 24, 1947, pp. 109–113.

Abstract of a chapter in volume IV of the author's forthcoming book, A History of the American Chemical Industry, treating of the historical development of the synthetic MeOH process beginning with the work of Patart and the Badische Co. and following through the operations of the E. I. duPont de Nemours, Commercial Solvents, and other companies down to the present day.

HAYS, G. E. *See* abs. **2220.**

1372. HEALEY, F. H., CHESSICK, J. J., AND ZETTLEMOYER, A. C. Adsorption of Gases on Metals. Am. Chem. Soc., 119th Meeting Abs., April 1951, p. 15 G.

Reduced and unreduced samples of Mo powder were studied by means of B. E. T. adsorption techniques. N, A, and O isotherms were measured at —195° and —183°. The Mo sample, originally 99.9% pure, was reduced with H_2 at several temperatures. The chemisorption of O_2 at —195° was taken to be a measure of the extent of reduced surface. Samples reduced at temperatures below approximately 500° showed no ability to chemisorb O_2, although there was an apparent increase in surface area. At about 540° some sintering was noted. Isosteric heats of adsorption were calculated for some of the reduced and unreduced surfaces. The value of V_m for the unreduced surface was found to be the same for A, N, and O. This finding led to a disagreement in areas calculated on the basis of closest packing of the adsorbate.

1373. HEAT ENGINEERING. Hydrogen Manufacture. Vol. 21, 1946, pp. 30–32.

Catalytic process is described that produces H_2 or a mixture of H_2 and CO in any ratio desired, from light hydrocarbons, such as natural gas, refinery gas, propane, or butane. Applicability of the process to synthesis of alcohols and to Fischer-Tropsch process is suggested. The H_2 produced varies in purity 98.5–99.9%. Gives simplified flow diagram.

1374. HEBDEN, D. Catalytic Synthesis of Methane From Carbon Monoxide and Hydrogen as a Means of Gas Enrichment. Thesis, Univ. of Leeds, 1943.

———. *See* abs. **690.**

1375. HECKEL,—. [Influence on the Grain Solidity of Cobalt Catalysts.] FIAT Reel K–29, 1938, frames 6,989–6,990, PB 70,218; TOM Reel 296.

Influences of various starting substances and additions and of various methods of precipitation, washing, forming, and reduction upon the grain solidification of the finished Co catalysts are tabulated.

1376. ———. [Examination of Kieselguhr.] FIAT Reel K–29, 1938, frame 7,029, PB 70,218; TOM Reel 296.

Compilation of the results of comparative washing tests on different test portions of kieselguhr, with 2 different cleansing apparatus, is given in a table. Differences in the results are explained by the different types of nozzles used.

1377. ———. [Thorium Content of Mixed Catalysts.] FIAT Reel K–29, 1938, frames 7,037–7,039, PB 70,218; TOM Reel 296.

Reduction of the Th content in mixed Th–Mg catalysts to about 2–3% ThO_2 is without noteworthy influence on the yield. 1 graph.

1378. ———. [Influence of the Reduction and the Type of Kieselguhr on the Catalytic Efficiency of Catalysts.] FIAT Reel K–29, 1938, frames 7,040–7,047, PB 70,218; TOM Reel 296.

It is established by tests that the method of reduction of catalysts with kieselguhr as carrier substance is without much influence, whereas, of all the kieselguhrs examined, the kieselguhr designated S–11 had the best reaction with regard to longevity and yield. 5 diagrams.

1379. ———. [Japanese Kieselguhrs as Carrier Substances for Catalysts.] FIAT Reel K–29, 1938, frames 7,048–7,056, PB 70,218; TOM Reel 296.

Japanese kieselguhrs are especially good as carrier substances for catalysts. 3 tables and 3 graphs.

1380. ———. [Tests on a New Catalyst Carrier—Eirichkorn.] FIAT Reel K–29, 1938, frames 7,077–7,081, PB 70,218; TOM Reel 296.

Results of a catalytic examination of catalysts, prepared by use of a new carrier called Eirichkorn are given but not described in detail. Compared to normal catalysts, Eirichkorn improved the activity of mixed Th–Mg catalysts, but deteriorated Th catalysts. 2 diagrams.

1381. ———. [Preparation of Cobalt Catalysts by Compression.] FIAT Reel K–29, 1938, frames 7,185–7,188, PB 70,218; TOM Reel 296.

It is shown that an increase of the Co density can be obtained by repeated pressing under dust conduction. The influence on the activity of such compressed catalysts is still being examined. 2 graphs.

1382. ———. [Use of Nickel and Cobalt-Nickel Catalysts in the Gasoline Synthesis.] FIAT Reel K–29, 1938, frames 7,316–7.319, PB 70,218; TOM Reel 296.

It is possible to prepare, by use of appropriate activators, a mixed Co–Ni catalyst with more than 50% Ni, which, in the normal pressure synthesis, does not produce a smaller yield compared to the pure Co catalyst. A Ni catalyst of equal value cannot be made as yet. The reaction of the Co–Ni mixture in the medium pressure process has still to be worked out. 1 table.

1383. HECKEL, H. [Influence of Kieselguhr on the Activity of the Catalyst.] FIAT Reel K–20, frames 103–108, 1937, PB 70,211; TOM Reel 287.

Tests were made covering chemical components, physical properties, microscopic structure, and activity. The solubility in acid and H_2O has no influence on the activity. Physical tests showed that a high loss of ignition diminishes the activity of the catalyst.

———. *See* abs. **402, 2875, 2876.**

HEDIN, R. *See* abs. **1385, 1387.**

HEDLEY, T. J. *See* abs. **2319.**

HEDVALL, J. A., AND BERG, A. [Magnetic Transformation and Catalytic Activity. VI. Catalytic Experiments with $MgO.Fe_2O_3$ and Different Kinds of Iron and Steel in the Region of the Loss of Their Ferromagnetic Properties.] *See* abs. **1389.**

HEDVALL, J. A. AND BYSTRÖM, H. [Magnetic Transformation and Catalytic Activity. V. Course of the Catalytic Hydrogenation of Liquid Unsaturated Compounds in the Region of the Curie Interval of Ferromagnetic Catalysts.] *See* abs. **1388.**

1384. HEDVALL, J. A., AND GUSTAVSON, E. [Catalytic Activity and Ferromagnetism. I.] Svensk Kem. Tid., vol. 46, 1934, pp. 64–65; Chem. Abs., vol. 28, 1934, p. 4971.

It has been shown recently that the reactivity of solids is increased by phase transformations that do not affect the lattice structure. Hence, it is important to investigate whether the disappearance of ferromagnetism produces a similar change. For this purpose experiments were made on the reaction $N_2O=N_2+O$, with pure Ni as the catalyst, at 330°–380°, since no alteration in the Ni lattice has been observed in a temperature interval of 1,000°. Between 330° and 359° the decomposition was constant, but at approximately 359° there was an abrupt rise in the decomposition-temperature curve. The Curie temperature for this specimen of Ni was 358°–360°. Control experiments with N_2 or O_2 instead of N_2O gave curves without this sharp break, as did experiments with N_2O over NiO. Experiments with other samples of Ni with different Curie points showed the same agreement between the temperature at which the break occurs and the Curie temperature. The sudden application of a magnetic field, either above or below the Curie point, produced no appreciable effect on the decomposition.

1385. HEDVALL, J. A., HEDIN, R., AND PERSSON, O. [Ferromagnetic Transformation and Catalytic Activity. II] Ztschr. physik. Chem., vol. 27, B, 1934, pp. 196–208; Chem. Abs., vol. 29, 1935, p. 1314.

Catalytic effect of Ni on the reaction $N_2O \rightarrow N_2+O$ is suddenly changed at the Curie point, where the amount decomposed increases rapidly. This is another example of the theory of the change of reactivity in transitions that do not result in the change of the lattice symmetry.

1386. HEDVALL, J. A., AND SANFORD, F. [Effect of Ferromagnetic Transformation on the Catalytic Power of Nickel in the Reaction $2\ CO=CO_2+C$. III.] Ztschr. physik. Chem., vol. 29, B, 1935, pp. 455–463; Chem. Abs., vol. 30, 1936, p. 369.

Four kinds of Ni catalysts were prepared and carefully analyzed for impurities. The Curie point was determined for each. The reaction $2\ CO=CO_2+C$, catalyzed with this Ni, was then studied, and, as with other reactions, the rate increased sharply at the Curie point. The effect of impurities on the reaction also was studied, as well as the condition of formation of Ni carbide and its effect on the reaction.

1387. HEDVALL, J. A., AND HEDIN, R. [Ferromagnetic Conversion and Catalytic Activity. IV. Hydrogenation of Carbon Monoxide and Ethylene Over Nickel and Carbon Dioxide Formation From Carbon Monoxide Over the Heusler Alloy, $MnAlCu_2$.] Ztschr. physik. Chem., vol. 30, B, 1935, pp. 280–281; Chem. Abs., vol. 30, 1936, pp. 1621–1622.

Rates of the reactions change discontinuously at the Curie point when the ferromagnetic properties of the catalyst disappear. A commercial thermal-conductivity apparatus was used successfully for analysis of the $CO–CO_2$ mixture.

1388. HEDVALL, J. A., AND BYSTRÖM, H. [Magnetic Transformation and Catalytic Activity. V. Course of the Catalytic Hydrogenation of Liquid Unsaturated Compounds in the Region of the Curie Interval of Ferromagnetic Catalysts.] Ztschr. physik. Chem., vol. 41, B, 1938, pp. 163–166; Chem. Abs., vol. 33, 1939, p. 458.

Hydrogenation of castor oil and cottonseed oil was studied in the presence of the catalysts Ni–Cu and Pd–Co and in the region of the Curie point (150°–200°). A sudden increase in the catalytic activity is noted at the Curie point.

1389. HEDVALL, J. A., AND BERG, A. [Magnetic Transformation and Catalytic Activity. VI. Catalytic Experiments With $MgO \cdot Fe_2O_3$ and Different Kinds of Iron and Steel in the Region of the Loss of Their Ferromagnetic Properties.] Ztschr. physik. Chem., vol. 41, B, 1938, pp. 388–395; Chem. Abs., vol. 33, 1939, p. 1579.

Reactions of $2\ CO+O_2=2\ CO_2$, $CO+H_2=C+H_2O$ and $CO+3\ H_2=CH_4+H_2O$ were studied on the catalysts synthetic Mg ferrite, pig Fe, and a W–Cr steel. The activity of the catalysts increases at the Curie point.

HEDVALL, J. A., AND HEDIN, R. [Ferromagnetic Conversion and Catalytic Activity. IV. Hydrogenation of Carbon Monoxide and Ethylene Over Nickel and Carbon Dioxide Formation From Carbon Monoxide Over the Heusler Alloy, $MnAlCu_2$.] *See* abs. **1387.**

HEDVALL, J. A., AND SANDFORD, F. [Effect of Ferromagnetic Transformation on the Catalytic Power of Nickel in the Reaction $2\ CO=CO_2+C$. III.] *See* abs. **1386.**

HEDVALL, J. A., HEDIN, R., AND PETERSON, O. [Ferromagnetic Transformation and Catalytic Activity. II.] *See* abs. **1385.**

1390. HEIDENREICH, R. D., STURKEY, L., AND WOODS, H. L. Decomposition of Martensitic Steel Above and Below 300°. Nature, vol. 157, 1946, p. 518; Chem. Abs., vol. 40, 1946, p. 5382.

Electron microscope and electron-diffraction methods were used to study metallurgical structures in a plain

C steel, 0.9%, 0.15% Si, 0.0056% N. Martensite aged at 200° gives a fine dispersion of hexagonal Fe_3N but no Fe_3C. Above 300° the reaction product is Fe_3C. A specimen aged at 200° shows both Fe_3N and Fe_3C after 30 min. at 350°. A mechanism is suggested: (1) $Fe+C_{solution}$, $+N_{solution}$, martensite, $\xrightarrow{200°}Fe_3N$ or $Fe_3(CN)+C_{solution}$; (2) $Fe+C_{solution}$, martensite, $\xrightarrow{400°}Fe_3C+N_{solution}$; (3) Fe_3N or $Fe_3CN+C_{solution}$, $\xrightarrow{350°}Fe_3C+N_{solution}$. The preparation of satisfactory surfaces involved (1) abrasion through 4/0 metallographic paper; (2) electrolytic polishing; (3) etching 60–90 sec. in 2% HCl and 1% $FeCl_3$ in MeOH; (4) rinsing (a) 50:50 Me_2CO–MeOH+0.5% HCOOH, (b) 50:50 Me_2CO–MeOH, (c) dry C_6H_6; (5) drying in an air blast.

HEIN, L. B. *See* abs. **701a.**

1391. HEINEMANN, F. Fischer-Tropsch Hydrocarbon Synthesis—Its First Development. Petrol. Refiner, vol. 28, No. 1, 1949, pp. 126–127.

Brief account of the patent development of the Fischer-Tropsch process, with biographical notes and photographs of the inventors.

1392. HEINEMANN, H. Digest of United States Patents on the Recovery and Processing of Natural Gas and Its Constituents and on Hydrocarbon Synthesis. Petrol. Refiner, vol. 23, No. 7, 1944, pp. 172, 174, 178, 180, 182, 184.

15 United States patents dealing with synthesis of hydrocarbons from CO and H_2.

1393. ———. Foreign Processes for the Conversion of Methane to Hydrogen and Carbon Monoxide. Petrol. Refiner, vol. 23, No. 1, 1944, pp. 35–36; Chem. Abs., vol. 39, 1945, p. 2391.

Review with 16 refs.

1394. ———. Digest of United States Patents on Hydrogenation of Hydrocarbons and Carbon Monoxide. Petrol. Refiner, vol. 25, No. 1, 1946, pp. 168, 170, 172.

Abstracts of 27 United States patents from 1944 and 1945.

1395. HEISENBERG, W. [Theory of Ferromagnetism.] Ztschr. Physik, vol. 49, 1928, pp. 619–636; Chem. Abs., vol. 22, 1928, p. 4348.

An attempt to explain the Weiss molecular field on the basis of a quantum mechanics energy-interchange process similar to that recently applied by Heitler and London to the interpretation of homopolar valence forces. According to this, ferromagnetism is possible only when (1) the lattice is such that each atom has at least 8 neighbors, and (2) the principal quantum number of the electrons responsible for the magnetism must be $\lesssim 23$. These conditions together do not serve to distinguish Fe, Ni, and Co from all the other materials but Fe, Ni, and Co satisfy these conditions. The present paper is, therefore, regarded by Heisenberg as preliminary and further development is promised.

1396. HELD, W. [Production of Gases for Syntheses.] Petrol. Ztschr., vol. 35, No. 25, 1939, pp. 435–437; Chem. Abs., vol. 33, 1939, p. 9559.

Various processes for the production of gases to be used in syntheses are described; for example, H_2 or mixtures of H_2 with N_2 or CO, according to the Winkler, Koppers, Pintsch-Hillebrand, Wintershall-Schmalfeldt, Bubiag-Didier, and Lurgi methods.

1397. ———. [Production of Hydrocarbons by Synthesis.] Petrol. Ztschr., vol. 35, 1939, pp. 493–495; Chem. Abs., vol. 34, 1940, p. 240.

Surveys coal-hydrogenation process and the Fischer-Tropsch synthesis very briefly. Gives some figures on the requirements of Fischer-Tropsch plants, including data on quantities of H_2 needed and amounts of metals required for furnaces and containers. The influence of catalyst, temperature, and pressure is discussed.

HELLBRÜGGE, J. *See* abs. **163.**

1398. HELLER, O. [Production of Water Gas and Gas for Synthesis From Pulverized Fuels.] Chim. et ind., Special No., June 1933, pp. 466–467; Chem. Abs., vol. 27, 1933, p. 5937.

So-called cellular gas producer, German Patent 520,739, is described. In it a high-grade water gas can be produced by treating pulverized coal with steam superheated to 1,000°. With a specially designed producer and air heated to a high temperature, gas of suitable composition for the synthesis of NH_3 can be produced directly from bituminous coal. By combining the process with a treatment with O_2, water gas virtually free from CH_4 and N_2 and suitable for the production of H_2 can be produced. The possibility of easily regulating the temperature and the amount of steam permits obtaining a mixture of CO and H_2 for the synthesis of MeOH. Gasification and cracking of tar and mineral oils can be carried out efficiently. Tars and mineral oils can readily be treated to obtain either a high calorific gas or mixtures of hydrocarbons with high gasoline and benzene contents.

HELLER, W. *See* abs. **3064.**

1399. HELMERS, C. J., CLARK, A., AND ALDEN, R. C. Catalytic Treatment of Synthetic Gasoline. Oil Gas Jour., vol. 47, No. 26, 1948, pp. 86, 89, 91, 92.

In the synthesis of olefinic gasoline from CO and H_2 with a fluidized Fe-base catalyst, the oxygenated compounds remaining therein must be removed as they have properties undesirable in a motor fuel. Since they are present only in small amounts, their removal does not materially affect the octane rating of the fuel. Any major improvement in octane rating of the synthetic gasoline, therefore, requires improvement in the rating of the hydrocarbons present. In the case of olefins, this is most readily accomplished by isomerization. The Perco catalytic desulfurization process was investigated in connection with this upgrading of olefinic synthetic gasolines. Briefly this process entails a mild vapor-phase treatment of the gasoline over bauxite catalyst. The gasoline is vaporized and preheated to 700°–800° F., and the superheated vapors are passed through the catalyst bed at 30–50 lb. pressure. The flow rate is 1–3 vol. of gasoline per hour per vol. of catalyst, or approximately 150–450 bbl. of gasoline per ton of catalyst per day. The results show a considerable improvement in the octane number up to a maximum in the temperature range 700°–750° F. at a constant flow rate of 1.5 vol. gasoline per vol. of catalyst per hr. Doubling the flow rate and increasing the temperature to 850° F. gives about the same octane improvement. It is assumed that the isomerization is primarily a shift of the double bond rather than a branching of the chain. Improvement was noted in the blending value of Perco treated gasoline with polymer gasoline, the gum content, and the storage stability. The oxygenated compounds originally present in the synthetic gasoline appear to be decomposed in passing through the catalyst bed, as is evident from the composition of the gas produced in the treatment.

1400. HENDRICKS, S. B. Crystal Structure of Cementite. Ztschr. Krist. (in English), vol. 74, 1930, pp. 534–545; Chem. Abs., vol. 24, 1930, p. 5560.

From data published by Westgren and Phragmen a complete structure determination is made for Fe_3C. The space group is $V16/h$. Atomic positions are derived. The structure is of the coordination type.

———. *See* abs. **390, 836.**

1401. HENK, H. J. [Inhibiting the Autoxidation of Fats and Oils.] Seifensieder-Ztg., vol. 64, 1937, p. 942; Chem. Abs., vol. 32, 1938, p. 1961.

Brief review of the status of production of fatty acids.

HENKE, G. *See* abs. **164.**

HENSELING, F. *See* abs. **2219.**

HENSINGER, G. *See* abs. **1969.**

HERBERT, W. *See* abs. **137.**

1402. HERBERT, W., AND RUPING, H. [Recovery With Activated Carbon of Benzine and Gas Oil From the Residual Gases From the Synthesis of Benzine by the Fischer-Tropsch-Ruhrchemie Process.] Chem. Fabrik, vol. 13, 1940, pp. 149–153; Chem. Abs., vol. 34, 1940, p. 4888.

Activated C Supersorbon absorbs 20% of benzine before permitting any loss in the exit gas from the absorber, and with proper operation, 1 lb. will produce over 1,000 lb. of product. With the plant operating for total benzine recovery the steam for regenerating is 2.5 lb. per lb. of benzine. The recovery of oil gas (3- and 4-C hydrocarbons) is about 95%, at which capacity the steam consumption is 3.5–4.0 lb. per lb. product. When both products are recovered simultaneously at atmospheric pressure from a residual gas containing 35–45% CO_2, the CO_2 is absorbed to such an extent that it amounts to 50% of the recovered gases, and when the hydrocarbons are liquefied, it is absorbed and lowers the calorific value. The compression efficiency also is lowered. These difficulties are overcome by the fact that toward the end of charging activated C with compounds of different molecular weights there is an enrichment of the heaviest molecules at the entrance side of the apparatus and of the lightest at the exit side, so that a fractional separation can be effected during regeneration. A flowsheet of a plant is shown, with some operating directions. At present 22 plants are operating or under construction with a daily capacity of about 1,400 tons of total product. Results with activated C and with oil washing are compared.

1403. HERBST, H. [Cracking of Tar and Mineral Oil at Ordinary Pressure Without Hydrogen as Opposed to Berginization.] Petrol. Ztschr., vol. 22, 1926, pp. 947–949; Chem. Abs., vol. 21, 1927, p. 2378.

Brown-coal coke may be gasified and synthetic petroleum products obtained from it.

1404. HERBST, M. [Temperature Resistance of a New Hexagonal Iron Carbide in Catalysts for the Hydrocarbon Synthesis According to F. Fischer.] FIAT Reel R–19, 1942, frames 7,136–7,147, P. B. 73,594; TOM Reel 300.

Tests described in the report concern a new hexagonal Fe carbide (Fe_2C) discovered in 1938 and found in the Fe catalysts used for Fischer gasoline synthesis. The X-ray examination showed that the new Fe carbide is an essential constituent for the activity of the Fischer catalysts. In the temperature range 290°–330°, the new Fe carbide is converted into the Fe_2C described by Hägg. This conversion temperature is considerably higher when the Fe catalysts contain Cu. It was determined that with a Cu content of 2% the conversion temperature is about 350°–400° and with 7.4% of Cu, 430°–450°. It may be seen that cuprous Fe catalysts in the Fischer synthesis are less sensitive to temperature, and that a catalyst with 7% Cu tolerates a temperature 100° higher than a catalyst free of Cu. Includes 2 tables.

1405. HERINGTON, E. F. G. Ethylene and Acetylene Adsorption in Hydrogenation Catalysis. Trans. Faraday Soc., vol. 37, 1941, pp. 361–366; Chem. Abs., vol. 35, 1941, p. 7274.

Conditions of atomic separation for the chemisorption of C_2H_2 and C_2H_4 on the crystal facets of Ni and Co are compared. Whereas C_4H_4 should be held on the short spacing, 2.47 Å., C_2H_2 will be held on the long, 3.50Å. Adsorbed C_2H_4 has no free valences, whereas C_2H_2 is potentially reactive. This is in agreement with experience, since C_2H_2 will polymerize in the presence of H_2 and a Co catalyst, although C_2H_4 is merely hydrogenated to C_2H_6. Support for these views is found in the different behaviors of these gases in the Fischer-Tropsch synthesis: When C_2H_4 or C_2H_2 is introduced in the mixture of CO and H_2 used in this synthesis, C_2H_4 is incorporated in the oil products and in addition yields liquids containing O_2; on the other hand, it was found that the products from a mixture of C_2H_2, CO and H_2 are indistinguishable from a mixture of the C_2H_2 plus H_2 and CO plus H_2 products and do not contain appreciable quantities of O-containing compounds.

1406. ———. Study of the Mechanism of Polymerization Reaction by Means of Size-Distribution Curves. Trans. Faraday Soc., vol. 40, 1944, pp. 236–240; Chem. Abs., vol. 38, 1944, p. 6170.

Degree of polymerization must be known to obtain information on the mechanism. A great simplification in the theoretical treatment, together with the avoidance of many of the practical difficulties, results if the reaction is allowed to proceed to a small extent (5–10%), preferably in dilute solution. 3 types of distribution curves are distinguished: (1) The molecular yield decreases continuously as the chain length increases; this can be terminated either by monomer formation, disproportionation, or transfer in conjunction with either of these; (2) the curve rises from 0 at very small chain length, passes through a maximum, and then decreases as chain length increases, terminated by some combination of mechanisms; (3) the curve commences at real finite values, passes through a maximum and decreases; may be terminated either by (a) monomer formation, disproportionation or transfer, where velocity of termination/propagation increases with chain length, or (b) transfer and combination occurring at the same time. Distribution curves taken in conjunction with other considerations can extend knowledge of polymerization reactions greatly.

1407. HERRINGTON, E. F. G., AND RIDEAL, E. K. Poisoning of Metallic Catalysts. Trans. Faraday Soc., vol. 40, 1944, pp. 505–516; Chem. Abs., vol. 39, 1945, p. 2248.

Phenomena of poisoning are examined to determine whether they are compatible with the hypothesis that uniform crystal facets rather than active patches are the sites of catalytic activity. These considerations are restricted to the active hydrogenating catalysts, for example, Ni, Co, Pt, Pd, in the face-centered cubic form, where the reaction velocity in simple hydrogenation is usually of zero order in respect to the material undergoing hydrogenation. It is assumed that the rate is proportional to the surface concentration of the given reactant. If after poisoning with a substance that occupies 1 active center, a fraction θ of the active spots is bare and an isolated group of n centers is required for reaction, then the number of unpoisoned groups is proportional to θ^n. With this mechanism, the plot of activity against poison concentration is linear throughout the entire poison range only when $N=1$. Much of the observed behavior during the poisoning of heterogeneous catalysts can be duplicated by the poisoning of a uniform set of sites. It is stated that an explanation of catalytic behavior requiring active spots appears in many cases to be unnecessary.

1408. HERINGTON, E. F. G., AND ROBERTSON, A. Influence of Reaction Mechanism on Size Distribution in Polymers. Trans. Faraday Soc., vol. 38, 1942, pp. 490–501; Chem. Abs., vol. 37, 1943, p. 1318.

Where the polymer grows by successive addition to active radicals, the distribution curves of reaction product can be derived for the general case where the

ratio of termination coefficient to the propagation coefficient is considered to vary with chain length. It is assumed first that the initiation rate remains constant over the period considered. Only those polymerizations are considered in which the mean life of the active chain centers is very small compared with the half life of the total reaction, so that application of the stationary state treatment is permissible. It is most desirable to have approximate instantaneous experimental distribution curves.

1409. HERINGTON, E. F. G., AND WOODWARD, L. A. Experiments in the Fischer-Tropsch Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. Trans. Faraday Soc., vol. 35, 1939, pp. 958–966; Brennstoff-Chem., vol. 20, 1939, pp. 319–324; Chem. Abs., vol. 33, 1939, p. 9583.

Catalyst of the following composition by weight was used throughout: Co : ThO_2 : kieselguhr=100 : 18 : 100. Oil synthesis can be insured by breaking in the catalyst in a suitable manner, that is, by keeping the temperature well below 150° when the synthesis gas is first admitted (following the treatment with H_2), the temperature should then be raised very slowly. Under otherwise similar conditions of reaction, a high H_2 : CO ratio in the ingoing gas favors the formation of hydrocarbons of lower molecular weight. Most of the revivifying effect of the H_2 on a used catalyst is shown to be due to chemical interaction. The addition of S compounds during the reaction at first causes an increased production of hydrocarbons of higher molecular weight. Treatment with H_2 at 375° destroys the preferential S resistance of centers, so that, with a partly poisoned catalyst, an increase in poisoning may result owing to redistribution of the S.

HERRMANN, K. *See* abs. **1356.**

1410. HERROUN, E. F., AND WILSON, E. Magnetic Susceptibility of Certain Natural and Artificial Oxides. Proc. Phys. Soc. (London), vol. 33, 1921, pp. 196–206; Chem. Abs., vol. 15, 1921, p. 3023.

Susceptibility of Fe_2O_3, as occurring in nature, varies through a wide range, but in the case of artificial preparations the range of variation seems to be much greater. The highest susceptibility exhibited by Fe_2O_3 occurs when either FeO or Fe_3O_4 is oxidized at a high temperature in the anhydrous condition. From hydrated Fe_3O_4, the susceptibility, though considerable, is much less. The lowest susceptibility is obtained from native hematites or naturally oxidized chalybite or by the ignition or precipitation of ferric salts. It appears that the passage through the stage of Fe_3O_4 impresses more pronounced magnetic properties upon the resulting Fe_2O_3. The susceptibilities of a number of ferrites were measured, of which that of Cu ferrite is most conspicuous, being higher than those of Co or Ni ferrites or any similarly constituted compound except Fe_3O_4 itself. Heating feebly magnetic Fe_2O_3 with a basic oxide, as CaO or MgO, increases susceptibility (confirming List and others). When higher susceptibility has been produced by heating Fe_2O_3 with a basic oxide, such as Ag_2O or HgO, subsequent removal of the metal leaves the Fe_2O_3 in a magnetic condition. The chemical compounds formed when Fe_2O_3 is replaced by Al_2O_3 show no definite increase in susceptibility, which is in marked contrast with the ferrites. In the cases of Co and Mn the susceptibilities of the different oxides show a steady decrease with increase of O_2, and, unlike Fe, there is no increase in the susceptibility of Co_3O_4 and Mn_3O_4 corresponding with Fe_3O_4. Although the susceptibility of Cu is negative, that of each of its oxides is positive but small in magnitude.

HETHERINGTON, H. C. *See* abs. **150.**

1411. HEUBLUM, R. [Synthetic Fatty Acids in the Production of Soap.] Riv. ital. essenze, profumi, piante offic., olii vegetali, saponi, vol. 20, 1938, pp. 236–237, 304–305; Chem. Zentralb., 1939, I, p. 4133.

Patent review of the synthesis of fatty acids with a discussion of their use in soapmaking.

HEWLETT, H. *See* abs. **45.**

1412. HEYD, F. Water-Gas Generation From Coal and Coke. Gas- u. Wasserfach, vol. 75, 973–974; Chem. Abs., vol. 27, 1933, p. 827.

While Heyd agrees in general with Dolch, he stresses the effect of the ash content of cokes as an important factor in attaining the water-gas equilibrium (abs. **407, 713, 714, 2436**).

1413. HIBSHMAN, H. J. Separation of Iso- and Normal Paraffins by Adsorption. Ind. Eng. Chem., vol. 42, 1950, pp. 1310–1314; Chem. Abs., vol. 44, 1950, p. 9143.

Activated C selectivity adsorbs n–C_5, –C_6, and –C_7 paraffins from iso-octane at room temperature. Based on experimental data, a flow plan for a continuous separation of iso-octane and heptane is presented by using fluidized solids technique. C introduced at the top of a column falls countercurrently to the feed and liquid reflux streams introduced at the center and bottom, respectively. The C withdrawn at the bottom contains heptane in high purity, which is removed from the C by washing with pentane, the pentane and heptane being separated by distillation. The pentane on the C need not be removed before the C is reused, since it appears in the filtrate with the iso-octane and is separable by distillation. The filtrate is 90% pure iso-octane. The process is analogous to the conventional extraction and distillation.

1414. HIDAKA, T. Winkler Water-Gas Producer. Jour. Fuel. Soc. Japan, vol. 19, 1940, pp. 1008–1015; in English, vol. 20, pp. 1–6a; Chem. Abs., vol. 35, 1941, p. 3062.

Describes the principle of the Winkler water-gas producer. Gives method and the results of operation.

HIDETAKA, S. *See* abs. **2504.**

HIEBER, G. *See* abs. **165.**

1415. HIGHTOWER, J. V. Organics From Natural Gas. Chem. Eng., vol. 56, No. 1, 1949, pp. 92–94, 132–135.

MeOH, formaldehyde, and acetaldehyde are produced by oxidation of natural gas components near Winnie, Tex., by the McCarthy Chemical Co. The rated maximum amount of feed gas processed by the chemical plant is 100,000,000 cu. ft. per day. O_2 of 90–95% purity is provided by a large, low-temperature unit of Hydrocarbon Research process design. The operation is described by the aid of a flowsheet.

1416. HILBERATH, F. [Composition of Synthetic Benzine From Carbon Monoxide and Hydrogen (Kogasin) and Suitability of Its Monoolefins for Production of Lubricating Oils.] Thesis, Keil, 1940, 79 pp; Feuerungstech., vol. 29, 1941, p. 191; Chem. Abs., vol. 36, 1942, p. 4316.

Fraction boiling below 100° of a Fischer-Tropsch synthetic benzine was separated into paraffins and olefins by means of Hg acetate, and the properties of narrow fractions of each series of hydrocarbons were determined. Some hydrocarbons of high purity were isolated. Various methods of determining the I value of olefins were compared. The Kaufmann and Gross-Getringhaus methods proved satisfactory. Monoolefins were polymerized with $AlCl_3$. n–C_7H_{16} proved a suitable chemically indifferent solvent for this purpose. The viscous oils obtained were compared with those obtained in the same manner from known olefins. The yield, viscosity, and pole height of the lubricating oils (mostly high-grade) depend on the structure of the olefins and particularly on the position of the double linking, for example, *tertiary* olefins yield oils with

poor pole heights. Results are presented in tables and curves.

———. *See* abs. **1823, 1824, 1825, 1826.**

HILDITCH, T. P. *See* abs. **74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86.**

1417. HILDITCH, T. P., AND HALL, C. C. Methanol Synthesis. Catalytic Processes in Applied Chemistry, D. Van Nostrand Co., New York, 2d ed., 1937, pp. 97, 99, 115.

1418. HILES, J., AND THOMPSON, J. K. Fischer-Tropsch Process. Fuel, vol. 21, 1942, p. 115.

Editorial covering developments in the United States at Bureau of Mines.

1419. HILL, D. G., AND KISTIAKOWSKY, G. B. Hydrogenation Over Metallic Cesium. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 892–894; Chem. Abs., vol. 24, 1930, p. 2663.

Catalytic combination of H_2 with C_2H_4 or CO but not with N_2 occurs appreciably over metallic Cs at room temperature, though much more rapidly at 200°. The rate of combination is much retarded by the gradual formation of cesium hydride.

1420. HILPERT, S., AND DIECKMANN, T. [Iron Carbides and Their Catalytic Action on the Decomposition of Carbon Monoxide.] Ber. deut. chem. Gesell., vol. 48, 1915, pp. 1281–1286; Chem. Abs., vol. 9, 1915, p. 2847.

According to Boudouard, the oxides of Fe, Co, and Ni are the principal factors in the decomposition of CO; according to Schenk and Zimmermann, the free metals, not the oxides, act as catalysts. In their experiments Hilpert and Dieckmann confine themselves to a study of the catalyst. In every case pure Fe_2O_3, which had been heated previously, was used. The CO was carefully purified and dried. At 950° the tendency of CO to separate C is very slight. In spite of this, it is surprising that at this temperature the oxide is reduced to pure Fe. After 10 hr. at this temperature a grayish metallic product was obtained, which analyzed 99.8% Fe. At 850° the formation of carbide occurs rapidly, and at the same time the separation of C occurs. Below 800° the separation of C occurs very rapidly. The evident conclusion is that not the Fe itself but a carbide hastens the reaction. The material showed no trace of magnetic properties at 200°. Since pure Fe loses its magnetic property at 750° and the carbide at 200°, only the carbide could have acted as catalyst. The mechanism of the process probably is that the apparently stable carbide Fe_3C is broken down by the action of CO into a series of compounds rich in C, such as Fe_2C and FeC. These are very unstable and tend to form Fe_3C again, with separation of C.

HINSHELWOOD, C. N. *See* abs. **2746, 3263, 3407.**

1421. HINSHELWOOD, C. N., AND HARTLEY, H. Influence of Temperature on Two Alternative Modes of Decomposition of Formic Acid. Jour. Chem. Soc., vol. 123, 1923, pp. 1333–1338; Chem. Abs., vol. 17, 1923, p. 2865.

1422. HINSHELWOOD, C. N., AND TOPLEY, B. Energy of Activation in Heterogeneous Gas Reactions With Relation to the Thermal Decomposition of Formic Acid Vapor. Jour. Chem. Soc., vol. 123, 1923, pp. 1014–1025; Chem. Abs., vol. 17, 1923, p. 2810.

1423. HINSHELWOOD, C. N., HARTLEY, H., AND TOPLEY, B. Influence of Temperature on Two Alternative Modes of Decomposition of Formic Acid. Proc Roy. Soc. (London), vol. 100, A, 1922, pp. 575–581, Chem. Abs., vol. 17, 1923, p. 914.

HINTERMAIER, A. *See* abs. **2877.**

HIRAO, T. *See* abs. **1930.**

HIROSE, S., NOBORI, N., AND NOGUCHI, M. Manufacture of Fatty Acids by the Oxidation of Paraffin. IV. Composition of Refined Fatty Acids. *See* abs. **1684.**

———. Manufacture of Fatty Acids by the Oxidation of Paraffin. V. Methanol-Soluble Portion of the Unsaponifiable Matter. *See* abs. **1685.**

HIROTA, K. *See* abs. **1756, 1757, 1758.**

1423. HIRSCH, E. [Conversion of Methane.] Mém. soc. ing. civils France, vol. 85, 1932, pp. 286–302; British Chem. Abs., 1932, B, p. 919; Chem. Abs., vol. 27, 1933, p. 2282.

Experimental data on the critical temperature range, rate of flow through the reaction chamber, and the optimum H_2O : vapor ratio are given for the conversion of CH_4 in natural and coke-oven gas into H_2 or H_2–CO mixtures suitable for synthesis purposes. The difficulty of maintaining the strongly endothermic reaction at 1,200° is met by the use of specially designed regenerative heat exchangers.

1425. ———. [Manufacture of Synthetic Gasoline by the Société Courrières-Kuhlmann—Fischer–Tropsch Process.] Mém. soc. ing. civils France, vol. 90, 1937, p. 756–767. Chem. Abs., vol. 32, 1938, p. 9463.

From 1 $m.^3$ of the mixture of CO+2 H_2 a yield of 120–130 gm. of primary products was obtained. This mixture of open-chain paraffins and olefins has the composition: Gaseous products (C_3H_8, C_3H_6, C_4H_{10}, C_4H_8) 8%; primary gasoline (boiling point<200°) 60%; gas oil (b. p.>200°) 22%; solid paraffins (m. p. 20°–100°) 10%. The primary gasoline can be used after a simple treatment. The heavier liquid hydrocarbons are converted to gasoline (octane index 65) by cracking. The octane index can be raised by admixture with alcohol or benzene or addition of $PbEt_4$. Primary gasoline is recovered from the gas oil by distillation.

1426. ———. [Heat Removal From Exothermic Catalyst Reactions.] Chaleur et ind., vol. 19, 1938, pp. 394–398; British Chem. Abs., 1938, B, p. 1012.

Methods adopted in MeOH synthesis and the production of hydrocarbons by the Fischer–Tropsch process are given.

1427. ———. [Manufacture of Synthetic Gasoline According to the Fischer-Tropsch Process by the Société Courrières-Kuhlmann.] Rev. Carburants France, vol. 1, No. 12, 1938, pp. 505–509.

Describes process. The yield of hydrocarbons is about 65% theoretical. The primary products consist of 8% gases; propane, propylene, butane, and butylene; 60% gasoline distilling below 200° C.; 22% gas oil distilling above 200°; and 10% solid paraffins melting at 20°–100°. The gasoline fraction is cracked to raise the octane number. This yields 80% motor fuel of 65 octane number, with very high Pb susceptibility. The gas oil has a cetene number of over 100 and can be blended with heavy oils of various origins. The Courrières-Kuhlmann Co. has built a synthesis unit of 20,000 tons annual capacity.

HIRSCH, J. H. *See* abs. **117.**

1428. HIRSCHFELDER, J. O., AND BOYD, C. A. Physical-Chemical Approach to Reaction Kinetics. Jour. Chem. Education, vol. 27, 1950, pp. 127–135; Chem. Abs., vol. 44, 1950, p. 4759.

Discussion of the principles of reaction mechanism, catalysis, and reaction rates. 14 refs.

1429. HIRSCHKIND, W., AND LOWDERMILK, F. R. Fischer-Tropsch and Allied Processes. CIOS Rept. XXVII–82, 1945, 24 pp., PB 474; British Coal Utilization and Research Assoc., Monthly Bull. 10, 1946, abs. 942; TOM Reel 239.

Report of a visit to the Kaiser Wilhelm Institute für Kohlenforschung at Mülheim. Several complete plants and pilot plants were investigated. Flow sheets

and full operating conditions are given for: (1) Manufacture of synthesis gas from purified and H_2-enriched water gas (80,000 m.³ per hr.); (2) normal pressure synthesis (description of steel converter embodying catalyst 30% Co, 10% ThO_2 per MgO, 60% kieselguhr), the product was largely straight-chain paraffins, with a large quantity of liquid and small amounts of gases and solids; (3) medium-pressure synthesis, 11 atm. pressure. With Co catalyst, 190°–200°, products were equally liquids and solids. With Fe catalyst, 225°–240°, products were largely liquids with small amounts of solids and gases and more unsaturates than with Co; (4) olefin synthesis. The synthesis gas has a H_2: CO ratio of 1:1.25. 2 trains are used: 1 at 10–12 atm.; 2 at 1 atm. for working up the residual gases from 1. Co catalysts are used for both. Yields: Train 1, 10 gm. liquefiable gas and 120 gm. liquid per m.³ feed gas; train 2, 30 gm. solid products and 160 gm. liquid and gaseous products per m.³ feed gas.; (5) aldehyde synthesis. In the Oxo process aliphatic aldehydes are formed by catalytic reaction of water gas on olefins. The aldehydes are reduced to alcohols for production of detergents by sulfonation. The olefins are C_{11}–C_{17} with the double bond at the end of the chain. The reaction was carried out batchwise at temperatures rising 125°–145° and at 150 atm. pressure using the Co catalyst. A plant costing 11,000,000 RM was built having a capacity of 10,000 tons higher aliphatic alcohols C_{12}–C_{18}. Estimated cost of product 0.90–0.95 RM per kg., market price 2.50 RM per kg. 1 lb. olefin was equal to about 1 lb. distilled alcohol. Raw material and power consumption were as follows: Power 1.5 million kw.-hr, per yr. at 0.025–0.03 RM; H_2O 200m.³ per hr.; water gas 750 m.³ per hr. at 0.03–0.035 RM per m.³; olefins 1,250 kg. per hr. at 0.38–0.40 RM per kg.; H_2 400 m.³ per hr. at 0.60–0.70 RM per m.³; steam 300 tons per day.

1430. HIRST, L. L. Methanol Synthesis From Water Gas. Chemistry of Coal Utilization, vol. 2, 1945, pp. 1846–1868.

Review. Bibliography of 230 refs.

———. *See* abs. **155, 156, 1677a, 3211, 3212.**

1431. HIRST, L. L., DRESSLER, R. G., AND BATCHELDER, H. R. Bureau of Mines Completes Gas-Synthesis Plant. Valve World, vol. 48, No. 1, 1951, pp. 98–103.

Describes recently completed gas-synthesis demonstration plant at Louisiana, Mo. The sections of the plant are those for oxygen production, coal gasification, synthesis-gas purification, hydrocarbon synthesis, and distillation and product recovery.

HIRTZ, H. *See* abs. **2304, 2305.**

1432. HOCHSTRASSER, J. [Catalytic Synthesis of Hydrocarbons by the Fischer-Tropsch Process.] Rev. quim. ind., Buenos Aires, vol. 2, No. 19, 1949, pp. 10–13, 20; British Chem. Abs., 1950, B, I, p. 484.

Summary of effects of temperature, pressure, proportions of initial constituents fed to reaction chamber, and shape of reaction chamber on the type and quantity of the finished product. Contrasts process with the high-pressure Synthol process developed by the I. G. Farbenindustrie A.-G. Discusses use of Fe and thoriated Co catalysts.

1433. HODGINS, E. Coal. I. Industrial Darkness. II. Coal Miner Speaks. III. Fuel Revolution. Fortune, vol. 35, No. 3, 1947, pp. 85–95, 221–232; No. 4, pp. 99–105, 238–254.

Discusses the economy of the coal industry and lays special emphasis on the inefficiency of the methods for mining, transporting, and consuming it. In attempting to answer the question, "What shall we do about it?", the technology of the modern developments in the processing of coal and its consumption is presented. The one imperative requirement appears to be that coal must be gasified, and it is from this viewpoint that the subject matter of this article is developed. Various developments are discussed: Underground gasification, total gasification by producer gas methods, such as the Winkler and Lurgi processes, the Bergius process of coal hydrogenation, the Fischer-Tropsch catalytic gas-conversion process, in particular the Americanized version, the Hydrocol process, and the power-gas turbine. Only coal hydrogenation and shale oil are ruled out as being uneconomical compared with other processes. The most favorable method of coal beneficiation from an economic standpoint appears to be total gasification under pressure and oxidation at the mine into a high B. t. u. (600 B. t. u. and above) gas, supplemented if desired by a phase of the Fischer-Tropsch reaction to convert part of the CO and H_2 into a rich blending gas, thus producing a rich fuel gas capable of pipeline transportation in direct competition with transported coal or petroleum at the point of consumption. Alternative methods are presented such as the method planned by the Pittsburgh Consolidation Coal Co. that leads from coal to gas, gasoline, and chemicals, or the Hydrocol process or a modification thereof adapted to coal instead of natural gas. It is believed that, given consistent development of the new technology, consumption of coal would rise to an enormous extent.

HOENE, J. V. *See* abs. **3262.**

1434. HOFER, L. J. E. Preparation and Properties of Metal Carbides, With Critical Comment as to Their Significance in the Fischer-Tropsch Synthesis. Bureau of Mines Rept. of Investigations 3,770, 1944, 39 pp.; Chem. Abs., vol. 38, 1944, p. 5647.

Probable physical and chemical characteristics of the Fischer-Tropsch (abs. **1026**) carbides are summarized tabularly. The kinetics of the formation of carbides of Fe, Co, and Ni were studied, and the results of various authors were correlated. 3 reactions were isolated: (1) A rapid reaction proceeding on the surface before it has been covered with carbide and reaction products; (2) a slow reaction, which may take weeks for completion. At the end of this reaction, the catalyst has a definite composition, by weight of carbide, corresponding to Fe_2C, Ni_3C, and Co_2C. Some Fe_3C may be formed. This slow reaction is identified with carbide formation in the lattice; (3) if the temperature is above a characteristic value for each metal, C is formed. It continues until the Fe is diluted to 1% of the total Fe–C mass. The Fe and any metal with it is distributed through the C in a finely divided state. Above the critical temperature mixtures of Fe and C corresponding to almost any composition can be prepared. The C-forming reaction is apparently 1st order. All the carbides of Fischer-Tropsch catalysts are more unstable than the true refractory carbides. As Fe, Co, and Ni the carbides are unstable with respect to C and metal. For all known Fischer-Tropsch catalysts, the ratio of C-atom radius to metal-atom radius exceeds 0.58. This seems to be a condition necessary for Fischer-Tropsch activity. The carbides are more or less distorted interstitial compounds with the C inserted into the interstices of the distorted metal lattice. The C does not exist in the ionic form. It is bound to the metal by essentially intermetallic bonds. This may be true of the surface carbide. It is inconceivable that carbide formation in the body of the catalyst will not profoundly modify the properties of the catalyst. Metal-to-metal distances will change. The electrical and magnetic properties will not remain the same. H_2, dissolved in the lattice, probably will not behave the same, partly because many of the interstices in the metallic lattice are filled. The absorption of reagents and desorption of the products probably are modified by the carbides. C formation, by carrying away active cen-

ters and producing irreducible residues on the catalyst, would tend to poison it.

1435. ———. Introduction to the Carbides of Iron and Their Physical and Chemical Properties. Bureau of Mines Tech. Paper 718, 1949, pp. 1–15.

Introduction to the main report by Pichler and Merkel, entitled "Chemical and Thermomagnetic Studies on Iron Catalysts for the Synthesis of Hydrocarbons." Presents a comprehensive, annotated literature review with critical comments on present-day knowledge concerning Fe carbides, their types, formation, and properties, with special reference to their application to the carbide theory on the production of hydrocarbons by the hydrogenation of CO over Fe catalysts. Special consideration is given to the conditions of formation and the identification of 2 new Fe_2C carbides—the carbides (I) and (II) of Pichler and Merkel, the former having the Curie point at 265° and the latter at 380° identifiable with the hexagonal, close-packed Fe carbide of Halle and Herbst. Appendixes A–D present the evidence in the form of translations of laboratory memoranda on the discovery of the Halle and Herbst carbide. Recent investigations at the Bureau of Mines indicate that carbide (I) is identical with the Hägg carbide.

———. *See* abs. **47, 52, 54; 586, 3297, 3647.**

1436. Hofer, L. J. E., and Cohn, E. M. Studies of Ferromagnetic Materials. Consolidated Eng. Corp. Recordings, vol. 4, No. 1, March 1950, p. 5.

Measurement of the magnetic properties of ferromagnetic substances is a convenient method for investigating their composition and chemical reactivity. 2 of these properties, the Curie point and the specific magnetization, can be determined from the thermomagnetic curve, which is obtained by means of the magnetic balance. Typical thermomagnetic curves are shown. The material was a mixture of 2 modifications of Fe_2C, the Hägg carbide (Curie point, 250°), and the hexagonal close-packed carbide (Curie point, 380°), containing about 10–30% Hägg carbide as estimated from specific magnetizations. The apparatus is illustrated and described.

1437. ———. Synthesis of Cementite. Jour. Chem. Phys., vol. 18, No. 5, 1950, pp. 766–767; Chem. Abs., vol. 44, 1950, p. 6367.

Describes new method for synthesizing cementite, which overcomes the difficulties of the presently known methods. It is based on the fact that, in partly carburized Fe containing either or both modifications of the Fe carbide, Fe_2C, the carbides will begin to react with the free Fe at a relatively low temperature (above 260°) and will have reacted completely below 500° to form well-crystallized cementite. This reaction, $Fe_2C+Fe \rightarrow Fe_3C$, thus requires substantially lower temperatures than any other known series of reactions producing cementite uncontaminated by free C, and the synthesis is comparatively simple to carry out. The operation is described with the aid of a thermomagnetic graph.

1438. ———. Thermomagnetic Determination of Hägg Carbide in Used Iron Fischer-Tropsch Catalysts. Am. Chem. Soc., 117th Meeting Abs., March-April, 1950, p. 36–J; Anal. Chem., vol. 22, 1950, pp. 907–910.

Being capable of measuring the Curie points and magnetic moments of ferromagnetic materials, the magnetic balance is suitable for relatively rapid qualitative and quantitative determination of the ferromagnetic phases in used Fe Fischer-Tropsch catalysts. Because of the nature of the samples and the method, special consideration must be given to the magnetic field strength, elastic effects, remanent force, sampling technique, shape of sample, and heating schedule. These points are discussed, and it is shown how a composite thermomagnetic curve may be resolved into its components when their characteristic magnetic constants are known. In connection with X-ray and chemical analyses, and by means of a few simple equations, the relative abundance of ferromagnetic phases can be calculated. This procedure is illustrated for the 3-component system $Fe_2C—Fe_3O_4—\alpha—Fe$, and the significance of the magnetically nondetectable Fe is discussed.

1439. ———. Some Reactions in the Iron–Carbon System. Application to the Tempering of Martensite. Nature, vol. 167, 1951, pp. 977–978.

Precipitated Fe–Cu–K_2O (100 : 10 : 0.32) catalyst was reduced with H_2 at 220° C. and carburized with CO at 188° C. to a C : Fe weight ratio of 0.06966. This preparation, consisting of metallic Fe and hexagonal close-packed Fe carbide, was used as a model for the thermomagnetic study of the reaction that occur during the tempering of carbon-martensite. The results indicate that the 1st tempering reaction (below 200° C.) may be the decomposition of martensite to hexagonal carbide and metallic Fe, and that the 2d reaction (at 200°–240° C.) is the decomposition of the retained austenite into the same products. Between 240° and 300° C., the hexagonal carbide is converted to Hägg carbide (*see* abs. **1446**) and above 300° C., Fe and Hägg carbide react to form cementite (*see* abs. **1437**). Above 470° C., the rate of decomposition of Hägg carbide into cementite and free Fe becomes appreciable (*see* abs. **586**). Thus, the 3 stages of tempering are essentially confirmed by the reactions observed in the catalyst model, except that an intermediate reaction (formation of Hägg carbide) is postulated that has not yet been observed in martensite.

1440. Hofer, L. J. E., and Peebles, W. C. Preparation and X-Ray Diffraction Studies of a New Cobalt Carbide. Jour. Am. Chem. Soc., vol. 69, 1947, pp. 893–899; Chem. Abs., vol. 41, 1947, p. 4363.

CO reacts with finely divided Co at 226°–230° to form a product of the composition corresponding to the formula Co_2C (9.3% C). This product reacts completely with H_2 at 240°–250° to give Co metal and CH_4. The carburization of Co at temperatures higher than 230° leads to C contents higher than 9.3%. However, only C up to 9.3% reacts with H_2 at 240°–250° to form CH_4. Carbon in excess of this amount reacts with H_2 only at temperatures above 350°. The paper reports the results of studies on the carburization of Co by CO at various temperatures, and the reaction of H_2 with, and X-ray analyses of, the resulting products. The results indicate that the easily hydrogenated C produced by the action of CO on finely divided Co metal is combined with Co to form a new crystalline species, Co_2C, whose structure is distinct from either α– or β–Co. X-ray diffraction data indicate that the difficulty hydrogenated C is in the form of finely divided C crystallites. Lattice parameter measurements of α–Co gave no evidence of any solid solution of C in α–Co in a partly carburized sample.

1441. ———. X-Ray Diffraction Studies of the Action of Carbon Monoxide on Cobalt–Thoria–Kieselguhr Catalysts. I. Jour. Am. Chem. Soc., vol. 69, 1947, pp. 2497–2500; Chem. Abs., vol. 42, 1948, p. 1483.

Reduction of the Fischer-type and Hall-type Fischer–Tropsch catalysts at 400° leaves the Co in the face-centered cubic β form, which does not convert readily to the hexagonal close-packed α form. On carburization of the reduced catalyst, the Co is converted to the same carbide previously reported by the authors (abs. **1440**). The carburization of α–Co and β–Co as associated with kieselguhr, ThO_2, and MgO proceeds at nearly the same rates and results in the same crystalline carbide. Hydrogenation of the carbide forms CH_4 and the stable α–Co. The cycle of carbiding the Co

in the reduced catalyst and hydrogenating the carbide so formed can be repeated apparently indefinitely at 210°.

1442. HOFER, L. J. E., PEEBLES, W. C., AND BEAN, E. H. X-Ray Diffraction Studies of the Action of Carbon Monoxide on Cobalt–Thoria–Kieselguhr Catalysts. II. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 2698–2701.

Below 235±10° CO reacts with finely divided Co to form only Co_2C, above this temperature inert free C also is formed. The results of a study of the reactions occurring above this critical temperature are presented. Reduced Co–Th–kieselguhr catalysts produced increasing amounts of free C and decreasing amounts of Co_2C on carburization with CO at increasing temperatures in the range 243°–298°. At the high temperatures, the maximum amount of carbide is formed within the 1st 5 hr. of carburization. Free C tends to make the catalyst inaccessible to further carbide formation either by poisoning or by mechanical blocking. Carbide inhibits free–C deposition. *See* abs. **1441.**

1443. HOFER, L. J. E., AND PEEBLES, W. C. X-Ray Diffraction Studies of the Carburization of a Cobalt–Thoria–Kieselguhr Fischer–Tropsch Catalyst. Am. Chem. Soc., 111th Meeting Abs., 1947, p. 1–E.

Catalyst containing Co–ThO_2–kieselguhr (100 : 18 : 100) was prepared essentially by the method of Fischer and Koch, reduced with H_2 at 400°, and then treated with CO at 210°. The reaction was followed gravimetrically in the manner of Bahr and Jessen. At 210° the weight increase owing to carburization stopped when the ratio C : Co in the catalyst was nearly the same as that in Co_2C. The C deposited at 210° could be rapidly converted to CH_4 and traces of higher hydrocarbons by treatment with H_2 at 210°. X-ray diffraction analysis showed that the ThO_2 and kieselguhr in the catalyst were amorphous, as was also the Co oxide before reduction. After reduction, however, the Co was in the form of cubic β–Co, which is the form stable above about 360°. No trace of any hexagonal α–Co lines could be detected. Upon carburization, lines of a new phase appeared, which previously have been identified as owing to a new Co carbide. After hydrogenation of the carburized catalyst, the lines of hexagonal α–Co appeared.

1444. ———. X-Ray Diffraction Patterns of Solid Aromatic Hydrocarbons. Anal. Chem., vol. 23, No. 5, 1951, pp. 690–695.

Investigations into the basic aspects of coal hydrogenation have led to the preparation of a series of highly purified solid aromatic hydrocarbons that are of interest to the coal-tar, fuel, and other industries and to the field of medicine. For the positive identification of solid crystalline aromatic hydrocarbons X-ray diffraction analysis is proposed. X-ray powder diffraction patterns of 59 hydrocarbons have been obtained using Fe-target radiation. Enough impurities to lower the melting point by as much as 15° C. do not appreciably modify the diffraction patterns. The patterns are very characteristic; those of closely related compounds and even isomers are unique and can readily be identified.

1445. HOFER, L. J. E., COHN, E. M., AND PEEBLES, W. C. Isothermal Decomposition of the Carbide in a Carburized Cobalt Fischer–Tropsch Catalyst. Jour. Phys. and Colloid Chem., vol. 53, 1949, pp. 661–669; Chem. Abs., vol. 43, 1949, p. 6064.

In a previous study of Co catalysts, a new Co carbide Co_2C was prepared and identified, and the rates of formation and of hydrogenation of this carbide in the standard Co–ThO_2–kieselguhr Fischer–Tropsch catalyst were observed. A study now is made of the thermal stability of this Co carbide as it occurs in a carburized catalyst. The rate of isothermal decomposition was studied magnetically and chemically 300°–360°. The Co carbide in the preparation used was either paramagnetic or very weakly ferromagnetic. In the range from about 80–25% Co carbide, the decomposition time curves were linear, and hence the reaction was of apparent zero order in that range. An empirical activation energy of 54.3 kcal. per mole was found for the range of apparent zero order. The details of a magnetic method are described, by means of which the complete course of a reaction in the solid state can be followed under certain conditions.

1446. ———. Modifications of the Carbide, Fe_2C—Their Properties and Identification. Jour. Am. Chem. Soc., vol. 71, 1949, pp. 189–195; Chem. Abs., vol. 43, 1949, p. 3699.

Purpose of this paper is to determine the relationship between the Fe_2C carbides that were reported in thermomagnetic studies and those reported in X-ray diffraction studies. The existence of 2 carbides of Fe with formula Fe_2C and having Curie points at 247° and 380° has been confirmed. A hexagonal close-packed carbide of Fe has been prepared. This carbide has properties similar to those of the carbide described by Halle and Herbst. The identity of the 380° Curie-point carbide of Pichler and Merkel with the hexagonal carbide has been established. The identity of the 247° (265° according to Pichler and Merkel) Curie-point carbide with the Hägg carbide has been established. The carbides reported by Hofmann and Groll and by Tutiya seem to be the hexagonal carbide. The hexagonal carbide decomposes above about 300° to Hägg carbide, which in turn decomposes at about 550° in 1 hr. to cementite and free C.

1447. ———. Isothermal Decomposition of Nickel Carbide. Jour. Phys. and Colloid Chem., vol. 54, No. 8, November 1950, pp. 1161–1169; Chem. Abs., vol. 45, 1951, p. 1850.

Thermal stability of Ni_3C was studied magnetically and by X-ray diffraction 320°–355° on a fully carburized and on an almost fully carburized sample. An induction period precedes the decomposition. This period is analogous to that found for the decomposition of austenite. There is no detectable structural change in the carbide during the induction period. The carbide decomposed into free metal and free C without intermediate formation of a lower carbide. Shortening the induction period by temporary overheating did not affect the zero-order rate of the decomposition, except when the normal induction period was completely suppressed. In that case, the zero-order rate was approximately doubled. In the range 70–10% Ni_3C, the decomposition rate was constant; hence, the reaction was of apparent zero order in that range. Empirical-activation energies were found for the induction periods and quasi-zero-order range of decomposition of both the fully carburized carbide and the almost fully carburized carbide.

HOFER, L. J. E., PEEBLES, W. C., AND BEAN, E. H. X-Ray Diffraction Studies of the Action of Carbon Monoxide on Cobalt–Thoria–Kieselguhr Catalysts. II. *See* abs. **1442.**

1448. HOFER, L. J. E., PEEBLES, W. C., AND DIETER, W. E. Magnetic and X-Ray-Diffraction Studies of Unreduced Ferric–Oxide Fischer–Tropsch Catalysts. Jour. Am. Chem. Soc., vol. 68, 1946, pp. 1953–1956; Chem. Abs., vol. 41, 1947, p. 644.

Catalysts prepared by precipitation with K_2CO_3 or KOH from a solution of a ferric salt are inactive in the Fischer-Tropsch synthesis if the original solution contains chloride anion and are active if the original solution contains nitrate ion only. This difference in activity is an extremely marked one. The catalysts precipitated in the presence of chloride ion in no case produced more than 2 or 3 gm. of liquid hydrocarbons per $m.^3$ of synthesis gas, while catalysts precipitated in

the presence of nitrate ion, in some cases, gave yields as high as 70 gm. per m.³ X-ray diffraction patterns showed that all the catalysts contained identifiable crystalline constituents. In the case of active catalysts, this was α–Fe_2O_3 (I), α–FeOOH (II), or both. In the case of the inactive catalysts, there was one exception, β–FeOOH (III). The magnetic susceptibility of the active catalysts was higher ($100–300\times10^{-6}$) than that of either (I) (25×10^{-6}), (II) (42×10^{-6}), (III) (40×10^{-6}). The magnetic susceptibilities of the inactive catalysts were quite close to the expected 40×10^{-6}. It should be remembered that both (II) and (III) decompose to (I) below 200°, so that the inactivity accompanying the presence of (III) in raw catalysts is not due to the (III) itself, but to some characteristic that it transmits to the ultimate catalyst. This hypothesis is supported by a subsequent investigation of the inactive, chloride-precipitated catalyst, which contained no (III). Repetition of the procedure leading to this catalyst showed that it was formed from (III) as an intermediate and, hence, had the undesirable poisoning characteristic owing to (III). That the chloride ion is not directly responsible for the poisoning action is shown by the fact that good active catalysts can be made starting with $FeCl_2$, in which case no (III) can be formed. Catalysts prepared by precipitation of hot $FeCl_3$ with K_2CO_3 contain β–$Fe_2O_3 \cdot H_2O$ when freshly precipitated, and they are inactive as Fischer-Tropsch catalysts whether or not they contain β–$Fe_2O_3 \cdot H_2O$ after washing and drying. Catalysts prepared by precipitation of $Fe(NO_3)_3$ solutions with K_2CO_3 or KOH contain α–Fe_2O_3 and in some cases α–$Fe_2O_3 \cdot H_2O$ and are active in the Fischer-Tropsch synthesis. The magnetic susceptibility of active raw Fe_2O_3 catalysts was considerably greater than that of any Fe_2O_3 or Fe_2O_3 hydrate, which would be identified in the diffraction pattern of the catalysts. The magnetic susceptibility of those catalysts containing β–$Fe_2O_3 \cdot H_2O$ was very much lower than that of the active catalysts and did not greatly exceed that of β–$Fe_2O_3 \cdot H_2O$. Several suggestions are proposed to account for the deactivation of the catalyst.

1449. HOFER, L. J. E., PEEBLES, W. C., AND GUEST, P. G. Preparing Extruded Specimens for X-Ray Diffraction Analysis. Anal. Chem., vol. 22, No. 9, 1950, pp. 1218–1219.

Details of the equipment and the method.

1449a. HOFER, L. J. E., ANDERSON, R. B., PEEBLES, W. C., AND STEIN, K. Chloride Poisoning of Iron–Copper Fischer-Tropsch Catalysts. Jour. Phys. and Colloid Chem., vol. 55, 1951, pp. 1,201–1,206; Chem. Abs., vol. 46, 1952, p. 233.

Catalysts prepared from ferrous, ferric, and cupric ion solutions are active only when they contain sizable amounts of Fe^{++}. The β–$Fe_2O_3 \cdot H_2O$ catalysts contain up to 0.92% Cl, the poisoning effect of which accounts for the inactivity of this catalyst. Activity is not affected by the presence of Cu.

HOFFMAN, D. S. *See* abs. **2310.**

HOFFMAN, H. M. *See* abs. **2574.**

1450. HOFMANN, F. [Oil Syntheses.] Österr, Chem.-Ztg., vol. 32, 1929, pp. 210–212; Petrol. Ztschr., vol. 26, 1930, pp. 283–284; Chem. Zentralb., 1930, I, p. 1561; Chem. Abs., vol. 24, 1930, p. 2868.

Lecture.

HOFMANN, H. *See* abs. **3374.**

1451. HOFMANN, K. [Heterogeneous Water Vapor and Carbon Dioxide Dissociation Equilibria Over Iron and Its Oxides. I.] Ztschr. Elektrochem., vol. 31, 1925, pp. 172–176; Chem. Abs., vol. 19, 1925, p. 2293.

From data contained in the literature derived equations for the heterogeneous equilibrium of the system Fe–O–C over Fe_3O_4/FeO: $\log K_{2pK} = (-1645/T) + 1.935$; FeO/Fe: $\log K_{3pK} = + (949/T) - 1.140$; Fe_3O_4/Fe: $\log K_{4pK} = + (261/T) - 0.325$. For the system Fe–O–H over the same solid phases the equations are $\log K_{2pW} = - (3237/T) + 3.509$; $\log K_{3pW} = - (834/T) + 0.636$; $\log K_{4pW} = - (1482/T) + 1.411$. K_{pW} and K_{pK} represent the constants of the homogeneous dissociation equilibrium of water vapor and CO_2, respectively. From the discussion of the heterogeneous equilibrium of CO_2 and H_2O over Fe and its oxides from the standpoint of the phase rule Hofmann concludes that a true chemical equilibrium does not obtain in a *blast furnace.*

1452. ———. [Reduction Mechanism of Iron Oxides in a Gas Stream. II.] Ztschr, angew. Chem., vol. 38, 1925, pp. 715–721; Chem. Abs., vol. 19, 1925, p. 3197.

Blast-furnace process is imitated in a simplified manner, using pure H_2 gas and various Fe_2O_3 and Fe_3O_4 preparations. The reaction products are analyzed, and the results are given in curves of H_2 adsorption in relation to time and reduction in relation to temperature. Equilibrium reactions indicate only the tendency of the reaction, because the result is determined by the surface conditions. Fe_2O_3 shows 100% reduction at 550° and 1,000°, with minima at 750° (a) and 925° (b). Granules of 0.05–0.02 mm. diameter are best. Fe_3O_4 exhibits the same character, but is harder to reduce (ferric ferrate). FeO was not found below 564°. Fe_3O_4 forms only in slow processes. The reduction minima are explained (a) by adhesion and (b) by the β–γ transformation. They can be suppressed by addition of MgO. Acid admixtures (SiO_2) do the same but form irreducible slag above 700°.

1453. HOFMANN, K. A., AND GROLL, H. [Production of Ammonia and Hydrocarbons From Lignite Coke by the Action of Steam at 500°.] Ztschr, angew, Chem., vol. 40, 1927, pp. 282–287; Chem. Abs., vol. 21, 1927, p. 1880.

Although at 900° $C + H_2O = CO + H_2$, and at lower temperatures the reaction $C + 2H_2O = CO_2 + 2H_2$ is favored, at 500° both reactions are too slow to be of technical importance. By the use of catalysts, however, reactions involving the addition of H_2 (obtained either from the above reactions or added as such) to the primary tar and to the N_2 present are accelerated. Thus Fe induces the transformation of 15% H_2 into CH_4, Ni, 30%, and Mn, 45%. With Mn and Co oxides together, still higher yields are obtained. It is assumed that metallic carbides, finely divided and rich in C, are formed, and that the H_2 reacts with them to form the hydrocarbons. Experiments are described showing the methods used for activating the C; the effects of H_2 on low temperature lignite coke at 500°, with the production of large yields of hydrocarbons and NH_3; and the influence of catalysts, such as the oxides of Fe, Ni, Mn, and Mn–Co.

1454. HOFMANN, K. A., AND SCHIBSTED, H. [I. Reducibility of Formic Acid. II. Preparation of Formaldehyde and Methyl Alcohol From Formates.] Ber. deut. chem. Gesell., vol. 51, 1918, pp. 1389–1398, 1398–1418; Chem. Abs., vol. 13, 1919, pp. 720–723.

It was found that the initial decomposition temperature of metallic formates increases regularly with an increase in the basic properties of the metal; for example, formate of Cu, 170°; of Pb, 195°; of Ni, 210°; of Ca, 335°; etc. At different temperatures above the initial decomposition temperature, a given formate may decompose in any of several ways; the formate of Li at temperatures 400°–500° may yield MeOH, acetone, HCOOH, CO_2 and H_2O; of Mg above 340° MeOH, acetone, and HCHO; of Cu and Ni, MeOH; of Zn, HCHO and MeOH; of Sn, HCHO but no MeOH; of Al, neither HCHO nor MeOH. These facts may be applied to the transformation of HCOOH in the vapor phase in the presence of chemically unchanged catalysts if the catalyst and temperature are so chosen as to allow for the possibility of formate formation. Un-

der these circumstances cyclic processes involving the synthesis and decomposition of formates may be adapted to the preparation of MeOH and HCHO. The best catalysts for the preparation of aldehyde were found to be ZnO or ThO_2 deposited on asbestos.

1455. HOFMANN, U. [Deposition of Carbon From Carbon Monoxide and Benzine in the Presence of Iron. I.] Ber. deut. chem. Gesell., vol. 61, B, 1928, pp. 1180–1195; Chem. Abs., vol. 22, 1928, p. 4289.

Continuation of the study of black C crystals. In previous work on thermal decompositions of hydrocarbons, temperatures under 700° could not be employed. With an Fe catalyst C separates from CO at 400°–700°, and from benzine at 700°–900°. The form or previous history of the Fe is without influence. The C samples so obtained were distinctly crystalline by X-ray analysis, the grain size increasing with temperature of deposition. Numerous density, chemical, and activity tests also depend on temperature. The fact that crystals of C can be obtained at so low a temperature indicates formations of a carbide with the Fe with subsequent decomposition. The formation of Fe_3C is not proved by X-ray analysis. However, at 400° with CO and at 700° with benzine diffraction lines appear for an unknown substance, which is called X-carbide, richer in C than Fe_3C.

1456. ———. [Deposition of Carbon From Carbon Monoxide or Benzine in the Presence of Iron. II. Crystalline Carbon With High Adsorptive Power.] Ber. deut. chem. Gesell., vol. 61, B, 1928, pp. 2183–2194; Chem. Abs., vol. 23, 1929, p. 751.

C obtained from CO or benzine by the method previously described or precipitated in the presence of $Fe(CO)_5$, although crystalline, is highly adsorptive. The adsorptive power cannot be attributed to the presence of amorphous C. It is due to a very loose, crystalline structure, presenting an enormous surface.

1457. HOFMANN, U. AND GROLL, E. [Separation of Carbon From Carbon Monoxide in Iron. III. Formation of Iron Oxides and Iron Carbides in the Solid Phase.] Ztschr. anorg. u. allgem. Chem., vol. 191, 1930, pp. 414–428; Chem. Abs., vol. 24, 1930, p. 5581.

O_2-free CO was passed over pure Fe, prepared from $Fe(CO)_5$. The solid phase was examined with X-rays by the method of Debye-Scherrer. Up to 450°, graphite and Fe_3O_4 were found with little Fe and Fe_3C; 450°–650°, graphite and FeO and small quantities of Fe_3C; 450°–650°, graphite and FeO and small quantites of Fe_3C, Fe and Fe_3O_4; above 655°, Fe, C and Fe_3C but no FeO or Fe_3O_4. At 320° and 275°, CO was passed over pure Fe_2O_3. X-ray examination showed Fe_3O_4 and Fe_3C in the solid phase. Unknown lines were attributed to a C-rich carbide, Fe_2C, which is unstable at higher temperature. Benzine vapors passed over Fe at 700°, together with O_2-free N_2, gave C, Fe, and cementite in the solid phase. The results are discussed with reference to the phase diagram of Schenck, abs. **3054.** Attempts to detect oxoaustenite in the solid phase were unsuccessful. Acording to Schenck (abs. **3053**), this occurs in carbonization above 575°. The CO–CO_2 analyses obtained at 700° are within this field but only cementite and α Fe were found in the solid phase. The latter was cooled both in H_2O and in liquid N_2, but since the mass is in the form of a fine powder because of the separation of C cooling may not be rapid enough to prevent decomposition of oxoaustenite.

HOFMANN, U. *See* abs. **1356.**

HOFMANN, U., AND GROLL, E. Separation of Carbon From Carbon Monoxide in Iron. III. Formation of Iron Oxides and Iron Carbides in the Solid Phase. *See* abs. **1457.**

1458. HOHENADEL, H. P. Products From Synthesis of Petroleum and Natural Gas. Oil Weekly, vol. 120, No. 12, 1946, pp. 27–28; Min. and Met., vol. 26, 1945, pp. 576–578; Chem. Abs., vol. 40, 1946, p. 2964.

Brief review.

1459. HOKANSON, H. [Some Observations on the Motor-Fuel Supply.] Tek. Tid. Uppl. D. Mekanik, Skeppsbyggnadskonst Flygtek. Automobil Motortek., vol. 70, No. 38, 1940, pp. 74–76; No. 42, pp. 77–84; No. 46, pp. 85–89; No. 51, pp. 98–100.

Lecture on the production of motor fuel from petroleum and coal by high- and low-temperature carbonization, hydrogenation, and gasification, as well as from gases by the Fischer–Tropsch process.

1460. HOLADAY, W. M., ALBRIGHT, R. E., UPJOHN, T. E., AND STEFFENS, L. R. Fuels—Their Present and Future Utilization. Oil Gas Jour., vol. 48, No. 27, 1949, pp. 277–304; Petrol. Processing, vol. 4, No. 11, 1949, pp. 1233–1244.

Trends in energy consumption; utilization developments; future availability of fuels are discussed in a paper presented at the annual American Petroleum Institute meeting, November 1949. Presents potential and practical possibilities for converting natural gas, coal, and oil shale into liquid fuels. Exhaustion of petroleum supplies is too remote to warrant active development of the above additional sources of liquid fuels at present. Of the 3 sources, shale oil appears to offer the best prospects.

HOLDEN, J. H. *See* abs. **3306.**

HOLLIMAN, W. C. *See* abs. **3220.**

1461. HOLLING, —. [Comparison of the Catalytic Cracking of Gas Oil From the Fischer-Tropsch Synthesis and From Naphtha.] FIAT Reel K–29, frames 6,603–6,615, PB 70,218; TOM Reel 296.

Tests have proved that, in catalytic cracking of gas oil from the Fischer synthesis, aviation fuels cannot be obtained as in the cracking of gas oil from naphtha under approximately the same conditions. The output of gasoline is smaller also when Fischer gas oil is used. 3 tables and 5 diagrams.

1462. HOLLINGS, H. Removal of Sulfur Compounds From Gas. Inst. Gas Eng., Pub., No. 175/64, 1937, pp. 4–7, 51–64; Gas Jour., vol. 220, 1937, pp. 475–476, 479–485, 667; Gas World, vol. 107, 1937, pp. 379–383, 471–476, 563. Chem. Abs., vol. 32, 1938, p. 6437.

In recent years, large-scale removal of S from gas has depended upon removal of benzene. The active C process removes about 75% of total S compounds. The normal oil washing removes only about ½ this amount. In a modified process, gas is washed with relatively large volumes of oil to remove CS_2. The oil is regenerated by treatment with K_2CO_3 solution to remove CO_2 followed by alcoholic caustic soda. The K_2CO_3 is regenerated by heat. The reaction with alcoholic caustic soda forms Na xanthate; CS_2 and MeOH are recovered by acidification and distillation. This process does not remove any substantial amount of benzene as wash oil becomes saturated with hydrocarbons. A catalytic process (abs. **1258**) seems best.

1463. ———. Wintershall A.–G., Lützkendorf. CIOS Rept. XXXII–90, 1945, 37 pp.; PB 2,233; Bureau of Mines Inf. Circ. 7369, 1946, 21 pp.; TOM Reel 197.

Report deals with the Schmalfeldt gasification plant for making synthesis gas, the Fischer–Tropsch plant, the hydrogenation plant, and the catalyst factory and includes a report on lubricating oil from Hanover and Austrian crude. The Schmalfeldt gasification process consists of gasification of brown coal in the entrained state by hot (1,000°) recycled synthesis gas. The plant was intended to supply synthesis gas for the Fischer–Tropsch plant, but later a hydrogenation plant was added and the gas requirement increased. The

original designed output per gasifier unit (2 generators in series) was 20,000 m.³ per hr. This was increased to 30,000 m.³ by the use of O_2. The gasification period was 4.5 sec. at 30,000 m.³ of gas per hr. and 6.0 sec. at 20,000 m.³ In addition to 4 gasifier units, there were 5 producer units, each making 30,000–35,000 m.³ of gas per hr. The gasification time was 11 sec. Producer gas also was made by gasification of entrained brown-coal dust, but without recycling of gas or the use of O_2. A mixture of gases was used to heat the gasification units (for each unit 24,000 m.³ per hr., consisting of 3,000–4,000 m.³ of rest gas from the Fischer–Tropsch plant and 21,000–20,000 m.³ of producer gas). The composition of the synthesis gas with and without O_2 was, respectively: CO, 25 and 28%; H_2, 50 and 56%; CO_2, 18 and 10%, CH_4, 3.5 and 3%, N_2, 3.5 and 3%. The H_2 for the hydrogenation plant came from the Wintershall generators. The cost of raw water gas is given as 2.70 pf. per m.³ and of H_2, 7.30 pf. per m.³ The Fischer-Tropsch plant consisted of 144 catalyst chambers, generally worked in 2 stages with a 1-stage conversion of about 50%. In 1940 and 1941 yields were 130 gm. per m.³ of synthesis gas by changing the catalyst every 1.5–2 mo. Total annual production was about 30,000 tons. The catalyst (Co, 100 parts; MgO, 10; ThO_2, 5; with 1.7–2.3 lb. of kieselguhr per lb. of Co) was made and regenerated in an adjacent catalyst factory. Gives details of the method and of the operation of the plant, which hydrogenated the residues from the lubricating oil plant. A table showing capital costs, broken down for the various plants, is presented.

1464. ———. Lurgi High-Pressure Gasification. Gas Jour., vol. 248, 1946, pp. 889, 890, 895–897, 899; BIOS Final Rept. 521, 1945, 75 pp., PB 32,578; TOM Reel 227.

Reviews the literature on the gasification of coal with steam and O_2 under pressure and describes the plant and its operation in detail. Gives flowsheets. In general, it was found that lean, hard coal could be gasified under pressure satisfactorily, while gas-flame coals usually required pretreatment to reduce the caking properties. The proportion of CH_4 formed on gasification increased with increasing pressure and decreases with increasing temperature. By gasification at 20 atm. it is possible to produce a gas with calorific value of 5,000 kcal. per *N* m.³ In actual practice the theoretical value is not obtained. However, the more reactive the fuel gasified, the nearer does the gas approach the ideal. Operating data, analyses and costs are tabulated. Describes operation of the A.-G. Sachsische Werke at Böhlen in detail, and covers the experiment to produce synthesis gas from hard coal in less detail.

1465. Hollings, H., and Griffith, R. H. Activated Adsorption of Hydrogen. Nature, vol. 129, 1932, p. 834; Chem. Abs., vol. 26, 1932, p. 4224.

Adsorption of hydrocarbons at high temperatures (up to 450°) takes place with every metal or metallic oxide so far investigated (Cr, Ti, Fe, Cu, Mo, Zn, Cd, Ca, Zr, Mg, Sn, Co, Al, Mn, and W). The velocity and extent of adsorption vary greatly in different cases and are also considerably influenced by the presence of impurities.

1466. Hollings, H., and King, J. G. Lurgi Gesselschaft für Wärmetechnik, Lurgi Haus, Frankfurt-am-Main. 5 and 7. High-Pressure Gasification. CIOS Rept. XXXII–91, 1945, pp. 6–7, 11; PB 1,722 and PB 4,328.

3 plants are gasifying brown coal under high pressure: Zittau, Böhlen and Brüx, the last 2 having productive capacities of 150 and 100 million cu. ft. per yr., respectively. The process had been investigated for production of synthesis gas from bituminous coal, but no plant had been installed. The process uses 0.5–0.2 m.³ of O_2 per m.³ of gas. The purity of the O_2 utilized depends upon the reactivity of the fuel, the higher the reactivity the lower the purity. Zittau had used O_2 of 72–75% purity. The maximum size of the generator at present is 2.5 m. An Fe, 100; Cu, 10; Al_2O_3, 9; kieselguhr 120 catalyst made by Lurgi Gesellschaft is used at a temperature 70° higher than in the Fischer process. The total cost of producing O_2 in the standard Linde-type plant is estimated at 2.2–2.5 pf. per *N* m.³ for plants producing 1,000–2,000 *N* m.³ per hr., of which 40% is for depreciation, 40% for power, and 20% for wages, maintenance, and chemicals. For large units of 17,000 m.³ per hr. the cost would be 1.5 pf., of which 0.4 pf. would be for depreciation.

1467. ———. Lurgi Gesellschaft für Wärmetechnik, Lurgi Haus, Frankfurt-am-Main. 6. Lurgi and Fischer-Tropsch. CIOS Rept. XXXII–91, 1945, pp. 8–11, PB 1,722 and PB 4,328; TOM Reel 197.

Because of outstanding developments in the Fischer process, Lurgi had been granted full rights by Ruhrchemie A.-G. for constructing Fischer-Tropsch plants, with interchange of technical information. Although it is conceded that hydrogenation is more suitable for the production of high-octane fuel, nevertheless, because of its better applicability to the treatment of high-ash coals and the production of wax and other products, the Fischer-Tropsch process is of considerable potential importance from the chemical point of view. Operation under medium pressure enables the quality of the product to be rather closely controlled. Some tabulated data are given on the yields of products obtained at 7–10 atm., 190°–225° with a Co catalyst and at 20 atm., 230° and 275° with two Fe catalysts in 3, 2, and 1 stages, respectively. Yields per m.³ of high–CO: H_2 ratio water gas were 160, 170, and 135 gm., respectively. The Fe catalyst developed by Lurgi is stated to work at 218°–230°, 10 atm., and H_2: CO ratio =2, a 2d stage of conversion being necessary. It has the composition Fe, 100; Cu, 25; Al_2O_3, 9; K_2O, 2; SiO_2, 30. It is insinuated that the double-tube, medium-pressure oven is not very satisfactory, with operation at 20 atm. pressure. Its temperature limit is 230°. The average cost per kg. of product is given as 24 pf. The average price of all products is 45 pf. Capital cost is set at 800–900 RM per yr. per ton of liquid products. A recent plant was quoted at 600 RM.

1467a. Hollings, H., Hopton, G. U., and Spivey, E. Lurgi High-Pressure Gasification. Gas Jour., vol. 248, 1946, pp. 889, 890, 895–897, 899; BIOS Final Rept. 521, 1945, 56 pp.; TOM Reel 227; PB 32,578; Chem. Abs., vol. 41, 1947, p. 847.

Critical examination of the working results of the plants of the Lurgi Co. in Germany. The fuel is dried in the top of the generator by the hot gases in exit. The latter leave at a temperature 300°–600° and a pressure of about 20 atm. The dried fuel passes down through the generator, and is carbonized by contact with the hot gases. The yield of tar plant and its operation are described at some length. It had a capacity of 150,000,000 m.³ of town gas per yr. and used dried brown-coal lumps and broken briquets as fuel. A diagram is attached. The O_2 consumption is 0.145 m.³ per m.³ of purified gas; steam consumption, 1.47 kg.; over-all power consumption for production of O_2, 1.1–1.2 kw.-hr. per *N* m.³; and the cost, 2.2 pf. per m.³, including capital charges. The total power consumption for gas manufacture including O_2 production is 0.22 kw.-hr. per *N* m.³ of purified gas. Based on costs of fuel at 6.50 RM per ton, H_2O at 6 pf. per m.³, power at 1.1 pf. per kw.-hr., labor at 0.4 pf. per m.³, maintenance cost at 0.4 pf. per m.³, and O_2 at 2.2 pf. per m.³, the total cost of gas is 3.8 pf. per m.³ After deducting a byproduct credit of 1.4 pf. per m.³, the net cost is 2.4 pf. per m.³ The Fischer-Tropsch pilot-plant unit was originally installed by Lurgi Gesellschaft

Wärmetechnik m. b. H. to study detoxification of town gas but was later turned over to the production of hydrocarbons at 18 atm. pressure, 250° and with a precipitated Fe catalyst. The unit never operated satisfactorily and made only a few short runs. The yield of liquid and solid product was only 40 gm. per m.^{3}

1468. HOLLINGS, H., HOPTON, G. U., NEWMAN, L. L., HORNE, W. A., AND SPIVEY, E. A. G. Sächsische Werke, Böhlen, Germany. CIOS Rept. XXX–13, 1945, 12 pp., PB 977; TOM Reel 197.

Deals with the low-temperature carbonization plant, the Lurgi high-pressure gasification plant, and the experimental high-pressure Fischer-Tropsch plant. The carbonizing plant is the standard Lurgi "Spulgas" design. Its primary object was to produce tar for hydrogenation in the adjoining Brabag I plant. The Lurgi high-pressure gasification is comparable to that from low-temperature carbonization. The fuel must not cake during carbonization. The carbonized fuel passes down into the combustion zone in the base of the generator where it reacts with steam and O_2. As the gases ascend through the fuel in the combustion zone, it is cooled and reactions leading to the formation of CH_4 occur. Analyses of the gas range 10–25% CH_4. All solid, noncaking fuels are suitable for pressure gasification, such as brown coal or lean hard coal. Artificial aging can be used to reduce the caking properties of coals which are unsuitable without treatment.

1469. HOLM, M. M., NAGEL, R. H., REICHL, E. H., AND VAUGHN, W. E. Oxo Process. FIAT Final Rept. 1,000, 76 pp., PB 81,383.

Historical development of the Oxo process is outlined, and the work of the I. G. Farbenindustrie A.-G. at Leuna and the Ruhrchemie A.-G. at Oberhausen-Holten discussed. The 10,000 ton-per-day plant at Holten is the only commercial plant in existence, and it was never in actual operation. The more recent development at Ruhrchemie A.-G. considered in this report covers: Production of Oxo olefins by cracking of wax; conversion of Oxo alcohol to soaps by fusion with caustic; conversion of Oxo aldehydes to soap by the Canizzaro reaction; the manufacture of highly branched alcohols by alodol condensation of the lower aldehydes and the production and oxonation of olefins in the C_{30} range for use in cosmetics, emulsifiers, etc. The main contribution of Leuna to the Oxo problem was the development of the original Ruhrchemie A.-G. process to a continuous operation. Also described is the modification of Dr. Reppe at Ludwigshafen in which the hydrogenation is carried out over a fixed catalyst bed consisting of Cu chromite instead of Co with Co carbonyl as the active ingredient as at Leuna and Ruhrchemie A.-G. A commercial development of the process under construction at the end of the war was the Bombrini plant in Italy for the manufacture of propionaldehyde by the oxonation of C_2H_4. Some discussion is made of the possible mechanism of the process but without conclusion. A bibliography of references to TOM reels is appended.

HOLMES, J. *See* abs. **2284.**

1470. HOLMES, J. AND EMMETT, P. H. Alteration of the Size and Distribution of Pores in Charcoals. Jour. Phys. and Colloid Chem., vol. 51, 1947, pp. 1276–1307; Chem. Abs., vol. 42, 1948, p. 1102.

Pore-size and surface-area alterations produced in 4 gas-mask charcoals by various combinations of steaming, hydrogenation, oxidizing, sintering, or impregnating with NiO, CuO, Mo_2O_3, Na_2CO_3, Fe_2O_3, or Cr_2O_3 were studied. Adsorption isotherms for N_2 at −195° were used to judge the changes in pore-size distribution and surface area. The samples included 2 charcoals made by the $ZnCl_2$ process, 1 steam-activated coconut shell charcoal, and 1 made from coal by a combination of calcination and steam activation. The various treating procedures are discussed in terms of 6 possible types of pore alteration that can be produced. The results can be summarized by saying that suitable combinations of the treating process seem capable of increasing the relative proportion of any particular size of pore that it is desired to produce in the charcoals.

1471. HOLROYD, R. Report on Investigations at the I. G. Farbenindustrie A.-G. Works at Ludwigshafen and Oppau. CIOS Rept. XXX–103, 1945, 69 pp., PB 23,750; Bureau of Mines Inf. Circ. 7,375, 1946, 75 pp.; TOM Reel 197.

This report contains information on the following subjects: (II) Synthesis-gas production, pressure operation of the water-gas shift, and the CH_4—O_2 process for synthesis gas and for C_2H_2 production (costs for the latter); (IV) MeOH and higher alcohols synthesis; (V) hydrogenation and related processes, bituminous and brown coal, bituminous and brown-coal tars, 300 and 700 atm. vapor phase, Dehydrierung-Hoch-Druck process, isooctane and alkylate production, fuel for jet planes, costs of hydrogenation process 200,000 ton-per-year basis, methods of manufacture of catalysts for hydrogenation, and related processes; (VII) Fischer-Tropsch synthesis—Michael gas-recycle fixed-bed catalyst and the foam processes; (VIII) miscellaneous chemical processes; (IX) plant operation at Heydebreck, Auschwitz, and Politz-Stettin; (X) negotiations between I. G. Farbenindustrie A.-G. and Japan, with flow sheets and data on hydrogenation of Utibuti coal; (XI) Wickel pressure vessels; (XII) development of high-pressure vessels; (XIII) H_2-resistant steels.

1472. ———. I. G. Farbenindustrie A.-G. Works at Ludwigshafen and Oppau. II–B. Synthesis Gas Production—Pressure Operation of the Water-Gas Shift Reaction. CIOS Rept. XXX–103, 1945, pp. 2–5, PB 23,750; Bureau of Mines Inf. Circ. 7,375, 1946, pp. 2–5; TOM Reel 197.

There are 3 advantages in using the pressure process for CO conversion: (1) Compression of the gases for removal of CO_2 is eliminated. The saving from this source is greater when H_2 or NH_3—synthesis gas is the required product than when synthesis gas for MeOH or Fischer-Tropsch is being made. (2) The equilibrium of the reaction $CO+H_2O=CO_2+H_2$ is unaffected, the volume of gas that can be treated is simply increased, and no change in reaction temperature or catalyst (91% Fe_2O_3+7% Cr_2O_3) is necessary. (3) The makeup steam requirement is reduced from 400 gm. to 250 gm. per m.^{3} of inlet gas. The potential disadvantage is corrosion owing to an increased concentration of dissolved CO_2, O_2, and S gases in the water. This is combatted by using a 17% Cr steel where contact with the liquid water is made. A description of the plant with diagrams is given. A pressure of 12–30 atm. is used. With a catalyst volume of 10 m.^{3}, a 25–30 atm. pressure plant has a capacity of 25,000 m.^{3} per hr. of inlet gas, as compared with only 3,000 m.^{3} at atmospheric pressure. This increase in unit capacity may not result in any reduction in capital cost per m.^{3} of synthesis gas product because special steels are required and a larger % spare capacity has to be installed. For regular production of 100,000 m.^{3} per hr., 5 pressure units with a total capacity of 125,000 m.^{3} per hr. would have to be installed as against 11 atm. units with a total capacity of 110,000 m.^{3} per hr. Not all of the 7 plants that have been installed have found the process satisfactory. It is said that the output of the plant has been limited, corrosion troubles have been severe, and the life of the catalyst has been shortened by deposition of scale on it.

1473. ———. I. G. Farbenindustrie A.-G. Works at Ludwigshafen and Oppau. II–C. Methane–Oxygen Process for Synthesis-Gas Production. CIOS

Rept. XXX–103, 1945, pp. 6–9, PB 23,750; Bureau of Mines Inf. Circ. 7,375, 1946, pp. 5–9; TOM Reel 197.

General description of the process, the operation, and the equipment is given for a plant treating 6,000–7,000 m.^{3} per hr. of coke-oven gas. Synthesis gas may be produced from pure gaseous hydrocarbons, coke-oven gas or purge gas from MeOH synthesis. S content must be low, the presence of even 15 mg. per m.^{3} of feed necessitates an increase in reaction temperature of about 200°. The first step of the process consists of burning the preheated hydrocarbon (650°) with O_2 or O_2-enriched air, the amount of O_2 being substantially the theoretical requirement for the reaction $CH_4+\frac{1}{2}\ O_2=CO+2H_2$. The second step consists of the conversion of residual CH_4 by the CH_4-steam reaction and the attainment of the water-gas equilibrium. The composition of the final gas is CO_2, 7%; CO, 23.8%, H_2, 69%; and CH_4, 0.2%. The consumptions per m.^{3} of CH_4 fed are O_2, 0.487 m.^{3}; steam, 0.107 kg.; cooling water at 15°, 9.6 kg. No cost data are given.

1474. ———. Visit to Oil Centers in Leuna, Lutzkendorf, Zeitz, Böhlen, Stassfurt and Factories in Russian-Occupied Territories. PB Rept. 38, 1945, 6 pp.

Brief account of activities at plants in Leuna, Lutzkendorf, Zeitz, Böhlen, Stassfurt, Blechhammer, Brüx, Politz, Heydebrech, Moosbierbaum, and Oppau (Ludwigshafen). The chief research and development work at Leuna has been in connection with production of high aromatic content gasoline. Synthesis gas and H_2 were made at Lutzkendorf by the Wintershall-Schmalfeldt process. At Blechhammer a pressure process was used for conversion of water gas to H_2.

———. I. G. Farbenindustrie A.-G. Works at Leuna. XXVI. German Oil-Production Data—Fischer-Tropsch Plants. *See* abs. **1481.**

1475. Holroyd, R., and Others. Report on Investigations at the I. G. Farbenindustrie A.-G. Works at Leuna. CIOS Rept. XXXII–107, 1945, 135 pp., PB 6,650. Bureau of Mines Inf. Circ. 7,370, 1946, 135 pp. TOM Reel 197; Chem. Abs., vol. 40, 1946, p. 6235.

This report comprises 27 sections as follows: I. Gas production. II. Ammonia synthesis. III. Methanol and higher alcohol synthesis. IV. Hydrogenation. V. Dehydrierung-Hoch-Druck process. VI. Hydroforming process. VII. Arobin process. VIII. Catalytic cracking. IX. Dehydrogenation of butane–alkylation. X. Isomerization of normal butane. XI. Synthetic lubricating oil—Leuna. XII. Synthetic lubricating oil—Schkopau. (A) Synthetic lubricating oil—Stettin—Pölitz. XIII. Aviation fuel manufacture and engine testing. XIV. Oxo process. XV. Synol process. XVI. Mersol process. XVII. Methylamine. XVIII. Manufacture of carboxylic acids. XIX. Polymerization of C_6 and C_7 olefins. XX. Fertilizers and nitric acid. XXI. Synthesis of toluene from benzene and methanol. XXII. Catalyst preparation. XXIII. Metallurgy. XXIV. Blechhammer. XXV. Brüx. XXVI. General oil production data. XXVII. Use of bottled propane and butane for road vehicles.

1476. Morley, R. J. I. G. Farbenindustrie A.-G. Works at Leuna. III. Methanol and Higher Alcohol Synthesis. CIOS Rept. XXXII–107, 1945, pp. 15–17 PB 6,650. Bureau of Mines Inf. Circ. 7,370, 1946, pp. 15–17.

About 12,000 tons per mo. of MeOH was produced and used for motor fuel, CH_2O manufacture and for solvents. The plant for making isobutanol (higher alcohols) was very similar to that used for MeOH synthesis as also was the synthesis gas. The catalyst was the same a for MeOH (Zn+Cr) with 2% K_2O added; maximum catalyst temperature was 450°. Plant output was 12,000 tons per mo. of which 12% was isobutanol. The composition of the crude was: MeOH 50–55%; H_2O 22–25%; dimethylether 1–3%; n–propanol 1–2%; isobutanol 11–12%; alcohols, ketones, hydrocarbons, etc., C_5 2%, C_6 and C_7 2.5%, C_8 and C_9 1–2%, C_{10}–C_{14} 1%; yellow oil containing 70% olefins 1–2%; fractions 110°–160° and 160°–250° each 3–4%. The MeOH was separated and repassed through the converter to produce more higher alcohols. Working-up of the crude can be followed by reference to a flow sheet. The dimethylether (purified to 98%) was used for making dimethylsulfate and dimethylaniline. The purified propanol was used for cosmetics and solvents; other material was converted to propionic acid or reacted with CH_2O to yield trimethylolethane which, when reacted with the oxidized acids from the 160°–200° fraction, yielded a substitute for castor oil. Some propanol was used in the production of glycerin. Isobutanol was converted to isobutylene and thence to isooctane or to Oppanol (polyisobutylene); some was used as acetates as lacquer solvents and some for making Koresin a CH_2O resin; other amounts were converted to isobutylamine. Some of the fractions 110°–130° and 130°–160° were used as acetates as solvents (Intrasolvane); the fraction 110°–160° was used to make Palatinol HS, esters of phthalic acid, used as plasticizers. The fraction 200°–250° was used in the manufacture of esters, lubricants and driers. Higher fractions could not be used.

1477. Howes, D. A., Allen, J. G., and Schindler, H. I. G. Farbenindustrie A.–G. Works at Leuna. XIIA. Synthetic Lubricating-Oil Manufacture at Stettin–Pölitz. CIOS Rept XXXII–107, 1945, pp. 81–83 PB 6,650. TOM Reel 197. Bureau of Mines Inf. Circ. 7370, 1946, pp. 81–83.

Under closely controlled conditions, a mixture of Fischer-Tropsch wax (maximum melting point 176° F.), and a special wax from brown coal tar distillation (made by a combination cracking-hydrogenation process) is cracked under closely controlled conditions to give 95–97% olefins. These are polymerized at atmospheric pressure in the presence of $AlCl_3$ catalyst. Ultimate yields are % by weight: Gas 27–30, lubricating oil 49–52, diesel oil 6–7, steam cylinder oil 8–11. 2 grades of lubricating oil have been made: Engler viscosity at 100° 3.0 and 5.5–5.6. Production capacity of the plant was 1,000–1,200 ton per mo.; actual production was about one-half this amount.

1478. Haensel, V. and Jones, J. P. I. G. Farbenindustrie A.–G. Works at Leuna. XIV. Oxo Process. CIOS Rept. XXXII–107, 1945, pp. 87–92. PB 6,650; Bureau of Mines Inf. Circ. 7370, 1946, pp. 87–92.

Oxo process consists of the reaction of olefins with water gas in the presence of Fischer–Tropsch catalyst to give aldehydes, which are hydrogenated to alcohols in a subsequent step. The raw materials processed at Leuna were Kogasin and yellow oil, an olefinic by-product of the higher alcohols process. The chemistry of the process is outlined and flow sheet is attached. The catalyst has the approximate composition, Co 30%, ThO_2 2%, MgO 2%, kieselguhr 66%. Process conditions and operating details are given. An essential of any scheme for operating the Oxo process is that the synthesis gas rate in both the Oxo and hydrogenation stage must be sufficiently high to ensure efficient stirring and complete suspension of the catalyst. A large excess of synthesis gas is not necessary. Intead of 220–240 atm. pressure, the Oxo stage might be operated at 40–50 atm., but with a lower throughput and at a higher temperature than 150°. 1 of the difficulties sometimes encountered was that unless the conditions in the Oxo stage are carefully controlled, olefin polymerization takes place, and these polymers, after hydrogenation, are difficult to separate from the higher boiling alcohol products. In addition to Kogasin and yellow oil, Leuna had investigated the treatment of cracked petroleum oil. The crude product con-

tained 16–17% of alcohols which may be separated from the hydrocarbons by forming boric esters. Only about 60% of the olefins were converted, of which approximately 80% were recovered as alcohol. *See also* abs. **1174.**

1479. HAENSEL, V., JONES, J. P., AND HORNE, W. A. I. G. Farbenindustrie A.-G. Works at Leuna. XV. Synol Process. CIOS Rept. XXXII–107, 1945, pp. 93–97. PB 6,650; Bureau of Mines Inf. Circ. 7370, 1946, pp. 93–97.

Synol process consists essentially of the reaction of a CO–H_2 mixture (1 CO : 0.7–0.8 H_2) at 18–25 atm. and 190°–200° over a sintered-Fe catalyst such as is used for NH_3 synthesis. The liquid product consists principally of alcohols and hydrocarbons, the former consisting essentially of straight-chain primary alcohols. Operation was still in the pilot-plant stage; 2 plants existing, 1 a 4-stage unit with tubular reactors with capacity of 3–5 tons per month, and a recycle plant with a single plate-type reactor with a capacity of 10–15 tons per month. A 2-stage process with gas recycle was under consideration. Both processes are illustrated by flowsheets. Optimum yield of liquid products is estimated at 155–165 gm. per $m.^3$ of $CO+H_2$ and appears to consist of 35–50% alcohols, 25–40% olefins and 20–35% paraffins, the alcoholic content being greatest in the temperature range 150°–200°. Neither type of reactor was satisfactory, the catalyst caked badly in both and was very difficult to remove. A new design is proposed and illustrated in a diagram. The sintered Fe catalyst, for which preparation is described, has the analysis: Fe_3O_4 97%, Al_2O_3 2.5%, K_2O 0.2–0.6%, S 0.6%, C 0.03%, apparent density 2.0. Reduction takes place with pure H_2, atmospheric pressure and 450°. The essential features of the reduction are: Maintenance of a high H_2 rate corresponding to a minimum linear velocity of 20 cm. per sec. and a minimum space velocity of 2,000 l. per hr. per l. of catalyst, and efficient drying of H_2. The time required is about 50 hr. The method proposed and shown by the flowsheet for the separation of alcohols from the crude synol depends on the formation of boric acid esters.

1480. UNDERWOOD, A. J. V. I. G. Farbenindustrie A.-G. Works at Leuna. XVI. Mersol Process. CIOS Rept. XXXII–107, 1945, pp. 101–103, PB 6,650; Bureau of Mines Inf. Circ. 770, 1946, pp. 98–99.

Mersol reaction consists in treating paraffin hydrocarbons with SO_2 and Cl to produce sulfonyl chlorides which are saponified to give sodium sulfonates. The product capacity of the Leuna plant was 50,000 tons per yr. The raw material was a Kogasin fraction b. 220°–320°. Preliminary hydrogenation at 200–230 atm. with a Ni–W–S catalyst is necessary to convert olefins to saturated compounds to prevent absorption of Cl. The Mersol reaction is carried out in 12–16 hr. at ordinary temperature and pressure using ultraviolet light to catalyze the reaction. The product, Mersol D, contains about 82% sulfonyl chlorides and 18% unreacted hydrocarbons. The reaction is not carried to completion in order to avoid the formation of higher sulfonyl chlorides which give inferior products on saponification. The soaps made therefrom, called Mersolates, are used mainly for soap powders. They are not as good as natural soaps for removing dirt, but are better grease removers and thus have the advantage for wool washing. By carrying the reaction with SO_2 and Cl only to the extent of 30–33%, a product called Mersol 30 is obtained and is made into flakes. Mersol D can only be made from Kogasin but Mersol 30 can be made from other materials. Kogasin has the advantage that it is more transparent to ultra violet light. The paraffinic Fischer–Tropsch material is preferred as it requires a smaller hydrogenation plant and the consumption of Cl is less. This applies even more strongly to natural petroleum fractions. With Kogasin at 30 pf. per kgm. and petroleum oil at 18 pf., there is not much difference in the final cost of the product.

1481. HOLROYD, R. I. G. Farbenindustrie A.-G. Works at Leuna. XXVI. German Oil Production Data—Fischer-Tropsch Plants. CIOS Rept. XXXII–107, 1945, pp. 132–133; TOM Reel 197; Bureau of Mines Inf. Circ. 7370, 1946, pp. 132–133; PB 6,650.

Plants:	*Total gasoline capacity tons per year*
1. Ruhrchemie A.-G	72, 000
2. Victor Rauxel	40, 000
3. Rheinpreussen	70, 000
4. Krupp Benzin	60, 000
5. Essener Benzin	80, 000
6. Hoesch Benzin	47, 000
7. Schwarzheide	170, 000
8. Schafgotsch	40, 000
9. Lutzkendorf	(70, 000) [1] 12, 000
Total	591, 000

[1] Under construction.

HOLT, A. *See* abs. **471.**

1482. HONDA, K. Double Diagram of the Iron-Carbon System. Trans. Am. Soc. Steel Treating, vol. 16, 1929, pp. 183–189; Chem. Abs., vol. 23, 1929, p. 4430.

This is an argument, based principally on X-ray data, in favor of the single diagram for the Fe–C system.

1483. HONDA, K., AND MURAKAMI, T. Thermomagnetic Properties of the Carbides Found in Steels. Sci. Repts. Tôhoku Imp. Univ., vol. 6, 1917, pp. 23–29; Chem. Abs., vol. 11, 1917, p. 2887.

To obtain the carbides, rods of C and W steels were annealed at 880°–920° and cooled very slowly. The rods were then polished and turned down until they were 7 mm. thick and 10 cm. long. The rods were used as anodes in dilute HCl, and by electrolysis the carbides were obtained. The Fe cementite was obtained as a gray powder and the double carbide as a black powder. The former contained 6.08% C and 93.5% Fe; the latter 8.10% C, 31.71% Fe, and 53.70% W. The Fe cementite is ferromagnetic and in a field of 500 gauss its specific magnetization is 19.7. The critical temperature, above which the carbide is paramagnetic, is 215°. In its free state the cementite is decomposed almost completely into its components by heating long enough at 900°. The double carbide found in low W-steels also is ferromagnetic, and its specific magnetization in a field of 500 gauss is 15.5. Its critical temperature lies at 400°. It is decomposed into its components by heating it to 850°. The conclusion, however, may not apply to the double carbide as it exists in low-W steel because its boundary condition is quite different in the steel than when existing by itself in the free state.

1484. HONDA, K., AND NISHIYAMA, Z. Nature of the Tetragonal and Cubic Martensites. Trans. Am. Soc. Steel Treating, vol. 20, 1932, pp. 464–470; Sci. Repts. Tôhoku Imp. Univ., vol. 21, 1932, pp. 299–331; Chem. Abs., vol. 27, 1933, p. 253.

X-ray analyses show martensite to be a solid solution of C in Fe, divided into 2 distinct kinds, α in quenched steels and β in quenched and tempered steels. β-Martensite is a solid solution, the C atoms being present within the space lattice of Fe. It is very probable that in α-martensite each of the C atoms occupies 1 of the face centers of the tetragonal lattice, and in β-martensite a position ($\frac{1}{2}$, $\frac{1}{4}$, 0) of the cubic lattice. The mechanism for the transition is austenite→α-martensite→β-martensite.

1485. HONDA, K., AND TAKAGI, H. Magnetic Transformation of Cementite. Sci, Repts. Tôhoku Imp. Univ.,

vol. 4, 1915, pp. 161–168; Engineering, vol. 100, 1915, pp. 665–667; Chem. Abs., vol. 10, 1916, p. 740.

By cooling, the magnetic transformation of cementite begins at 215°, and by heating it ends at the same temperature. This is the critical temperature of the cementite. In former experiments steels with a C content 0.14–1.5% showed almost the same critical temperature as the latter steels. Since the ferromagnetic compounds of Fe have critical temperatures peculiar to them it may be concluded that the carbides may have different critical temperatures. But, since the various steels, with 0.14–4.2% C, show a single transformation between room temperature and 700°, it is probable that the only carbide existing at ordinary temperature is cementite.

HONGO, M. *See* abs. **1911, 1912, 1913, 1914.**

1486. HOOG, H. Netherland Report on Additional Information on Various Catalytic Processes in Western Germany. I. BIOS Miscell. Rept. 112, 1947, 50 pp.; PB 96,550.

Report is made of a trip through the British zone in February 1947, for the purpose of collecting information supplementing previous CIOS and BIOS reports. Some of the subjects reported are: (1) Development of the Fischer-Tropsch catalyst (Co–Th–Mg–kieselguhr) by Ruhrchemie A.-G.; preparation of the Fe catalyst with determination of the degree of reduction by the method $Fe+2\ FeCl_3 \rightarrow 3\ FeCl_2$ with titration by $KMnO_4$. Details are given by Dr. Rottig in an appendix. (2) status of the Oxo process at Sterkrade-Holten with some description of the reactors and filters and discussions of the catalysts and reaction conditions by Dr. Roelen. (3) catalytic oxidation of hydrocarbons in the liquid phase at I. G. Farbenindustrie Werke, Uerdingen. (4) catalytic hydrogenation of various products such as aldol, C_2H_2 to C_2H_4 at Hüls, and methanization of town gas at Ruhrchemie A.-G., Sterkrade-Holten by Dr. Roelen. (5) manufacture of Fischer-Tropsch cobalt catalyst at Sterkrade-Holten. (6) compression and storage of water gas, manufacture of CO at I. G. Farbenindustrie A.-G., Leverkusen. Appendix: A new method for the determination of the metallic iron in reduced iron catalysts by Dr. Rottig of Ruhrchemie A.-G., Oberhausen-Holten. Several diagrams of apparatus are shown.

1487. ———. [Fuel Synthesis and Other Catalytic Processes in West Germany.] Chem. Weeblad, vol. 45, 1949, pp. 201–203.

Digest of a paper presented to the Netherlands Chemical Society July 1948 is given. A survey is made of processes for production of motor fuel with brief descriptions. The Oxo process is emphasized.

1487a. ———. Slurry Process Versus Fixed-Catalyst-Bed Operation. Proc. 3d World Petrol, Con., The Hague, May–June 1951.

Catalyst slurry process was chosen for pilot plant development. Improvements instituted included the use of low-quartz catalyst to reduce mechanical wear; the use of short contact time and operating temperatures on the low side of the maximum range with recycling of unconverted olefins; preheating of the olefin feed and water gas to effect rapid initiation of the reaction; the use of a high-pressure cooler and cold-separator system to reduce Co hydrocarbonyl content of recycle gas and oil contamination in recycle pumps; and a specially designed decobalting system to prevent excessive Co deposition in the preheating section for the decobalter feed and in the decobalter proper. A special feature, added to the Leuna process for producing C_7–C_9 alcohols, was a catalytic after-hydrogenation for removing color-producing unsaturated aldehydes in refining the final alcohols.

1488. HOOVER, C. R., DORCAS, M. J., LANGLEY, W. D., AND MICKELSON, H. G. Catalytic Preparation of Unsaturated Hydrocarbons From Carbon Monoxide and Hydrogen. Jour. Am. Chem. Soc., vol. 49, 1927, pp. 796–805; Chem. Abs., vol. 21, 1927, p. 1444.

Mixture of approximate equal parts of CO and H_2 with a trace of O_2, when passed at a space velocity of 1,500–2,000 over a Ni-Pd catalyst supported on Al or pumice stone, produced 1–3% of C_2H_4 at temperatures in the neighborhood of 100°; the catalyst lost 0.5% of its efficiency in 30 hr. Other catalysts in order of decreasing activity were Ni–Cu–Pd, Fe–Ni–Pd, Ni–Pt, Cu–Co–Fe, Cu–Pd, Cu–Co–Ni, C–Pd, Ni–Cu, Cu–Co. While saturated hydrocarbons were not specially sought, Ni and Ni–Pd catalysts yielded from 20–25% CH_4 at temperatures in the neighborhood of 250°. The catalysts showed little decrease in activity after several days' use.

HOPTON, G. U. *See* abs. **1467a, 1468.**

1489. HORIBA, S., AND RI, T. Decomposition of Carbon Monoxide in the Presence of Reduced Nickel. Bull. Chem. Soc. Japan, vol. 3, 1928, pp. 18–25; Chem. Abs., vol. 22, 1928, p. 1520.

Improved apparatus for the investigation of contact catalysis has been described. The decomposition of CO in the presence of reduced Ni in the vicinity of 230° is a unimolecular reaction.

1490. HORN, —. Composition of the Reaction Products From the Fischer-Tropsch Benzine Synthesis. FIAT Reel A–26, frames, 2999–3008, Oct. 15, 1940; PB 70,249.

Compilation of data collected from the literature showing the analyses of the various fractions from C_3–C_4 to the heavy paraffins and the saturated acids.

1491. HORN, O. [Development and Present Status of the Benzine Synthesis.] Forschungen u. Fortschr., vol. 7, 1931, p. 185; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 693–694.

Brief review from 1925 to date.

———. *See* abs. **1827, 2249.**

1492. HORNE, W. A. Interrogation of Prof. Franz Fischer at Munich, Germany. FIAT Final Report 90, 1945, 3 pp.; PB 1,253; TOM Reel 199.

Isosynthesis process produces iso-octanes by the polymerization or alkylation of isobutylene obtained by the dehydrogenation of isobutane and isopentane produced by synthesis from CO and H_2 at 300–600 atm. and 400°–500° in the presence of a Th catalyst activated with 10–20% of Al_2O_3. The product contains higher-boiling constitutents consisting of naphthenes, aromatics, ethers, and alcohols. The proportions of these and of the isoparaffins can be varied by changing the operating conditions and the catalyst; the addition of ZnO favors the formation of naphthenes and aromatics, of Al_2O_3, the isoparaffins. In preparing a Th–ZnO catalyst, its activity with respect to the formation of liquid hydrocarbons can be virtually doubled by pouring the nitrate solution into the soda solution, the reverse of normal precipitation. Attempts have been made to replace the Th in the catalyst with other elements but unsuccessfully; a part only (25%) can be substituted by either Al_2O_3, ZnO, or a mixture of both. Mention is made of Fe synthesis, Ni catalysts, suspended catalysts, and isomerization of Fischer-Tropsch products with $AlCl_3$ promoted by HCl, but no details are given.

1493. ———. Review of German Synthetic Lubricants. Ind. Eng. Chem., vol. 42, 1950, pp. 2428–2436.

Brief review is presented of the processes used in Germany during World War II to manufacture syn-

thetic lubricating oils. These lubricants were of 2 general classes, hydrocarbons and nonhydrocarbons. The former consisted of ethylene polymers, polymers prepared from mixtures of higher boiling olefins produced by the vapor-phase cracking of Fischer-Tropsch wax or gas oil, and the condensation product of chlorinated paraffins and naphthalene. I. G.-Pölitz, Rhenania-Ossag (Harburg) and Ruhrchemie A.-G. (Holten) had developed methods for the polymerization of higher olefins from the Fischer-Tropsch process. These are briefly described with the aid of flow diagrams. The composition and applications of the lubricating oils produced are presented.

———. *See* abs. **872, 873, 874, 875, 876, 877, 878, 1468, 1479.**

1494. HORNE, W. A., AND FARAGHER, W. F. Interrogation of Dr. Pier and Staff. I. G. Farbenindustrie A.-G. Ludwigshafen and Oppau. II. Synthesis of Hydrocarbons From Water Gas—Michael Process. FIAT Rept. 426, 1945, pp. 1–8, PB 1367 and 7745; TOM Reel 199; Bureau of Mines Inf. Circ. 7376, 1946, 27 pp.; Coke Smokeless–Fuel Age, 1946, pp. 194–195.

Four processes developed to the pilot plant scale by the I. G. Farbenindustrie A.-G. at Ludwigshafen under the direction of Dr. Michael are described. *The fixed-bed circulating-gas process* uses a fixed catalyst made by pasting powdered Fe carbonyl with a concentrated borax solution equivalent to about 1% on the Fe and sintering 1 c. of the paste at 800°–850° for 4 hr. and cooling in an H_2 atmosphere. The synthesis gas is recirculated over this in the ratio of 100 vol. of old gas to 1 vol. of new, having a $CO:H_2$ ratio of 1:1 or 4:5, a S content of less than 2 mg. per m.^{3} and no CO_2, so that the rise in temperature in the catalyst bed is not over 10°. The gas velocity is about 1 m. per sec. and the time of contact 0.5–1 sec. The flow must be nonturbulent. Operating pressure is 20 atm. and the temperature 300°–325°. The yield of hydrocarbons per m.^{3} of catalyst is 700–800 kgm. per day recovered in 3 stages of condensation. 1 m.^{3} of 4 CO : 5 H_2 gas yields about 35 gm. of CH_4 and C_2H_6 and 160 gm. of useful products; the gasoline having an octane number of 68–70 and the gas oil a cetene number of 45–50. *In the oil-circulation process* an oil fraction from the synthesis product is circulated over the catalyst to remove the heat of reaction and prevent excessive production of C and CH_4. The process operates at 20–25 atm. pressure and temperatures of 260°–300° in the first stage and 280°–330° in the second. It uses the same catalyst as the first process. The gas has a CO : H_2 ratio of 55 : 45 and the yield per liter of catalyst per hr. is 20–25 gm. of all products and per m.^{3} of synthesis gas 150 gm., the gasoline having an octane number of 62–65 and gas oil a cetene number of 70. *Foam process* has for its object the production of a higher proportion of olefins in the product. It operates in the liquid phase using a finely divided catalyst suspended by an ascending stream of gas. The catalyst is made by precipitation of Fe_2O_3 and is pasted into granules with a solution of K_2CO_3, dried, reduced by H_2 at 350°–450° and ground fine in a ball mill mixed with gas oil. A gas of composition CO : H_2=1 : 1 or 4:5 is used at 20 atm. pressure and 250°. The time of reaction is 3 minutes. The temperature rise through the reaction chamber is about 10°. Conversion to useful products is about 70% and the CO_2 content of the exit gas is 40–45%. The yield per day per m.^{3} of reaction products is 350–450 kg. The gasoline has a 70% olefin content and the gas oil 40–50%. *In tubular reactor process*, the operating pressure is 20 atm. and the temperature 230°–250°. The synthesis gas has a $CO:H_2$ ratio 4:5 to 5:5. The catalyst is made by mixing Fe_2O_3 with 5–25% of alkali earth and 1–2% of K_2CO_3, pelleting, heating to 850°, cooling to 350°–450° and reducing in H_2. It has a high activity at 240° and below. Conversion is 70–80%, giving 0.35–0.45 kg. per liter per day of products all of high olefin content.

1495. ———. Interrogation of Dr. Pier and Staff. I. G. Farbenindustrie A.-G. Ludwigshafen and Oppau. IV. Oxidation Process. Fatty Acid Production. FIAT Final Rept. 426, 1945, pp. 9–11; Bureau of Mines Inf. Circ. 7,376; PB 1,367 and 7,745; TOM Reel 199.

Paraffin waxes produced by the hydrogenation of brown coal, from crude petroleum oils and from the Fischer–Tropsch synthesis, have been oxidized successfully to fatty acids. The molten wax is blown with air in pure Al towers in presence of Mn compounds, such as $KMnO_4$ or Mn soaps; addition of 0.08–0.15% of Na or K carbonate improves the quality of the products. A temperature of 130°–160° is maintained until oxidation begins and is then lowered to 100°–120°. The lower the oxidation temperature, the smaller is the formation of peroxides, but the longer the reaction time. The airflow is continued for 10–30 hr. until approximately 30% of the paraffin is converted. The product has an acid number of 75 and a saponification number of 130–150. The oxidation product is saponified with aqueous NaOH (20–25% at 80°), heated in an autoclave to 130°–150° under pressure, the soap solution and the unsaponifiable product separating in layers, the former at the bottom. The upper layer is recycled to the oxidation tower, the lower heated in a pipe still to 280°–350° at 80–100 atm., the pressure being released flashing the water vapor and the remaining unsaponifiable material. The molten soap from the flash tower is dissolved in water and hydrolyzed with H_2SO_4. The fatty acid is washed and distilled under a vacuum of 3 mm. Based on 100 parts of paraffin the following 3 fractions are obtained: Acids C_3–C_{10} boiling up to 150°, 7–15%; soap acids C_3–C_{10} boiling 150°–240°, 45–55%; higher acids C_{16}–C_{25} boiling 240°–300°, 2–5%; residue 5–20%. The plant at Oppau had a capacity of 20,000 ton of paraffin wax per yr.

1496. HORNE, W. A., AND JONES, J. P. Fischer–Tropsch Unit at Leipzig Gas Works. CIOS Rept. XXVII–68, Item 30, 1945, 10 pp. PB 294; TOM Rept. 11, TAC Rept. SnMc–5, TOM Reel 198; Gas Age, vol. 97, No. 3, 1946, pp. 28, 68; Chem. Abs., vol. 41, 1947, p. 1828.

Installation was for the purpose of enriching city gas. The synthesis gas, a 2 : 1 mixture of water gas and coke-oven gas (CO : H_2=1 : 2), after purification, was to be passed at 1,200 mm. Hg in parallel flow into 4 units of 3 standard plate reactors operating at 185°–200° and atmospheric pressure, each reactor containing 10 m.^{3} of Co catalyst of 350 kg. per m.^{3} density. Pressure drop through the catalyst bed was expected to be 500 mm. Hg. Boiler condensate from the gas works was to be used as the heat-exchange medium. The residual gas from the reactors containing about 21.3% CO, 37.5% H_2, 23.6% CH_4, 8.1% CO_2, and 8.5% N_2 was to be returned to the gas works for admixture with water and coke-oven gas and used for city gas. The expected yield of liquid hydrocarbons was about 100 gm. per m.^{3} of gas consisting of about ⅓ each of benzine, medium oil, and wax.

1497. HOSELITZ, K. Iron-Nickel Phase Diagram by Magnetic Analysis and the Effects of Cold Work. Jour. Iron Steel Inst. (London), vol. 149, I, 1944, pp. 193P–211P; Chem. Abs., vol. 38, 1944, p. 1198.

Small prismatic samples of Fe–Ni alloys in the range 3–50 at. % Ni were heated to 1,000° for 4 hr., quenched

in cold water, and cooled to —180° for 48 hr. to insure a single-phase state. The magnetic saturation intensities were determined over a wide range of temperatures. It was found that annealing of cold-worked alloys gave inconclusive results. Cold work on quenched alloys produced definite changes in the alloys, notably in the range 29–35% Ni; this indicates a distinct separation into 2 phases. In alloys with less Ni the changes are small, since these samples are not far from their equilibrium state. The boundaries of the heterogeneous ($\alpha+\gamma$) region extended from 5% Ni to 34% Ni at 365°. Below this temperature the rates at which equilibria states are approached become extremely slow. It was estimated that the time for complete change is about 10 yr. at 325° and of the order of 40 yr. at 300°.

HOSELITZ, K., AND SUCKSMITH, W. Magnetic Study of the 2-Phase Iron-Nickel Alloy. II. *See* abs. **2695.**

HOSHINO, S. *See* abs. **1906a.**

HOT, M. *See* abs. **248, 249.**

1498. HOUDREMONT, E., KLINGER, P., AND BLASCHCZYK, G. [New Electrolytic Isolation Procedure for Determining Iron Carbide.] Tech. Mitt. Krupp, Forschungsber., vol. 4, 1941, pp. 311–328; Arch. Eisenhüttenw., vol. 15, 1941, pp. 257–270; Chem. Zentralb., 1942, I, p. 2167; Chem. Abs., vol. 37, 1943, p. 3017.

In the electrolytic apparatus the anode compartment is separated from the cathode compartment by a diaphragm, which consists of a clay plate impregnated with agar agar. The sample of steel is made the anode in a neutral anolyte of such chemical composition that no precipitation of ferrous salt results from hydrolysis. The used anolyte contains ferrous salt from the anode and is therefore heavier than the original solution, so that it falls to the bottom of the anode chamber from whence it can be withdrawn and fresh anolyte introduced through a filtering arrangement. The anolyte consists of a 15% Na citrate solution containing about 1.2% KBr and 0.1% KI. The solution is diluted with boiled water and freed from O_2 before it is driven by N_2 or H_2 gas pressure into the anode compartment. The cathode is formed from Cu gauze dipping in 10% $CuBr_2$ solution. An ampere-hour counter, an ammeter, and a voltmeter are introduced into the electrical circuit as parts of the apparatus. To control the anode potential, which is important for the isolation of carbides, a measuring cell is introduced, which consists of a calomel cell with siphon and a Pehavi measuring instrument. For the isolation of the carbide, the apparatus is provided with a contrivance whereby the carbide can be removed while under a neutral gas atmosphere. In the experiments made with this apparatus, Fe_3C was the only carbide that could be isolated from either hypoeutectoidal or hypereutectoidal steel, produced under all conditions of heat-treatment. The literature often contains contrary statements, which doubtless are caused by decomposition of the very reactive lamella of carbide.

1498a. HOUGEN, O. A., AND WATSON, K. M. Solid Catalysts and Reaction Rates—General Principles. Ind. Eng. Chem., vol. 35, 1943, pp. 529–541; Chem. Abs., vol. 37, 1943, p. 4,294.

Effect of solid catalysts on the reaction rates of liquid- or gas-phase chemical reactions is discussed on the basis of the following steps: (1) The mass transfer of reactants and products to and from the gross exterior surface of the catalyst particle and the main body of the fluid, (2) the diffusional and flow transfer of reactants and products in and out of the pore structure of the catalyst particle when reaction takes place at interior interfaces, (3) the activated adsorption of reactants and activated desorption of products at the catalytic interface, (4) the surface reaction of adsorbed reactants to form activation adsorbed products. Equations are derived for the effects of adsorption, catalyst activity, particle size, porosity, flow conditions, poisons, and diluents as well as pressure temperature and concentration. It is suggested that the constants of the rate equation be determined by experiment with a differential reactor containing a thin bed of catalyst at a uniform temperature. Methods of integrating the rate equation are given to determine the volume of reactor to produce a specified catalytic conversion.

1499. HOWARD, F. A. Conversion of Coal to Oil and Gas. Oil Gas Jour., vol. 46, No. 42, 1948, p. 70; Min. and Met., vol. 29, July 1948, pp. 388–395.

Paper presented at the 166th meeting of the American Institute of Mining and Metallurgical Engineers at New York is abstracted. The development of coal liquefaction and the synthesis of liquid fuel from natural gas are traced, and some evaluation is given of the processes in comparison with the petroleum process. Whether water gas or natural gas is converted into liquid products, the process is the same and requires the same equipment and experience, the essential difference at the present time being that a more efficient method of coal gasification must be developed. In comparing the hydrocarbon synthesis process with the high-pressure hydrogenation process, the former looks the more attractive from both commercial and military standpoints in that the capital cost and steel requirement have been estimated to be as much as 50% lower. From a construction standpoint, the building of a synthetic-fuel industry does not seem to be the best solution of either the immediate shortage or the immediate military problem. It will be a slow and costly development as compared with the expansion of facilities for producing, refining, and transporting more crude oil and natural gas, and it will represent a worse drain on our economy.

1500. ———. Synthetic Fuels. Combustion, vol. 20, No. 5, 1948, pp. 47–50; Oil Gas Jour., vol. 47, No. 29, 1948, p. 61; Mech. Eng., vol. 71, No. 1, 1949, pp. 26–27.

In an address before the National Coal Association, the development of destructive hydrogenation and the hydrocarbon synthesis processes for producing oil from coal is traced, and the present economic status is discussed. Methods are suggested for building up a national synthetic-fuel industry in this country. A definite program should be laid out whereby industry and Government would cooperate in creating the necessary foundation. There are 3 lines of endeavor: (1) Further technical development and pilot-testing of modernized coal gasification. This should be left to private industry without Government subsidy. (2) The preparation of complete and reliable project plans for large synthesis units at fixed locations preferably capable of great expansion. The actual engineering cost would be met by Government funds under contract with the industrial units involved. (3) The collection of field engineering and geological data on location, quality, and mining conditions of coal and shale reserves suitable for conversion to permit the drafting of a master plan for a national synthetic-fuel industry. This could be contracted for and supervised by the Army engineers.

1501. HOWAT, D. D. Synthesis of Oils From Industrial Gases—Fischer-Tropsch and Allied Processes. Chem. Age, vol. 44, 1941, pp. 57–60; Chem. Abs., vol. 35, 1941, p. 2302.

Review with 16 refs.

1502. ———. Large-Scale Production of Oxygen. Chem. Age, vol. 56, 1947, pp. 767–771, 801–805, 812, 835–837; vol. 57, 1948, pp. 81–85.

General review of the development of methods for the production of O_2, touching upon the work of Ruhe-

mann, Frankl, Linde, Kapitza, and Claude. Economic aspects are set forth.

HOWE, K. E. *See* abs. **739.**

1503. HOWES, D. A. Synthesis of Methanol and Higher Alcohols From Water Gas. Sci. Petrol., vol. 4, 1938, pp. 2812–2821.

This paper reviews the historical development of the process, discusses the equilibrium data, classifies and describes the catalysts for synthesizing MeOH and the higher alcohol from water gas, and explains the mechanism of formation.

1504. ———. Interrogation of A. Bollhorn, E. Grages and Dr. Gross of Deutsche Erdoel A.-G., Berlin. Production of Vaseline From Fischer-Tropsch Wax. BIOS Final Rept. 326, 1945, p. 17, PB 27,705, TOM Reel 227.

At the Research Station, Berlin, an inferior grade of vaseline has been made experimentally by dissolving Fischer-Tropsch wax in liquid paraffin. The wax is dissolved in ethylene dichloride and the fraction of the required melting point obtained by fractional crystallization. It is then refined by treatment with H_2SO_4 at 160°–180° until water-white.

———. *See* abs. **873, 874, 875, 876, 877, 878.**

1505. HOWES, D. A., AND RAMPTON, H. C. Properties of Hydrocarbon Gas Turbine Fuels. Internat. Cong. Pure Appl. Chem., July 1947, 11th Cong., London; Jour. Inst. Petrol., vol 35, 1949, pp. 419–435; Chem. Abs., vol. 43, 1949, p. 7662.

Summary is presented on the properties of hydrocarbons boiling within the range 65°–300°, with particular reference to their use as constituents of fuels for gas turbines. These various properties, determined by chemical composition and configuration, are closely interrelated and they lie mostly between the extremes set by the paraffins and the aromatics, respectively. This means that any gas-turbine fuel comprised entirely of hydrocarbons will have properties within this range. Information is given on the hydrocarbon compositions of petroleum, Fischer-Tropsch, hydrogenation, and shale-oil fractions, and attention is drawn to the present lack of knowledge concerning hydrocarbon compositions in fractions boiling above the motor gasoline range. This is due to the considerable difficulties encountered in analysis. Methods of analysis are reviewed and the possibilities of synthetic methods for producing gas-turbine fuels of different hydrocarbon compositions are summarized. No synthetic process exists at the present time for producing fuels in the 65°–300° boiling range, which would appear to be ideally suited to the aero-gas turbine. Such processes as alkylation, polymerization, catalytic cracking, etc., are not suitable methods for producing turbine fuels, since the products contain appreciable amounts of aromatics or olefins that have not yet been found acceptable in turbine fuels. The same objection applies to the products of Fischer-Tropsch type processes. 1 of the 1st problems to be solved is how to use fuels containing olefin hydrocarbons satisfactorily in aero-gas turbines.

HOWES, D. A., ALLEN, J. G., AND SCHINDLER, H. I. G. Farbenindustrie A.-G. Works at Leuna. XII A. Synthetic Lubricating-Oil Manufacture at Stettin-Pölitz. *See* abs. **1477.**

1506. HOWEY, J. H. Magnetic Behavior of Nickel and Iron Films Condensed in a Vacuum Upon Various Metal Backings. Physiol. Rev., vol. 34, 1929, pp. 1440–1447; Chem. Abs., vol. 24, 1930, p. 4674.

1507. HOYT, L. F. German Chemical Developments in Synthetic Detergents and Wetting Agents. PB Rept. 3,868, 1945, 151 pp.

Detailed report on development and uses of synthetic detergents, Igepons, based on natural fats or oils or on synthetic fatty acids, were produced to the limit of available materials. Igepals, based on ethylene oxide, provided a variety of detergents and emulsifiers for technical purposes. Higher alcohols of suitable chain length and quality were produced by the reduction of the corresponding synthetic fatty acids derived from the oxidation of paraffin. Outstanding large-scale development of synthetic detergents was based on the production of Mersols from byproducts of the Fischer-Tropsch synthesis of hydrocarbons from coal. Appendix IV has a chart showing compounds derived from some byproducts of Fischer-Tropsch process.

1507a. HRADEK, V. [Conversion of Light Hydrocarbons Into Carbon Monoxide and Hydrogen.]Paliva, vol. 31, 1951, pp. 266–277; British Abs., 1952, B, I. p. 639.

Thermodynamics of all possible 20 reactions during the conversion of CH_4 with O_2, steam and CO_2 are discussed. It is found that: (1) Below the minimum temperature of 920° K. a conversion of CH_4 by O_2 is not possible without liberation of C; (2) the liberated C is mainly due to the reaction $CH_4+O_2 \rightarrow C+H_2O$; (3) the conversion of CH_4 by steam needs a higher temperature (1,000°); (4) the same applies for the conversion by CO (about 900°); (5) the rising of temperature favors all cases of CH_4 conversion, lowers the amount of steam and reduces the possibility of free C formation to compare quantitatively these facts the equilibrium constants are calculated from the free energies and the limiting conditions at which C is not liberated are determined.

1508. HSIUNG, S. Y., AND KUNG, K. M. A Study on the Synthesis of Liquid Fuels From Carbon Monoxide and Hydrogen. Jour. Chinese Chem. Soc., vol. 8, 1941, pp. 112–122; Chem. Abs., vol. 37, 1943, p. 6107.

Preliminary report on the use of Ni and Co catalyst on kieselguhr in the synthesis of liquid fuels from CO and H_2. A procedure is suggested for eliminating the CH_4 reaction, which involves the passage of CO over the catalyst before the introduction of the CO–H_2 mixture. A mechanism of the CO pretreatment is suggested.

HSU, W. W. *See* abs. **468.**

1509. HUBMANN, O. Production of Synthesis Gas From Wyoming Subbituminous Coal. General Investigation of Methods and Flowsheet for Plant to Process Eight Million Cubic Feet per Day. Bureau of Mines Spec. Rept., Nov. 1946, 23 pp.; TOM Reel 242, Rept. 9.

To obtain general information on the advantages and disadvantages of various methods of producing synthesis gas from a coal like the Wyoming coal, 4 methods are considered suitable for treating this coal, and calculations are made of the investment and production costs for a plant with a capacity of 100,000 N m.^{3} per hr. of synthesis gas. The high content of H_2 of Wyoming coal promises very high tar content and consequently very favorable conditions for utilizing it for producing motor fuels by a combination of carbonization, byproduct gasification with the synthesis of hydrocarbons, and hydrogenation of tar. The 4 methods investigated are: Lurgi pressure gasification; combined carbonization-gasification with O_2 and with burning of the coke and cracking of the carbonization gas; the same with use of air in the 1st step and O_2 in the 2d, with burning of the carbonization gas and gasification of the coke; and the Koppers complete gasification of powdered coal. Cost of equipment is taken from figures available from German sources. Corresponding figures for the United States are calculated with the ratio of 1 RM : $0.50 for the investment cost and 1 RM : $1.00 for the cost of labor, with a rough adjustment for special work.

Investment costs and production figures for 100,000 N m.³/hr. of synthesis gas

	I Gasification of pulverized coal (Koppers)	II Lurgi pressure gasification	III Carbonization with O_1, gasification with O_2	IV Carbonization with air; gasification with O_2
Investment cost:				
Million RM	49.5	54.0	50.2	46.6
Million dollars	24.75	27.0	25.1	23.3
Coal consumption, tons per year	740,000	945,000	995,000	925,000
Laborers	420	600	550	450
Wages:				
Million RM	1.05	1.5	1.37	1.13
Million dollars	1.05	1.5	1.37	1.13
% of production cost	11.0 20	13.5 24.5	12.8 23.4	11.5 21.5
Production cost per year:				
Million RM	9.6	11.14	10.66	9.79
Million dollars	5.18	6.13	5.81	5.27
Tar production, tons per year	----------	44,200	65,800	60,500
Value of tar:				
Million RM	----------	4.86	6.58	6.05
Million dollars	----------	1.33	1.65	1.51
% of production cost	----------	43.5 21.6	62.0 28.3	62.0 28.5
Production cost, 1,000 N m.³				
Million RM	10.9	7.2	4.60	4.24
Million dollars	5.9	5.40	4.70	4.25

Further calculations on 3 so-called pioneer plants A, B, and C: Carbonization gas-producer plant; Koppers pulverized-coal gasification; and Lurgi pressure gasification give production costs per 1,000 N m.³ on the basis of capacities of 8,000,000 cu. ft. of ideal gas per day and 320 operating days, respectively, of $9.30, $11.80, and $11.50. Here again the combined carbonization-gasification method is found to be the most favorable one. It is proposed to erect 2 units of carbonization-gasification type with the necessary equipment for operating each of the units for the production of gas as well as for the carbonization of coal and the production of coke as this seems the safest, the cheapest, and the most flexible method with respect to the requirements of a pilot-experimental plant, which should be able to handle various types of coal from such standpoints as tar recovery and alteration of the CO : H_2 ratio. It also might prove an economical method for the treatment of oil shales with more than 10% of oil.

1510. ———. Production Costs of CO–H_2 Mixtures for Different Methods of Gasification With Oxygen and Various Fuels. Bureau of Mines Spec. Rept., 1947, 35 pp.

Describes various methods of gasification and their operating principles. The technical performance and the possible improvements of these methods with some directives in the selection of the gasification method best suited for a specific purpose are presented. The many factors entering into the investment and production costs are discussed in detail and extensive calculations are made in arriving at an approximate idea of the economic advantages and disadvantages of the various processes. The most important investment and operating figures are compared and the data tabulated. They show that such costs, O_2 and power costs included, are lowest with methods using a fixed fuel bed, and that a fluidized fuel bed or a powdered fuel requires additional costs for a lower efficiency and higher investment costs because of the necessity of pulverizing the coal and handling large volumes of gas with a high dust content. However, gasification of pulverized coal is the only method of utilizing caking coals for the production of synthesis gas. Therefore, it should be developed as the most important base of a large-scale industry in the eastern coal fields. Furthermore, the Winkler process (fluidized fuel bed), though slightly cheaper in operating costs, may lose its interest as soon as the pulverized-coal gasification has been developed further, especially if this latter method could be operated under several atmospheres pressure.

HUFF, W. J. *See* abs. **738.**

HUFFMAN, E. H. *See* abs. **1729.**

1511. HUFFMAN, J. R., AND DODGE, B. F. Decomposition of Methanol Over Catalysts Composed of Oxides of Zinc and Chromium. Ind. Eng. Chem., vol. 21, 1929, pp. 1056–1061; Chem. Abs., vol. 24, 1930, p. 334.

Parallelism between the decomposition and synthesis of MeOH at 350° over a series of ZnO–Cr_2O_3 catalysts is not complete but is surprisingly good. Both results show the maximum rate for a catalyst containing 4 Zn : 1 Cr. At about 60% Cr there is a rapid decrease in the activity for decomposition. From 60–100% Cr, there is very little activity for decomposition into CO and H_2, which is contrary to the results for synthesis. A steady decrease in the activity of the catalysts for the decomposition, but not for the synthesis, was observed in all cases. The decomposition over these catalysts was quite complex, the products being CO, H_2, CO_2, CH_4, unsaturated compounds, HCO_2Me, HCHO, Me_2O, and small quantities of unidentified substances.

1512. HUGEL, G. [Synthetic Gasoline and Its Derivatives.] Ann. combus. liquides, vol. 11, 1936, pp. 719–733; Chem. Abs., vol. 30, 1936, p. 8570.

Describes coal-hydrogenation process employed by the Compagnie de Béthune, the Fischer process and the products obtained from it.

1513. ———. [Hydrogenation in France and Foreign Countries.] Sci. et ind., Tech ind. pétrole, No. 271, 1936–1937, pp. 71–79; Chem. Abs., vol. 31, 1937, p. 5976.

Outline of the hydrogenation processes of International Hydrogenation Patents Co., Ltd., of Vallette, of Audibert and of Fischer.

HUGEL, R. *See* abs. **1980.**

1514. HUGGETT, J., AND CHAUDRON, G. [Temperatures of Magnetic Transformations in the System Iron-Iron Sesquioxide.] Compt. rend., vol. 184, 1927, pp. 199–201; Chems. Abs., vol. 21, 1927, p. 1218.

System Fe_2–O_3–Fe_3O_4 shows two points of transformation, 1 at 590°, corresponding to Fe_3O_4, and the other at 650°, corresponding to a solid solution of Fe_3O_4 in Fe_2O_3. These transformations are rigorously reversible. The system Fe_3O_4–FeO has a transformation point at 570° for the Fe_3O_4. In the system FeO–Fe, the temperature of transformation is the same as that of Fe, or 765°.

1515. HUGILL, J. T. Tonnage Oxygen for Chemical Industry. Canadian Chem. Process Ind., vol. 13, 1947, pp. 1115–1120; British Abs., 1948, B, I, 300.

Review of developments with description and flow

sheet of 100-ton-per-day Air Liquide-Frankl O_2 plant (Air Liquide Oxyton).

HUHN, W. *See* abs. **1571.**

1516. HULL, A. W. Crystal Structure of Iron. Phys. Rev., vol. 9, 1917, pp. 84–87; Chem. Abs., vol. 12, 1918, p. 2064.

In the X-ray analysis of Fe a special procedure is necessary on account of the difficulty of obtaining large crystals. (The large crystals of pure ferrite, reaching a length at times of several inches, which are met with in blast-furnace "bears", are not considered.) Single crystals about 6 mm. square and 2 mm. thick were isolated from a sample of Si steel. The value of $d_{100}=1.43\times10^{-8}$ cm. requires 2 atoms for a cube of side $2d_{100}$. A lattice having atoms at cube corners and cube centers satisfies this condition and gives the observed spacing for other planes. Pure Fe was then investigated in the form of a fine powder. A narrow beam of rays from a W target passed through the powder and formed on the plate a kind of generalized Laue photograph in which every possible plane in the crystal structure had an equal opportunity of reflecting and reflected all wave lengths present. What was actually observed was the position of the *K* lines, which with the tube running at 110,000 volts, stood out very clearly. Their reflection in different planes appeared as concentric, nearly circular lines whose distance from the center should be inversely proportional approximately to the spacing of the planes. On the assumption that the atoms were arranged on a centered cubic lattice, and that the scattering electrons in each atom were concentrated at its center, the calculated spacings agree remarkably well with the observed values but fail to account for the following facts: (1) That the intensity of the lines falls off continuously with increasing distance from the center; (2) that the 1st-order (100) reflection is much too weak for its position; and (3) that the 2d-order (100) reflection is entirely lacking. In calculating intensities it is assumed (1) that the rays, when they reach the crystal, consist of long trains of waves, to which the electromagnetic theory is applicable; (2) that the scattering is due entirely to the electrons in the atoms, each of which scatters independently and equally; (3) that the number of electrons in an atom is equal to its atomic number; and (4) that the electrons have fixed positions in the atom, about which they move in very small orbits.

1517. HUME-ROTHERY, W., RAYNOR, G. V., AND LITTLE, A. T. Lattice Spacings and Crystal Structure of Cementite. Jour. Iron Steel Inst. (London), vol. 145, 1942, pp. 143P–152P; Iron and Steel (London), vol. 15, 1942, pp. 318–320; Chem. Abs., vol. 36, 1942, p. 3465.

Cementite examined by Lipson and Petch (abs. **2120**) was prepared by passing CO over Fe_2O_3 at 550°. It evidently had been partly decomposed during annealing and had lattice spacings different from the cementite used in the present study, which was extracted from steel by electrolytic attack in HCl. The values obtained by Debye-Scherrer photographs in a 19-cm. camera are: $a=4.5155$ Å., $b=5.0773$ Å., $c=6.7265$ Å. at 25°. Samples from 3 steels of commercial purity gave the same results. Analysis confirmed the composition Fe_3C. The structure of cementite can be derived from that of martensite by a simple shearing process. The ready formation of cementite from martensite (compared to formation from austenite) suggests that the relative positions of Fe and C atoms in martensite enable this transformation to take place with small atomic movements at a low temperature. 2 refs.

HUNSMANN, W. *See* abs. **853.**

HUNTER, W. *See* abs. **409.**

HUNTOON, R. T. *See* abs. **3262.**

1518. HUPPERT, O. [Hydrogenation of Coal and Oil.] Petrol. Ztschr., vol. 26, 1930, pp. 1250–1251; Chem. Abs., vol. 25, 1931, p. 1359.

Coal is liquefied by hydrogenation under high temperatures and pressure with or without catalysts and indirectly by hydrogenation of CO obtained from coal.

HURD, N. L. *See* abs. **1105.**

1519. HURST, W. W. and RIDEAL, E. K. Promoting Action of Palladium on Copper. I. Catalytic Combustion. Jour. Chem. Soc., vol. 125, 1924, pp. 685–694; Chem. Abs., vol. 18, 1924, p. 1775.

Ratio CO : H_2 burned in a mixture of the gases containing O_2 at the surface of Cu, and Cu containing, admixed with it, varying quantities of Pd has been measured. A real specific promoting effect was observed and the addition of Pd to Cu definitely increased the ratio CO : H_2. The promoting action of Pd on Cu is ascribed to a peculiarity of the Cu–Pd interface. The anomalous activities of molecules at interfacial boundaries and points of discontinuity are cited in favor of this view.

1520. ———. Promoting Action of Palladium on Copper. II. Adsorption of Hydrogen and Carbon Monoxide. Jour. Chem. Soc., vol. 125, 1924, pp. 694–705; Chem. Abs., vol. 18, 1924, p. 1775.

Adsorption of H_2 and CO and of mixtures of these gases by Cu and a Pd-promoted Cu catalyst has been studied, by means of a device based on the difference in thermal conductivity of the gases. Definite proof has been obtained that in general both gases are adsorbed, and that the composition of the adsorbed gas phase is independent, not only of the composition of the gas phase, but also of the nature of the adsorbent. The addition of Pd to the Cu produces an increase in the CO adsorption and a decrease in the H_2 adsorption, as well as a relative increase in the CO of the adsorbed phase in the presence of both gases. Arguments are advanced for the hypothesis that polar molecules are adsorbed at low temperatures and high pressures in multimolecule layers, and nonpolar molecules in unimolecule layers.

1521. HUSMANN, W. [Effluents From Fischer-Tropsch Plants Erected Under the German 4-Year Plan.] Gesundh.-Ing., vol. 62, 1939, pp. 299–304; Chem. Abs., vol. 34, 1940, p. 5624.

Phenols, S, and NH_3 are recovered from the effluents at hydrogenation works using the I. G. Farbenindustrie A.-G. process. The slightly acidic effluents from Fischer-Tropsch synthetic petrol works are treated by biomechanical methods. The strongly acidic effluent from synthetic fatty acid works is made harmless by separating the crude paraffin wax and neutralizing.

1522. HUTCHISON, W. K. A Plant for the Removal of Sulfur Compounds by Oil Washing. Inst. Gas Eng., Copyright Pub. 175/64, 1937, pp. 8–44, 51–64; Gas Jour., vol. 220, 1937, pp. 475–476, 479–485, 667; Gas World, vol. 107, 1937, pp. 379–383, 471–476, 563; Chem. Abs., vol. 32, 1938, p. 6437.

S was determined by drawing products of combustion of a free-burning flame of gas in purified air through an accurately neutralized solution of H_2O_2 of about 5 vol. strength and titrating H_2SO_4 formed with standard alkali with methyl red indicator. S compounds likely to be present in purified coal gas are CS_2, COS, thiophene and its homologs, mercaptans, sulfides, and disulfides, the last 3 representing less than 5% of the total S. As much as 18% of S in some coal gas is in a compound completely absorbed by alcoholic KOH, similar to CS_2 but more volatile, perhaps COS. Methods for determination of each are described, and analyses of 9 coal gases are tabulated. Partition factors for benzene and CS_2 were determined for 10

oils; this factor is largely instrumental in determining the quantity of oil to circulate. Sludge formation increased rapidly with temperature but varied widely in different oils, gas oils being most unstable. Washing with 80% H_2SO_4, followed with 10% NaOH and distilling greatly reduced sludge formation in gas oil. Specific gravity of oil used should be far enough from H_2O to reduce likelihood of emulsion formation. Viscosity should be as low as possible; doubling viscosity will increase the size of heat exchangers one-third and increase back pressure one-half. The mean boiling point should be high and distillation range narrow. The relations between rate of oil circulation, partition factor, and the characteristics of the washing plant; the conditions governing the performance of the stripping plant; and the effect of individual efficiencies of the two parts on the performance as a whole are analyzed. Some of the features of the plant are described, including power and heat, pumps, vacuum system and heat exchangers. The process differs from others in the larger quantity of oil circulated and lower ratio of steam to oil in stripping. The most favorable stripping conditions were distillation at 80° and 200 mm. abs. pressure; exhaust steam at a m. pressure can be used at this temperature. After 7 months' operation, total S removal is 70–76%. CS_2 removal is 90%.

1523. HÜTTIG, G. F. Course of Chemical Reactions in Which Solid Substances Are Involved. I. Historical Basis. Kolloid Ztschr., vol. 94, 1941, pp. 137–147; Chem. Abs., vol. 35, 1941, p. 3857.

Review of the development of theoretical chemistry is given.

1524. ———. Kinds of Chemical Reactions and Their Systemization. II. A Comprehensive Treatise on the Course of Chemical Reactions in which Solid Materials are Involved. Kolloid Ztschr., vol. 94, 1941, pp. 258–283; Chem. Abs., vol. 35, 1941, p. 5379.

Reactions of solids are divided into 5 classes on the basis of the number of components. These classes are further divided into subgroups on the basis of such considerations as the existence of polymorphic forms, fusibility, volatility of reactants and products, surface effects, and homogeneity of the mixture. A bibliography of 142 refs. is included.

1525. HÜTTIG, G. F., AND WEISSBERGER, E. [Catalytic Activity of Platinum Metals in the Decomposition of Methanol.] Siebert Festschr., 1931, pp. 173–178; Chem. Abs., vol. 26, 1932, p. 4233.

Catalytic activity of metals of the Pt group deposited on asbestos on the reaction of $MeOH \rightarrow 2H_2+CO$ is generally very erratic in the early stages of use but finally reaches a constant value that decreases in the order Pd, Os, Rh, Ru, Ir, Pt. In the 1st few hr. the activity of Os rises to more than 15 times its final constant value, then falls rapidly, whereas the values for Pd, Pt, and Rh undergo relatively little variation. The ultimate values are in all cases much higher than that of a ZnO catalyst.

HUTTON, R. S. *See* abs. **2752.**

HUZIMURA, T. *See* abs. **2506.**

I

IBING, G. *See* abs. **1828, 1829, 1830.**

ICHIMARU, T. *See* abs. **2507.**

1526. ICKES, H. L. Coal's New Horizons. Coal Age, vol. 48, 1943, pp. 54–64; Petroleum (London), vol. 6, No. 7, 1943, p. 110.

Not until 1937 did an experimental plant for producing liquid fuels by direct hydrogenation come into production. That plant, erected by the Federal Bureau of Mines at Pittsburgh, Pa., has a capacity of 100 lb. of coal per day. It is to be supplemented with another plant for the investigation of indirect hydrogenation. Direct hydrogenation gasoline has an octane rating of 70–75, which can be increased to 85–90 by adding tetraethyl lead. Gasoline made by the indirect hydrogenation has a low octane number and must be cracked to make it usable as motor fuel, but the diesel fuel made by this process is of excellent quality.

1527. I. G. FARBENINDUSTRIE A.–G. [History of Methanol Synthesis.] Ztschr. angew. Chem., vol. 40, 1937, p. 166; Chem. Abs., vol. 21, 1927, p. 1249.

1528. ———. Oxidation of Paraffin by Air or Oxygen for the Production of Fatty Acids. TOM Reel 54, May 1937, bag 3414, target 30/4.17, item 11.

This is a lengthy and detailed report of the experimental work by the I. G. Farbenindustrie at its experimental plant and by the Standard Oil Co. at Baton Rouge on the production of fatty acids by the oxidation of paraffin. Much is said concerning the oxidation and saponification procedures and the purification of the fatty acids, as well as their composition and analysis.

1529. ———. [Supervision of the Purity of Oxygen and Nitrogen Produced by the Liquefaction of Air.] TOM Reel 195, Part 10, Item 3, Frames 31,234–31,246, 1939.

Description of a new method, based on the heat conductivity of O_2 and N_2, by which impurities of even 0.1% can be detected rapidly and efficiently. Several tables and graphs are included, depicting the effect of various phenomena encountered in the determination of impurities on the sensitivity of the measuring apparatus.

1530. ———. [Collection of Patents on Paraffin Oxidation.] FIAT Reel J–281, frames 2755–2776, May 24. 1940; TOM Reel 285; PB 74,562.

Claims of 62 I. G. patents and patent applications in the field of paraffin oxidation are presented. Only 3 specific references are made to Fischer-Tropsch products. The corresponding foreign patents are listed.

1531. ———. [Flowsheet of the Winkler Plant and Miscellaneous Plant-Cost Data Sheets.] TOM Reel, 115, Item 4, 1941–1944, 28 pp.

Contribution of the Merseburg Ammonia Works, Leuna, Plant Control Department. The Winkler-plant flowsheet is laid out as a schematic drawing of the installation, showing relative sizes of the various units. The plant-cost sheets include: Energy data for the overall hydrogenation process including hydroforming and hydrocarbon separation; a flowsheet for the treatment of rich and lean hydrogenation gases; graphs of output of pure hydrogenation gas as a function of CH_4 % in Winkler output gas; computations of the analysis of pure hydrogenation gas for various CH_4 %; test analyses of hydrogenation gas output for different 24-hr. shifts; and analytical report on gasoline synthesis for a typical month.

1532. ———. [Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen With an Iron Catalyst According to the Emulsion Method.] TOM Reel 148, Rept. LU 558, No. N–25, June 23, 1942, 2 pp.

Tabular data summarize the products obtained in a 10-week run on a 1.5 $m.^3$ furnace at 250° and 20 atm. with a 55 : 45 mixture of $CO : H_2$ and a daily yield of 0.3. In smaller experiments a high percentage of high-boiling products was obtained. The paraffin content was as high as 40%. Some of the products were worked up to yield alcohols, sulfonates, fatty acids, lubricating oils, and leather oils.

1533. ———. Comparison of Products of Vapor-Phase and Foam-Phase Syntheses at Different Temperatures. Bureau of Mines Transl. T–436, January 1948, 4 pp.

Paper from Dr. Pier's files, high-pressure experiments, Ludwigshafen 558. Results of a few tests, and tabulated comparisons of products from the Synol process at Leuna, from the straight vapor-phase reactors, and from the gas circulation reactors. The products are expressed as free and total alcohol.

IGARASHI, H. *See* abs. **1345.**

IGAWA, S. *See* abs. **3607, 3608, 3609, 3610, 3611.**

IHARA, K. *See* abs. **1910.**

1534. IIZIMA, S. [Sorption of Hydrogen by Reduced Nickel. I. Quantities of Hydrogen Adsorbed by, and Diffused in, Pure and Contaminated Reduced Nickel, Isothermal Adsorption Lines and Heat of Adsorption.] Sci Papers Inst. Phys. Chem. Research (Tokyo), vol. 22, 1933, pp. 285–300. Chem. Abs., vol. 28, 1934, p. 2589.

Adsorption of H_2 by reduced Ni is due to both adsorption and diffusion. Quantitative distinction is drawn between the amount of H_2 adsorbed and the amount diffused. Isotherms showing the quantities of H_2 adsorbed under low pressures agree with the Freundlich equation. Heats of adsorption are calculated by means of the Clapeyron equation, and an average of 16,350 cal. per mol. is obtained. Reduced Ni that was brought into contact with air before the adsorption studies showed lower adsorptive capacity for H_2. The heat of adsorption in one such case was 6,479 cal. per mol.

1535. ———. [Sorption of Hydrogen by Reduced Nickel. II. At Low Temperatures.] Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 23, 1933, pp. 34–43. Chem. Abs., vol. 28, 1934, p. 2589.

Adsorption of H_2 under low pressures by reduced Ni was measured at 100°, 19°, 0°, —45.2°, —78.5°, —112° and —183.5°. The results of Nikitin, see abs. 2469, at 19° were not confirmed. Ni and H_2 did not form a compound at 19°. Isobars all showed maxima 0°–20°, and minima were found between —80° and —180°. The lower the equilibrium adsorption pressure the lower the temperature of the minimum. Irregularities in the isothermal at —183° are accounted for on the basis of local heating of the adsorbent due to adsorption of large quantities of H_2. The isothermal is smooth when H_2 is admitted slowly.

1536. ———. [Sorption of Hydrogen by Reduced Nickel. III. Heat Treatment of Reduced Nickel and Its Relation to the Sorption Velocity and to the Quantity of Hydrogen Sorbed.] Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 23, 1933, pp. 164–172. Chem. Abs., vol. 28, 1934, p. 2589.

Reduced Ni was successfully heat treated in H_2 for 1 hr. at temperatures ranging 300°–500°. Between each heat treatment the adsorptive capacity for H_2 at 0° and 20.3 cm. pressure was measured. Increasing temperatures of heat treatment shortened the time necessary for adsorption to reach equilibrium and diminished the quantity of H_2 adsorbed. The velocity with which A diffused into reduced Ni was unaffected by heat treatment up to 500°.

1537. ———. [SORPTION of Hydrogen by Reduced Nickel. IV. The Velocity of Sorption of Hydrogen at the Early Stage.] Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 26, 1935, pp. 45–69; Chem. Abs., vol. 29, 1935, p. 3893.

Rate of sorption of H_2 by reduced Ni was measured at 0°, 10°, 21°, 30°, 40°, 50°, 60°, 70° and 100° for various pressures of H_2. Except for the first 15 sec. after the introduction of H_2 the rate of sorption was followed up to 90 min. The results indicate 3 types of sorption. A rapid adsorption of the van der Waals type occurred during the 1st minute or 2. This was followed by a period of activated adsorption. Slow diffusion then followed and this was attributed to the diffusion of H from the surface to the interior of the metal as well as the slow distribution of H over the surface of the metal.

1538. ———. [Adsorption of Hydrogen on Reduced Nickel. Studies at Low Temperatures.] Rev. Phys. Chem., Japan, vol. 12, 1938, pp. 1–14; Chem. Abs., vol. 32, 1938, p. 6124.

Adsorption velocities were studied at 6 temperatures between —23° and —130°. The adsorption occurring 1 min. after the start consists of several activated adsorptions with markedly different velocities. The heat of activation of a particular adsorption was found to be 7,100 cal. Adsorption isotherms for some particular adsorptions were found, which gave a heat of adsorption of 10,600 cal.

1539. ———. [Adsorption of Hydrogen on Reduced Nickel.] Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 38, No. 1006, 1941, p. 183; Rev. Phys. Chem. Japan, vol. 14, 1940, pp. 128–136; Chem. Abs., vol. 35, 1941, p. 3138.

Some additional facts are noted in the study of the adsorption of H_2 on reduced Ni. The adsorption and desorption of H_2 on reduced Ni is irreversible with change of temperature. It is difficult to desorb H_2 by evacuation at low temperatures. The amount of activated adsorption decreases markedly with rise in reduction temperature used in preparing reduced Ni. The maximum and minimum points on the adsorption isobar should vary with the activity of the reduced Ni and the pressure of the gas. Van der Waals adsorption accounts for the adsorption at —183°.

IMAI, O. *See* abs. **1909.**

1540. IMHAUSEN, A. [Coal as Raw Material for Soaps]. Fette u. Seifen, vol. 44, 1937, pp. 411–415; Chem. Abs., vol. 32, 1938, p. 823.

Lecture is given outlining the history and chemistry of the processes for production of fatty acids by oxidation of paraffin hydrocarbons, which in turn may be synthesized by the Fischer-Tropsch contact process from water gas produced from coal.

1541. ———. [Early History and Chemistry of the Industrial Synthesis of Fatty Acids.] Chem.-Ztg., vol. 62, 1938, pp. 213–215; Brennstoff-Chem., vol. 19, 1938, p. 232.

Process recently developed by the I. G. Farbenindustrie for the production of fatty acids involves the catalytic oxidation of a suitable fraction of the high-molecular hydrocarbons obtained from the Fischer-Tropsch process. The reaction mechanism is not very well known. Whether the O_2 molecule ruptures a C–C bond of the hydrocarbon with the formation of a dialkylperoxide or whether it becomes enclosed in a molecule of paraffin with the formation of an alkylhydroperoxide is not yet clear. The O_2 could, in the primary step, unite with a molecule of paraffin with the formation of a molecular compound. The formation of an olefin by dehydrogenation, whose double bond then reacts further with O_2, is conceivable. The peroxides then become further oxidized with the formation of alcohols and aldehydes from which the fatty acids arise by way of the peracids. Alcohols and aldehydes are, thus, the intermediate products of fatty acid oxidation. There is also the possibility of ester formation from 2 mol. of aldehyde. Esters could be produced also by the reaction of the intermediately formed alcohols with the fatty acids. Side reactions are favored thereby so that the fatty acids are sensitive to further oxidation and can react with O_2 more easily than do the hydrocarbons. In this way undesired oxyacids are formed, which easily form lac-

tones with the intermolecular splitting off of H_2O, and, if the oxy-group of the one acid reacts with the carboxyl-group of another, estolides are formed. Moreover, the oxyacids easily split off H_2O with the formation of unsaturated acids. The oxidation also can lead to ketocarboxylic and dicarboxylic acids. It has been found possible, however, to suppress all these side reactions in favor of the desired formation of normal fatty acids so that today a large part of the soap used in Germany is made from synthetically produced fatty acids.

1542. ———. [Soaps From Synthetic Fatty Acids.] Kolloid-Ztschr., vol. 85, 1938, pp. 234–246; Chem. Abs., vol. 33, 1939, p. 1979.

Manufacture of soap from synthetic fatty acids on a commercial scale is described. Hydrocarbons were produced by the reaction of CO, from coal or lignite, with H_2 in the presence of a catalyst. These hydrocarbons were oxidized, by air, to fatty acids, consisting mainly of C_{10}–C_{22} chains. These acids were purified by boiling to remove the low-boiling fatty acids, and saponified to soaps or esterified to fats. The soaps produced in this manner were similar to soaps from natural fatty acids in their surface tension, viscosity, foam-producing properties, gold number, turbidity formation, and detergent properties. Experiments on the production of edible fats from synthetic fatty acids were successful on a laboratory scale.

1543. ———. [Importance of Synthetic Fatty Acids for the German Fat Economy.] Kolloid-Ztschr., vol. 103, 1943, pp. 105–108; Chem. Abs., vol. 37, 1943, p. 6917.

Process for manufacturing synthetic fatty acids is described based on the oxidation of the residue obtained during the hydrogenation of CO. This residue of the synthetic-fuel plants is first fractionated then oxidized to fatty acids. The product is washed to removed the catalyst, saponified, and the unsaponifiables are steam-distilled and returned to be oxidized again. The soap is acidified, the fatty acids are distilled and fractionated. These acids have 10–20 C atoms in the chain and are similar to natural fatty acids, except that the synthetic product contains acids with both even and uneven C atoms. The product is used for soap and, after esterification with glycerol, for cooking fats and for artificial butter.

1544. IMHAUSEN, K. H. [Synthesis of Edible Fats.] Ztschr. Ver. deut. Ing., vol. 91, 1949, pp. 463–467; Chem. Abs., vol. 44, 1950, pp. 4695, 5615.

Fischer-Tropsch process yields 10–15% of paraffinic residue boiling 320°–450° (chain length, C_{20}–C_{30}) suitable for producing synthetic fatty acids. The conversion uses finely distributed air of atmospheric pressure at temperatures slightly above 100° in the presence of Mn catalyzers. The process takes 15–30 hr. in Al or special steel towers 11 m. high and 2.6 m. in diameter. Oxidation requires approximately 50 $m.^3$ per hr. per ton of paraffin. The reaction is exothermic. The product is washed in towers and saponified with 30% Na_2CO_3 and 45% NaOH at 95°. Nonsaponifiables are separated, and the soap is heated 320°–350° to remove H_2O and paraffins, which are recycled along with the previously recovered nonsaponified material. The soap is dissolved and converted into fatty acid and Na_2SO_4 by means of 75% H_2SO_4. The crude fatty acid is fractionated under 4–10 mm. absolute pressure at 320° into C_5–C_9, C_{10}–C_{17}, C_{18} and higher, and residue. Yield is 70–80%.

IMHOFF, D. H. *See* abs. **202.**

INABA, T. *See* abs. **1120.**

1545. INDUSTRIAL and ENGINEERING CHEMISTRY. Methanol Developments. Vol. 17, 1925, pp. 772–773.

Full significance of the synthesis of MeOH and petroleumlike compounds from CO and H_2 has not been realized. The significant thing is not so much whether production will be undertaken in the United States or even the price at which foreign producers will demonstrate their ability to send this chemical to us. It is rather the patent situation that is causing the gravest concern in the light of the controversy taking place between Badische Anilin- und Soda-Fabrik. versus Patart. Present production in Germany is about 1,000 ton monthly; the estimated total for 1925 is 15,000 ton. Production costs are believed to be about 13% of the cost of MeOH by wood distillation. It is stated that at 1 plant the cost has been reduced to $0.03 per kg.

1546. ———. Synthetic Manufacture of Methanol. Vol. 17, 1925, pp. 981–982; Chem. Abs., vol. 19, 1925, p. 2928.

British Patent 229,715 is reproduced in full, together with a statement of conclusions drawn from this patent and from other literature as to proper apparatus and conditions necessary in MeOH synthesis. The essential features are as follows: (1) A gaseous mixture of CO and H_2 in which there are at least 2 vol. of H_2 : 1 of CO; (2) catalyst, a number of which are available, consists chiefly of ZnO with admixture of Cr_2O_3 and metallic Cu or CuO; (3) absence of alkali in the catalyst, which would cause decomposition of the MeOH produced and production of higher alcohols, H_2O, and oily and tarry bodies therefrom; (4) proper apparatus made of alloy steel and lined with Cu, Al, or Zn capable of withstanding very high pressure, at least 250 atm., and containing a heating element so that the incoming gases will come in contact with the catalyst at a temperature around 250°–300° C. without coming in contact with Fe, Ni, or Co; (5) condensation of the MeOH produced, and the recirculation of the residual gases brought again to the proper concentration by the addition of H_2 and CO.

1547. ———. Pressure-Synthesis Operations of the DuPont Ammonia Corp. Vol. 22, 1930, pp. 433–437.

Outstanding characteristics in the pressure-synthesis industry are exemplified by a survey of the synthetic NH_3 plant at Belle, W. Va. Because of the extremely high capital investment necessary, a plant of 300 ton-per-day capacity is probably the minimum economic size that can be constructed if costs are low enough to make a satisfactory rate of return in this field. Furthermore, the size of such operating units as compressors and converters is increasing to such a degree that this factor of unit size controls very largely the desirable overall plant capacity. Also, the enormous research and development expense must be distributed over a fairly large output, if reasonably low expense is to be shown per unit of output. Assuming that the 300 ton-per-day plant is the smallest that should be projected, then the total capital requirement, at the commonly accepted figure of $250-per-yr.-per-ton of NH_3, would be about $25,000,000.

1548. ———. Gasoline From Natural Gas. Vol. 37, No. 7, 1945, Adv. Sect., p. 5.

It has been reported that gasoline can be made at about $0.05 per gal. using the Fischer-Tropsch process and natural gas (abs. **2516** and **2997**). Our natural-gas resources are estimated at 111 trillion cu. ft. The price ranges from $0.015–$0.05 per 1,000 cu. ft. It is claimed that with gas at $0.05, it is possible to make a $0.05 per gal. gasoline having an octane rating of 75, a diesel oil with a 90–100 diesel index, and various chemicals in the form of oxygenated compounds. Using natural gas, 440 lb. or 10,450 cu. ft. is needed to make 1 bbl. of gasoline, about 8% less than by European methods. Conversion of all available natural gas would produce 11 billion bbl. of gasoline, enough to last 18 yr. at the 1940 rate of consumption. A plant capable of making 300,000 bbl. per day, American design, would cost 660 million dollars, as com-

pared with a plant of European design, which would cost 1.4 billion. As to costs, without depreciation, before taxes, and without profit, gasoline can be made at $0.036 per gal. with $0.05 natural gas. With depreciation, without taxes and profit, cost would be $0.048 per gal. At present, refinery costs, with $1.20 crude, are $0.051 and $0.053 for the same conditions.

1549. INDUSTRIAL AND ENGINEERING CHEMISTRY, NEWS EDITION. Soap Production From Paraffin to be Doubled. Vol. 16, 1938, pp. 193–194.

First experimental plant in Witten on the Ruhr, Germany, now produces 20,000 tons of fatty acids from paraffin per yr. A second plant of 20,000-ton capacity is under construction. The new soaps do not differ from the customary soaps either in odor or in characteristics in use. The paraffin is produced in the synthesis of gasoline.

1550. ———. Coal Hydrogenation. Japan. Vol. 19, 1941, p. 70.

In addition to coal hydrogenation, research was conducted on the synthesis of motor fuel from CO and H_2. The Fischer-Tropsch synthetic fuel plant of the Mitsui Mining Co. has been partly completed with test runs under way, but none of the other Mitsui plants under construction will be ready for production before 1942. The National Gas Institute of the Formosan Government-General has completed 2 pilot plants. One will produce carbon black, the other H_2–CO mixture for gasoline synthesis. Synthetic MeOH is manufactured by 6 companies, with an aggregate capacity of 19,650 tons per-yr.

1551. INDUSTRIAL BULLETIN OF ARTHUR D. LITTLE, INC. Gas From Gas. No. 224, 1946.

Review of the Hydrocol development at Brownsville, Tex.

1552. INDUSTRIAL CHEMIST AND CHEMICAL MANUFACTURER. Oxygen in Water-Gas Manufacture. Vol. 19, 1943, pp. 13–17, 57–60.

Review of processes. Describes Winkler, Lurgi, and Thyssen-Galocsy processes briefly, with details of recent installations in Germany, particularly in combination with low-temperature carbonization plant.

1553. ———. Thirty Years of F. Fischer's Work. Vol. 20, 1944, pp. 257–259.

On October 1, 1943, F. Fischer handed over to Prof. Karl Ziegler the direction of the Kaiser Wilhelm Institut für Kohlenforschung in Mülheim-Ruhr. Review work by Fischer at Mülheim. Up to 1924, the institute was occupied largely with researches upon the constitution of coal; after that date, with problems of gas chemistry, leading up to full-scale application of the Fischer-Tropsch synthesis.

1554. ———. Operation of Two Fischer-Tropsch Plants. Vol. 22, No. 256, May 1946, pp. 253–257.

Report on the operation and production of the Rheinpreussen plant at Moers-Meerbeck and the Ruhrbenzin A.-G. plant at Sterkrade-Holten.

1555. ———. Mersol and Hostapon—Manufacture of Sulfonated Detergents in Germany. Vol. 23, 1947, pp. 242–249; CIOS Rept. XXVI–2, PB 6, 684, and XXXII–107, PB 6,650; BIOS Final Rept. 805, PB 49,196.

The nature, manufacture, and uses of Mersol and Hostapon are given. Mersol is a mixture of sulfochlorinated paraffins in the C_9–C_{18} range, made by the action of SO_2 and Cl in the presence of ultraviolet light on a hydrogenated Fischer-Tropsch Kogasin distillate (Mepasin). The reaction is known as the Reed reaction. Hostapon is a mixture of alkyl sulfonic acids produced directly by the sulfo-oxidation of Mepasin, the reaction being promoted either by ultraviolet light or with acetic anhydride. The Fischer-Tropsch fraction used for starting material was the 220°–330° C. or the 230°–320° C. cut. Flowsheets, detailed descriptions of the processes, and the outputs from the plants are given.

1556. ———. Synthetic Fatty Acids. I. II. Vol. 23, 1947, pp. 652–656, 755–763.

Information in this article is drawn mainly from BIOS final reports 86, PB 18,911; 275, PB 23,808; and 805, PB 49,196, and FIAT reports 407, PB 7,738, and 426, PB 7,745. The raw materials used by the Germans to produce synthetic fats consisted of Fischer-Tropsch wax, gatsch boiling at 320°–450°, waxes from hydrogenation of brown coal, and even petroleum derivatives of waxy character. Plants were operated by the Deutsche Fettsäurewerke at Witten-Ruhr, by the I. G. Farbenindustrie at Ludwigshafen-Oppau and Heydebreck, by Hubbe and Fahrenholtz at Magdeburg, and by Ruhrchemie in a 3-ton per month pilot plant at Sterkrade-Holten. The intake capacity of these plants was approximately 100,000 tons per year, with a rated yield of 75–80% of fatty acids. The process of Ruhrchemie developed by Velde utilized the harder, long-chain waxes and produced fatty acids of high molecular weight. The raw wax was heated to 125°, treated with nitrosyl sulfuric acid for 8–12 hr., the acid was separated and the waxy product washed, dried, melted again, kneaded with caustic and, after saponification was complete, extracted with a Fischer-Tropsch motor-gasoline fraction boiling at 80°–100°. The separated wax was returned to the process, while the soap was treated with dilute H_2SO_4, washed, and dried. The material so made was called OP32, and the yield was about 80% on the wax used. It was yellow to brown in color, hard, and solidified at 80°, its acid No. was 145–150 and its saponification No. 150–155. The I value was nearly zero.

1557. ———. Synthetic Oil in Japan—an Attempt to Gain Self-Sufficiency. Vol. 23, 1947, pp. 333–340.

Complete plants at the end of the war numbered 2 for hydrogenation, 5 for Fischer-Tropsch, and 14 for low-temperature carbonization. The output of synthetic oil, excluding Manchuria, for 1944 was 113,000 kl., of which 770 kl. were hydrogenation products, 18,000 kl. Fischer-Tropsch oils, and 95,000 kl. low-temperature carbonization oils. Outputs are discussed in detail.

1558. ———. Igepon, Igepal, and Tylose. 1948, pp. 108–117.

Survey of Germany's efforts to produce synthetic detergents. Fatty acids and fatty alcohols from Fischer-Tropsch waxes were a considerable source of the raw materials. The importance is drawn mainly from CIOS Reports XXVI–2, PB 6,684; XXX–10, PB 954; and BIOS Final Report 711, PB 45,243; and BIOS Miscellaneous Report 11.

1559. INSLEY, E. G. Study of Finely Divided Metals and a Method for Their Preparation. Jour. Phys. Chem., vol. 39, 1935, pp. 623–636; Chem. Abs., vol. 29, 1935, p. 5327.

Adsorption of H, C_2H_4 and C_2H_6 was determined at 0° and compared with the rate of hydrogenation of C_2H_4 and Cu, Ni, Co, and Fe catalysts prepared from both the oxides and the amalgams. Ni, Co, and Fe, but not Cu catalysts prepared from amalgams, showed hydrogenating activity as high as those prepared from the oxides. The adsorption of H_2 on Ni was studied over the temperature range —80°–150°.

1560. INSTITUTE OF GAS TECHNOLOGY. Fischer-Tropsch Process. An Annotated Bibliography. Rept. for Technical Sec. Postwar Planning Cooperating Com., October 1945, 82 pp., 423 refs., 49 tables and 16 figs.

Very comprehensive review of the Fischer-Tropsch process is given. It embraces the following: Chapter I Introduction; II Historical development; III Products of the reaction, (1) nature, (2) treatment, (3) lubricating oil from primary products, (4) products of Robinson-Bindley process; IV Variables affecting the reaction, (1) catalyst, (2) pressure, (3) temperature, (4) time factor, (5) CO : H_2 ratio, (6) constituents other than CO and H_2 in the synthesis gas; V Thermodynamics of the reaction; VI Mechanism of the reaction; VII Industrial production, (1) production of CO–H_2 mixtures, (2) removal of S from synthesis gas, (3) contact chambers, (4) product recovery; VIII Industrial application of the Fischer-Tropsch synthesis; IX Integration of Fischer-Tropsch synthesis of hydrocarbons in gas plants; Appendix I the Sabatier synthesis; II Conversion factors. A tabulated compilation of every published type of Fischer-Tropsch catalyst, the best catalyst of each type on the basis of yield is included. *See* abs. **1562, 1563, 1564, 1565, 1566.**

1561. ———. Fischer-Tropsch Process. Rept. for Tech. Sec. Postwar Planning Cooperating Com., August 1945, pp. 19–33.

General review of published information with a summary of plant and operating costs taken from the Hearings before the Senate Committee on Senate Bill S–1243. Recommendations to the American gas industry as to the disposition of the process are: That no research be done on the production of liquid fuels by the Fischer-Tropsch process; that research be conducted on directing the Fischer-Tropsch synthesis to the production of gaseous hydrocarbons; and that the developments of the Fischer-Tropsch synthesis by the petroleum industry be followed closely.

1562. ———. Fischer-Tropsch Process, an Annotated Bibliography. Rept. for Tech. Sec., Postwar Planning Cooperating Com., October 1945, p. 19.

Compilation of every published type of Fischer-Tropsch nickel catalyst

Composition	Ratio of constituents, wt. basis	Reaction temp., ° F.	Yield of primary product, liquid, and solid hydrocarbons, gal./1,000 ft.³	Remarks
Ni	100	446	0.03	
Ni-kguhr	100:100	446		Also when prepared by ignition.
Ni–Al_2O_3-kguhr	100:15:100	446	.27	
Do	100:10	379	.77	
Ni–Cr-kguhr	100:8:125	401	.16	
Ni–Mn-kguhr	100:18:125	399	.60	
Do	100:18:125	399	.83	
Do	100:18:125	399	.77	
Ni–ThO_2-kguhr	100:18:100	347	.78	
Do	100:18:100	383	.74	
Ni–U_3O_8-kguhr	100:18:100	392	.61	
Ni–Co–Al_2O_3-kguhr	100:50:12:30:125 (sic)	374	.88	
Ni–Mn–Al_2O_3-kguhr	100:20:25:120	374	1.03	
Do	100:20:10:100	388	.96	
Do	100:20:5:66	347	.91	
Do	100:15:5:125	401	.86	
Ni–Mn–Cr-kguhr	100:18:1:125	401	.60	
Do	100:12:3:125	401	.55	
Ni–Mn–Cu-kguhr	100:15:0.5:125	399	.32	
Ni–Mn–fuller's earth-kguhr	100:15:75:75	401	.52	
Ni–Mn–K_2CO_3-kguhr	100:18:0.35:125	399	.43	
Ni–Mn–K_3HPO_4-kguhr	100:18:0.4:125	406	.53	
Ni–Mn–Mo-kguhr	100:12:3:125	401	.52	
Ni–Mn–Na_2CO_3-kguhr	100:18:4.8:125	401	.45	
Ni–Mn–Rb_2CO_3-kguhr	100:18:0.6:125	403	.74	
Ni–Mn–ThO_2-kguhr	100:15:3:125	401	.80	Space velocity, 130.
Do	100:15:3:125	401	.94	
Ni–Mn-starch-kguhr	100:25:300:125	394	.16	
Ni–Mn–U_3O_8-kguhr	100:20:8:125	392	1.07	
Do	100:12:3:125	401	.70	
Ni–Mn–W-kguhr	100:12:3:125	401	.68	
Ni–Co–Mn–Al_2O_3-kguhr	100:50:12:4:125	374	.88	
Ni–Co–Mn–ThO_2-kguhr	100:50:12:3:125	374	.93	
Do	100:50:12:3:100	374	[1] 1.02	
Ni–Mn–U_3O_8–Al_2O_3-kguhr	100:20:8:4:125	392	1.14	
Ni–Mn–U_3O_8–ThO_2-kguhr	100:20:8:4:125	392	1.16	
Ni–Mn–U_3O_8–WO_2-kguhr	100:20:8:4:125	392	1.12	

[1] At 5 atm. pressure.

1563. ———. Fischer-Tropsch Process, an Annotated Bibliography. Rept. for Tech. Sec., Postwar Planning Cooperating Com., October 1945, p. 23.

Compilation of every published type of Fischer-Tropsch cobalt catalyst

Composition	Ratio of constituents. wt. basis	Reaction temp., ° F.	Yield of primary product, liquid and solid hydrocarbons, gal./1,000 ft.³	Remarks
Co	100	410	0.33	
Co–Al	100:20	419	.07	
Co–Cr	100:20	419	.10	
Co–Mg	100:20	419	.34	
Co–Mn	100:20	419	.47	
Co–ThO_2	100:18	392	.10	
Co–Zn	100:20	419	.31	
Co–Cu–ThO_2	100:33:15	482	.09	

Compilation of every published type of Fischer-Tropsch cobalt catalyst—Continued

Composition	Ratio of constituents, wt. basis	Reaction temp., ° F.	Yield of primary product, liquid, and solid hydrecarbons, gal./1,000 ft.[3]	Remarks
Co-Cu-ThO_2	100:12:2	387	[1] 6.20	
Co_2O_3-MnO_2-CuO	100:75:50	523	.03	
Co-Mn-kguhr	100:15:-	392	.90	
Co-ThO_2-kguhr	100:18:100	374	.97	
Co-ThO_2-kguhr	100:18:100	392	[1] 6.97	Middle pressure.
Co-ThO_2-kguhr	100:18:100	----------	[1] 7.56	
Co-Cu-MgO-sugar-char	100:35:15:-	473	.33	See footnote 1.
Co-Cu-MgO-pumice	100:35:15:-	473	.50	See footnote 2.
Co-Mn-Al-kguhr	100:15:5:-	419	.57	
Co-Mn-Cu-kguhr	100:15:10:-	401	.81	
Co-Cu-MnO_2-ThO_2-kguhr	100:5:12:4:125	365–410	1.11	
Co-Cu-ThO_2-Ce-kguhr	100:11:22:2.6:-	392	.25	Ignition of nitrates gave slightly higher yield.
Co-Cu-Th-starch-kguhr	100:12.5:3.76:150:125	410	.83	
Co-Cu-Th-U-kguhr	100:12.5:1.88:1.88:125	410	.50	
Co-Cu-Th-U-kguhr	100:12.5:1.88:1.88:125	410	1.00	
Co-Cu-U-starch-kguhr	100:12.5:3.76:150:150	414	.87	
Co-Mg-Cu-Cr-(?)	100:25:12.5:12.5:-	410	.39	CO:H_2=1:1.
Co-Mg-Cu-Mo-(?)	100:25:12.5:12.5:-	410	.35	CO:H_2=1:1.
Co-Mg-Cu-Th-kguhr	100:25:12.5:5:75	455	.42	
Co-Mg-Cu-Th-(?)	100:25:12.5:5:-	410	.54	CO:H_2=1:1.
Co-Mg-Cu-U-(?)	100:25:12.5:12.5:-	410	.56	CO:H_2=1:1.
Co-Mg-Cu-W-(?)	100:25:12.5:12.5:-	410	.44	CO:H_2=2:3.
Co-Mn-Cu-Th-kaolin	100:25:12.5:5:125	471	.46	
Co-Cu-Th-U-starch-kguhr	100:12.5:1.88:1.88:150:125.	410	.97	
Co-Mg-Cu-Th-Ce-(?)	100:30:10:5:0.77:	455	.47	
Co-Ni-Mn-U_3O_8-ThO_2-kguhr	100:43:21:7:4:125	392	1.04	
Co-(Ni,Fe,CaO,S,Mn)-ThO_2-kguhr	100:(1.72):8:	----------	.84	Naphthene production (?)

[1] Lb. per 1,000 cu. ft.
[2] Reference gives yield ten times larger. A source of error has been assumed.

1564. ———. FISCHER-Tropsch Process, an Annotated Bibliography. Rept. for Tech. Sec., Postwar Planning Cooperating Com., October 1945, p. 27.

Compilation of every published type of Fischer-Tropsch nickel-cobalt (1 : 1) mixed catalyst

Composition	Ratio of constituents, wt. basis	Reaction temp., ° F.	Yield of primary product, liquid and, solid hydrocarbons gal./1,000 cu. ft.	Remarks
(Ni-Co)-Mn-Al_2O_3-kguhr	(100):15:5:125	410	0.71	
(Ni-Co)-Mn-Cr_2O_3-kguhr	(100):15:5:125	410	.70	
(Ni-Co)-Mn-ThO_2-kguhr	(100):15:5:125	410	.89	
(Ni-Co)-Mn-U_3O_8-kguhr	(100):15:5:125	392	.96	
(Ni-Co)-Mn-U_3O_8-kguhr	(100):20:20:125	383	1.20	
(Ni-Co)-Mn-U_3O_8-kguhr	(100):19.5:19.5:-	----------	1.14	
(Ni-Co)-Mn-U_3O_8-ThO_2-kguhr	(100):15:5:3:125	374	1.14	Variation of Ni:Co ratio from 30:70 to 70:30 has no effect.

1565. ———. Fischer-Tropsch Process, an Annotated Bibliography. Rept. for Technical Sec. Postwar Planning Cooperating Com., October 1945, p. 28.

Compilation of every published type of Fischer-Tropsch iron catalyst

Composition	Ratio of constituents, wt. basis	Reaction temperature, ° F.	Yield of primary product, liquid and, solid hydrocarbons gal. per 1,000 ft.[3]	Remarks
Fe-Cu-kguhr	100:20:-	518	0.17	
Do	100:25:-	518	[1] 1.63	
Do	100:25:-	518	[1] 2.18	Electrolytic washing.
Do	100:25:-	518	[1] 2.18	
Do	100:200:-	527	.17	
Do	100:100:-	527	.14	From 0.005–0.2 mol. Na_2CO_3 has no effect on yield.
Do	100:35:125	495	.45	
Fe-Cu-MgO	100:100:15	518	.06	
Fe-Cu-Na_2O_3	100:100:-	518	.17	
Fe-Cu-Co-kguhr	100:25:5:125	482	.54	
Fe-Cu-K_2CO_3-kguhr	100:25:3:125	495	.54	CO:H_2 ratio.
Fe-Cu-MgO-Na_2CO_3	100:100:15:2	500–536	.08	
Fe-Cu-Ni-asbestos	100:25:2.8:-	509	.31	
Fe-Cu-Ni-kguhr	100:25:5:125	482	.54	
Fe-Cu-K_2CO_3-kguhr	100:25:2:125	482	.23	
Fe-Cu-K_2CO_3-Al_2O_3-kguhr	100:25:2:2:125	482	.54	
Do	100:25:5:2:125	495	.28	
Fe-Cu-K_2CO_3-Cr_2O_3-kguhr	100:25:5:2:125	495	.09	

See footnote at end of table.

Compilation of every published type of Fischer-Tropsch iron catalyst—Continued

Composition	Ratio of constituents, wt. basis	Reaction temperature, ° F.	Yield of primary product, liquid and, solid hydrocarbons gal. per 1,000 ft.[3]	Remarks
Fe-Cu-K_2CO_2-MgO-kguhr	100:25:2:2:125	495	.61	
Do	100:35:2:2:125	482	.31	
Fe-Cu-K_2CO_3-MnO_2-kguhr	100:25:2:2:125	495	.61	
Do	100:25:2:2:125	482	.54	
Fe-Cu-Mn-KOH-kguhr	100:25:2:2:125		.59	
Fe-Cu-ThO_2-K_2CO_3-kguhr	100:25:5:2:125	495	.47	
Do	100:25:2:2:125	482	.45	
Fe-Cu-U_3O_8-K_2CO_3-kguhr	100:25:5:2:125	495	.54	
Fe-Cu-Zn-K_2CO_3-kguhr	100:25:5:2:125	495	.17	
Fe-Cu-Al_2O_3-Mn-KOH-kguhr	100:25:3:2:120 (sic)	482	.65	
Fe-Cu-Mn-Ni-ThO-kguhr	100:25:15:10:125 (sic)	495	.14	
Fe-Cu-Ni-Th-Ce-asbestos	100:25:6.25:0.74:0.10:-	509	.55	Yield of gaseous.
Fe-Cu-Ni-ThO_2-U_3O_8-kguhr	100:25:5:5:5:125	495	.16	

[1] Lb. per 1,000 cu. ft.

1566. ———. Fischer-Tropsch Process, an Annotated Bibliography. Rept. for Tech. Sec., Postwar Planning Cooperating Com., October 1945, p. 29.

Compilation of every published type of Fischer-Tropsch alloy catalyst

Composition	Ratio of constituents, weight basis	Reaction temperature, °F.	Yield of primary product, liquid and solid hydrocarbons, gal. per 1,000 cu. ft.	Remarks
Co-Al	?	392	1.20	
Co-Si	?	428	.75	
Do	100:100	401	.47	
Do	100:100	446	.55	
Ni-Al	?	348	1.15	
Do	100:100	383	.52	Increase in Al or temperature decreased yield.
Do	100:100	401	.41	
Ni-Si	100:100	401	.47	
Ni-Co-Si	100:100:200	383	.90	Yield varied with diameter of reaction tube.
Do	100:100:200	396	.58-.79	
Do	100:100:200	388	.66	
Ni-Fe-Al	100:100:200	446	.32	
Ni-Mn-Si	100:20:100	410	.36	
Ni-Co-Mn-Si	100:100:20:200	419	.80	

1567. ———. Utilization of Off-Peak Gas Capacity. Rept. for Tech. Sec., Postwar Planning Cooperating Com., August 1945, pp. 35–47.

Discusses the possibilities of utilizing spare water-gas equipment for producing synthesis gas for making synthetic MeOH or synthetic gasoline by the Fischer-Tropsch process. The conclusion is that the utilization of spare water-gas capacity during off-peak periods for the above purpose is not economically feasible. It is proposed, however, that the feasibility of producing lamp black or carbon black be investigated, as this proposition is economically possible.

1568. IPATIEFF, V. N. [Pyrogenic Contact Reactions of Organic Compounds. I, II, III.] Ber. deut. chem. Gesell., vol. 34, 1901, pp. 596–600, 3579–3589; vol. 35, 1902, pp. 1047–1057, 1057–1064; Jour. Chem. Soc., 1901, I, p. 248; 1902, I, p. 4; 1902, II, p. 335.

MeOH is decomposed by heat into trioxymethylene, a decomposition facilitated by Zn, but Fe causes a further decomposition into H_2 and CO. In presence of graphite, MeOH yields considerable quantities of CH_4. When MeOH is passed through a red-hot Fe tube, considerable quantities of HCHO are produced together with combustible gases and about 3% of C. The oxides of Zn, Fe and Cr are classified as dehydrogenation catalysts.

1569. ———. [Pyrogenetic Contact Reactions of Organic Compounds. IV. A New Method of Preparing Olefins.] Ber. deut. chem. Gesell., vol. 36, 1903, pp. 1990–2003; Jour. Chem. Soc., 1903, I, p. 593.

1570. ———. [Pyrogenetic Contact Reactions of Organic Compounds. V. Contact Isomerism.] Ber. deut. chem. Gesell., vol. 36, 1903, pp. 2003–2013; Jour. Chem. Soc., 1903, I, p. 594.

1571. IPATIEFF, V. N., and HUHN, W. [Pyrogenetic Contact Reactions of Organic Compounds. VI. Contact Isomerism.] Ber. deut. chem. Gesell., vol. 36, 1903, pp. 2014–2016; Jour. Chem. Soc., 1903, I, p. 595.

1572. IPATIEFF, V. N., and LEONTOWITSCH, W. [Pyrogenetic Contact Reactions of Organic Compounds. VII. Contact Metamerism.] Ber. deut. chem. Gesell., vol. 36, 1903, pp. 2016–2019; Jour. Chem. Soc., 1903, I, p. 598.

1573. IPATIEFF, V. N. [Catalytic Reactions at High Temperatures and Pressures. VIII, IX.] Jour. Russian Phys.-Chem. Soc., vol. 36, 1904, pp. 786–813, 813–835; Ber. deut. chem. Gesell., vol. 37, 1904, pp. 2961–3005; Jour Chem. Soc., vol. 2, 1904, pp. 644–645.

Investigation of the decomposition of alcohols at high temperatures and pressures in presence of Fe catalyst leads to the conclusion that increase of pressure diminishes the decomposability of alcohols, and

although the course of the reaction is the same as under ordinary pressure, yet the products of the reaction, especially the gases formed, differ in composition from those obtained under atmospheric pressure. The decomposition of primary, secondary, and tertiary alcohols differs as regards both the products formed and the velocity which may be taken as approximately proportional to the rate of increase of pressure. Investigation of the decomposition in presence of alumina as catalyst of alcohols in closed vessels under high pressures and at definite temperatures shows that the alcohols undergo decomposition into olefins and H_2O just as is the case under ordinary pressure. The temperatures at which the catalytic decompositions occur are, however, higher than under atmospheric pressure. But it is found that at temperatures lower than those at which the olefins are formed from primary alcohols, 1 mol. of H_2O is given up by 2 mol of alcohol, an ether being formed. This reaction is reversible, the ether again yielding the alcohol under the influence of alumina. At higher temperatures the ether undergoes further decomposition into olefins and H_2O. At still higher temperatures the olefins and also the aldehyde formed by the hydration of the ether are decomposed, yielding gaseous products partially similar to those formed during catalysis by Fe.

1574. ———. [Catalytic Synthesis of Methane.] Jour. prakt. Chem., vol. 87, 1913, pp. 479–487; Jour. Russian Phys.-Chem. Soc. vol. 45, 1913, pp. 433–442; Chem. Zentralb., 1913, II, p. 234; Chem. Abs., vol. 7, 1913, p. 3126.

It has been assumed that the catalytic synthesis of CH_4 from C and H_2 in presence of reduced Ni is facilitated by the formation of hydrides of the metal. Ipatieff ascribes catalysis to the presence of metallic oxides, which may serve both as oxidizing and reducing agents. In this case the scheme is as follows: Actor H–NiO catalyzer; Actor H–C acceptor. The NiO oxidizes the C to CO_2, and the latter is reduced by the H_2 according to the reversible reaction: $CO_2+4H_2 \rightleftharpoons CH_4+2H_2O$. As the H_2O produced is decomposed by the metal with regeneration of metallic oxide, the process is continuous, a small amount of the latter being enough for synthesizing a considerable amount of CH_4. The correctness of this view is supported by the fact that at least a small amount of H_2O is necessary in this, as in many other reactions and that the reaction represented by the above equation is reversible. This is proved by numerous experiments made at different temperatures and pressures, and with different concentrates of the gases. The results of these experiments are summarized as follows: The reduction of CO_2 by H_2 does not go to completion, whether the H_2 or the CO_2 is in excess; when a large excess of CO_2 is used, the relative amount of H_2 left unchanged decrease with an increase in the original concentrate of the CO_2; both NiO and reduced Ni catalyze the reduction, while CuO is considerably less effective; with theoretical amounts of the 2 gases the reaction of reduction tends to reach a certain limit. Several tables illustrate the results.

1575. ———. [Displacement of Metals and Their Oxides by Hydrogen Under Pressure at High Temperatures.] Chim. et ind., Spec. No., April 1928, pp. 411–414; Chem. Abs., vol. 22, 1928, p. 4287.

Effects of CO on $CuSO_4$ solutions at 160°–220° and 20–100 atm. for 16 hr. were studied. It was found that H_2O and CO reacted to give HCOOH, which decomposed to give $2H_2$ and CO_2.

1576. ———. Hydrogenation Developments in Russia. Nat. Petrol. News, vol. 23, No. 25, 1931, pp. 61–64; Chem. Abs., vol. 26, 1932, p. 1424.

Decomposition and synthesis investigations of organic compounds were made possible with the development of high-pressure and high temperature methods. The reduction of CO by H_2 at atmospheric pressure with catalysts produces liquid and solid homologs of CH_4. The formation of metal carbides appears to be an intermediate stage of the reactions involved. A gasoline produced similarly from water gas was shown to be highly unsaturated, and several O_2 compounds were isolated.

1577. ———. Mixed Catalysts. Nat. Petrol. News, vol. 32, No. 32, 1940, pp. R–280–282; Petrol. Refiner, vol. 19, 1940, pp. 250–255; Science, vol. 91, 1940, pp. 605–608; Chem. Abs, vol. 34, 1940, p. 6512.

According to a theory formulated by Ipatieff, increased activity is not explained satisfactorily as a purely physical effect of the promoters resulting in arrested recrystallization and preservation of the surface. Experiments with promoted catalysts led this author to conclude that a new source of energy contributes to catalysis. He assumes that contact of the metallic promoter with the basic catalyst produces electric energy. Ipatieff believes that the metallic oxide promoters participate in the reaction according to their chemical nature, thus assisting the catalyst in utilizing the reaction energy. This would mean, for instance, that ThO_2 in a Co–ThO_2–kieselguhr catalyst acts not only by its stabilizing influence on the specific structure of the catalyst but actually takes part in the reaction as a dehydrating agent. An activating agent may thus operate by physical, chemical, or physicochemical means.

———. *See* abs. **3091a.**

1578. IPATIEFF, V. N., AND DOLGOV, B. N. [Study of Catalysts for the Synthesis of Methanol.] Jour. Chem. Ind. (U. S. S. R.), vol. 8, 1931, pp. 825–829; Chem. Abs.,. vol. 26, 1932, p. 80.

Decomposition of MeOH over various catalysts was studied as a guide to the discovery of the catalyst most active for the MeOH synthesis. Zn–Cr catalysts are best, though Zn and ZnO also may be used. Asbestos forms a better support than pumice. For best results the Zn–Cr nitrates are precipitated from dilute solution by dilute alkaline carbonates, which produce a more active catalyst than the hydroxides on the asbestos at 60°–80°. The density of the catalyst on the support should be high. The catalyst is then reduced by H_2 or MeOH vapors. Zn catalysts are less easily poisoned by PH_3 than those of Cu. Nitrates of Ce, Th, and UO_2 serve as activators in small amounts, but in larger quantities they reduce the catalytic activity. On standing, the activity of all the catalysts decreases.

IPATIEFF, V. N., AND HUHN, W. [Pyrogenetic Contact Reactions of Organic Compounds. VI. Contact Isomerism.] *See* abs. **1571.**

IPATIEFF, V. N., AND LEONTOWITSCH, W. [Pyrogenetic Contact Reactions of Organic Compounds. VII. Contact Metamerism.] *See* abs. **1572.**

1579. IPATIEFF, V. N., AND MONROE, G. S. Synthesis of Methanol From CO_2 and H_2 Over Copper-Alumina Catalysts. Mechanism of Reaction. Jour. Am. Chem. Soc., vol. 67, 1945, pp. 2168–2171; Chem. Abs., vol. 40, 1946, p. 1140.

Synthesis of MeOH from CO_2 and H_2 over Cu–Al_2O_3 catalysts was investigated over a catalyst temperature range of 282°–487° and a pressure range of 117–410 atm. Cu alone and Al_2O_3 alone had no catalytic effect. The most active catalyst had a Cu content of 8–28%, giving conversions of 94% at 410 atm. and catalyst temperature of 285°. Similar experiments with CO and H_2 gave conversions of 39–43%, with as much as 15 and 41% of the CO charge reacting to give CH_4 and dimethyl ether, respectively. When CO_2 was added to the CO (mol. ratio $CO:CO_2=3.1:1.0$) the MeOH conversion was raised to 64%, and the formation of dimethyl ether was reduced to about 1%. Results

obtained with aqueous CH_2O solutions indicate that the formation of MeOH from CO_2 and H_2 under pressure may proceed along 2 paths. After reduction of the CO_2 to the CH_2O stage, part of the MeOH is formed by direct hydrogenation of the CH_2O and part by the Cannizzaro reaction.

1579a. IPATIEFF, V. N., AND SCHMERLING, L. Alkylation of Isoparaffins. Advances in Catalysis, Academic Press, Inc., New York, 1948, vol. I, pp. 27–64.

Critical discussion of catalytic alkylation of isoparaffins with special emphasis on catalysis and reaction mechanism. 43 refs. listed.

1579b. IPATIEFF, V. N., MONROE, G. S., AND FISCHER, L. E. Low-Temperature Hydrogen Production. Ind. Eng. Chem., vol. 42, 1950, pp. 92–94; Chem. Abs., vol. 44, 1950, p. 3,221.

Experiments were conducted on the direct catalytic conversion of CH_4 and H_2O to H_2 and CO_2 at about 500°–800° and at atm. and at 250 p. s. i. pressure. Space velocities of CH_4 of about 120 per hr. and mole ratios of $H_2O:CH_4$ of about 5 at atm. pressure and 32 at high pressure were used. The most effective catalysts were NiO or NiO and CuO on kieselguhr and the optimum concentrations about 7% CuO, 70% NiO, and 23% kieselguhr. This gave 55–92% conversion of CH_4. Increase of temperature increased H_2 yield and formation of CO. Increase of pressure decreased CO formation and H_2 yield, but the latter effect was nullified by increasing the $H_2O:CH_4$ mole ratio.

1580. IREDALE, T., AND LYONS, L. E. Influence of Inert Gases on the Photodecomposition of Gaseous Acetone. Jour. Chem. Soc., November, 1944, pp. 588–590; Chem. Abs., vol. 39, 1945, p. 3735.

A study was made on the influence of CO_2 and N_2 at about atmospheric pressure on the photodecomposition of gaseous acetone at room temperature in light of wave length 2,400–3,100 A. The yield of CO was increased, no detectable amounts of biacetyl were formed, and the ratio C_2H_6: CO approached unity. The results are attributed to increased dissociation of acetyl radicals on collision into CO and methyl and/or to hindering diffusion of acetyl to the walls, where it associates to give biacetyl.

1581. IRON AND COAL TRADES REVIEW. Hydrocarbons From Water Gas. Germany. Vol. 129, 1934, p. 542.

Fischer experimental plant for the manufacture of synthetic benzine from coal, which is being erected by the Ruhrchemie A.-G., of Oberhausen-Holten, will probably be completed at the end of this year. The cost will be approximately RM 1,000,000. The Fischer process operates at normal pressure and commences with water gas made directly from coke; thus, it is not based on coal byproducts but on the raw fuel itself. The collieries in the Ruhr, which are associated with the I. G. Farbenindustrie in the development of coal hydrogenation, are awaiting the results of the plant erected at Oppau by the I. G., which operates on the modified Bergius process and is claimed to have a much greater output than that adopted by the Ruhrchemie. The full-scale plant to be erected at Scholven will probably be on this process. It remains to be seen whether, following the successful outcome of the I. G. trials, the Ruhr collieries will come to a general agreement with the I. G., especially if the expectations regarding the Fischer process are fulfilled.

IRSA, A. P. *See* abs. **3395, 3395a, 3501.**

ISHIBASHI, T. *See* abs. **3315, 3316, 3317.**

1582. ISHIGAKI, T. Determination of the Density of Cementite. Sci. Repts. Tôhoku Imp. Univ., vol. 16, 1927, pp. 295–302; Chem. Abs., vol. 21, 1927, p. 2643.

Results of all previous investigations are listed; they differ considerably. Ishigaki redetermines the density by extrapolating the density-concentration curves of annealed C steels and cast irons to the concentration of cementite. Hot-forged and annealed samples were used to eliminate minute intercrystalline cracks and gas enclosures. The density measurements are made with an accuracy of ± 0.0003 gm. by an application of Archimedes' principle. The density of cementite is 7.662, in satisfactory agreement with 7.68 found by Westgren and Phragmen by means of X-ray analysis. A table showing the influence of common impurities, other than C, upon the density of Fe is given.

ISHIKAWA, H. *See* abs. **1802, 1803.**

ISHIKAWA, S. *See* abs. **1867.**

ITO, S. *See* abs. **1918, 1919, 1920, 1921, 1922, 1923, 1924, 1925, 1926.**

1583. IURA, T. Synthetic Motor Fuels. Wisconsin Eng., vol. 49, No. 3, 1944, pp. 9, 29.
Review.

IVANNIKOV, P. Y. *See* abs. **1107.**

1584. IVANNIKOV, P. Y., FROST, A. V., AND SHAPIRO, M. I. [Effect of Ignition Temperature on the Catalytic Activity of Zinc Oxide.] Compt. rend., acad. sci. U. R. S. S., 1933, pp. 124–126; Chem. Abs., vol. 28, 1934, p. 1595.

Activity of ZnO as catalyst for the decomposition of MeOH vapor decreased sharply with rise in ignition temperature of the hydrate from which the ZnO was formed. The hexagonal lattice remained unchanged between 110°–1,300° and had the following parameters: $a=3.248\pm0.002$ Å. U.; $c/a=1.602\pm0.002$. The size of the crystallites remained unchanged 100°–500°; a rapid increase began at 770°. A comparison of the changes in activity and crystal size showed that the decrease in activity began sooner and proceeded more rapidly than the decrease in surface caused by sintering.

1585. IVANOFF, N. [Esterification of Fatty Acids With Glycerol.] Bull. mat. grasses inst. colonial Marseille, vol. 29, Nos. 1–2, 13–19, 1945; Chim. et ind., vol. 53, No. 1, 1945, p. 41; Chem. and Met. Eng., vol. 53, No. 3, 1946, p. 270.

Work done on the rate of esterification of fatty acids with glycerol showed what quantities of catalyst and glycerol should be used, as well as the most favorable temperatures in regard to rate of reaction and preparation of undecomposed products. It was found that the catalytic action of benzene-sulfonic acid and *p*-toluenesulfonic acid is practically the same. At 175°–185° and in presence of 0.22% catalyst, the reaction is virtually in equilibrium after 8 hr. of heating, the yield being 82%. With 0.5% catalyst the yield is still 82%, and the reaction stops after 5 hr. of heating. When the temperature is raised to 250°–260°, the reaction is rapid and the yield is 96–97%, but the product is partly carbonized at the end of 3 hr. The rate of esterification and the yield of esterified fatty acids increases very rapidly when the quantities of glycerol used are greater than those indicated in the theoretical formula for triglycerides, but then there is a distinct predominance of diglycerides. *p*-toluenesulfonic acid was found to be more advantageous than benezenesulfonic acid.

1586. IVANOV, K. I., AND GUSEV, V. I. [Properties of Zinc–Chromium Catalysts for the Synthesis of Methanol.] Jour. Chem. Ind. (U. S. S. R.), vol. 12, 1935, pp. 1143–1146. Chem. Abs., vol. 30, 1936, p. 1525.

When a catalyst of $8ZnO \cdot 1.5Cr_2O_3$ is first used, it is most efficient at 370°, but as its use is continued, the optimum temperature rises slowly to 400°. Very high rates of passing the gas over it favor MeOH formation, while low rates of passing the gas, or temperatures above 400°, begin to favor CH_4 formation.

1587. IVANOV, K. N. [Properties and Structure of the Copper-Methanol Catalysts.] Acta Physicochim., U. R. S. S., vol. 1, 1934, pp. 493–502; Chem. Abs., vol. 29, 1935, p. 6711.

Addition of ZnO increases somewhat, and of Cr_2O_3 very strongly, the activity of the catalyst. Very active catalysts, 5 times as active as any previously reported, were prepared, for example: Cu, 82; ZnO, 16; Cr_2O_3, 2; and Cu, 60; ZnO, 35.6; Cr_2O_3, 4.4. High ZnO (more than 30%) and low Cr_2O_3 (less than 2%) lead to rapid aging of the catalyst. Reduction of the dried mixed precipitate takes place in a H_2 stream at 200°–220°. X-ray studies indicate that the function of Cr_2O_3 is to preserve a small amount of CuO, and that the real active centers are the Cu–CuO interfaces. During use, ZnO with Cu forms α-brass, with an increase in lattice constant of Cu and a decreased catalytic activity.

1588. ———. [X-Ray Examination of Copper Methyl Alcohol Catalysts.] Mem. Inst. Chem. All-Ukrain. Acad. Sci. vol. 1, 1934, pp. 49–55 (in German, pp. 56–57); Chem. Abs., vol. 29, 1935, p. 7169.

Activation of CO and H_2 molecules by Cu–ZnO–Cr_2O_3 catalysts (I) is due to active Cu and CuO molecules, the dispersion of which is increased by the ZnO. Cr_2O_2 acts as a promoter forming solid solutions with CO. Inactivation of (I) is due to diminution in the dispersion of Cu, to reduction of active CuO, and to increase in the parameters of the Cu lattice consequent on conversion into α-brass.

———. *See* abs. **893, 2710, 2711, 2712, 2713, 2716, 2717.**

1589. IVANOV, K. N., AND KOZLOV, L. I. [Corrosion of Alloy Steels Under the Conditions of Methanol Synthesis.] Khim. Mashinostroenie, vol. 5, No. 6, 1936, pp. 36–39; Chim. et ind., vol. 38, 1939, p. 923; Chem. Abs., vol. 32, 1938, p. 2496.

Corrosion of steel during the synthesis of MeOH results mainly in the production of Fe carbonyl. The metals alloyed with the steel can reduce corrosion, but not suppress it completely. The most resistant steels are those with high Cr content (13–15%); their corrosion is practically nil up to 100° and above 300°, Cr–V steel, on the other hand, is unsuitable. To secure practically absolute resistance, the steel should be covered with a protective lining such as a surface layer of a high=Cr, Fe–Cr alloy.

1590. IVANOV, K. N., KOZLOV, L. I., AND SOFER, M. A. [Properties of Zinc–Chromium Catalyst for the Synthesis of Methanol.] Jour. Chem. Ind. (U. S. S. R.), vol. 13, 1936, pp. 406–408; Chem. Abs. 30, 1936, p. 4630.

Presence of Pb and Cu in the catalyst lowers its productivity somewhat. More than 1% of sulfide or sulfate S lowers the productivity and increases the amount of esters in the MeOH. Above 400°, this effect is not so important. The presence of even 0.1% of Fe is very harmful, though FeO does not shows this effect.

1591. IVANOVSKIĬ, F. P., AND BRAUDE, G. E. [Low-Temperature Catalysts for the Conversion of Carbon Monoxide.] Jour. Chem. Ind. (U. S. S. R.), vol. 15, No. 1, 1937, pp. 14–19; Chem. Abs., vol. 32, 1938, p. 3100.

Catalysts deposited on grog are not strong enough for industrial use. The best catalysts are mixtures of about 35% CuO and 65% CoO containing some $K_2Cr_2O_7$, fused and reduced with H_2 at 300°. Such catalysts are poisoned by H_2S.

1592. IVANOVSKIĬ, F. P., BRAUDE, G. E., AND PANINA, A. M. [New Catalysts for the Conversion of Carbon Monoxide.] Jour. Chem. Ind. (U. S. S. R.), vol. 10, No. 2, 1934, pp. 37–44; Chem. Abs., vol 28, 1934, p. 3845.

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Fe catalysts should be heated for 2 hr. at 700° before use to give them the greatest stability. Co catalysts are very active but are mechanically weak. Addition of MgO strengthens them but lowers their activity. Siderite is a good catalyst, but it loses its activity on prolonged use. The loss may be prevented by addition of 0.7% by wt. of $K_2Cr_2O_7$ to siderite that has been heated for 6 hr. at 500°–525°. Such a catalyst gives 94–96% conversion. Addition of too much $K_2Cr_2O_7$ weakens the catalyst. H_2S lowers its activity. Titanomagnetite, Fe chromite, and bauxite are unsatisfactory as catalysts.

1593. IVANOVSZKY, L. Natural Gas; Possibilities of Exploitation in Great Britain. Petroleum, vol. 5, 1942, pp. 133–134; Chem. Abs., vol. 37, 1943, p. 1030.

Possibility of using CH_4 from natural gas as starting material and possibly fuel in the Fischer-Tropsch and Bergius processes for the production of motor fuel in Great Britain is briefly discussed. Reports of a 1938 drilling campaign indicate that a group of Scottish gas wells could supply more than 10,000,000 cu. ft. per day, while by horizontal drilling and vacuum extraction from coal seams, 1,000 cu. ft. (equivalent to 7 gal. of gasoline) could be extracted per ton of coal—or a total of 1,400 million gal. of gasoline per yr. based on a production of 200,000,000 ton per yr.

1594. ———. [Synthetic Waxes—Attempted Classification and Definition.] Chim. et ind., vol. 63, 1950, pp. 239–245; Chem. Age, vol. 62, 1950, p. 610.

Waxes may be classified as (a) natural-animal, vegetable, mineral, (b) refined (natural), (c) chemically modified, (d) synthetic, (e) compound. The term "synthetic" should be restricted to waxes that differ essentially from the raw materials used and result from chemical processes, which are often complicated. From the strictly scientific point of view, they are to be regarded as products of important chemical changes and partial synthesis. There are 3 synthetic processes: Hydrogenation of CO (Fischer–Tropsch waxes); low-temperature hydrogenation of C (T. T. H. waxes); and ethylenic polymerization (alkathenes, polythenes). Conversion of these hydrocarbon waxes into those of fatty acids, alcoholic or ketonic waxes, or of esters or other condensation waxes, leads to a series of purely synthetic waxes, if the hydroxylated consituents used are themselves synthetic, but the conception of true or purely synthetic has only theoretical interest. It is more important to inquire if the synthetic waxes are true replicas of the corresponding natural substances. In some cases this is so, as with the hydrocarbon waxes, which are similar to paraffin wax; and in some other cases there are analogies or similarities. In such instances the synthetic product may be superior or inferior to its natural analog, but in any case offers greater variety of properties. The difference between the natural ester waxes and the synthetic residues is that the latter contain various glycols, etc., but do not contain fatty alcohols of high molecular weight in appreciable quantities. Some, therefore, are completely saponifiable, while others (pseudo-esters) are virtually unsaponifiable.

IWAMOTE, T. *See* abs. **3199.**

IWAMURA, E. *See* abs. **2205.**

IWAO, M. *See* abs. **1927, 1928, 1929.**

1594a. IYENGAR, I. M. S. Fluidization. Jour. Sci. Ind. Research (India), vol. 9A, 1950, pp. 314–322; Fuel Abs., vol. 11, No. 7, 1952, abs. 677.

Fluidization technique is described and its application to the production of water gas from coal, catalytic cracking of petroleum oils, Fischer-Tropsch synthesis of liquid fuels, oxidation of naphthalene, washing of coal, and removal of S from town's gas is discussed.

J

1595. JACK K. H. Iron–Nitrogen, Iron–Carbon, and Iron–Carbon–Nitrogen Interstitial Alloys: Their Occurrence in Tempered Martensite. Nature, vol. 158, 1946, pp. 60–61; Chem. Abs., vol. 40, 1946, p. 6392.

Prolonged reaction of CO with Fe nitrides below 500° eliminates N, forming Fe percarbide (C, 30.5–32.1 atomic %). The unit cell is orthorhombic; it contains 4 $Fe_{20}C_9$ molecules. Above 500° the product of the same reaction is cementite. Both of these Fe carbides are metastable; Fe percarbide decomposes *in vacuo* to C+cementite; cementite to α —Fe+C. The rate of decomposition is negligible below 350°.

1596. ———. Binary and Ternary Interstitial Alloys. I. Iron-Nitrogen System: The Structures of Fe_4N and Fe_2N. Proc. Roy. Soc. (London), vol. 195, A, 1948, pp. 34–40; Chem. Abs., vol. 43, 1949, p. 3765.

ζ-Fe_2N phase is prepared by passing NH_3 over Fe at temperatures not exceeding 450°. The positions of N in γ (Fe_4N) and in ζ-phases are determined. Both are fully ordered interstitial alloys. In ζ the Fe atoms are in approximately hexagonal close-packed array. In each layer plane of octahedral interstices one-half of their number is occupied such that each N atom is allowed to have unoccupied holes above and below it in adjacent planes.

1597. ———. Binary and Ternary Interstitial Alloys. II. Iron–Carbon–Nitrogen System. Proc. Roy. Soc. (London), vol. 195, A, 1948, pp. 41–55; Chem. Abs., vol. 43, 1949, p. 3765.

Reaction of CO with nitrides of Fe and of NH_3 with carbides of Fe gave new Fe carbonitrides, a series of new ternary interstitial alloys. Carbonitrides with structures similar to corresponding Fe nitrides extend from Fe_8N_4 to Fe_8C_3N. The latter is isomorphous with Fe_2N. Phase fields are described. Prolonged reaction of CO with nitrides of Fe leads to elimination of the N. Below 500° the product is Fe percarbide; above this temperature it is cementite.

1598. ———. Binary and Ternary Interstitial Alloys. III. Iron–Carbon System: The Characterization of a New Iron Carbide. Proc. Roy. Soc. (London), vol. 195, A, 1948, pp. 56–61; Chem. Abs., vol. 43, 1949, p. 3765.

Fe percarbide has a narrow range of composition and is identical with a carbide previously assumed to be an Fe_2C. The unit cell is either orthorhombic or hexagonal, the former having approximately 80 Fe atoms. An empirical formula $Fe_{20}C_9$ is proposed. Fe_2C has probably not yet been prepared. Cementite and the percarbide are both metastable. Fe percarbide decomposes giving cementite and C while cementite gives α –Fe and C. The rates of decomposition of the 2 carbides are negligible below 350°.

1599. ———. [Results of Further X-Ray Structural Investigations of the Iron–Carbon and Iron–Nitrogen Systems and of Related Interstitial Alloys.] Acta cryst., vol. 3, 1950, pp. 392–394; Chem. Abs., vol. 44, 1950, p. 10641.

Tempering of C–martensite, the structure of N–austenite, N–martensite, and the tempering of N–martensite, the structure of ϵ–Fe and the $\epsilon \rightarrow \zeta$ transition, and the hexagonal Ni, Ni nitride, and Ni carbonitrides are discussed.

1600. ———. [X-Ray Structural Investigations of the Iron–Carbon and Iron–Nitrogen Systems and of Related Interstitial Alloys.] Acta cryst., vol. 3, 1950, pp. 392–393; British Abs., 1951, I, A, p. 41.

Three tempering stages of C martensite are discussed. The loss of tetragonality of martensite during the 1st tempering stage is due to the precipitation of a close-packed hexagonal Fe carbide, structurally similar to ϵ–Fe_2N. The unit-cell dimensions are a 2.73 Å, c 4.33 Å. The behavior of N martensite on tempering is quite different from that of the corresponding C alloys. At temperature <250° a new phase, α'', is formed as an intermediate in the decomposition α'–γ'. This α'' phase is relatively stable, with a 5.72Å, c 6.29 Å. The structures of ϵ–Fe nitrides and the ϵ–ξ transition are discussed. The hexagonal structure of Ni_3N is confirmed, the unit-cell dimensions being a 2.6677 Å±0.0005 Å, c 4.3122 Å±0.0005 Å. There appears to be no evidence as yet for the existence of a hexagonal allotrope of Ni.

———. *See* abs. **578a, 1218.**

JACOB, K. *See* abs. **2434.**

JACOBS, J. *See* abs. **1255.**

1601. JACOBSON, B., AND WESTGREN, A. [Nickel Carbide and Its Relation to the Other Carbides of the Series of Elements Scandium–Nickel.] Ztschr. physik. Chem., vol. 20, B, 1933, pp. 361–367; Chem. Abs., vol. 27, 1933, p. 2860.

X-ray analysis was made of Ni_3C. The elementary cell has dimensions a=2.646 Å. U., c=4.329 Å. U. and c: a=1.636. The results do not agree with the rule of Hägg for the structure of hydrides, borides, carbides, and nitrides of the transition elements.

JACOBUS, G. *See* abs. **385.**

JACOBY, J. *See* abs. **2219.**

1602. JACQUÉ, L. [Action of Hydrogen on Carbides of Iron and Chromium.] Compt. rend. vol. 206, 1938, pp. 1900–1902; Chem. Abs. vol. 32, 1938, p. 6170.

H_2 at a pressure of 100 kg. per cm.^{2} at 550° in 50 hr. entirely decomposes cementite, prepared by the action of KCN or NaCN on Fe at 650°. At lower temperature and pressure the removal of C was less complete, thus under 50 kg. per cm.^{2} at 500° the amount of C remaining was 2.5–3.5%, at 550°, 1.6–2.3. Treated similarly, H_2 had no appreciable effect on Cr carbides, whether Cr_7C_3, Cr_5C_2, or Cr_3C_2.

1603. ———. [Thermodynamics and Catalysis in the Synthesis of Fuels Under Pressure.] Centre de perfectionnement technique, Cours confs., No. 1318, February 1945, 31 pp.; Chim. et ind., vol. 55, 1946, p. 445.

Application of thermodynamics to the study of reactions permits a formula being established giving as a function of temperature and pressure the equilibrium concentrations of the constituents of the reaction. It has been established that the paraffins and the polymethylenes are relatively the most stable hydrocarbons at low temperature (below 500°), while the aromatics and olefins are the most stable at high temperature. Except for C_2H_2, no hydrocarbon is thermodynamically stable compared with its elements above 577°. In most reactions for synthesis of motor fuels, equilibrium is not attained in practice. It is often necessary to operate at a velocity high enough to avoid side reactions. A study of the kinetics of the reactions enables suitable reaction conditions to be selected, especially from the point of view of the dissipation of the heat of reaction.

———. *See* abs. **3723.**

1604. JACQUE, L., GIVAUDON, J., SCHMITT, P., AND DELION, R. [Preparation of Pure Paraffin Hydrocarbons by the Superfractionation of Synthetic Gasoline.] Rev. Inst. franç. petrol. et Ann. combust. liquides, vol. 1, December 1946, pp. 137–140; Chem. Abs., vol. 42, 1948, p. 4325.

By superfractionating a hydrogenated synthetic Fischer gasoline, the authors have prepared fractions of pentane, hexane, heptane, octane, and nonane, which analyze 8–9%, 22–23%, 20–25%, 20–22%, 10–15% of gasoline, respectively. The utilization of hexane for precipitating the asphaltic substances of lubricating oils and that of heptane as standard motor fuel for determining the octane numbers with the Cooperative Fuel Research motor is shown.

JAECKEL, B. *See* abs. **2139.**

1605. JAEGER, A. [Reduction of Carbon Monoxide to Formaldehyde and Methanol at Ordinary Pressure.] Ges. Abhandl. Kenntnis Kohle vol. 7, 1926, pp. 51–54; Chem. Zentralb. 1926, I, p. 3393; Chem. Abs., vol. 21, 1927, p. 3531.

Survey of literature.

———. *See* abs. **982.**

1606. JAEGER, A., AND WINKELMANN, H. [Reduction of Carbon Monoxide Under Ordinary Pressure.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 55–62; Chem. Abs., vol. 21, 1927, p. 2550.

Yields of CH_4 and of mixed oxides of C obtained by passing a mixture of 26% of CO and 67% of H_2 over a Ni pumice catalyst are, respectively, 12 and 12% at 220°, 54 and 7% at 245°, and 66 and 6% at 250°. The optimum temperature for CH_4 formation lies in a narrow zone at 250°. A mixed Cu–Ni catalyst yielded only 6% of CH_4; no C_2H_4 could be detected when a Pd catalyst was used. Contrary to the results of French Patent 519,649, no CH_2O is formed when a mixture of CO, HCl, and H_2 is passed over CuCl, Cu, Fe, or Ni at 200°–300°; it is produced in considerable amounts, however, when formic acid vapor mixed with H_2 is passed over metals at lower temperatures, over indifferent substances at higher temperatures, or through an empty glass tube at 700°–750°. CO and steam yield small quantities of formic acid when passed over hydrated SiO_2 at 320°; at 450° in a quartz tube about 1.5% of the CO is converted into CH_2O. This yield decreases with rising temperature and increasing streaming velocities (100 cm.^{3} per min.), and no CH_2O is formed at all when Cu or Ni pumice catalysts are used or when the steam is replaced by H_2. H_2 free from H_2S or prepared by dehydrogenation of tetralin (tetrahydronaphthalene) does not reduce CO to CH_2O at 400°. CH_2O likewise is not obtained by reducing the compound $K_3Fe(CN)_5CO$ with H_2.

1607. JAHN, H. [Studies on the Decomposition of Simple, Organic Compounds by Zinc Dust.] Ber. deut. chem. Gesell., vol. 13, 1880, pp. 983–990.

By passing MeOH over a heated mixture of Zn and ZnO, decomposition takes place giving a gas containing 30% CO, the rest being H_2 containing a trace of CH_4.

1608. JAHN, K. [Formaldehyde From Water Gas.] Ber. deut. chem. Gesell., vol. 22, 1889, p. 989.

CH_2O was produced by passing $CO+H_2$ over a catalyst of Pd sponge.

1608a. JAIN, B. C. Synthetic Liquid Fuel. Trans. Indian Inst. Chem. Engr., vol. 3, 1949–1950, pp. 79–104; Chem. Abs., vol. 46, 1952, p. 5,819.

Review of various processes for the synthesis of liquid fuels from coal and account of current economics of the processes. Among the techniques discussed are coal hydrogenation and Fischer-Tropsch. German and American work is cited. Excellent summaries are given of catalyst, operating conditions and yields for all modifications of the basic processes.

1609. JÄNECKE, E. [System: Fe–C–O.] Ztschr. anorg. Chem. vol. 204, 1932, pp. 257–290; Chem. Abs. vol. 26, 1932, p. 5530.

Comprehensive survey of recent work, with extensive bibliography. Jänecke's diagram has been somewhat modified, and the equilibria at various pressures and temperatures have been calculated. The heat of formation of cementite is −6.5 kcal. and that of pearlite −2.77 kcal. Contrary to previous views, there is a maximum pressure in the univariant system: Fe–austenite–FeO–gas at 820°. The equilibria in the Fe–C–O system between 500° and 1,000° and 0.2 and 5 atm. are represented by a 3-dimensional model.

1610. JANTZEN, E., RHEINHEIMER, W., AND ASCHE, W. [Composition of a Fatty Acid Mixture Obtained by the Oxidation of Synthetic Paraffin.] Fette u. Seifen, vol. 45, 1938, pp. 388–393, 613–615; Chem. Abs., vol. 33, 1939, p. 1527.

Paraffin produced by the Fischer-Tropsch process was oxidized in the presence of H_2O, the H_2O was removed, and the neutral oil was separated from the soap solution. After the fatty acids were liberated with acid, they were steam distilled, neutralized, and the lactones were extracted with petroleum ether. After the purified mixed fatty acids were liberated with acid, their constants were determined to be: Average molecular weight 229.8, I No. 486, OH No. 3.7, and solidifying point 26.2°. The fatty acids were converted to the Me esters and carefully fractionally distilled. The Me esters of all the fatty acids and, after saponification, all the fatty acids within the range C_8–C_{17} were isolated in pure form. The largest fraction (16.0%) was myristic acid, while acids above C_{17} amounted to 13.29%. Small amounts of unsaturated acids and acids containing OH or CO groups introduced slight irregularities into the curves showing boiling point, melting point and n_D^{36} as a function of the amount of fatty material distilled over. It is concluded, as regards the mechanism of oxidation, that all the CH_2-groups are equally susceptible to oxidation.

1611. JÄPPELT, A., AND STEINMANN, A. [Production of Synthesis Gas in the Technical Research Plant "Reiche Zeche," Freiberg i. Sa.] Braunkohle, vol. 35, 1936, pp. 353–357, 372–377; Chem. Abs., vol. 30, 1936, p. 5757.

Describes process (abs. **3101**) from operating standpoint with heat and material diagrams.

1612. JARZYŃSKI, A. [Synthesis of Liquid Fuels.] Przemysl Chem., vol. 26, 1947, pp. 164–175; Chem. Abs., vol. 43, 1949, p. 5570.

Reviews catalytic hydrogenation of coal and C oxides. Describes discovery, mechanism, and development of the Fischer-Tropsch synthesis to large-scale operation in Germany. Reviews other German catalytic processes developed during World War II, such as the production of synthetic lubricants, toluene, and higher alcohols. Discusses German commercial utilization of Fischer-Tropsch waxes.

1613. ———. [Synthetic Liquid Fuels.] Nafta, vol. 3, 1947, pp. 245–248; Chem. Abs., vol. 43, 1949, p. 3591.

Review of the manufacture of gasoline by hydrogenation of coal or from $CO+H_2$ and synthesis of CH_4 is presented.

1614. JASPER, T. M. Building of Containers for Severe Service. Ind. Eng. Chem., vol. 20, 1928, pp. 466–470.

Precautions are outlined to be observed in designing containers to operate under high pressure and temperature.

1615. ———. Building Vessels for High-Pressure and High-Temperature Service. Mech. Eng., vol. 52, 1930, pp. 193–200.

Discusses research work on vessels that has been carried to the point of practical application by pointing the way to correct design and fabrication in the production of containers for high-pressure and high-temperature service.

JEFFERSON, M. E. *See* abs. **390.**

JELLINEK, E. *See* abs. **2935.**

1616. JELLINEK, K., AND DIETHELM, A. [Producer-Gas Equilibrium at High Pressures.] Ztschr. anorg. Chem., vol. 124, 1922, pp. 203–229; Chem. Abs., vol. 17, 1923, p. 461.

Equilibria in the reaction $C+CO_2 \rightleftharpoons 2CO$ were investigated for temperatures between 800° and 1,000° and for pressures up to 50 atm. for the so-called amorphous coals. The apparatus used for the determination was a specially constructed electric furnace (described in detail) for determinations up to 150 atm. and 1,300°. The equilibria for both amorphous coals and graphite agree very closely. Complete agreement also was found, up to the temperatures investigated, between the producer-gas equilibria and the law of mass action. It is true probably at still higher pressures. Primarily the generator reaction is probably a heterogeneous gas reaction, by which the validity of the law of mass action at high pressures is established. The integration constant of the isochor reaction in the producer gas equilibria agrees fully with that calculated from the chemical constants in Nernst's heat theory. It follows from the producer-gas equilibrium and the CO_2 dissociation equilibrium that, with virtually approachable temperatures and pressures, the maximum work performed by the reaction $C+O_2 \rightleftharpoons CO_2$ is equal to the heat tone in case the initial O_2 pressure and the final CO_2 pressure are alike and the reaction takes place isothermally and reversibly.

1617. JELLINEK, M. H., AND FANKUCHEN, I. Application of X-Ray Diffraction to the Study of Solid Catalysts. Advances in Catalysis, Academic Press, Inc., New York, 1948, vol. I, pp. 257–289.

General discussion is presented of the techniques of X-ray diffraction applicable to the study of catalysis with a few specific applications.

1618. JELLINEK, O. [Conversion of Coal Into Oil.] Umschau, vol. 30, 1926, pp. 533–538; Chem. Zentralb., 1926, II, p. 1481.

Describes Bergius process and the Fischer synthesis.

JENCKEL, E. *See* abs. **3062.**

JENNINGS, W. H. *See* abs. **368.**

1619. JENNY, F. J., AND CONWAY, M. J. Equipment for Low-Cost Oxygen Production. Oil Gas Jour., vol. 45, No. 23, 1946, p. 91.

Digest of a paper presented at the 1946 national conference on petroleum mechanical engineering, American Society of Mechanical Engineers. Describes production of O_2 by the liquefaction and fractionation of air as practiced on a pilot-plant scale. The unit operations involved consist essentially of compression, heat exchange, refrigeration, and fractionation. The first of 2 large plants is now under construction at Brownsville, Tex. It will operate in connection with Hydrocol process for the treatment of natural gas to produce motor fuel, diesel fuel, and crude alcohols. A second unit, to be built for a major oil company, also will supply O_2 for a Hydrocol plant similar in size and operation to the Brownsville plant. These 2 plants will compress approximately 250,000,000 cu. ft. of air per day to 75–85 p. s. i. g.

1620. JENSON, O. Carbonization by Electricity. Gas Jour., vol. 261, 1950, pp. 270–271.

Abstract of a paper presented at the United Nations Scientific Conference on the Conservation and Utilization of Resources, Lake Success, N. Y., is reviewed. A new electric process is described for the carbonization of noncoking bituminous coal, Spitzbergen. Carbonized briquets made from the crushed coal are charged into the top of the vertical shaft and preheated by hot gases. A diagram of this operation is shown. At the lower end of the shaft is an electric furnace containing 2 sets of 3-phase electrodes. The carbonized and conductive briquets form the resistor element, which provides the heat for the process. Cold gas, introduced at the base of the furnace, cools the hot coke and is preheated. The gas is heated further to 1,000° in the electric furnace and reacts with the hot C, forming CO and H_2. As the hot gas rises in the furnace, its sensible heat serves to carbonize the coal briquets. One short ton of coal yields 1,250–1,300 lb. coke briquets, 20–25 gal. low-temperature tar, and 24,000 cu. ft. of gas. Power consumption is about 40 kw.-hr./M cu. ft. of gas produced. The gas has a H_2: CO ratio of 2.6, and to produce synthesis gas, H_2: CO=2, it is only necessary to add blue water gas, for example, by adding steam to the circulating gas. A plant for the synthesis of gasoline capable of converting 1.5 million short tons of Spitzbergen coal annually will yield about 700,000 tons of low-ash coke briquets, 750,000 bbl. of low-temperature coal tar, and 2 million bbl. of gasoline and diesel fuel. The power requirements would be about 300,000 kw. Estimated production cost for the gasoline will be about $0.20/gal.

JERDAN, D. S. *See* abs. **296.**

JESSEN, V. *See* abs. **133, 134.**

JINKINGS, A. J. *See* abs. **326.**

JINTA, T. *See* abs. **1119, 1120.**

1621. JOCHUM, P. [Enrichment of the Methane Content of Technical Gases, and the Production of a Carbon Monoxide-Free Illuminating Gas.] Jour. Gasbeleucht., vol. 57, 1914, pp. 73–80, 103–111, 124–131, 149–151; Chem. Abs., vol. 8, 1914, p. 1660.

Previous attempts to form CH_4 from the CO and H_2 of illuminating gas by the catalytic action of Ni have met with difficulty, owing to the poisonous effect of S compounds or the fouling of the catalyzer by tars or deposited C. The optimum conditions for the reaction are determined, using synthetic mixtures of CO and H_2 in the ratios 1:1, 1:3, 1:5, these being the proportions named in the 3 most-important patents. The latter also approximates ordinary coal gas and is the subject of the patents of the Cedford process, the most nearly successful of all. The main reaction goes readily at low temperatures and CO_2 also is reduced easily. But, with high concentrates of CO or high temperatures, the reaction $2\,CO \rightleftharpoons CO_2+C$ makes its appearance. This is partly counteracted by $C+2\,H_2 \rightleftharpoons CH_4$. The experiments were carried out with Ni reduced from the nitrate on unglazed porcelain. The analyses of the final gas were calculated back and checked very closely with the original mixtures, showing the accuracy of manipulation and absence of serious side reactions. With 1:1 mixtures, the CH_4 could not be carried above 40%, and at this point much CO_2 was formed from the second reaction above. With 1:3 mixtures, the yield was 50–65% and some CO_2 was formed; but with 1:5, no trace of CO_2 appeared, though the CH_4 could not be raised above 35%. However, in this latter gas, the contraction owing to the reaction was less, so that the net yield of CH_4 was greater than where the concentration of CH_4 was higher. Most of these experiments were run at the rate of 8 cc./min. in a tube 16 mm. in diameter, though it was found that up to 200 cc./min., no CO_2 appeared. The optimum temperature for 1:5 mixtures is 280°. With mixtures of C_2H_4 and H_2 in the theoretical amounts for $C_2H_4+H_2 \rightleftharpoons C_2H_6$ no difficulty was met and a gas of 80% C_2H_6 with virtually no C_2H_4 could be obtained at 150°. As the temperature rose the reaction $C_2H_6 \rightleftharpoons CH_4+H_2+C$ appeared, and at 320° a gas of 90% CH_4 with no H_2 and only traces of C_2H_6 was obtained. This decomposition is at decidedly lower temperatures than noted by Sabatier, probably owing to a better catalyzer. With synthetic illuminating gas (9% CO, 50% H_2, 38% CH_4) no difficulty was found in preparing a gas of 85% CH_4, no trace of CO, and less than 1% of CO_2. This was at 300° and the

velocity was increased to 90 cc./minute without CO appearing in the end products. With actual city gas, purified from S, after 24 hr. CO began to appear. This was due to tarry materials collecting on the catalyzer; for when the gas was passed through CO_2 snow and ether on its way to the catalyzer, a gas of 85% CH_4, wholly free from CO, and with only traces of CO_2, was still obtained after 62 hr. Though this process as applied to commercial illuminating gas means a loss of heat (with $CO:H_2=1:5$ a net loss of 14% and with illuminating gas a loss of 11%), the resulting gas has a much higher heating value/m.^{3} and as such is more valuable. The main disadvantage is the cost of purification by freezing, which will be partly offset by the benzene recovered. As a process for the manufacturing of CH_4 as a material for chemical industries, it could hardly compete with natural gas. Reviews most-important patents in this field.

1622. JOHANSSON, A., AND VON SETH, R. Carburization and Decarburization of Iron. Surface Decarburization of Steel. Jour. Iron Steel Inst. (London), vol. 114, 1926, pp. 295–358; Engineering, vol. 122, 1926, pp. 460–464; Chem. Abs., vol. 20, 1926, p. 3429.

In an atmosphere of CO_2–CO the main course of the reaction is $3Fe+2CO=Fe_3C+CO_2$. The theoretical considerations involved are discussed and experiments are described, which were to determine the equilibrium of the reaction and establish isotherms at 1,100°, 1,000°, 900°, 800°, 750°, and 710° on steels in which C ranges from 0.03 to 2.32%. The equilibrium $Fe_3C+2H_2=3Fe+CH_4$ is also studied.

1623. JOHANSSON, A., VON SETH, R., AND ELFSTROM, N. [Investigations on the Surface Decarburization of Steel.] Jernkontorets Ann., vol. 116, 1932, pp. 565–655; Chem. Abs., vol. 27, 1933, p. 3429.

Equilibrium isotherms have been determined for the systems $3Fe+2CO\rightarrow Fe_3C+CO_2$ (1) and $3Fe+CH_4\rightarrow Fe_3C+2H_2$ (II) between 680° and 1,100°. The isotherm for (1) at 710° shows a decreasing CO_2 pressure with increasing C content, a result which is inconsistent with the assumption that C is insoluble in ferrite below the Ac_1 point. Above 900°, FeO cannot be reduced to metallic Fe free from C. At 680° the reaction proceeded too slowly for establishing equilibrium, but a mutual solubility of cementite and ferrite was indicated. From 900°–1,100° the activity coefficient of C was found to be nearly unity in cementite and Mn steels. By varying the $CO_2:CO$ ratio in carburetted gas, either carburizing or decarburizing conditions may be established. At 1,250° and 1,320° the solubility of C in molten Fe was 4.4 and 4.56%, respectively. In (II) the rate of reaction was found to be a maximum at 950° but was noticeable at 600°, and falling again above 1,000°. Ni, Mn, W, and Cr steels gave about the same rate as unalloyed steel. No decarburization was found with N_2 and none with air at 750°, 710°, or 650°, probably because a protective oxide layer prevents diffusion of gas to the Fe surface. 26 refs.

1624. JOHNSON, A. F., AND GRAYSON-SMITH, H. Magnetic Susceptibilities of Iron-Group Salts at Low Temperatures. Canadian Jour. Research, vol. 28 A, 1950, pp. 229–241; Chem. Abs., vol. 44, 1950, p. 8178.

Magnetic balance of the Sucksmith-ring type is described. This apparatus is used to measure the susceptibilities of hydrated and anhydrous $CR_2(SO_4)_3$ and the nitrates of Cr, Co, and Ni. The presence of small amounts of ferromagnetic impurity is corrected by making measurements at several values of the field strength. The reciprocal susceptibility $1/\chi$ is plotted against the absolute temperature to evaluate the Weiss constant θ.

1625. JOHNSON, C. A., BUSCHOW, H. F., AND CARLSMITH, L. E. Gasification of Coal. FIAT Final Rept. 938, April 22, 1947, 34 pp.; PB 80330.

Of the various processes proposed by the Germans for converting coal into synthesis gas by continuous gasification with O_2, 2 of the more recently developed processes are of interest for possibly providing gas for Fischer-Tropsch liquid-fuel plants. These are the Lurgi high-pressure and the Thyssen-Galocsy processes, both of which use O_2. The Koppers combination low-temperature carbonization and gasification process, which has been used for producing synthesis gas on a large scale, also is studied. The Lurgi process operates at a high pressure (20 atm.), assuring low velocities (small equipment), eliminating the necessity of compressing the gas ahead of the Fischer-Tropsch units, simplifying recovery of condensables in the gas, and providing another variable (pressure) for control of gas composition. This process will utilize a wide variety of coal. The Thyssen-Galocsy process operates at a temperature high enough to melt the ash, which is withdrawn as a fluid, thereby eliminating the frequently encountered problem of clogging of the generator by sintering of low-melting-point ash coals. Furthermore, the equipment is unusually simple. The Koppers process operates at atmospheric pressure and does not use O_2. It consists in distilling coal briquets, followed by partial gasification of the semicoke with hot steam lower in the retort, finally cooling and removing the coke and gasifying it in conventional gas producers. The producer gas is burned in regenerators and used to superheat steam (1,300°), which is reacted with the semicoke to form the synthesis gas. Several diagrams of the 3 processes are reproduced. A summary also is given of the status of the Fischer-Tropsch process.

JOHNSON, H. H. *See* abs. **3146.**

1625a. JOHNSON, M. F. L. and RIES, H. E. Structure of Cobalt Catalysts Supported on Diatomaceous Earth. Am. Chem. Soc., 121st Meeting Abs., March–April, 1952, p. 12–M.

Various points are presented as evidence for the existence of catalyst–support interaction in the case of Co oxide precipitated in the presence of a diatomaceous earth support. These include measurements of adsorption isotherms, the degree of reduction to Co metal, and the use of area–temperature sintering curves to characterize gels. The adsorption isotherms for this type of catalyst all have the same characteristics: A nearly asymptotic approach to P_0, representing interparticle condensation, plus a sharp break at 0.5 relative pressure and a volume adsorbed corresponding to the volume of small pores.

1626. JOHNSON, R. C. Anthracite as Fuel for Synthesis-Gas Production. Trans. 7th Ann. Anthracite Conf., Lehigh Univ., May 1949, pp. 69–82; Fuel Abs., 1950, Abs. 140.

American anthracite industry has in store and is producing many million tons of 2 low-cost byproduct fuels suitable for manufacture of synthesis gas: (a) Silt, a mixture of coal, bone, and slate with basically the same composition as commercial anthracite at the mine at which it is produced, except that the ash content is higher; and (b) bone coal, anthracite interspersed with small slate bands; its ash content varies 25–30% and is governed by the gravity at which it is separated from rock and other refuse. Investigations of different processes for gasification of these fuels are in progress. The Anthracite Institute has been operating a fluidized-bed gas-producer pilot plant using silt; results are encouraging. There has been no trouble with the fluidization of the bed, but it has been difficult to obtain the desired bed temperatures for

production of the best quality gas. The silt can be used in conventional gas generators if it is briquetted.

JOHNSON, R. T. *See* abs. **2128a.**

JOHNSTON, H. L. *See* abs. **654a.**

JOHNSTONE, H. F. *See* abs. **424a.**

1627. JOKLIK, A. [Methane Cracking and Carbon Monoxide Conversion in Gas Works.] Gas, Wasser, Wärme, vol. 4, 1950, pp. 247–258; Fuel Abs., vol. 9, No. 3, 1951, abs. 1625.

Reforming of gases of all kinds that contain CH_4 (natural gas, residual gases from benzine synthesis plants ond oil refineries, and sewage gas) can be used to supplement the production of town gas. This can be achieved by a combination of CH_4 cracking with CO conversion. The combined process also can be used in the manufacture of town's gas from coal gas. An account is given of the properties of various mixing gases and town's gases and of the suitability of CH_4, cracked gases, and partly converted cracked gases for town gas production.

JOLLEY, L. J. *See* abs. **304, 1328, 3699.**

1628. JOLLEY, L. J., AND BOOTH, N. Underground Gasification of Coal. Gas Research Board Inf. Circ. 2, Pub. 22; Gas World, vol. 128, 1948, pp. 588–595; Fuel, vol. 24, May–June 1945, No. 2, pp. 31–37; No. 3, pp. 73–79.

Bibliography of 123 refs. (*see* abs. **3698**). Extensive review of the literature on underground gasification, particularly of Russian sources, appears. The average output/man employed was increased from 30 tons of coal/month by mining methods to the thermal equivalent of 100–120 tons by underground gasification; in large installations it might reach 500–600 tons. The cost of standard coal in Russia in 1939 was 22–30 rubles (18–25 s.)/metric ton. The cost of production of 1,000 kcal. of gas of low calorific value (100–150 B. t. u./cu. ft.) is stated to be 0.15–0.20 kopek (0.375–0.5 d.) and that of high-calorific-value gas to be 0.4 kopek (1.0 d./therm). (The above figures do not appear to include labor costs.) The cost of low-calorific-value gas is about ⅓ that of producer gas. The net cost (exclusive of capital charges) of gas from normal producer installations is 0.74–1.21 kopeks/1,000 kcal. (1.84–3.0 d./therm), while that of gas from underground installations is 0.27–0.68 kopek/1,000 kcal. (0.7–1.7 d./therm). The capital cost of underground gasification plant is stated to be 60–70% of that of a plant employing an above-ground producer. In the Stream method 80–90% of the capital cost represents surface work and 14–15%, the preparation of panels. The percolation method is stated to reduce capital investment by 15–20%. For a combined underground gas-electric power generating station the capital cost is 1,500 rubles/kw. installed power and the prime cost of power, 4–6 kopeks/kw.-hr. The cost of an O_2 plant is estimated to amount to 70% of the total outlay cost and the cost of gas made with an O_2 blast 3 times that made with an air blast.

1629. JOLLEY, L. J., AND MORCOM, A. R. Ruhrchemie A.-G., Sterkrade-Holten. BIOS Final Rept. 1038, December 1946, 15 pp., PB 75,817.

This report presents additional details on: (1) The pelleting and grading of precipitated catalysts on kieselguhr by 4 improved methods, (2) organic S removal, and (3) the production of C_2H_2 and cyanides from CH_4 and natural gas. A flowsheet of the scrubbing process for C_2H_2 production is included. (*See* abs. **873, 874, 875, 876, 877, 878, 1327.**)

JONAKIN, J. *See* abs. **810a.**

1630. JONES, A. L. Liquid Thermal Diffusion—a Continuous Separation Process. Petrol. Processing, vol. 6, No. 2, 1951, pp. 131–135.

Liquid thermal diffusion is a process in which a mixture of liquids is passed through the slit formed by 2 smooth, parallel surfaces in close proximity of about 1/32 or 1/16 in. One of the surfaces is heated, and the other is cooled so that a temperature gradient exists across the slit. Because of the temperature gradient and the thermal convection currents set up in the liquid, some types of molecules preferentially concentrate near the hot wall and are moved to the top of the slit while other types concentrate near the cold wall and are moved to the bottom of the slit. The exact mechanism is not known as yet. It appears, however, that the direction and degree of concentration are dependent upon the relative shapes of the molecules present in the mixtures. Separations can be made of compounds having the same molecular weights or identical boiling points. Even isomers have been separated. The effects of variables such as column height, slit width, and temperature are discussed. The process is covered by United States Patents 2,541,069, 2,541,070, and 2,541,071.

JONES, H. O. *See* abs. **700.**

JONES, H. R. *See* abs. **15a.**

1631. JONES, I. H. Gasification of Brown-Coal Briquets in Pintsch-Hillebrand Water-Gas Generators at Wesseling, Germany. FIAT Final Rept. No. 425, November 1945, 12 pp. PB 22,441.

Report on generators that were developed especially for employing brown-coal briquets formed from brown coals that have an ash that will not exhibit incipient fusion below about 1,290°–1,300°. Detailed information on the technical and constructional features is supplemented by a list of refractories and their properties.

———. *See* abs. **451, 452, 453.**

1632. JONES, J. P. Some German Solvent Extraction Developments. I. Nat. Petrol. News, Tech. Sec., vol. 38, No. 6, 1946, pp. R83–88. CIOS Rept XXXI–85, 1945, 73 pp., PB 1850.

Series of papers based on interviews with the Edeleanu G. m. b. H. describing the methods developed and used by it for the solvent extraction of low-temperature carbonization tar for the production of fuels and waxes. Of special interest is a paper presented by E. Terres, general manager, before the Deutschen Braunkohlen-Industrie Verein on The Use of Selective Solvents to Extract Fractions from Synthetic Oil from Coal (translated and introduced by Jones). This paper reviews the development of refinery methods using selective solvents, discusses the mechanism of selective solvent extraction and describes the procedure for the treatment of mineral oils, shale oil and tar. The selective treatment of the low-temperature-carbonization tar includes 3 principal stages: (1) Extraction of wax-containing fraction with SO_2; (2) extraction of the resulting SO_2 extract with naphtha after addition of the waxfree fraction; and (3) fractional separation of hard and soft wax with dichloroethane from the SO_2 raffinate after removal of SO_2.

1633. ———. Some Solvent-Extraction Developments in Germany. II. Nat. Petrol. News, Tech. Sec., vol. 38, 1946, pp. R181, 182, 184. CIOS Rept. XXXI–85, 1945, 73 pp. PB 1850.

Second part of this report discusses the separation of low-temperature carbonization tar distillate into raffinate and extract by means of SO_2 and the use of naphtha to separate the extract. Also described is the use of triangular coordinate graphs to supply data on the relationship between solvent, raffinate and extract phases necessary for commercial operations.

1634. ———. Some Solvent-Extraction Developments in Germany. III. Commercial Methods for Manufacturing Wax in Germany. Nat, Petrol. News,

Tech. Sec., vol. 38, No. 14, 1946, pp. R273, 274, 276, 278–279, 282; CIOS Rept. XXXI–85, 1945, 73 pp., PB 1850.

Both hard and soft wax were made by solvent extraction with SO_2 from tar distillate obtained by the low-temperature carbonization of brown coal and, to a limited extent, from shale oil. Centrifuging was used followed by 2-stage extraction also with SO_2. Dichloroethane was used in the dewaxing step. The extract solution from the tar distillate was processed into diesel fuel. A study was made of wax properties.

1635. ———. Some Solvent-Extraction Developments in Germany. IV. Continuous Band Filter to Produce an Oil-Free Hard Wax. Nat. Petrol. News, Tech. Sec., vol. 38, No. 18, 1946, pp. R344–346, R348; CIOS Rept. XXXXI–85, 1945, 73 pp., PB 1850.

Description with drawings is given of an entirely new type of commercial wax filter. This continuous band filter was developed by the GERMAN EDELEANU COMPANY to meet the wartime need for a commercial grade of hard wax substantially free from oil. The wax slurry was treated with one or more portions of solvent, the liquid being removed by suction from the bottom of moving pans. The entire filter was enclosed in a pressure shell. Also described is a supplementary straight-line graph method for recording and evaluating data from the solvent extraction of oils. This method was found to supply information on raffinate and extract solutions not obtainable through the more familiar triangular coordinate system discussed previously. A method was also developed and described in this article for determining the wax content of a wax-oil mixture by measuring the amount of polarized light which will pass through a thin layer of the mixture. The method is based on the fact that wax crystals are doubly refractive while oil is not.

———. *See* abs. **1478, 1479, 1496.**

1636. JONES, N. C. Activation of Halogen and Carbon Monoxide. Jour. Phys. Chem., vol. 33, 1929, pp. 1415–1427; Chem. Abs., vol. 24, 1930, p. 275.

Charcoal activates Cl and Br but does not activate CO, H_2, or O_2 to any appreciable extent. HBr was made rapidly by passing a current of H_2 containing Br over charcoal (99.3% conversion at 200°). In the $COCl_2$ synthesis over charcoal Cl is activated, but CO is not, since neither H_2CO nor MeOH could be synthesized from CO and H_2 over charcoal, nor could CO_2 be made from CO and O_2 over charcoal. Hopcalite activates O_2 but does not activate either CO or H_2. No reaction between CO and H_2 could be observed but CO, H_2, and benzene are easily burned with air over hopcalite. Although benzene seldom burns until the temperature attains 490°, over hopcalite benzene vapor burns completely to CO_2 and H_2O at 78°. Evidence is presented that CO is a better reducing agent than H_2 by a margin of 30°–50°. Neither Fe nor Ni activates CO at a point where it reacts with molecular H_2. CO must be essentially electropositive in character, since it reacts much more readily with O_2 and Cl than it does with H_2, even when all 3 of the latter gases are activated. CO reacts only with activated monatomic H and not with molecular H_2. CO does not react with electronegative H_2 at a temperature lower than 500°. With CaH_2 at this temperature CO gives the same reaction that is produced by CO_2. This work supports the theory of Fischer and Tropsch (abs. **1018** and abs. **1021**) for the mechanism of the hydrogenation of CO at ordinary pressure.

JONNARD, A. *See* abs. **619a.**

1637. JORDAN, R. E. Gas Liquefaction and Synthesis Under Pressure. Synthesis of Ammonia and Methanol. Proc. World Eng. Cong., Tokyo, 1929, vol. 31, 1931, pp. 139–152; Chem. Abs., vol. 25, 1931, p. 5253.

Claude process for the purification of coke-oven H_2 and synthesis of NH_3 and CH_3OH are described.

1638. JORGENSEN, S. M. Pressure-Vessel-Design Calculations. Petrol. Refiner, vol. 24, No. 10, 1945, pp. 381–384; Chem. Abs., vol. 40, 1946, p. 3.

Numerous equations and formulas are listed for calculating combined loads on pressure vessels.

1639. JORIS, G. G., AND TAYLOR, H. S. Exchange Reactions of Nitrogen Isotopes on Iron and Tungsten Surfaces. Jour. Chem. Phys., vol. 7, 1939, pp. 893–898; Chem. Abs., vol. 33, 1939, p. 9128.

Activities of Fe synthetic–NH_3 catalysts and of W filaments in promoting the reaction between N_2^{15} and N_2^{14} were studied from room temperature to 725° with Fe and to 900° on W. In contrast to the exchange reaction of molecular H_2 isotopes, the exchange reaction of N_2 molecules is very slow, being first measurable above 450°. The exchange is accelerated by the presence of H_2. The exchange involves, as the slow process, either the rupture of valence bonds of adsorbed molecular N_2 on the surface or migration of N atoms over the surface, and that H_2 accelerates such processes. The temperature coefficient of exchange in a N_2 : 3 H_2 mixture is about 50 kcal. The data suggest that measurements of the velocity of N adsorption at about 400° on synthetic–NH_3 catalysts are measurements of true activated adsorption.

JOSEPH, T. L. *See* abs. **3370.**

JOUBERT, D. B. *See* abs. **1743.**

1640. JOURNAL of the FUEL SOCIETY OF JAPAN. Synthetic Benzine. Vol. 13, 1934, pp. 3–4; Brennstoff-Chem., vol. 15, 1934, p. 132.

Survey of Japanese work on benzine synthesis from CO and H_2 at ordinary pressure. Especially considered is the work of Fujimura and Tsuneoka who have obtained with a Ni–Mn–Th catalyst a maximum yield of 137 cc. of liquid products per $m.^3$ of mischgas. Tsutsumi was able with a catalyst (no specifications given) to increase the yield to 155 cc. per $m.^3$

1641. ———. Production of Gasoline by the Fischer Process. Vol. 15, 1936, p. 89.

Mitsui Trading Co. and the Mitsui Mining Co. will erect a plant of 10,000,000 gal. annual capacity in the spring of 1937 at the Miike colliery for producing gasoline by the Fischer process. On completion of this plant, a large-scale plant will be constructed in Hokkaido.

1642. ———. Japanese Plant. Vol. 16, 1937, p. 49.

Mitsui Trading & Mining Co. will erect new Fischer-Tropsch synthesis plants in Manchukuo and North China in addition to the one at Miiki. An annual production is planned of 85,800,000 gal. of motor fuel and 250,600,000 gal. of heavier oils by the Fischer-Tropsch process.

1643. ———. Studies on Gasoline Synthesis. Vol. 16, 1937, pp. 10–11; vol. 17, 1938, p. 29.

Review touching upon the research on catalysts and the influence of reaction conditions on the yield and composition of the oils obtained in the Fischer-Tropsch process.

1644. ———. Production of Synthetic Petroleum From Coke-Oven Gas. Vol. 17, 1938, p. 74.

Showa Steel Co. has decided to produce petroleum from coke-oven gas by the Fischer process. A production of 200,000 tons per year is contemplated.

1645. ———. Oil in Japan. Vol. 18, 1939, p. 7; Fuel, vol. 19, 1939, p. 99.

Synthetic-oil industry is expanding radiply. 2 plants employing the Fischer process are nearing com-

pletion at Miike and Chinchou. Their combined output will be 60,000 tons of synthetic gasoline per year. The Hokkaido Artificial Petroleum Co. will construct a plant with an annual production of 140,000 tons of synthetic oil. This is to be completed by the end of 1940. Research is in progress, and it is stated that satisfactory yields of hydrocarbons, free from O_2 compounds, have been obtained at initial pressures of 40 atm., using a catalyst of Co–ThO–kieselguhr.

1646. JOURNAL OF THE SOCIETY OF CHEMICAL INDUSTRY (JAPAN). Synthetic Petroleum Industry in Japan and Manchoukuo. Vol. 43, 1940, suppl., pp. 265–266.

Patents of the Fischer-Tropsch process were bought through the Mitsui Trading Co. in 1936, and a full-size pilot plant situated at Miike started operation in June of this year. 3 larger plants are now under construction at Hokkaido, Amagasoki, and Chinchow.

JOVITSCHITSCH, M. Z. *See* abs. **2142.**

1647. JULIARD, A., RAYET, R., AND LUDE, A. Kinetic Study of the Dissociation of Carbon Monoxide Accompanying the Reduction of Metallic Oxides. Disc., Faraday Soc., 1948, No. 4, pp. 193–196; British Abs., 1950, B, I, p. 415.

Kinetics of the reduction of NiO and Fe_2O_3 by CO have been examined by simultaneously measuring, as functions of time, the rates of oxide reduction and of CO dissociation. Absolutely pure Ni does not catalyze CO dissociation. Ni charged with H_2 catalyzes the dissociation probably on account of C nuclei formed by reduction of CO by traces of active H adsorbed on Ni crystallites. In the Fe system the Boudouard reaction does not occur under conditions unfavorable to the formation of metallic Fe. CO dissociation apparently requires the presence of an interfacelike Ni or NiO or Fe–Fe_3C or the prior formation of C nuclei.

JUNGE, C. H. *See* abs. **3146.**

JUNGERS, J. C. *See* abs. **695, 2153, 2460, 2461, 3398.**

1648. JUNGERS, J. C., AND COUSSEMANT, F. [Effect of Adsorption on the Course of Catalytic Reaction.] Jour. chim. phys., vol. 47, 1950, pp. 139–144; Chem. Abs., vol. 44, 1950, p. 10,441.

Kinetics of gas-phase and liquid-phase catalytic reactions are interpreted in terms of the relative adsorptions of reactants and products. Reactions discussed include the hydrogenation of CO and CO_2 to CH_4 over Ni (abs. **2153, 2460**), of C_6H_6 to cyclohexane in the presence of CO_2 (abs. **2461**), of acetone to isopropyl alcohol; C_2H_2 to C_2H_4 (abs. **695**), and the dehydrogenation of a secondary alcohol to a ketone (abs. **3398**). The hydrogenation of PhOH to cyclohexanol takes place through the intermediate formation of cyclohexanone. A quantitative evaluation of the adsorption coefficients and the several reaction velocity constants is made. Similarly, the hydrogenation of naphthalene to decahydronaphthalene takes place through the formation of 1,2,3,4-tetrahydronaphthalene. Intermediates in the hydrogenation of C_6H_6 to cyclohexane are not detected. The possible use of C_2H_2, CO_2, or other compounds as acceptors for H_2 in dehydrogenation catalysis is discussed.

JÜNGLING, K. *See* abs. **207.**

JUSTICE, J. L. *See* abs. **3240.**

JUZA, R. *See* abs. **1948, 2483.**

1648a. JUZA, R., AND PUFF, H. [Crystal Structure of Cobalt Carbide.] Naturwissenschaften, vol. 38, 1951, pp. 331–332; Chem. Abs., vol. 46, 1952, p. 2,870.

Co_2C crystallizes in the rhombic system; a=2.885, b=4.454, c=4.360 A; 2 CO_2C in the unit cell, d_r=7.76; space group $D\ 2^{14}_h$; 4 Co in 4 cOy ¼ with y=0.158. The structure is a rhombically deformed dense hexagonal packing. Close agreement with these results is obtained by recalculation of data of Hofer and Peebles (abs. **1440**).

1649. JUZA, R., AND SACHSZE, W. [Metal Amides and Metal Nitrides. XII. The System Nickel–Nitrogen.] Ztschr. anorg. Chem., vol. 251, 1943, pp. 201–212; Chem. Abs., vol. 37, 1943, p. 6175.

Nickel nitride, Ni_3N, theoretical N content 7.37%, was prepared by passing a rapid stream of NH_3 over 10–20 mg. of Ni powder, prepared from Ni $(CO)_4$, at 445° for 3 hr. It was also prepared from $NiF_2.2\ NH_4F$ and $NiBr_2$ but there is no particular advantage in using the halides. The nitride is tested for metallic Ni contamination by testing in a magnetic field of 11,000 gausses strength. Ni_3N is a black-gray material, easily ground in an agate mortar, and is stable to O_2 and moisture. NaOH solution has no action either hot or cold. Acid solutions and acids react slowly to explosively, depending on concentration and temperature. The density at 25° was 7.66 which is lower than the calculated density of 7.91 from x-ray data. X-rays showed hexagonal close packing of the Ni atoms, with lattice constants, a 2.664, c 4.298, and c a 1.613. The structure agrees with the ϵ-phase of Fe_2N. The N atoms are located at the center of an octahedron of Ni atoms, at a distance of 1.877 from the Ni atoms, and 3.423 from the other N atoms. The N atoms are interstitial and the structure differs completely from that of Cu_3N. From an x-ray study it is estimated that the solubility of N_2 in Ni does not exceed 0.07% by weight.

1650. HAHN, H., AND MÜHLBERG, H. [Metal Amides and Metal Nitrides. XX. The System Iron–Nickel–Nitrogen.] Ztschr. anorg. Chem., vol. 259, 1949, pp. 121–134; Chem. Abs., vol. 44, 1950, p. 992.

Alloys of Fe and Ni containing 10, 20, 30, 40, 50, 60, 70, 80, 90, and 95 at. % Fe were nitrided at 300°–1,000° in a stream of NH_3. The optimum temperature range for uptake of N was 350°–600°. The weight % N in the nitrided alloys varies linearly with the atomic % Fe. The uptake of N can be increased further by pretreatment of the alloy with NH_3 at 600°–800°, quenching to room temperature, and finally prolonged nitriding at 400°–500°. For alloys treated this way which contain 50% Fe or more, the % N again varies linearly with the % Fe; with alloys containing less Fe, the % N approximates that for Fe_4N. Debye–Scherrer diagrams were made of the pure and nitrided alloys. There were 2 alloy and 2 nitride phases found. A cubic face-centered alloy (I) occurs in alloys containing 10–70% Fe and is the only phase if the % N is below 5. This phase resembles γ–Fe in dissolving N with an increase in the lattice constant a. A cubic body-centered alloy phase (II) is stable for Fe above 70%, N up to 3%, and at nitriding temperatures up to 450°; above 450° it changes to (I) with a greatly enlarged lattice. Like α–Fe, (II) takes up only very little N in solid solution. A cubic face-centered nitride phase (III) is stable up to 70% Fe, while above this a hexagonal nitride phase (IV) also occurs. (III) corresponds to Fe_4N with some of the Fe replaced by Ni. The constant a increases with % N and its increase with the % Fe parallels that for the pure alloys. (IV) resembles Fe_2N except that a little of the Fe is replaced by Ni. The decomposition temperatures of the nitrided alloys are low, ranging 360°–500° with increase in the % Fe.

K

KADOTA, N. *See* abs. **2205.**

1651. KAFUKU, K., AND OGURA, T. Reaction Between Methane and Water Vapor. Jour. Chem. Soc. Japan, vol. 56, 1935, pp. 1145–1159; Chem. Abs., vol. 30, 1936, p. 1542.

Yield of H_2 and CO from CH_4 and H_2O vapor was best by using Ni as catalyst with low pressure and high temperature, 5 mm. and 1,000°. Use of Ni with Al_2O_3, MgO, or pumice was more effective.

1652. KAGAN, G. B., AND LITVIN, M. Z. [Gasification of Low-Grade Fuels with a Steam-Oxygen Mixture Under Pressure.] Khim. Tverdogo Topliva, vol. 8, 1937, pp. 1155–1165; Chem. Abs., vol. 32, 1938, p. 4309.

Lurgi process for gasification of Aleksandriiskii brown coal, peat, and anthracite was investigated. The steam–O_2 mixture should contain 75% steam for brown coal and peat and 85–90% for anthracite. A gas of calorific value 4,500 cal. per $m.^3$ can be obtained. The cracking of tar formed in the low temperature carbonization zone affected the composition of the gas. The gas with highest calorific value was obtained in the gasification of bituminous fuel. The fuel containing ash up to 30% and moisture 25–30% can be used for the gasification. 12 refs.

1653. KAGAN, M. Y., MOROZOV, N. M., AND PODUROVSKAYA, O. M. [Sorptive Properties of Mixed Catalysts. I. Sorption of Ammonia on Synthetic-Ammonia Catalysts in Connection with the Function of Promoters.] Jour. Phys. Chem. (U. S. S. R.), vol. 8, 1936, pp. 677–688; Chem. Abs., vol. 31, 1937, p. 2078.

Pure Al_2O_3 has a high adsorptive capacity for NH_3 up to 600°–700°, with a heat of adsorption of 30 cal. per mol. for 2 $cm.^3$ per gm. Al_2O_3, or 18 cal. for 6 $cm.^3$ per gm. of Al_2O_3. In the adsorption layer at 500°, NH_3 breaks up into H and a surface-bound radical. Addition of K_2O to the Al_2O_3 decreases the sorptive capacity and the heat of adsorption to about ⅔. Fe additions also decrease adsorption to about ⅓, with a smaller effect at higher temperatures.

KAGAN, Y. B. *See* abs. **152, 152a.**

KAGANOVA, E. M. *See* abs. **2714.**

1654. KAINER, F. Di5. Kohlenwasserstoff-Synthese nach Fischer-Tropsch. Springer-Verlag, Berlin, Germany, 1950, 322 pp.; rev. in Chem. and Eng. News, vol. 29, No. 28, 1951, pp. 2860, 2862.

This book is based to a great extent on patents and patent applications issued during the development of the hydrocarbon synthesis. The value of these patent references could be increased, however, by mentioning their dates of application and publication. No attempt is made to compare, critically, results of research work done by different researchers or to contribute substantially to the theories or to explain the mechanism of the involved reaction. Any revision of this book should contain more data regarding the basic facts of the synthesis and fewer data on the preparation of specific, and for a great part on relatively unimportant, catalysts (45 pp. are given over to kieselguhr catalysts). The section (73 pp.) on synthesis products presents considerable useful information on the different methods used in Germany for recovering and refining the synthesis products and further shows that hydrocarbon synthesis is not only of importance for the manufacture of liquid fuels but for the production of raw materials for many other industrial processes.

1655. KAISER WILHELM INSTITUT FÜR KOHLENFORSCHUNG. [Report of the Middle-Pressure Synthesis With Iron.] June 1940, 75 pp.; OTS Bib. Tech. Rept., vol. 12, No. 6, 1949, p. 228; PB 98,743.

Survey is made of work carried out on the middle-pressure synthesis with Fe catalysts. Precipitation, alkalization, induction, synthesis-gas production, apparatus, pelleting of catalyst, and further processing of primary products are discussed. This report appears to be the same as H. Pichler, TOM Reel 49, frames 541–662, June 1940, Bureau of Mines Transl. T–424, December 1947, and TOM Reel 101, first 48 pp., trans. by M. Leva.

1656. ———. [Direct Synthesis of Isoparaffins From CO and H_2.] TOM Reel 134, Item IV–3, December 1942; TOM Reel 259, Item 20, frames 1055–1071.

It was discovered that catalysts based on Th are particularly well suited for the synthesis of branched hydrocarbons from CO and H_2. The best Th catalysts are produced by precipitation of Th salt solutions, generally by precipitation of the basic carbonate by Na_2CO_3 from the nitrate solutions. The lifetime of the Th catalyst is very long under the conditions of isosynthesis and can easily be regenerated. A water gas of $CO : H_2$ ratio of 1 : 1–1.2 : 1 is used for the synthesis. The type of reaction products obtained is dependent on certain conditions such as composition and method of production of the catalyst, the temperature and pressure, the residence time of the gas in the catalyst space, operation in 1 or more stages, the material of the reaction tubes, etc. With a pressure of 150 atm. and a flow rate of the gases corresponding to 10 l. final gas per hr. per 28 gm. catalyst, the amount of alcohol and other O_2-containing compounds, which prevail below 375°, decreases rapidly with rising temperature. Mostly liquid branched aliphatic hydrocarbons are formed, 375°–425°. With rising temperature, the amount of naphthenes gradually increases, reaching 50% at 450°–460°. Between 450° and 500° aromatics are identified. The amount of gaseous products increases from less than 10% at 375° to 50% at 440°, with isobutane the highest, and at 450°–460° ⅓ of the total products consists of this hydrocarbon. Unbranched aliphatic hydrocarbons appear in only very small amounts. N-butane results in amounts of about 10% of the isobutane. With a constant temperature of 450°, the reaction begins at 6 atm. pressure and at 30 atm. a 22% conversion of the CO takes place with a production of 5.1 gm. C_3+n-C_4, 5.4 gm. iso–C_4 and 16.1 gm. liquid hydrocarbons/$N-m.^3$ entering gas. The amount of products from a single operation increases with rising pressure, reaching at 500 atm. 46.5 gm. iso–C_4 and 40.5 gm. gasoline plus oil. The yield of liquid hydrocarbons was greater with V_2A stainless-steel pipes than with Cu pipes. The conversion of CO increases with rising pressure in a single operation, likewise at 50–100 atm., providing several operations instead of 1 are performed. Graphical and tabular data show the influence of temperature and pressure on the type and yield of products, as well as their distillation range and the composition of the various fractions. The composition of the reaction products can be varied within rather wide limits by choosing the synthesis conditions. The gasoline obtained at 450° and 150 atm. and hydrogenated had an octane number, after adding 0.08 vol. % of Pb, of 95; at 370° and 150 atm. 89.6%.

KALLENBERG, S. *See* abs. **2336.**

KALLENBERGER, R. H. *See* abs. **576.**

1657. KALLING, B. Use of Oxygen in Metallurgical and Other Thermochemical Processes. Iva, vol. 19, 1948, pp. 44–59; Chem. Abs., vol. 42, 1948, p. 6291.

Reviews cost of production of O_2 and its uses in metallurgy and in production of synthesis gas.

KALYANASUNDARAM, A. *See* abs. **3013.**

KAMIIKE, O. *See* abs. **2414, 2415, 2416, 2417, 2418, 2419, 2421, 2422, 2423, 2424, 2425, 2426.**

KAMIIKE, O., KATAOKA, S., NIBAYASHI, M., AND NEGISHI, R. Hydrocarbons From Carbide. II. Non-catalytic Polymerization Under Ordinary Pressure—Analysis and Liquid Products. *See* abs. **2420.**

1658. KAMURA, H. Reduction of Ferric Oxide and Iron Ores by Hydrogen. Jour. Iron Steel Inst., vol. 112, II, 1925, pp. 279–298; Chem. Abs., vol. 19, 1925, p. 3451.

Samples of pure Fe_2O_3 and of hematite were heated to 500°–800° in a combustion tube, and H_2 was passed over them, the volume of gas used and the % of reduction to Fe being recorded at definite time intervals. At 500° the time required for 90% reduction of the hematite was 78 min.; at 600°, 46 min.; at 700°, 39 min.; and at 800°, 30 min. The volume of H_2 used also decreased with rise of temperature. At about 570° the velocity of reduction increased rapidly and the volume of H_2 decreased suddenly, probably because reduction below this temperature was from Fe_3O_4 to Fe and above it from Fe_3O_4 to FeO and FeO to Fe. As velocity of reduction increases slowly above 600°, this would be the most economical reduction temperature.

1659. KAMZOLKIN, V. P., AND LIVSHITZ, V. D. [New Method for Obtaining Ammonia Catalysts From Natural Ural Magnetite.] Jour. Chem. Ind. (U. S. S. R.), vol. 13, 1936, pp. 398–401; Chem. Abs., vol. 30, 1936, p. 4630.

Ore is fused with Al_2O_3 and excess KNO^3, ground, and separated magnetically. Enough Fe is added to form Fe_3O_4, and the mixture is fused and separated as before. This treatment reduces the amount of SiO_2 to 0.5%.

1660. ———. Effect of Different Conditions of Reduction on the Activity and Structure of Iron Ammonia Catalysts. Jour. Chem. Ind. (U. S. S. R.), vol. 14, 1937, pp. 93–98; Chem. Abs., vol. 31, 1937, p. 3217.

Time required for reduction is very important. A natural magnetite should be reduced for 46 hr., an artificial one for 32 hr. These reductions are best run at 400°, 150 atm. and not too high a rate of gas flow.

1661. ———. [Poisoning Action of Water Vapor on Iron Catalysts for the Synthesis of Ammonia.] Jour. Chem. Ind. (U. S. S. R.), vol. 14, 1937, pp. 244–249; Chem. Abs., vol. 31, 1937, p. 4777.

H_2O poisons all Fe catalysts, but its action is stronger on less active catalysts. Poisoning is greater at higher pressures and lower temperatures. It is due to destruction of active centers on the catalyst surface.

1662. KAMZOLKIN, S. P., LIVSHITZ, V. D., and KOZHENOVA, K. T. [Reduction of Catalysts for the Synthesis of Ammonia.] Jour. Chem. Ind. (U. S. S. R.), vol. 12, 1935, pp. 687–690; Chem. Abs., vol. 29, 1935, p. 8244.

If the reduction is run at a temperature and pressure as low as possible, a more efficient catalyst is obtained.

KAN-KOGAN, K. I. *See* abs. **282.**

1663. KANTOROVICH, B. V. [Effect of Gas Pressure and Concentration on the Length of the Reaction Zone in Heterogeneous Processes.] Doklady Akad. Nauk S. S. S. R., vol. 71, 1950, pp. 315–318; Chem. Abs., vol. 44, 1950, p. 9220.

Mathematical equations are derived for several reaction conditions involving layers of solid particles or materials suspended in flames of reacting gases. Conclusions are: (1) For first-order reaction in a layer of solid particles, x, the length of the reaction zone, is independent of pressure in the kinetic region but directly proportional to pressure in the diffusion region; in either region, x is independent of the relative weight concentration of gas. (2) For first-order reaction in a stream of powdered material, x is inversely proportional to pressure in the kinetic region but independent of pressure in the diffusion region; in either region, x is inversely proportional to the relative weight concentration of reactive gas. (3) In reactions accompanied by a volume increase occurring in a layer of solid particles, x is independent of pressure in the kinetic region but is directly proportional to pressure in the diffusion region; x increases with increasing initial volume concentration. (4) In reactions accompanied by a volume increase occurring in a stream of powdered material, x is inversely proportional to pressure in the Kinetic region but independent of pressure in the diffusion region; x decreases with increasing initial volume concentration.

KAPPELMACHER, E. *See* abs. **2620a.**

1664. KAPUSTINSKIĬ, A. F., AND GOFMAN, E. [Equilibrium in the Reduction of Cobalt Oxide by Carbon Monoxide.] Jour. Phys. Chem. (U. S. S. R.), vol. 9, 1937, pp. 713–715; Acta Physicochim. U. R. S. S., vol. 6, 1937, pp. 487–490; Chem. Abs., vol. 31, 1937, p. 8329.

Over the range 993°–1,393° abs., the equilibrium is given by $\log K = -(1/R)\ [(-17.005/T) - 8.06 \log T + 0.00254\ T - 0.063\ T^2 + (38{,}100/T^2)] + 31.78$. The value of the free energy from the experimental data was $\Delta F_{208} = 11{,}400$ cal., as compared to the value 10,918 cal. calculated from data given by Emmett and Shultz (abs. **833**).

KARPINSKIĬ, M. N. *See* abs. **726, 727, 729, 1796.**

1665. KARPOV, A. Z. [Synthesis of Methanol From Carbon Dioxide and Hydrogen.] Org. Chem. Ind. (U. S. S. R.), vol. 6, 1939, pp. 574–577; Chem. Abs., vol. 34, 1940, pp. 5047, 6929.

MeOH is obtained in good yield by passing CO_2–H_2 mixture over a Zn–Cr–Ni catalyst at 370°. The gas from $COMe_2$–BuOH fermentation contains traces of S compounds, which inactivate the catalyst; such gases may be purified by passing over active C.

———. *See* abs. **724, 728, 3557.**

1666. KARZHAVIN, V. A. [Low-Temperature Conversion of Methane.] Jour. Chem. Ind. (U. S. S. R.), vol. 10, No. 2, 1934, pp. 31–33; British Chem. Abs., 1934, B, p. 611; Chem. Abs., vol. 28, 1934, p. 3873.

Complete conversion of CH_4 and H_2O into CO_2 and H_2 at 500°–600° is possible only when the CO_2 produced is immediately removed from the reaction gases by CaO. The reaction is catalyzed by Ni, which is, however, rapidly inactivated by traces of S in the gas.

1667. ———. Natural Gas. Conversion to Carbon Monoxide and Hydrogen. Ind. Eng. Chem., vol. 28, 1936, pp. 1042–1044; Chem. Abs., vol. 30, 1936, p. 6923.

Process of converting natural gas to CO and H_2 by the use of steam is tested on a commercial scale by heating natural-gas–steam mixtures in regenerative apparatus packed with grog, then passing over a Ni catalyst. The CH_4 content of the resultant gas was 0.8%. For conversion, 1.9 $m.^3$ of steam is added to 1 $m.^3$ of natural gas, producing 3.3 $m.^3$ of gas, containing H_2 64 and CO 22%, respectively. Total consumption of natural gas per $m.^3$ of pure N_2–H_2 mixture is 0.44 $m.^3$, including gas used for conversion and for heating. 1 $m.^3$ of reaction chamber space gives 24 $m.^3$ of converted gas per hr.

1668. ———. [Catalytic Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Uspekhi Khim., vol. 15, No. 3, 1947, pp. 327–352; Chem. Eng., vol. 55, No. 7, 1947, pp. 276–277.

Critical review, with 59 refs.

1669. ———. [Heat Transfer in Apparatus for Catalytic Synthesis of Hydrocarbons and Water Gas.]

Khim. Prom., 1947, No. 5, pp. 14–19; Chem. Abs., vol. 43, 1949, p. 2343.

Method for calculating the heat transfer in catalytic synthesis of hydrocarbons from CO and H_2. This method is applicable to both tubular and plate reactors. The temperature varies considerably along the catalyst, and for best results, the cooling should be adjusted to the conditions of each particular sector of the catalyst.

1670. KARSHAVIN, V. A., AND LEIBUSH, A.-G. [Continuous Process for Conversion of Gases Containing Methane and Other Hydrocarbons.] Jour. Chem. Ind. (U. S. S. R.), vol. 10, No. 1, 1934, pp. 34–38; U. O. P. Co. Survey Foreign Petroleum Literature, Transl. S–396, 1946; British Chem. Abs., 1934, B, p. 611.

Hydrocarbon constituents are converted into CO and H_2 by passing the gas, mixed with air, over Ni at 1,000°–1,100°; at lower temperature the Ni is inactivated by 0.2–0.25% of S in the reaction gases.

1671. KARSHAVIN, V. A., BOGUSLAVSKI, I. M., AND SMIRNOVA, Z. M. [Catalysts for Methane Conversion.] Jour. Chem. Ind. (U. S. S. R.), vol. 10, No. 8, pp. 31–40, 1933; U. O. P. Co. Survey Foreign Petroleum Literature Transl. S–394–A; British Chem. Abs., 1934, B, p. 82.

Process of conversion of CH_4–H_2O mixtures into CO and H_2 is best catalyzed by fireclay containing 6.4% of reduced Ni at 1,000°. The activity of the catalyst is increased by up to 1% MgO and diminished by more than 1% MgO. Loss of Ni as $Ni(CO)_4$ and inactivation by formation of carbide are virtually negligible. H_2S and organic S compounds, initially, slightly depress the activity, which then remains constant. Deposition of soot takes place to an extent, increasing with the content of higher hydrocarbons in the mixture.

1672. KARŽHAVINA, N. A. [Catalytic Formation of Methane From Carbon Monoxide in Industrial Gases.] Jour. Chem. Ind. (U. S. S. R.), vol. 13, 1936, pp. 598–602; Chem. Abs., vol. 30, 1936, p. 6534.

CH_4 cannot be profitably produced from ordinary blast-furnace gas, but if the gas has been produced by blowing O_2 into the furnace, a gas can then be obtained containing up to 60.6% CH_4, after adsorption of CO_2. The best catalyst for the conversion with steam consists of 84% Ni and 16% Al_2O_3, at about 400°.

1673. KARZHEV, V. I., AND SEVER'YANOVA, M. G. [Catalytic Cracking of the Synthin Fraction.] Khim. Tverdogo Topliva, vol. 9, 1938, pp. 71–76; Chem. Abs., vol. 32, 1938, p. 9436.

Synthin fractions boiling at 80°–150°, 150°–200°, and 200°–250° were introduced from burettes by drops into a quartz tube placed in an electric furnace. The catalysts were placed in the tube in a 25-cm. layer in that portion of the tube that had a constant temperature. The product was passed through with a constant velocity of 5 $m.^3$/hr. The temperature of experiments was varied within the range 475°–550°. The following catalysts were used: Cr–Cu–P, H_3PO_4, activated coal as a carrier, Cr–Cu and Cr prepared by special method (not disclosed) the best being the last catalyst. The catalytic cracking of various fractions of synthin over the above catalyst at 475°–525° at atmospheric pressure yielded about 85–90% of liquid products and 10–15% of gaseous products. The practical formation of coke was not observed. The composition of the products obtained justifies the assumption that they have a high octane number.

KASAI, K. *See* abs. **1904.**

1674. KASE, T. Equilibrium Diagram of the Iron–Carbon–Nickel System. Sci. Repts. Tôhoku Imp. Univ., vol. 14, 1925, pp. 173–217; Chem. Abs., vol. 20, 1926, p. 570.

Thermal and magnetic analyses, hardness tests, and microscopic examinations are reported for the Fe–Ni system, and the binary equilibrium diagram is concluded to be of the solid-solution type. The A_3 change falls steadily with increasing Ni content down to −190° at 35% Ni and occurs in a temperature interval rather than at a point. Ni dissolves C up to 0.55%, forming a eutectic with C at 1318° and 2.22% C. Ni_3C is very unstable and cannot be detected with the microscope. The ternary diagram was worked out and is described and illustrated by a sketch of a model. Photomicrographs of typical structures also are shown. For etching specimens with over 25% Ni either strong HNO_3 or hot HCl was used. No ternary eutectic was found. A binary eutectic contains 4.3% C with no Ni and decreasing C down to 0.3% with increasing Ni up to 30%. Cementite occurs in the ternary alloys with 0 to about 30% Ni, with over 0.1% C. With increasing Ni, the A_1 transformation is lowered and is difficult to detect with over 10% Ni, but is almost independent of the C content. With increasing Ni, the A_2 and A_3 points are rapidly lowered, and the C content at the eutectoid point decreases down to 0.3% at about 35% Ni. 6 plates of curves accompany this paper.

1675. KASHIMA, S. Synthetic Methanol as a Fuel Substitute. Jour. Fuel Soc. Japan, vol. 15, 1936, pp. 57–59.

From the results of practical tests it is concluded that it is possible to use MeOH as a fuel for gasoline engines if the fuel : air ratio is increased. Since MeOH has a low calorific value, best results in lowering the fuel consumption are obtained by blending about 50% of benzol or gasoline with it. Compared with gasoline, the merits of MeOH are its high antiknock property and low freezing point, and its disadvantages are its high heat of vaporization and low calorific value.

1676. KASSEL, L. S. Limiting High-Temperature Rotational Partition Function of Nonrigid Molecules. VI. Methanol Equilibrium. Jour. Chem. Phys., vol. 4, 1936, p. 493–496; Chem. Abs., vol. 30, 1936, p. 6250.

Entropy of MeOH and the equilibrium constant for MeOH synthesis are calculated for 2 mol. models: 1 rotates freely and the other has a torsional oscillation about the CO bond.

KASSLER, R. *See* abs. **3187, 3188, 3457.**

1677. KASTENS, M. L., DUDLEY, J. F., AND TROELTZSCH, J. Synthetic Methanol Production. Ind. Eng. Chem., vol. 40, No. 12, 1948, pp. 2230–2240.

History of synthetic methanol both here and abroad is sketched, figures on the production and price since 1898 are presented, and present producers are listed. The main emphasis is placed on a description of the Sterlington, La., plant of the Commercial Solvent Corp., which uses natural gas catalytically reformed into synthesis gas with the addition of some CO_2 as the raw material. The plant operates at about 5,000 p. s. i. g. and 400°, as compared with current practice of 2,200–14,700 p. s. i. g. and 250°–400°.

1677a. KASTENS, M. L., HIRST, L. L., and DRESSLER, R. G. An American Fischer-Tropsch Plant. Ind. Eng. Chem., vol. 44, 1952, pp. 450–466.

Gives construction and operation details of the gas synthesis demonstration plant at Louisiana, Missouri. Pulverized coal is gasified with steam and oxygen to produce a synthesis gas which reacts in an agitating bed catalytic reactor cooled by concurrent flow of heavy oil. Capacity of the plant is 50–80 bbl. per day of liquid products with a conversion efficiency of about 80%. The hydrocarbon products consist of 70% gasoline, 10% Diesel oil, 10% heavy distillate, and 10% waxes. Oxygenated compounds made up about 10%

of the total product. The following subjects are discussed: Gasification, slagging type vertical gasifier, the Koppers horizontal gasifier and the Kerpely generator; gas purification; Linde–Frankl oxygen plant; gas synthesis; Fe catalyst production; operating performance; materials of construction; possibilities of pressure gasification; and utility requirements.

KATAOKA, S. *See* abs. **2419, 2420, 2422.**

KATAYAMA, I. *See* abs. **1880, 1881.**

KATAYAMA, I., MURATA, Y., KOIDE, H., AND TSUNEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLI. Activation of Catalysts by Slow Oxidation With Atmospheric Oxygen. *See* abs. **1877.**

KATO, J. *See* abs. **1930.**

1678. KATTWINKEL, R. [Determination of Aromatic and Unsaturated Hydrocarbons in Benzine by Means of Sulfuric Acid.] Brennstoff-Chem., vol. 8, 1927, pp. 353–358; Chem. Abs., vol. 22, 1928, p. 3039.

Previous methods based on the solvent action of H_2SO_4 for aromatics and unsaturates are discussed. Kattwinkel determines aromatics+unsaturates in a 10 cc. sample by shaking with 30 cc. of a mixture of 30 gm. P_2O_5 in 100 cc. H_2SO_4 (d. 1.840). Unsaturates alone are determined by shaking the sample with a mixture of 5 gm. boric acid in 100 cc. H_2SO_4 (d. 1.840). The boric acid mixture does not dissolve aromatics; P_2O_5 in H_2SO_4 catalyzes sulfonation and thus aids solution of aromatics.

1679. KAUFMANN, H. P. Effecting Separation by Adsorption in the Field of Fats. I. Experiments With Mixtures of Fatty Acids. Fette u. Seifen, vol. 46, 1939, pp. 268–273; Chem. Abs., vol. 33, 1939, p. 6073.

On passing solutions containing 2 or more fatty acids through columns of adsorptive materials, for example, Al_2O_3 or silica gel, certain fatty acids are more strongly adsorbed; this makes possible a partial, or under suitable conditions, a complete separation. Applications of such adsorption methods being developed include: Analysis of fatty acid mixtures, isolation of naturally occurring, sensitive fatty acids and commercial processing of fatty acid mixtures to isolate more valuable fractions.

KAULAKIS, A. F. *See* abs. **2347.**

KAUPP, E. *See* abs. **805, 806.**

KAVERIN, I. B. *See* abs. **1806.**

1680. KAWAI, S. Synthetic Fatty Acid Industry. Chem. Rev. (Japan), vol. 7, 1941, pp. 117–120; Chem. Abs., vol. 35, 1941, p. 7744.

———. Manufacture of Fatty Acids by the Oxidation of Paraffin. VI. Treatment of Paraffin With Aqueous Alcohol and Its Influence on Oxidation. *See* abs. **1686.**

———. Manufacture of Fatty Acids by the Oxidation of Paraffin. XX. Example of an Oxidation Experiment. *See* abs. **1693.**

———. Manufacture of Fatty Acids by the Oxidation of Paraffin. XXII. Thermal Decomposition of Oxidation Products and Crude Fatty Acids. *See* abs. **1695.**

———. *See* abs. **1696.**

1681. KAWAI, S. and MORITA, K. Manufacture of Fatty Acids by the Oxidation of Paraffin. I. Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, p. 619; Chem. Abs., vol. 43, 1949, p. 9029.

1682. ———. Manufacture of Fatty Acids by the Oxidation of Paraffin. II. Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, pp. 702–704; Chem. Abs., vol. 43, 1949, p. 9029.

Oxidation product of Fushun oil-shale paraffin treated 3 hours with concentrated NaOH solution in an autoclave at 260°–310° under 60–120 atm. yielded crude fatty acids of very low ester value and low OH value. These values decreased with increasing reaction temperature and pressure.

1683. KAWAI, S. and NOBORI, H. Manufacture of Fatty Acids by the Oxidation of Paraffin. III. Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, pp. 803–806; Chem. Abs., vol. 43, 1949, p. 9029.

Oxidation product of Fushun oil-shale paraffin was analyzed; the amount of each of the fatty acids from C_7 to C_{22}, the total acids over C_{23}, and the amount of alcohol-soluble unsaponifiable matter were determined.

1684. HIROSE, S., NOBORI, H., AND NOGUCHI, M. Manufacture of Fatty Acids by the Oxidation of Paraffin. IV. Composition of Refined Fatty Acids. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 541–544; Chem. Abs., vol. 43, 1949, p. 9029.

Refined fatty acids were prepared as follows: Oxidized paraffin was saponified and the unchanged paraffin was removed. The saponified product was treated at high temperature and the unsaponified matter was extracted with C_6H_6. The crude fatty acids were then distilled under reduced pressure. Properties of the distillates are tabulated.

1685. ———. Manufacture of Fatty Acids by the Oxidation of Paraffin. V. Methanol-Soluble Portion of the Unsaponifiable Matter. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 544–545; Chem. Abs., vol. 43, 1949, p. 9029.

Saponification of the oxidized product was carried out in the presence of MeOH at high temperature and pressure. The MeOH soluble portion of the unsaponifiable matter contained most of the intermediate oxidation products. Unchanged paraffins were insoluble in MeOH.

1686. Kawai, S. Manufacture of Fatty Acids by the Oxidation of Paraffin. VI. Treatment of Paraffin with Aqueous Alcohol and Its Influence on Oxidation. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 834–836; Chem. Abs., vol. 43, 1949, p. 9029.

Shale-oil paraffin was soluble in 95% alcohol to the extent of 2.6%. The iodine value of the alcohol-soluble portion was greater than that of the original paraffin. When the paraffin was distilled, the solubilities in 95% alcohol and iodine values of the lower boiling fractions were greater than those of the higher fractions. The oxidation velocity of paraffins, from which the alcohol-soluble portion was removed, was greater than that of untreated paraffins.

1687. Kawai, S. and Nobori, H. Manufacture of Fatty Acids by the Oxidation of Paraffin. VII. Oxidation of Fractions Obtained by Distillation of Paraffin. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 986–987; Chem. Abs., vol. 43, 1949, p. 9029.

Shale-oil paraffin, melting 47.5° and I value 9.1, was fractionated into 3 portions: b_5 below 190°, b_{4-5} 190°–240°, and the residue. 50 gm. of each fraction was oxidized at 130° by passing 2 l. per min. of air for 20 hr. The middle fraction gave a product with an acid value of 95, while the other fractions were much more difficult to oxidize. The acids obtained from the middle fraction were best for practical applications.

1688. KAWAI, S., NOBORI, H. AND NOGUCHI, M. Manufacture of Fatty Acids by the Oxidation of Paraffin. VIII. Composition of Fatty Acids From Oxidation of the Middle Fraction of Paraffin. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1084–1085; Chem. Abs., vol. 43, 1949, p. 9029.

Fatty acids obtained by oxidation of the middle fraction of shale-oil paraffin acid separation by distillation as Me esters included acids from caprylic to arachidic. The yield of acids was 74–78%, mostly in the C_{14}–C_{17} range.

1689. KAWAI, S. AND NOBORI, H. Manufacture of Fatty Acids by the Oxidation of Paraffin. IX. Oxidation of Paraffins of High Boiling Points. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1175–1176. Chem. Abs., vol. 43, 1949, p. 9029.

Paraffins of high boiling points in shale oil from Bujun, Manchuria, were oxidized with air. The crude fatty acids were separated from the unsaponifiable portion, and their properties and compositions were determined.

1690. ———. Manufacture of Fatty Acids by the Oxidation of Paraffin. X. Oxidation of the Mixture of Paraffins and Fatty Acids. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 167–170; Chem. Abs., vol. 43, 1949, p. 9029.

Shale oil, melting 45.5° and I value 11.1, from Bujun, Manchuria, was mixed with various fatty acids, such as caprylic or stearic acid, and air was passed at 110°. Comparatively small amounts of the acids were oxidized. If oxidation was carried out at 130°, lauric acid and stearic acid were oxidized.

1691. ———. Manufacture of Fatty Acids by the Oxidation of Paraffin. XI. Oxidation of Crude Fatty Acids. XII. New Method for Acceleration of the Oxidation. XIII. Oxidation of Unchanged Paraffins and the Properties of the Fatty Acids Produced. XIV. Properties of the Unsaponifiable Compounds Formed by Oxidation of Unchanged Paraffins. XV. Oxidation of a Mixture of Paraffins and Fatty Acids. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 372–386; Chem. Abs., vol. 43, 1949, p. 9030.

Crude fatty acids separated from the oxidation product of shale-oil paraffin from Bujun, Manchuria, were oxidized. When the crude acid was heated at 130°–140°, its acid value increased, and OH value and the content of oxidized acid decreased. When it was heated at 140°–150°, the color changed to dark brown. When the crude fatty acid was oxidized at 120°–130° by air in the presence of 0.1% $KMnO_4$, its acid value decreased, saponification value increased, OH value decreased, and oxidized acid disappeared. At the same time the color turned to orange-yellow. When the oxidation product of the crude fatty acid was treated with alcohol, the portion with low acid value, low saponification value, and large OH value was insoluble and was thus separated. The free fatty acid obtainable from this portion by saponification contained a large amount of oxidized acid.

1692. ———. Manufacture of Fatty Acids by the Oxidation of Paraffin. XVI–XIX. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 636–645; Chem. Abs., vol. 43, 1949, p. 9030.

XVI. Oxidation of tricosane. Tricosane obtained by hydrogenating laurone was oxidized by air at 120° in the presence of Mn soap. The product contained all the fatty acids from hendecanoic acid to arachidic acid with some hydroxy acids. The unsaponifiable portion of the product contained about 20% MeOH soluble material which consisted mostly of alcohols. XVII. Oxidation of hentriacontane. Hentriacontane obtained by the hydrogenation of palmitone was oxidized by air at 110° with Mn soap as catalyst. The fatty acids obtained consisted of all the acids from undecanoic to tricosanoic. The unsaponifiable portion contained about 6% MeOH soluble material consisting of alcohols, carbonyl compounds, etc. The MeOH insoluble fraction was more easily oxidized than triacontane. XVIII. Oxidation of the methanol-insoluble fraction of the unsaponifiable portion. The MeOH insoluble fraction of the unsaponifiable matter obtained on 3 successive oxidations of Fushun shale-oil paraffin described in part XIV (abs. **1691**) was oxidized by air at 130°–160° with the addition of 0.1% $KMnO_4$. These fractions were easier to oxidize than the original paraffin. Crude fatty acids containing no hydroxy acids were obtained. XIX. Treatment of raw fatty acid with solvents. Crude fatty acid obtained from the oxidation of Fushun shale-oil paraffin was separated into petroleum ether-insoluble and ether-soluble portions. The soluble portion was further separated into portions insoluble and soluble in 85% alcohol. The petroleum ether-insoluble portion was converted to the Me esters, and 37% was distilled. The distillate was was assumed to consist of Me esters of hydroxy acids having similar numbers of C atoms. The 85% alcohol-insoluble portion consisted of higher saturated fatty acids. From the portion soluble in 85% alcohol no lactones, lactides or similar compounds could be obtained by distillation.

1693. KAWAI, S. Manufacture of Fatty Acids by the Oxidation of Paraffin. XX. Example of an Oxidation Experiment. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 762–764; Chem. Abs., vol. 43, 1949, p. 9030.

Distillate, b_3 200°–250°, from shale-oil paraffin was oxidized 22.5 hr. by 4 l./min. of air/800 gm. paraffin at 110°–120° to yield 22.2% crude fatty acids. Of the crude fatty acids, 8% are insoluble in petroleum ether. Of the fatty acids soluble in petroleum ether, 89% are soluble in 85% alcohol. The distillation test on the fatty acids soluble in alcohol was carried out, and the properties of the distillates were examined.

1694. KAWAI, S. AND NOBORI, H. Manufacture of Fatty Acids by the Oxidation of Paraffin. XXI. Oxidation of High-Boiling Fractions of Paraffin (Suppl.). Jour. Soc. Chem. Ind (Japan), vol. 46, 1943, pp. 764–765; Chem. Abs., vol. 43, 1949, p. 9030.

High-boiling fraction of shale-oil paraffin, melting 47.6° and I value 9.2, was oxidized by air, 2 l./min./50 gm., at 150°. The acid value did not increase after 10 hours. The formation of oxidized acids and lower acids occurred some time after the high-boiling fraction of paraffin was oxidized.

1695. KAWAI, S. Manufacture of Fatty Acids by the Oxidation of Paraffin. XXII. Thermal Decomposition of Oxidation Products and Crude Fatty Acids. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 1058–1062; Chem. Abs., vol. 43, 1949, p. 9030.

Three oxidation products of shale-oil paraffin of different degrees of oxidation and the 3 crude mixtures of fatty acids obtained from them were, respectively, heated in a retort with or without the addition of acid clay, etc., and the properties of the distilled oils were examined and compared. The highly oxidized product and the crude fatty acids obtained therefrom yielded a smaller amount of distilled oil than the other products. The amount of acid clay added had a great effect on the yield and properties of the distilled oil. With increasing amounts of acid clay, the specific gravity of the distilled oil diminished, and the yield decreased. An increase in I value and a decrease in OH value were also noticed. The yield of olefinic material was greatest when the medium-oxidized product, that is, paraffin oxidized 20 hours at 120°–130°, was slowly heated with the addition of 10% acid clay.

1696. NOBORI, H., AND KAWAI, S. Manufacture of Fatty Acids by the Oxidation of Paraffin. XXIII. Oxidation of High-Melting Paraffins. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 1211–1212; Chem. Abs., vol. 43, 1949, p. 9031.

Paraffin, melting 59.4°, I value 3.22, from Bujun, Manchuria, was oxidized by air at 120°. The oxidation products contained C_{16}–C_{21} fatty acids. The paraffins were most easily oxidized in the middle of the chain.

KAWAI, S., AND NOBORI, H. Manufacture of Fatty Acids by the Oxidation of Paraffin. VII. Oxidation of Fractions Obtained by Distillation of Paraffin. *See* abs. **1687.**

———. Manufacture of Fatty Acids by the Oxidation of Paraffin. IX. Oxidation of Paraffins of High Boiling Points. *See* abs. **1689.**

———. Manufacture of Fatty Acids by the Oxidation of Paraffin. X. Oxidation of the Mixture of Paraffins and Fatty Acids. *See* abs. **1690.**

———. Manufacture of Fatty Acids by the Oxidation of Paraffin. XI. Oxidation of Crude Fatty Acids. XII. New Method for Acceleration of the Oxidation. XIII. Oxidation of Unchanged Paraffins and the Properties of the Fatty Acids Produced. XIV. Properties of the Unsaponifiable Compounds Formed by Oxidation of Unchanged Paraffins. XV. Oxidation of a Mixture of Paraffins and Fatty Acids. *See* abs. **1691.**

———. Manufacture of Fatty Acids by the Oxidation of Paraffin. XVI–XIX. *See* abs. **1692.**

———. Manufacture of Fatty Acids by the Oxidation of Paraffin. XXI. Oxidation of High-Boiling Fractions of Paraffin (supplement). *See* abs. **1694.**

KAWAI, S., NOBORI, H., AND NOGUCHI, M. Manufacture of Fatty Acids by the Oxidation of Paraffin. VIII. Composition of Fatty Acids From Oxidation of the Middle Fraction of Paraffin. *See* abs. **1688.**

1697. KAWAKITA, K. Chemisorption of Carbon Dioxide by Reduced Iron. I. Interaction of Carbon Monoxide and Carbon Dioxide With the Reduced Iron. Rev. Phys. Chem. Japan, vol. 8, 1934, pp. 89–116; vol. 11, 1937, pp. 39–53; Chem. Abs., vol. 31, 1937, p. 3759; vol. 32, 1938, p. 403.

In chemisorption of CO_2 by reduced Fe an irreversible sorption always takes place in the normal state of the activity of the catalyst, the amount of the sorption being proportional to the square root of time in the intermediate state of the sorption. The final pressure of CO_2 always approaches zero. Some selectivity of catalytic action was found with catalysts of various activities and mixtures of CO and CO_2. Sieverts' law, that the amount of sorption is proportional to the square root of the pressure, seems to hold. It is suggested the chain reaction is $Fe+(CO_2)_{ads.}=Fe_xO_y+(CO)_{ads.}$; $CO_{ads.}=1/2C+1/2(CO_2)_{ads.}$. Facts indicating these reactions are: (a) The catalyst, saturated with CO_2, recovers its activity, forming water, by its re-reduction with H_2; (b) the formation of free C was observed; (c) the sorption is irreversible and has some self-poisoning. The activity of the catalyst may be accomplished by saturating it with CO_2, by poisoning and by sintering.

1698. ———. Chemisorption of Carbon Dioxide by Reduced Iron. II. The Effect of Chemisorption on van der Waals Adsorption of Carbon Dioxide at 0°. Rev. Phys. Chem. Japan, vol. 12, 1938, pp. 105–114; Chem. Abs., vol. 33, 1939, p. 1568.

Chemisorption of CO_2 by reduced Fe at 300°–500° was studied by measurement of its van der Waals adsorption at 0°. The following 3 types of surfaces, obtained by pretreatment, were studied: (A) Fresh surface without chemisorption, (B) when reaction vessel is evacuated at 300°–400° after chemisorption and (C) when the reaction vessel is not evacuated or evacuated at 0° after chemisorption. The van der Waals adsorption was greater on surface (B) and less on surface (C) than on surface (A). The fraction of the surface covered with the adsorbed molecules and the total number of the elementary spaces in van der Waals adsorption at 0° were calculated. The relation between the fraction of surface covered with the adsorbed molecules and the whole surface was found to be $(B)\doteq(A)>(C)$. The relation between the total number of elementary spaces and the surfaces was $(B)>(A)>(C)$. Increase in van der Waals adsorption due to the chemical treatment at high temperature in the case of (B) is ascribed to increase in the total number of elementary spaces.

1699. ———. Chemisorption of Carbon Dioxide by Reduced Iron. III. Thermodynamic Consideration of the Chemisorption. Rev. Phys. Chem. Japan, vol. 13, 1939, pp. 87–95; Chem. Abs., vol. 33, 1939, p. 9084.

Free-energy equations are derived for the possible reactions in the chemisorption of CO_2 by reduced Fe, and the free-energy values are calculated for 360°. CO as an intermediate product is identified by its reduction of $PdCL_2$ solution. Fe_3O_4 is identified as a product. These facts and the free-energy values suggest that the chemisorption consists of the following reactions: $Fe+CO_2=FeO+CO$, $3FeO+CO_2=Fe_3O_4+CO$, $3Fe+4CO_2=Fe_3O_4+4CO$, $2CO=C+CO_2$. The apparent reaction of the system becomes $3Fe+2CO_2=Fe_3O_4+2C$.

1700. ———. Chemisorption of Carbon Dioxide by Reduced Iron. IV. Kinetics of the Chemisorption. Rev. Phys. Chem. Japan, vol. 14, 1940, pp. 1–10; Chem. Abs., vol. 34, 1940, p. 5717.

Kinetics of the chemisorption of CO_2 by reduced Fe are studied. There appear to be active centers of different character on the surface of the catalyst, some of which adsorb CO_2 and some CO. The apparent heat of activation is 37 kcal. per mol.

1701. ———. Chemisorption of Carbon Dioxide by Reduced Iron. Effect of the Chemisorption on van der Waals' Adsorption of Carbon Dioxide at 0°. Proc. Imper. Acad. (Tokyo), vol. 12, 1936, pp. 61–63; Chem. Abs., vol. 30, 1936, p. 7008.

Van der Waals' isotherms for the adsorption of CO_2 by reduced Fe at 0° are reproducible, equilibrium being attained within 1 min. The effect of the previous treatment of the reduced Fe (previous cycles, temperature of evacuation) and the pressure (0–20 cm. Hg) on the adsorption of CO_2 are shown graphically.

1702. ———. [Kinetics of the Reduction of Ferric Oxide.] Rev. Phys. Chem. Japan, vol. 14, 1940, pp. 79–85; Chem. Abs., vol. 35, 1941, p. 961.

Rate of reduction of Fe_2O_3 by H_2, dx/dt, measured in a static system, equals $kx^n(a-x)$, where x is the amount of H_2 reacted, a is the initial H_2 concentration, k is the rate constant, and n is a topochemical factor related to the number of reaction nuclei and to their rate of propagation. At 500° and 600°, many nuclei are formed at the start of the reaction and $n=0$, and the reaction is approximately 1st order. At 265° very few nuclei are formed initially and $n=1$, giving a maximum rate when $x=a/2$. n decreases as k increases. As the temperature increases above 265° the maximum rate is larger and appears earlier.

KAWAMICHI, K. *See* abs. **1854.**

1703. KAZANSKIĬ, B. A. [Synthesis of Liquid Fuel From Carbon Monoxide and Hydrogen.] Gosudarstvennoe Nauchno-Tekhnicheskoe Izdatel'stvo, U. S. S. R., 1940.

———. *See* abs. **797, 803, 2916.**

1704. KAZANSKIĬ, B. A., SERGIENKO, S. R., AND ZELINSKIĬ, N. D. Contact Cyclization of Paraffinic Hydrocarbons. Compt. rend. acad. sci. U. R. S. S., vol. 27, 1940, pp. 664–669 (in English); Chem. Abs., vol. 35, 1941, p. 1387.

Fraction of synthin, boiling at 83°–138°, containing 11.84% unsaturates and having 66.0 aniline point and 10 octane number, was passed over catalysts at 425°–500°, giving condensates having the following values

for % unsaturates, % aromatics, aniline point (maximum), and octane number: 90% silica gel and 10% Cr_2O_3 (preheated in H_2 to 450°) at 450°, 5.30, 11.37, 57.5, —; 1:1 mixture of silica gel–Cr_2O_3 (reduced in H_2 at 450°) at 425°–450°, 5.60, 14.5, 58.0, 22; 91.5% Cr_2O_3 and 8.5% NiO at 450°, 6.03, 16.38, 48.4, —; 85% Al_2O_3 and 15% UO_3 (preheated in N_2 to 450°) at 500°, 11.26, 11.40, 56.2, 26; 62% Al_2O_3, 24% Cr_2O_3, and 14% UO_3 (preheated in N_2 at 475°) at 475°, 9.78, 26.42, 32.3, —; 80% Al_2O_3 and 20% MoO_3 (preheated in N_2 to 450°) at 450°, 6.03, 15.74, 52.8, 24; and Zn chromate at 475°, 20.84, 1, 58.9, —. Platinized charcoal (containing 23% Pt and prepared by impregnating activated charcoal with H_2PtCl_6 solution and heating in H_2 at 300°–310°) at 300°–356° did not aromatize the synthin fraction. After removal of unsaturated hydrocarbons from the synthin fraction by means of Kattwinkel mixture (*see* abs. **1678**) the platinized charcoal at 350° aromatized the remaining hydrocarbons to approximately the same degree as with octane. Air blowing has no effect on the activity of Zn chromate catalyst.

1705. KAZANSKIĬ, B. A., PLATÉ, A. F. BULANOVA, T. F., AND ZELINSKIĬ, N. D. [Contact Cyclization of Paraffinic Hydrocarbons. Catalysts Containing Vanadium Pentoxide and Thorium Dioxide.] Compt. rend. acad. sci. U. R. S. S., vol. 27, 1940, pp. 658–663; Chem. Abs., vol. 35, 1941, p. 1386.

When a synthin fraction, boiling at 83°–138°, was passed over V_2O_5 at approximately 500°, NH_4VO_3 (preliminary heating to 500° in N_2 at 500° or Al_2O_3 at 450°–555°, there was virtually no formation of aromatic hydrocarbons. Alumina with 5–10% of V_2O_5 at 475°–500° catalyzes the formation of aromatic hydrocarbons from synthin fractions, which boil at 83°–138° and 162°–205°, respectively, but gradually loses its activity, becoming covered with C. The catalyst readily regains its original activity by heating in a current of air. Cr_2O_3 with 10% V_2O_5 at 450°–470° showed considerable catalytic activity but rapidly lost its activity. Parby kieselguhr with 10% V_2O_5 did not catalyze the formation of aromatic hydrocarbons from a synthin fraction boiling 83°–138°. Alumina with 10% ThO_2 catalyzed the formation of aromatic hydrocarbons from the same synthin fraction. The catalytic activity of alumina with 10% ThO_2 at 500° for the formation of aromatic hydrocarbons from the same synthin fraction increased slowly and then slowly decreased; the catalyst can be regenerated by heating with air. Alumina with 10% V_2O_5 and 2% ThO_2 at 475°–500° acted in the same manner as alumina with 10% V_2O_5. Activated charcoal with 10% ThO_2 at 450°–470° catalyzed considerably the formation of aromatic hydrocarbons from the synthin fraction, but the catalyst declined somewhat rapidly in activity and was not satisfactorily regenerated with air.

1706. KAZANSKIĬ, B. A., LIBERMAN, A. L., PLATÉ, A. F., ROZENGART, M. I., AND STERLIGOV, O. D. [Laboratory Method for Rapid Hydrogenation of Olefins at Atmospheric Pressure.] Doklady Akad. Nauk S. S. S. R., vol. 71, 1950, pp. 477–480; Chem. Abs., vol. 44, 1950, p. 8313.

Platinized C activated by a small amount of $PdCl_2$ or H_2PtCl_6 is a very active, rapidly acting catalyst for atmospheric pressure hydrogenation of olefins even without added solvents. A considerable economy in the amounts of catalysts needed is one of the results. Sample reductions were performed in a rocking flask with 50–200 ml. charges and platinized charcoal containing 0.01–0.05 gm. Pt to which was added 1–2.85 ml. of the activator solution (either 0.03 gm. Pt/ml. of H_2PtCl_6, or 0.018 gm. Pd/ml. of $PdCl_2$ solution); the reductions were complete in 3–8 hr. (usually 97%), and after filtration the products were distilled.

1707. KAZ'MIN, S. [Utilization of Cheremkhov Coals.] Planovoe Khoz., 1939, No. 11, pp. 131–134; Khim. Referat. Zhur., 1940, No. 7, p. 85; Chem. Abs., vol. 36, 1942, p. 5631.

Fine coal can be utilized by semicoking after briquetting. The heat capacity of semicoke is equal to that of the initial coal. The least expensive method for producing liquid fuel is by semicoking the coal and distilling the tar; the yield is 12%. The other methods used are hydrogenation of the coal, and synthesis from water gas produced from the coal.

1708. KEHDE, H., FAIRFIELD, R. G., FRANK, J. C., AND ZAHNSTECHER, L. W. Ethylene Recovery. Commercial Hypersorption Operation. Chem. Eng. Progress, vol. 44, No. 8, 1948, pp. 575–582; Chem. Abs., vol. 42, 1948, p. 8149.

Describes hypersorption process for the continuous separation of gases by selective adsorption on a moving bed of activated C; also operation and performance of the first full-scale commercial hypersorber built for the Dow Chemical Co. to recover small concentrations of C_2H_4 from a H_2–CH_4 stream at 75 p. s. i. g. From a feed gas containing 4.5–6.0 vol. % C_2H_4, a C_2H_4 product is obtained of 92–93% purity and 0.1% maximum CH_4 contamination. The H_2–CH_4 overhead stream contains less than 0.1% C_2H_4.

1709. KEĬER, N. P., AND ROGINSKIĬ, S. Z. [Investigation of the Heterogeneity of Active Surfaces by the Differential Isotopic Method. I. The Active Surface of Metallic Nickel and of Zine Oxide.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1950, pp. 27–38; Chem. Abs., vol. 44, 1950, pp. 5690–5691.

Heterogeneity of the surface of an active Ni catalyst, prepared by compression of Ni grains of 1.0–2.0 mm. diam. (by reduction of NiO in a stream of H_2 at 280°), specific surface area 1.5–2 m.²/gm., was demonstrated by experiments of consecutive adsorption, at room temperature, of H_2 and of D_2, or 1st of D_2, then of H_2, and thermal conductivity analysis of the gas given up in fractions on desorption at increasing temperatures. Before the adsorption experiments, 1.05-gm. samples of the catalyst were outgassed at up to 450° under 10^{-5} mm. Hg, reduced once more with H_2 at 450° and again outgassed at 530°. Between the 2 adsorptions, the catalyst was evacuated 1.5 min. to 10^{-5} mm. Hg, then the 2d gas was admitted. Data for a typical run are: 1st adsorption, D_2 under 1.48 mm. Hg, amount adsorbed in 9 min. at room temperature, 0.095 cc. (S. T. P.); after short evacuation, 2d adsorption, H_2 under 3.08 mm. Hg, amount adsorbed in 9 min. at room temperature, 0.04 cc., followed by 1.5 min. evacuation, the % of D_2 and of H_2, respectively, in the gas desorbed; at room temperature, 5 and 95; at 2°–65°, 0 and 100; at 170°–220°, 0 and 100; at 300°–320°, 40 and 60; at 420°–470°, 95 and 5; at 520°, 100 and 0; at 530°, 100 and 0. Consequently, the isotope adsorbed first is desorbed last. The same is observed in analogous runs with the order of the 2 adsorptions reversed; namely, 1st H_2, then D_2. In these experiments, the surface coverage is of the order of 5–10% of the total surface area. No specific effects owing to the chemical difference between H_2 and D_2 are observed. The conclusion is that active spots on the surface of Ni differ in their heats of adsorption and activation energies, and that there is no mixing of the molecules adsorbed on the surface. A gas of mixed composition is obtained only in desorption in an intermediate temperature range, which indicates limited mobility of the molecules in the adsorbed layer. On the basis of this finding, the exponential kinetic law established by Elovich and Zhabrova (abs. **814** and **815**) for the rate of adsorption of H_2 is rooted not in repulsive interaction between the adsorbed molecules but solely in the heterogeneity of the adsorbing surface. Analogous

experiments were made with ZnO, prepared by oxidation of Zn in the electric arc, and outgassable at up to 500° without decomposition; decomposition is noticeable only above 600°. On adsorption of H_2, the gas liberated in desorption at up to 500° is pure H_2; reaction between H_2 and ZnO takes place only above 500°, and then even under a pressure as low as 0.5 x 10^{-4} mm. Hg. If the 2 consecutive adsorptions are accomplished above 100°, only the gas adsorbed last is given up on heating; the isotope adsorbed first appears to have been spent. In room temperature adsorption, the 2d adsorbed gas is bound very weakly, and most of it is desorbed in the 1.5 min. evacuation at room temperature, which precedes the high-temperature desorption. Consequently, only the isotope adsorbed first is found in the gas desorbed on heating. This indicates that, under these conditions, only a very minor fraction of all active points has a high binding power for the adsorbed molecules, and these points are completely filled by the gas adsorbed first. This situation is changed when the 1st adsorption is done at 200°. Thus, with D_2 adsorbed first under 6.15 mm. Hg, 50 min. at 200° followed by slow 16 hr. cooling to room temperature, the amount of D_2 adsorbed was 0.2 cc. (S. T. P.); after short evacuation, H_2 was adsorbed under 6.65 mm. Hg, 34 min. at 115°, amount adsorbed 0.028 cc.; the composition of the gas given up on subsequent desorption at 170°–285°, 300°–325°, 395°–450°, 487°–495°, was (% D_2 and H_2), 15 and 85, 25 and 75, 20 and 80, 75 and 25%. Under these conditions, the gas adsorbed last is given up first, as in the case of Ni.

KEIL, W. Fat Acids With Odd Number of Carbon Atoms. V. Behavior of Branched Fat Acids in the Body. *See* abs. **1714.**

———. Fat from Fatty Acids With Odd Numbers of Carbon Atoms. III. *See* abs. **1712.**

———. Fats from Fatty Acids With Odd Numbers of Carbon Atoms. VI. *See* abs. **1716.**

———. See abs. **1711, 1713, 1717.**

KEIL, W., AND SCHILLER, G. Fats From Fatty Acids With Odd Numbers of Carbon Atoms. Addendum to III, IV, and V. *See* abs. **1715.**

1710. KEIL, W., APPEL, H. AND BERGER, G. [Fats From Fat Acids With Uneven Numbers of Carbon Atoms. I. Preliminary.] Ztschr. physiol. Chem., vol. 257, 1939, pp. 1–3; Chem. Abs., vol. 33, 1939, p. 3193.

1711. APPEL, H., BERGER, G., BÖHM, H., KEIL, W. AND SCHILLER, G. [Fats From Fat Acids With Uneven Numbers of Carbon Atoms. II.] Ztschr. physiol. Chem., vol. 266, 1940, pp. 158–173; Chem. Abs., vol. 35, 1941, p. 2582.

Cacao butterfat acids were reduced to the alcohols, converted to bromides with HBr and these to nitriles with CaCN and these hydrolyzed to fat acids with uneven numbers of C atoms. These, as well as the original fat acids, were resynthesized to "uneven" cacao fat and "even" cacao fat and compared with natural cacao fat and with each other. The synthetic fats were completely hydrogenated. The fats were fed at 5, 10 and 20% levels to rats. No significant differences in body weight, deposition of fat, residual fats after starvation, their I numbers, extent of resorption or dicarboxylic aciduria were observed. The resorption of the 3 fats is virtually equal in man.

1712. KEIL, W. [Fat From Fatty Acids With Odd Numbers of Carbon Atoms. III.] Ztschr. physiol. Chem., vol. 274, 1942, pp. 175–185. Chem. Abs., vol. 37, 1943, p. 5943.

Ether-soluble acids were determined in the urine of dogs on basal diet supplemented with different kinds of natural fat. 0.1–0.4 gm. were recovered/100 gm. fat fed daily for 3 days. Similar results were obtained with fats containing only odd number, straight-chain fatty acids. Triglycerides of synthetic branched-chain fatty acids gave an increased Et_2O-soluble fraction in the urine. Et branched-chain fatty acids are inefficiently attacked in the body and are eliminated, whereas 2–, 3– and 5–methyldodecanoic acids are not excreted significantly. A number of branched-chain fatty acids were synthesized.

1713. APPEL, H., BÖHM, H., KEIL, W. AND SCHILLER, G. [Fat From Fatty Acids With Odd Numbers of Carbon Atoms. IV.] Ztschr. physiol. Chem., vol. 274, 1942, pp. 186–205; Chem. Abs., vol. 37, 1943, p. 6713.

Growth and development of young male goats were the same when fed coconut oil or butterfat or a synthetic fat mixture (1) consisting of straight-chain odd- and even-numbered fatty acids. After prolonged feeding the resorption of I was 79%, of coconut oil 91 and of butterfat 92%. Body and depot fat of rats and goats fed saturated fats contained more than 60% saturated acids. Feeding I containing C_{10}–C_{23} fatty acids led to C_{13}–C_{17} fatty acids in depot fat, and odd-numbered C-chain fatty acids amounted to 33% of the total depot fatty acids. With I, C_{13} acids are the smallest to appear in depot fat, with coconut oil C_{12}, and with butterfat C_{14}.

1714. KEIL, W. [Fat Acids With Odd Number of Carbon Atoms. V. Behavior of Branched Fat Acids in the Body.] Ztschr. physiol. Chem., vol. 276, 1942, pp. 26–32; Chem. Abs., vol. 37, 1943, p. 6728.

Feeding to dogs of triglycerides of branched fat acids (I) with even or odd numbers of C atoms causes an increase in the amount of acid metabolic products in the urine.

1715. KEIL, W. AND SCHILLER, G. [Fats From Fatty Acids With Odd Numbers of Carbon Atoms. Addendum to III, IV, and V.] Ztschr. physiol. Chem., vol. 282, 1947, pp. 135–136; Chem. Abs., vol. 43, 1949, p. 6164.

Fats from fatty acids with odd numbers of C atoms whose metabolic fate in dogs has been reported, abs. 1714, were prepared by esterification with glycerol of the fatty acids resulting from air oxidation at 100°–150° of various paraffin preparations in the presence of suitable catalysts. The crude fatty acids were removed by extraction with aqueous alkali, reprecipitated by addition of mineral acid, distilled, and the fraction of chain-length C_{10}–C_{23} esterified. The resulting triglycerides were purified in the usual way. The acids prepared from Riebeck-paraffin fatty acids contained higher oxidation products (I), especially dibasic acids (II) (3–4%), HO, and Keto acids. The color of the resulting fats, G138/140, was improved by hydrogenation. The acids prepared from Fischer-paraffin fatty acids, containing (I), gave the fat G137, which was hydrogenated before use. The acids prepared from a paraffin resulting from the high temperature hydrogenation of lignite or lignite tar gave, without further purification, G284 on esterification. G301 was prepared from the same material as G284, after careful separation of the fatty acids from (I), especially (II), by chromatography on silica gel, and improvement of the triglyceride color by hydrogenation. G236 was prepared from the same starting material as G137, but with purification of the acids by chromatography as for G301. Prior crystallization of the lignite paraffin and chromatography of the crude acids gave, on esterification, G405, a product free of (II), and branched-chain acids (III). The fatty acids resulting from oxidation of pure eicosane contained no (III), and chromatography removed (II); on esterification, G273a resulted, but omission of chromatographic treatment gave G289 which contained some (II). G118/119 are comparable to G138/140 and were

prepared from the acids from oxidation of Riebeck paraffin.

1716. KEIL, W. [Fats From Fatty Acids With Odd Numbers of Carbon Atoms. VI.] Ztschr. physiol. Chem., vol. 282, 1947, pp. 137–142; Chem. Abs., vol. 43, 1949, p. 6165.

1717. APPEL, H., BÖHM, H., KEIL, W., AND SCHILLER, G. [Fats From Fatty Acids With Odd Numbers of Carbon. VII. Preliminary Communication Concerning Properties, Stability, Physiology, and Toxicology of Synthetic Fats From Paraffin Fat Acids.] Ztschr. physiol. Chem., vol. 282, 1947, pp. 220–244; Chem. Abs., vol. 43, 1949, p. 9487.

Synthetic fats prepared from glycerol and fat acids obtained by oxidation of paraffin from various sources are more resistant to oxidation and become rancid more slowly than natural fats. Of the fat acids not occurring in natural fats odd-numbered ones, approximately 48% in the synthetic fat, are metabolized by animals and man like natural fat. After feeding odd-numbered saturated acids with C_{11}–C_{19}, 9–10 unsaturated acids are found in depot fat. Branched-chain acids, approximately 15% of the synthetic fat and removable by recrystallization of the paraffin or the fat acids, when fed are mostly excreted in the urine as low-molecular branched acids, dicarboxylic acids, and unidentified acid products. Only a very small amount appears in depot fat. A diet high in branched-chain fats inhibits growth in rats and is toxic. Dicarboxylic acids from C_9–C_{16}, 3–4% of the synthetic fat and removable with alkali or by absorption, are excreted in the urine as degraded dicarboxylic acids from C_6–C_{10}. Unsaturated acids with double bonds mainly in 2–3 and 4–5 positions and with transconfiguration are present only in very small amounts. The unsaponified fraction consisting of paraffin, alcohols, and ketones is nontoxic in the low concentration, less than 1%, present in synthetic fat.

KEILIG, F. *See* abs. **2932, 2934.**

1718. KEITH, P. C. Gasoline From Natural Gas. Gas, vol. 22, No. 6, 1946, pp. 21–26; Nat. Petrol. News, vol. 38, No. 27, 1946, pp. R–506–511; Am. Gas Jour., vol. 164, No. 6, 1946, pp. 11–15; Oil Gas Jour., vol. 45, No. 6, 1946, pp. 102, 105, 107, 108, 111, 112; Am. Gas Assoc. Monthly, vol. 28, 1946, pp. 253–257, 296–297.

This is a discussion of the Hydrocol process developed by Hydrocarbon Research, Inc., studied in a 10-bbl. per-day pilot plant at Olean, N. Y., and to be put into commercial production by Carthage Hydrocol, Inc., at Brownsville, Tex., for converting CO and H_2, from the partial combustion of natural gas with O_2, to gasoline. A cheap, rugged, Fe-base catalyst giving high conversion has been developed. It operates by the fluid-catalyst technique. This catalyst, the cheap production of O_2, and a method for the almost total recovery of the exothermic heat, make it possible to synthesize gasoline that can compete with that from natural crude. The plant will include the largest O_2 plant in existence and will produce 40,000,000 cu. ft. of O_2 per day for use in the partial combustion of the natural gas. The synthesis process will effect a 90% conversion of synthesis gas to produce 5,800 bbl. of 88–90 octane no. gasoline per day in addition to 1,200 bbl. of 45–50 cetane no. diesel fuel and 150,000 lb. of mixed alcohols. Allowing $0.035 per gal. for the diesel fuel and $0.005 per lb. for the crude alcohols, gasoline will be produced at a cost of $0.0525 per gal. One of the important features in maintaining this cost level is the heat recovery through which 750,000 lb. of high pressure steam per hr. will be produced. Based on estimated gas reserves of 175 billion cu. ft., a synthetic crude supply is potentially available equivalent to the present crude petroleum reserves. Another important possibility is the use of waste refinery gases, which could yield as much as 7–8% of the country's present crude production. Furthermore, present developments indicate that the production of gasoline from coal might not be much more difficult with complete gasification of coal offering gas reserves of astronomical proportions.

1719. ———. Synthetic Fuels Promise to Bolster Petroleum Reserves. Chem. Eng., vol. 53, No. 12, 1946, pp. 101–103; Coal Age, vol. 51, No. 11, 1946, p. 134; Combustion, vol. 18, No. 6, 1946, pp. 55–57.

Lecture before the Princeton Bicentennial Conference. The successful conclusion of the coal-to-oil development will increase our potential oil resources materially. With the economic equivalence of gas-to-oil well on its way to being established, the indications are that the economic equivalence of coal-to-oil will follow shortly. German developments have greatly increased the efficiency of coal gasification, and it is reasonable to expect that, since American engineering has improved and lowered the cost of the synthetic oil processes, it can also greatly improve and lower the cost of coal gasification. The present German Lurgi process utilizes a highly reactive, noncaking brown coal, but there appears to be no basic reason why a relatively inactive, highly caking bituminous coal could not be similarly gasified to yield a 900–950-B. t. u. gas with a thermal efficiency or 80% plus. Development work is under way, and the indications are that it will be successful. The economic equivalence of brown coal to town gas having been demonstrated, the same for bituminous coal to town gas and pipeline gas should follow. Fuel transportation is an important factor in this respect. If coal can be economically transformed into gas and oil, it will be interesting to compare the cost of transporting energy as coal with cost of transporting it as gas and oil. The relative costs of transporting equivalent amounts of energy in the form of coal, oil and gas from West Virginia to New York are shown to be as follows: Coal $3.35, oil $0.73, gas $1.92. The transformation of coal into gas at 80% thermal efficiency appears economically superior to its transformation into oil. Operating cost for the former is estimated at about $1.00 per ton of coal, exclusive of all fuel charges; therefore, with coal worth $2.50 per ton in West Virginia the transportation of gas looks very attractive, especially gas of 1,000 B. t. u., the production of which seems feasible. The figures for the transportation of coal as oil do not look so attractive. Again, excluding fuel cost, the present predicted cost of transforming a high B. t. u., low-moisture, low-ash coal into oil is about $5.00 per ton or $1.93 per bbl. Until the capital and operating costs of converting coal to oil can be decreased, oil from coal will not compete with coal as an industrial fuel.

1720. ———. Expansion in Natural-Gas Synthesis. Oil Gas Jour., vol. 46, No. 31, 1947, p. 130.

Abstract of a paper presented before the Petroleum Engineers' Club of Dallas. It is estimated that within the next decade 10 Hydrocol plants may be built to meet the anticipated demand for liquid fuels. Natural gas however, should not increase greatly in price as coal conversion, which lurks in the background, would automatically place a competitive limit to natural-gas prices. The probable economic sequence of alternative future sources for petroleum products is outlined as follows: (1) Gasoline from gas, now commercially feasible with Hydrocol plants under construction at Brownsville and Hugoton; (2) gasoline from coal, with a plant under construction at Pittsburgh; (3) oil from coal, an economic probability in 8–10 yr. The relatively fixed market for chemical products of the type produced by the Hydrocol process incidentally, will increase the commercial success of the process. Development of the method of producing cheap O_2 is given recognition for the commercial success of the Hydrocol process.

1721. ———. Hydrocol Process Development. Petrol. Refiner, vol. 26, No. 4, 1947, pp. 171–172; Nat. Petrol. News, vol. 39, No. 14, 1947, p. 9; Chem. Eng. News, vol. 25, 1947, p. 1044; Petrol. Processing, vol. 2, 1947, p. 390.

Abstract of a paper presented at the 35th meeting of the Western Petroleum Refiners Association. By means of the Hydrocol process, a gasoline of 78–80 octane no., Cooperative Fuel Research Motor method, or 90–92, Research method, can be made from natural gas, plus a 39–40 gravity, A. P. I., diesel fuel of 50–75 cetane no. and a large amount of oxygenated compounds, such as alcohols, HCHO, acetone, etc. By using coal as a raw material, these same products are derived at a somewhat higher price. Thus the synthetic process, using coal, natural gas, or even refinery waste gas, has the 2-fold effect of (1) putting a definite ceiling on the price of natural gas and crude, and (2) setting at rest fears for what we shall use for fuel when and if reserves of crude and gas are exhausted. The possibility of using coal, supplies of which are sufficient to last 1,000 yr., puts a ceiling of not more than \$0.10–0.12 per 1,000 cu. ft. on natural gas and permits only a corresponding increase in the price of crude. The Hydrocol process also is of interest to the refiner, because it is the only other process, with the exception of polymerization and alkylation, by which the quality of the product can be enhanced without a corresponding decrease in quantity. It also may become a strong competitor of catalytic cracking and has the additional advantage of simultaneously utilizing both gases and refinery wastes. It is thought that by 1955 gasoline will be produced synthetically from synthesis gas made by coal gasification. It is estimated that a Hydrocol plant of 3,500-bbl.-per-day capacity would be practical.

1722. ———. Current Status of Synthetic Fuels. Oil Gas Jour., vol. 47, No. 25, 1948, pp. 56–57.

Abstract of a paper presented at the annual meeting of the Texas Mid-Continent Oil and Gas Association. The manufacture of gas from coal and oil from gas will be the dominating synthesis processes used to supplement United States crude supplies. Processes used for synthesizng oil from coal, gas from coal, oil from shale, and oil from gas are reviewed. The low-pressure process of converting coal to oil is uneconomical at present, as gasoline produced in this manner would cost about \$0.165 per gal., using coal worth \$3.00 per ton. Processes for synthesizing gas from coal will soon be commercialized, as gas with a B. t. u. content equivalent to that of natural gas can be manufactured and transported about 150 miles for approximately \$0.136 per 1,000 cu. ft. Because of the huge cash outlay involved, utilization of our shale deposits will not be immediate, although technically sound processes have been developed. In order for the process to be economical, plants of 100,000 bbl. capacity or larger involving a capital outlay of some \$500,000,000.00 will be required. Processing the shale oil would require a capital outlay of \$8,500.00 per bbl. of gasoline. At this time the only commercially feasible method is the synthesis of oil from gas. Such plants as those using Hydrocol process can be built for about \$3,800.00 per bbl. per day capacity. Allowing credit for byproducts, and a 10% amortization plus a 10% return on 50% of the capital and 4% on the remainder, gasoline can be produced at a cost of \$0.0833 per gal. from gas worth \$0.083 per 1,000 cu. ft. For gas worth \$0.163 the cost is about \$0.0993. There are 3 reasons why the oil industry has been slow in entering the gas-to-oil synthesis field: Newness of the process; lack of funds due to expansion of present equipment; and the tax position. There appears to be, however, no reason why the Government should assume control of the synthetic-oil industry.

1723. Keith, P. C., and Wilson, D. W. Manufacture of Low-Cost Oxygen. Blast Furnace, Coke Oven and Raw Materials. Am. Inst. Min. and Met. Eng., Proc., vol. 6, 1947, pp. 55–63.

Brief history of the development of modern O_2 plants is given, with a description of the principles involved in plants of the type now being built. It is estimated that the approximate capital cost of a plant producing 100 ton or 2,400,000 cu. ft. of 90–96% O_2 per day would be \$940,000.00 and for a 400-ton or 9,600,000-cu. ft. plant, \$1,900,000.

1724. Keller, K., and Klempt, W. [Catalytic Conversion of Gases Containing Methane Into Carbon Monoxide and Hydrogen.] Ber. Gesell. Kohlentech., vol. 3, 1930, pp. 230–261; British Chem. Abs., 1931, B, p. 325.

Reaction studied were (1) $CH_4+H_2O=CO+3H_2$ and (2) $CH_4+O=CO+2H_2$. The composition of the gas used was approximately 2% CO_2, 2% C_nH_m, 0.5% O_2, 6% CO, 26% CH_4, 55% H_2, and 8% N_2. Poisoning of the catalyst by S compounds present in the gas appears to be due to the formation of NiS, which, at suitable temperatures, can be decomposed by oxidation with steam and, thus, prevented from deactivating the catalyst completely. Since reaction (1) is endothermic, considerable difficulty was experienced in maintaining the catalyst at the high temperature required when pure steam was used. In the large-scale experiments, a study was made of the best method of combining reactions (1) and (2) to prepare a H_2–N_2–CO mixture in proportion suitable for the subsequent production of a H_2–N_2 mixture in the proportions of 3:1. A vertical furnace of alloy steel packed with catalyst was heated externally by gas, and the gas mixture with regulated volumes of steam and air was passed in at the base of the catalyst. With this furnace, which had a layer of catalyst 94 cm. long by 12 cm. in diameter, 6 $m.^3$ of gas, 3 kg. of steam, and 3 $m.^3$ of air per hr. produced a gas containing (%) CO_2, 2; CO, 17; H_2, 56.5; N_2, 24.5; CH_4, traces. The highest temperature in the tube was 1,050°. In the absence of air it was only possible to convert 3.5 $m.^3$ of gas per hr. into a CH_4-free mixture. Increase in the amount of steam does not in all cases increase the CH_4 conversion. In experiments on the carrying out of the reaction in two stages, the catalyst was divided into 2 separate portions. Gas and steam were passed through the first lower-temperature portion and air was added at suitable intervals along the second length of the catalyst. In this way the CH_4 content could be reduced to 0.03–0.09% when a 3:1 H_2–N_2 mixture was required.

1725. Kelley, K. K. Thermodynamic Consideration of the Synthetic Methanol Process. Ind. Eng. Chem., vol. 18, 1926, p. 78; Chem. Abs., vol. 20, 1926, p. 538.

Free energy and equilibrium constant of the reaction $CO+2H_2=CH_3OH(g)$ are calculated at various temperatures. $\Delta F°_{298}=-10.950$, $\Delta F°_{523}=0$, the working limit of the process at 100 atm. is 700° abs. The method of calculation is that of Lewis and Randall. Park's value for the entropy of liquid CH_3OH is assumed.

1726. ———. Heat Capacity of Methanol From 16° K. to 298° K. and the Corresponding Entropy and Free Energy. Jour. Am. Chem. Soc., vol. 51, 1928, pp. 180–187; Chem. Abs., vol. 23, 1929, p. 1344.

Heat of transition was found to be about 154 cal. per mol. and the entropy of liquid MeOH, based on specific heat measurements to 16° K, is 30.3 ± 0.2 E. U. per mol. at 157.4° K.

1727. ———. Thermodynamic Consideration of the Snythetic Methanol Process. Ind. Eng. Chem., vol. 21, 1929, pp. 353–354; Chem. Abs., vol. 23, 1929, p. 2350.

From new data the following free-energy values for the reaction: $CO(g)+2H_2(g)=CH_3OH(g)$ are obtained: $\Delta F°_{298}=-9{,}640$ cal., and $\Delta H_{298}=-25{,}150$ cal. $\Delta F°=-20{,}740+4500T\log 10T-0.01586T^2+IT$ where I= 69.4.

1728. ———. Data on Theoretical Metallurgy. VIII. Thermodynamic Properties of Metal Carbides and Nitrides. Bureau of Mines Bull. 407, 1937, 66 pp.; Chem. Abs., vol. 32, 1938, p. 2821.

Thermodynamic data relating to metal carbides and nitrides are collected and discussed with the view of obtaining usable heat and free energy of formation relations. Pertinent data are difficult to obtain experimentally and are rare; this fact necessitates frequent use of approximations and assumptions. CH_4 and NH_3 also are included because some of the reactions considered involve these substances. The carbides considered are those of Al, Ca, Cr, Co, Fe, Mn, Mo, Ni, Si, Na, Th, Ti, W, U, V and Zr. The nitrides include those of Al, Ba, Be, B, Ca, Ce, Cr, Fe, La, Li, Mg, Mn, Mo, Si, Sr, Ta, Th, Ti, U, V and Zr. The data are applied in a discussion of the following: (1) Carburization of Fe by CH_4, (2) debismuthizing of Pb by Ca through the medium of CaC_2, (3) partition of C between Mn and Fe in the γ range, (4) possibility of producing NH_3 direct from natural gas, (5) decarburization of Cr and (6) possibility of producing cyanides from CO and NH_3. Bibliography of 108 refs.

1729. KELLEY, K. K., BOERICKE, F. S., MOORE, G. E., HUFFMAN, E. H., AND BANGERT, W. M. Thermodynamic Properties of Carbides of Chromium. Bureau of Mines Tech. Paper, vol. 662, 1944, 43 pp.; Chem. Abs., vol. 38, 1944, p. 6183.

Describes preparation of carbides of Cr, and records some observations of the general properties of the carbides. Reports low-temperature specific-heat measurements in the temperature range 51°–298° K. for the carbides that are true compounds (Cr_3C_2, Cr_7C_3, and Cr_4C) and for the mixed carbide Cr_5C_2. The corresponding entropies are computed. High-temperature heat-content measurements from room temperature up to the limiting temperatures of available containers are reported for Cr_3C_2, Cr_7C_3, Cr_4C, and Cr_2O_3. Analytical representations of the results are given. C reduction of solid Cr_2O_3 takes place in four distinct, reversible reaction steps in which Cr_3C_2, Cr_7C_3, and Cr_4C are the intermediate compounds. Results of the equilibrium measurements obtained with described apparatus and methods are reported for each reaction step. The various data are correlated satisfactorily and thermodynamic values and functions are derived for the Cr carbides. Each carbide of Cr at temperatures below its melting point is stable with respect to decomposition into (1) the elements, (2) any lower carbide and C, and (3) any higher carbide and Cr. The intermediate carbide, Cr_7C_3, is stable with respect to decomposition into Cr_3C_2 and Cr_4C.

1730. KELLING, —. [Production of Branched-Chain Gas Oils and Aviation Gasoline From Fischer-Tropsch Synthesis Products.] TOM Reel 138, Doc. 22 (no date), 28 pp.

Comparison of the products obtained by subjecting Ruhrchemie Diesel oil to thermal cracking, Dubbs process, and to catalytic cracking, and an East Texas gas oil, 220°–350°, to catalytic cracking by the Houdry process. A flow sheet is given of the Ruhrchemie catalytic cracking process based upon the recovery of the exothermic heat developed during the catalyst-regeneration period for supplying heat to the catalytic cracking converters during the endothermic cracking period. The chief difficulty lies in regulating the amount of C deposited upon the fixed-bed catalyst during the endothermic cracking period.

KELLY, R. *See* abs. **53.**

1731. KEMMER, H. [Removal of CO From Illuminating Gas.] Gas- u. Wasserfach, vol. 72, 1929, pp. 744–751; Chem. Abs., vol. 23, 1929, p. 4799.

Catalytic processes may be used, such as the hydrogenation of the CO by passing the gas over a catalyst composed of active C impregnated with Ni containing about 18% ThO_2. A $CO:H_2$ ratio of 1:5 is required for quantitative conversion to CH_4. The Ni catalyst is strongly activated by the ThO_2 so that the reaction temperature can be kept low. The optimum temperature for CH_4 formation lies between 180°–190°. It is mentioned that with these catalysts in addition to CH_4 quite small amounts of heavy hydrocarbons would be formed.

1732. ———. [Gas Improvement by Refrigeration and Catalysis.] Gas u. Wasserfach, vol. 75, 1932, pp. 269–273; Chem. Abs., vol. 26, 1932, p. 3649.

Gas is cooled by the usual water cooler, and then passed through an electric tar precipitator, after which it is cooled to 0° by NH_3 liquor to remove NH_3 and part of the naphthalene, light oil, etc., while the remainder of the naphthalene and light oil is removed by oil scrubbing at −10°–15°. The gas is then further purified in the usual wet or dry S purifier. A 2-stage Altenkirch-Borsig absorption refrigeration system is used to cool the NH_3 liquor and oil; the operation of this apparatus is described. Flue gases supply the necessary heat for this refrigeration system. The gases may then be purified from remaining S by Lauta mass at 250°–300°, which removes the S to about 1–2 gm. per 100 $m.^3$ After saturation the Lauta mass may be regenerated. The best catalyst for removing CO was found to be one consisting of Fe 75, Ni 23 and Cr 2 parts, on active charcoal, or one of Ni and Al_2O_3 on pumice, said to be very insensitive to catalyst poisons. These catalysts permitted a 1-stage conversion of the CO to CH_4 and CO_2 at about 360° and with the gas saturated with moisture at 60°–70°. Energy losses on catalysts are said to be 0–2%. Costs of operation are given for German conditions.

1733.———. [Gas Industry and German Motor-Fuel Economics.] Gas- u. Wasserfach, vol. 77, 1934, pp. 877–883; Chem. Abs., vol. 29, 1935, p. 1609.

German requirements for motor fuel are discussed, together with the need of greater and more efficient benzene recovery, and means of increasing benzene yield, as by suction of distillation products from the interior of the coal charge. The relative advantages of the active C and wash-oil recovery processes for light oil are compared. Other sources of motor fuel are low-temperature carbonization of brown and bituminous coal and motor-fuel synthesis by the Fischer process; the suitability of the process for gasworks use is discussed. The use of compressed gas for motor fuel also is reviewed and costs are considered, as well as special equipment required for using gas with automotive equipment.

1734. ———. [Removal of Carbon Monoxide From City Gas.] Angew. Chem., vol. 49, 1936, pp. 133–137; Chem. Abs., vol. 30, 1936, p. 3204.

This is a description of a 2-stage process whereby a partial oxidation of the CO with steam over a Cr catalyst takes place, followed by a hydrogenation of the remaining 4–5% of CO to CH_4. This last reduction proceeds virtually quantitatively at 200°–250° over a Ni–Th catalyst by utilizing the H_2 formed in the first step. The 2-stage process should not cost more than 0.5 pf. per $m.^3$ To eliminate the existing difficulties of gas purification and to lower the working costs, it is proposed to combine the process with the synthetic production of fuel by the Fischer-Tropsch process.

KEMPKENS, J. *See* abs. **1988, 1989.**

1735. KENYON, R. L. Alcoholic Cousin—the Oxyl Process. Ind. Eng. Chem., vol. 42, No. 6, 1950, pp. 10–A, 12–A.

German associates of the Blaw-Knox Co. have developed a process for the production of alcohols from synthesis gas, and the Blaw-Knox Co. is prepared to build plants to produce them. Assurance is given that all but the lowest of these alcohols can be made and marketed in this country on a sound economic basis from natural or other synthesis gases. The Oxyl process, by means of a catalytic reaction within pressure and temperature ranges comparable to those of the Fischer-Tropsch, converts synthesis gas into a mixture of alcohols, C_1–C_{20}, saturated and unsaturated hydrocarbons. Conversion of the raw materials to alcohols is 80% or better, with the remainder of the product in hydrocarbons. One of the most important advances in the development of this process is an effective method of separation of the components of the reaction mixture. The individual alcohols can be isolated in a purity of 95% or better. The catalyst for the process is now available from Germany, but it will be prepared here when a plant using the Oxyl process is built and operated in the United States. For a small plant the cost of the catalyst will be high, but preparation in large quantities will bring the unit cost down considerably. It is estimated that plants for the Oxyl process can be built and operated economically in the United States under present conditions and prices at production capacities of 5–8 million lb. per yr. It is assumed that the plant will amortize itself in 3–5 yr.

1736. KEPPELER, G. [Gas for Syntheses From Peat. A Plant Trial in the Tiefstack Plant of the Hamburg Gas Works.] Chem. Fabrik, vol. 12, 1939, pp. 457–462; Chem. Abs., vol. 34, 1940, p. 609.

Pintsch-Hillebrand process for producing water gas is discussed, and a vertical section through the producer, a flow-sheet, and an elevation of the plant are shown. The apparatus was used on ordinary raw peat containing 28–30% H_2O, which was charged just after using lignite briquets, the experiments beginning about 70 hr. after starting to charge the peat, with temperatures of 1,200° and 1,300°. Data are given on heat balance, peat consumption, gas yields, and analyses, the latter averaging about 15, 27, 54, 2.5 and 1.8% CO_2, CO, H_2, CH_4 and N_2, respectively. States estimated plant and production costs based on Pintsch data, and it is concluded that a synthetic-gas plant is feasible in peat regions. Gives 5 refs.

1737. KEPPLER, W. [Fatty Acids.] Vierjahresplan, vol. 1, 1937, pp. 269–271; Chem. Zentralb., 1937, II, p. 1913.

Production of fatty acids from Fischer-Tropsch paraffin waxes and their application in the soap industry.

KERLOGUE, R. H. *See* abs. **404.**

1738. KERSHAW, J. B. C. World's Future Supply of Liquid Fuels. Engineer, vol. 143, 1927, pp. 244–245, 261–263; Chem. Abs., vol. 21, 1927, p. 1532.

Review.

KESTING, W. *See* abs. **3052, 3053.**

1739. KEULEMANS, A. I. M., KWANTES, A., AND VAN BAVEL, T. [Structure of Formylation (Oxo) Products Obtained From Olefins and Water Gas.] Rec. trav. chim., vol. 67, 1948, pp. 298–308; British Abs., 1949, A. II, p. 2; Chem. Abs., vol. 42, 1948, p. 8152.

Formylation of olefins by means of CO and H_2 at 120°–160° and 100–200 atm. in presence of the Fischer-Tropsch Co catalyst is studied with 16 alkenes containing 3–8 C, cyclopentene, and cyclohexene. The aldehydes formed are immediately hydrogenated in the same autoclave with pure H_2 to alcohols. Analysis of the products of reaction is simplified if the alcohols are dehydrated by pyrolysis of their stearates, and the olefins obtained are hydrogenated to alkanes.

KEUNECKE, E. *See* abs. **2295.**

1740. KEUNTZEL, W. E. Preferential Catalytic Oxidation of Carbon Monoxide in the Presence of Hydrogen. I. Activity of Two Water-Gas Conversion Catalysts, of Copper Oxide, of Manganese Dioxide, and of a Mixture of These Oxides. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 437–444; Chem. Abs., vol. 24, 1930, p. 2367.

Preferential oxidation of CO by O_2 in the presence of H_2, CO_2, a large excess of steam and various catalysts has been studied. An efficiency of 96% for 37 hr. was obtained with a 2-component hopcalite. Promoted Fe oxide and Co oxide governed only the water-gas reaction $CO+H_2O \rightleftharpoons CO_2+H_2$. CuO, MnO_2, and a 5-component hopcalite were catalytically active but suffered reduction and loss of activity.

1741. ———. Preferential Catalytic Oxidation of Carbon Monoxide in the Presence of Hydrogen. II. Activity of 2-Component Hopcalites. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 445–455; Chem. Abs., vol. 24, 1930, p. 2367.

Of the influent CO 97–99% was oxidized by free O_2 with a commercial hopcalite as catalyst in a temperature range of 160°–196°. The composition of the converted water gas used was: CO, 1.3; O_2, 1.5; CO_2, 28.0; H_2, 49.0; and N_2, 20.2% in the presence of 3 vol. of steam. The catalyst suffered a loss of O and of activity. The rapid dissipation of the heat of reaction was of importance. The steam acts to dissipate this heat and to inhibit the reduction of the catalyst.

1742. KEY, A., AND EASTWOOD, A. H. Removal of Sulfur Compounds From Coal Gas and Synthesis Gas at Atmospheric Pressure. 45th Rept. Joint Research Com., Gas Research Board, and University of Leeds. Gas Research Board Com. 14, 1945, 36 pp.; Fuel Abs., vol. 3, No. 2, abs. 442.

Most active catalysts for the synthesis of CH_4 and other hydrocarbons from CO and H_2 are poisoned by traces of S compounds, such as are present in gases resulting from the carbonization and gasification of carbonaceous fuels. Most attention has been given to processes involving the catalytic reduction of organic S. It was found that certain metallic sulfides have great activity in this direction at temperatures as low as 250° when supported on carriers, such as active C and activated Al_2O_3, which have high specific surface area and absorptive capacity. The catalyst that would give the most efficient organic S conversion in a normal coal gas is the Cu_2S–Cr_2O_3 preparation, but it is poisoned unless the acetylenic bodies in the coal gas are first removed by a pretreatment. On the other hand, Mo sulfide, which is not normally poisoned by coal gas, effects a rather smaller degree of conversion. A combination of the 2, however, the Mo preceding the Cu–Cr, overcame both these difficulties, and is the system that should be adopted to secure maximum conversion. It is problematical whether the employment of this combined system can be justified if the aim is merely to reduce the S content of a gas to 2–3 grains/100 cu. ft.

1743. KEYES, F. G., SMITH, L. B., AND JOUBERT, D. B. Equation of State for Methane-Gas Phase. Jour. Math. Phys., Massachusetts Inst. Tech., vol. 1, 1922, pp. 191–210; Chem. Abs., vol. 17, 1923, p. 668.

1744. KEYES, F. G., TAYLOR, R. S., AND SMITH, L. B. Thermodynamic Properties of Methane. Jour. Math. Phys., Massachusetts Inst. Technol., vol. 1, 1922, pp. 211–242; Chem. Abs., vol. 17, 1923, p. 668.

From the experimental values of the vapor points and densities of liquid CH_4, determined over the entire liq-

uid phase region by precision methods described in detail, a number of equations and thermodynamic constants are derived.

KHAĬKOVA, N. A. *See* abs. **891.**

1745. KHARKHOV, N. V. [Gasification of Finely Ground Coal in a Boiling Layer Using Steam-Oxygen Blast.] Kislorod (Oxygen), 1944, No. 2, pp. 12–21; U. O. P. Co. Survey Foreign Petroleum Literature Index, Aug. 2–9, 1946, pp. 22–23.

Pilot-plant work was begun in 1935 with a unit of capacity of 2,000–3,000 m.³ per hr. on the preparation of an NH_3 synthesis-gas mixture. Fuel of grain size, 10 mm. and less, was used. The blast passing through the 0.3–1.5-m. bed at a velocity of 2–3 m. per sec. brings the bed into a condition resembling boiling. The O_2-enriched air and steam are continuously charged both below and above the fuel bed. The O_2 content of the blast was 53–55%; in mixture with steam 23–24% when the steam amounted to 56–58%. The temperature of 850°–900° in the generator is enough to crack all volatile matter, and the resulting gas contains no tar or heavy hydrocarbons and but little CH_4. The lowest calorific value of the gas was 1,800 kcal. per cu. m.; this is raised to 2,200–2,300 kcal. per m.³ when pure steam-O_2 is charged. The gas has the composition, in vol. %: CO_2, 17.6; CO, 34.0; H_2, 29.2; N_2, 19.1; H_2S, 0.1; no CH_4, O_2, or olefins. Production of 1,000 cu. m. gas requires about 0.5 ton coal of 10% moisture, 180–190 cu. m. O_2 of 98% purity, 230 m.³ air, 280–300 kg. steam, but 500–550 kg. steam also is generated. Young fuels such as lignites are most suitable for the process. The size of the unit is virtually unlimited. In the N_2 industry, gas generators are being built of 15,000–20,000 m.³ per hr. capacity using waste O_2. The extent to which the method will find practical application will depend chiefly upon the supply of cheap O_2.

KHAZANOVA, N. E. *See* abs. **1985, 1986.**

1746. KHITAROV, P. I. [Study of Double Carbides of Manganese and Iron.] Vsesoyuz. Nauch.-Issledovatel. Inst. Metrol., Kratkiĭ Obzor Vazhneĭshikh Nauch.-Issledovatel. Rabot Lab., VNIIM, 1940, pp. 54–55; Chem. Abs., vol. 35, 1941, p. 5075.

By dissolving Fe–Mn of different compositions in dilute acids and salt solutions in the absence of air, it was possible to separate the double carbides corresponding by composition to $x Mn_3C.y Fe_3C$. Data on chemical and X-ray analysis and phase diagram of Fe–Mn–C show that these carbides are solid solutions and not double carbides. The carbides of Fe and Mn also form solid solutions in Fe–Mn.

1747. ———. [Double Carbides of Iron and Manganese.] Vsesoyuz. Nauch.-Issledovatel. Inst. Metrol., Sbornik Trudov, 1941, No. 3 (No. 48), pp. 35–64; Chem. Abs., vol. 39, 1945, p. 5232.

Double carbides of Fe and Mn having the typical formula of $x Fe_3C.y Mn_3C$ were obtained as residues after acid (or other) attack on ferromanganese (20–80% Mn, 5–8% C) in an atmosphere of N_2 or CO_2. By X-ray and phase studies these materials were shown to be solid solutions. Mn_3C (used for reference in the X-ray work) was made by heating a 4:1 mixture of Mn_3O_4 and lampblack for 10–15 min. at 1,300°–1,400°. By longer heating, homogeneous products were obtained with 7.3–7.6% C to which the empirical formulas $Mn_{11}C_4$ and Mn_5C_3 were assigned. 49 refs.

1748. KHODSCHAIAN, S. [Technically Important Gas Equilibria at Low Pressures.] Feuerungstech., vol. 26, 1938, pp. 109–112; British Chem. Abs., 1938, B, p. 1005; Chem. Abs., vol. 33, 1939, p. 4496.

Calculations show the position of equilibrium in various gas reactions, for example, dissociation of H_2, and in the water-gas reaction at elevated temperature and pressure up to 1 atm.

KHOMYAKOV, K. G. *See* abs. **3758a.**

1749. KHRIZMAN, I. A. [Catalytic Decomposition of Ammonia.] Acta Physicochim. U. R. S. S., vol. 4, 1936, pp. 899–910; Chem. Abs., vol. 30, 1936, p. 7987.

Kinetics of the decomposition of NH_3 on promoted Fe catalysts of the $Fe–Al_2O_3–K_2O$ type were investigated over the temperature range 300°–450°. Two values for the energy of activaton were found, 12.4 kcal. per mol. for temperature 300°–350°, and 39.7 kcal. per mol. above 350°. The 2 values were explained on theoretical grounds by assuming several surface reactions with different reaction rates. 13 refs.

1750. ———. [Stablization of Reduced Catalyst for Ammonia Synthesis.] Ber. Pissarjewsky Inst. physik. Chem., Akad. Wiss. Ukr. S. S. R., vol. 12, 1940, pp. 15–20; Chem. Abs., vol. 35, 1941, p. 2685.

NH_3 catalyst of the type $Fe–Al_2O_3–K_2O$ was 1st reduced with a dry mixture of H_2 and N_2 and then nitrided with dry NH_3. The temperature interval for reduction and nitriding was 350°–475°. The nitrided catalyst was cooled in a stream of NH_3 and tested for stability (reaction with moisture, CO_2 and O_2). The tests indicate that the stabilized catalyst may be transported from the place of manufacture to the NH_3 synthesis plant without loss of activity.

1751. KHRIZMAN, I. A., AND KORNIĬCHUK, G. P. [Role of Iron Nitride in the Catalysis of Ammonia.] Ber. Inst. physik. Chem., Akad. Wiss. Ukr. S. S. R., vol. 6, 1936, pp. 95–101; Chem. Abs., vol. 31, 1937, p. 6831.

NH_3 was decomposed catalytically in the interval 250°–470°, the catalyst being the nitride of activated Fe of the type $Fe–Al_2O_3–K_2O$. At 410° and higher, a stoichiometric mixture of N_2 and H_2 was obtained, at 410°–350° the products abounded in N_2, and at 350° and lower, the chief product was N_2 with traces of H_2. By comparing these results with those obtained when ordinary Fe was used, it becomes evident that the nitride hinders the decomposition of NH_3 and that Fe, and not the nitride, is the catalyst in the production of NH_3.

KHULLAR, M. L. *See* abs. **810a.**

1752. KHVATOV, A. D. [Dependence of the Energy of Activation on the Activity of the Catalyst.] Jour. Gen. Chem. (U. S. S. R.), vol. 9, 1939, pp. 819–824; Chem. Abs., vol. 33, 1939, p. 7653.

Surface of catalysts is not homogeneous. The most-active regions of the surface are first acted upon by chemical reagents, which decrease the activity of the catalyst almost 50%. In the experiments, the surface structure of Ni was changed by the reaction of $Ni(CO)_4$ formation, formed when a stream of CO is passed at 100°–150° over Ni, and again decomposed into Ni and CO at 300°–400° by passing definite amounts of CO and by determining the activation energy of CH_3CHO decomposition from the reaction $CH_3CHO \rightarrow CH_4 + CO$. The reaction velocity was determined by passing 1 l. of CO in 1 hr. over the catalyst at 100°. The $Ni(CO)_4$ formed was passed into a U tube heated to 350°, where it was decomposed into metallic Ni and CO. The deposited Ni was dissolved in HNO_3 and its amount determined by the method of Chugaev as Ni dimethylglyoxime. This experiment was repeated until the activity of the catalyst (measured by the reaction velocity) remained constant or changed only slightly. The reactions were performed in a quartz tube, 500 mm. long, 18 mm. diam., with 2 gm. of the catalyst, 2 cm. long. After the 1st action of CO a very sharp drop of the decomposition velocity was observed (26.6–47%). After the 2d CO action a smaller drop occurred at 250°–260°, and only a very small drop after the 3d CO action at 260°. It was

found that a minimum of Ni formation corresponded to the maximum activity drop of the catalyst. This verifies the hypothesis that the number of active regions on the surface of the catalyst can be very small. From the experimental data, the energies of activation for the different steps of the chemical action of CO on Ni were calculated from the equation of Arrhenius, and they were found to be the same in all cases (9,000±300 cal.). This shows that the energy of activation does not depend on the activity of the catalyst. Gives 6 diagrams, 7 tables, and 17 refs.

1752a. KIDDOO, G. Petrochemical Processes. Chem. Eng., vol. 59, No. 9, 1952, pp. 149–168; Chem. Abs., vol. 47, 1953, p. 298.

This report is a comprehensive review of the technology of the major processes used to make industrial chemicals from petroleum and natural gas hydrocarbons. It includes: Synthesis gas and H_2 from natural gas, aldehydes and alcohols by the Oxo process. HCN from natural gas and NH_3, chlorination of CH_4 and C_2H_4, C_2H_2 by cracking of hydrocarbons, C_2H_4 and C_3H_6 by thermal cracking, polymerization and alkylation processes, alcohols from olefins, ethylene and propylene oxides and glycols, ketones by dehydrogenation of alcohols, synthetic glycerol from C_3H_6, aldehydes and alcohols by hydrocarbon oxidation, butylenes and butadiene, aromatic hydrocarbons by catalytic reforming and oxidation of xylenes.

KIEHL, J. P. *See* abs. **1056, 1057.**

KIENITZ, H. *See* abs. **3011.**

1753. KILLIFFER, D. H. A Year's Progress in Chemistry. Ind. Eng. Chem., vol. 19, 1927, pp. 1077–1082; Chem. Abs., vol. 21, 1927, p. 3289.

Review. Among the subjects treated are liquid fuels from coal and synthesis of hydrocarbons.

KILPATRICK, J. E. *See* abs. **3589.**

1754. KIMPFLIN, G. [Work of the School of Louvain on Synthetic Motor Fuels.] Génie civil, vol. 119, 1942, pp. 279–281; Chem. Zentralb., 1943, I, p. 1237; Chem. Abs., vol. 38, 1944, p. 3443.

In the investigation of catalysts for the production of benzine from CO and H_2, Co from Katanga (98.57% Co; 0.24 Ni; 0.13 Fe; 0.32 CaO; 0.03 S; and 0.07 Mn activated with 18% ThO_2) yields 123.8 cc. benzine per m.^{3} of gas and under the same conditions a Co–Ni catalyst precipitated on kieselguhr with K_2CO_3 (Co, 3.6; Ni, 3.6; Mn, 1.4; M_3O_8, 1.4) yields 166 cc. benzine. The benzines contain, respectively, 12.6 and 9% olefins, 0.84 and 1.0% aromatic compounds, 18.8 and 24.6% naphthenes, and the remainder paraffinic hydrocarbons. Best results are obtained by maintaining the temperature constant by surrounding the contact oven with boiling aniline. A short description of the production of alcohols from CO and H_2 is given as well as the equilibrium value of CH_3OH and propanol at 25°, 300°, and 400°.

KIMUMAKI, J. *See* abs. **3176, 3177.**

KIMUMAKI, J., SHIRAI, S., AND FUJISAKI, T. Iron Catalyst for Synthetic Petroleum. III. Influence of Barium Nitrate on Iron Catalyst. *See* abs. **3178.**

1754a. KIMUMAKI, J., SHIRAI, S., AND OGAWA, T. Iron Catalyst for the Benzene Synthesis. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, suppl. bind. pp. 80–83; Chem. Abs., vol. 46, 1952, p. 1,186.

For the preparation of better Fe catalysts for the synthesis of benzene from gas mixtures of CO and H_2, it is important to consider the state of division of the alkali to be added, the effect of the duration, and of the degree of heating. In order to improve the state of division of the alkali, it is recommended to replace the alkali carbonates, which were used in most cases with alkali nitrate which is easily formed at the precipitation of the metal hydroxides by K_2CO_3. The alkali nitrate was left in suitable quantity in the precipitate by properly regulating its washing. This alkali nitrate is always converted at the reduction process into alkali carbonate, which causes a homogeneous distribution of the alkali on the surface of the diatomaceous earth. Superheating the catalyst often impairs the synthesis of benzene. The reduction with H_2 will, therefore, be avoided as much as possible, because higher temperatures are always needed for this purpose. It is concluded, that for the synthesis of benzene from natural gases, the selective adsorption of the alkali among the catalyst metals and the diatomaceous earth is of great importance.

KIMURA, K. *See* abs. **1927, 1928, 1929.**

1755. KIMURA, O. Hydrogenation and Polymerization Reaction of Acetylene. I. Reaction in Liquid Phase and the Effect of High-Tension Discharge. Bull. Chem. Soc. Japan, vol. 18, 1943, pp. 1–12. Chem. Abs., vol. 41, 1947, p. 4436.

Polymerization and hydrogenation reactions of C_2H_2 were studied in liquid paraffin in the presence of such catalysts as Ni, Co, Pd, and Ca. The polymerization reaction occurs more easily than hydrogenation. To avoid this defect in the process of obtaining liquid fuel from C_2H_2, high-tension discharge was applied to activate the H_2; the products were mainly liquid hydrocarbons.

———. *See* abs. **2414.**

1756. KIMURA, O., AND HIROTA, K. Hydrogenation and Polymerization Reaction of Acetylene. II. Polymerization Reaction by Use of the Thermal Diffusion Column. Bull. Chem. Soc. Japan, vol. 18, 1943, pp. 13–21; Chem. Abs., vol. 41, 1947, p. 4436.

Applying the thermal separation column of heated W wire at 700°–1,000°, C_2H_2 was converted into liquid hydrocarbons almost perfectly.

1757. ———. Hydrogenation and Polymerization Reaction of Acetylene. III. Kinetics of Polymerization by Use of Thermal Separation. Bull. Chem. Soc. Japan, vol. 18, 1943, pp. 45–53; Chem. Abs., vol. 41, 1947, p. 4436.

By using the thermal separation column with W wire as a reaction vessel, the reaction was found to be of the 2d order and the activation energy 44.8 kg.-cal.

1758. ———. Hydrogenation and Polymerization Reaction of Acetylene. IV. Kinetics of Polymerization by Use of Thermal Separation Column. Bull. Chem. Soc. Japan, vol. 18, 1943, pp. 273–277; Chem. Abs., vol. 41, 1947, p. 4436.

From the equation derived by the authors, the velocity constant K and the activation energy Q of C_2H_2 in the thermal separation column of Clusius and Dickel were computed: $K=8.7$ atm.$^{-1}$ sec.$^{-1}$ at 720° and $Q=44$ kcal.

KING, G. W. *See* abs. **2174.**

1759. KING, J. G. Production of Liquid Fuels From Coal. Jour. Soc. Chem. Ind., vol. 46, 1927, pp. 181–186T; Gas Jour., vol. 177, 1927, pp. 391–392; Chem. Age, vol. 16, 1927, p. 86; British Chem. Abs., 1927, B, p. 641; Chem. Abs., vol. 21, 1927, p. 2546.

Three main lines along which the problem of oil production from coal is being attacked are described and the latest results reviewed. The effect of temperature of carbonization on the constitution of low-temperature tar is illustrated by experiments carried out at the Fuel Research Station. There are indications that 550°–600° is a critical temperature so far as the tar is concerned when external heating is used. At 600° only 8.8% of the tar is saturated. On a large scale the yields of tar are not much greater than 16.5 gal. per ton of coal, and if 50,000,000 tons

of coal was carbonized only 150,000,000 gal. of motor spirit and 550,000,000 gal. of tar oils would be available—much less than the country's requirements. The Bergius process offers technically 100–130 gal. of oil per ton of coal or up to 60% by weight of suitable coals. The plant is described and yields are quoted. The catalytic production of alcohols and hydrocarbons from CO is showing considerable promise for the future, but so far results are only experimental. The recent work of Fischer and Tropsch in producing petroleumlike hydrocarbons shows particular promise. The catalysts used and the nature of the end products are described.

1760. ———. Complete Gasification of Coal and Methane Synthesis. Inst. Gas Eng., Pub., 197/80, 29 pp.; Gas Jour., vol. 224, 1938, pp. 457–460, 637; Gas World, vol. 109, 1938, pp. 372, 410–411; Chem. Abs., vol. 33, 1939, p. 6562.

Sized semianthracite coals of low caking power can be gasified successfully in a water-gas plant to yield 67,000 cu. ft. or 205 therms of gas per ton of coal. Rate of output of gas is similar to that obtained from sized coke. High-volatile coals of low or medium caking power can be gasified by using a recuperator and introducing a backrun into a cycle. The yield of gas is about 45,000 cu. ft. or 141 therms per ton of coal. Rate of output of the generator is 15–25% less than when sized coke is used in the same plant. A small proportion of the tar (about 2.5 gal. per ton of coal) escapes cracking and means must be provided for its recovery. By modifying cycles of operation, coal can be gasified to give a gas having a high ratio of H_2: C. Such a gas would be of value in connection with processes for catalytic synthesis of hydrocarbons. Mo catalysts were not entirely satisfactory for synthesis of CH_4 from coal gas. Activity of a ThO_2-promoted Co catalyst was unaffected by S, but decreased with time. The Fuel Research Station vortex burner was modified to gasify pulverized coal with steam and O_2 at atmospheric pressure.

1761. ———. Oil and Coal After the War. Petroleum (London), vol. 6, No. 12, 1943, pp. 180–181, 188.

Since the oils produced in the Fischer-Tropsch synthesis are mainly straight chain in character, the process has special significance in that the diesel-oil fraction has a high cetane value (120) and the oils are most amenable to cracking and chemical reconstruction. The significance of this process in postwar planning is, however, only partly in the field of fuel and is perhaps mainly centered in its value as a means of producing those olefins that are the starting point in the manufacture of so many of the new raw materials wanted in the chemical industry. It is, moreover, the only process from which satisfactory lubricating oil can be synthesized.

1762. ———. Research and the Gas Industry. Gas Jour., vol. 241, 1943, pp. 796, 799, 800, 805.

Lines of research commented on are: The utilization of 2d and 3d quality gas coals, complete gasification both by the Lurgi and the Leeds processes, CH_4 synthesis and liquid CH_4, the Fischer-Tropsch process, complete removal of S from town gas and high-pressure gas-distribution systems.

1763. ———. Better Utilization of Coal for the Production of Oil and Petrol. I. A Survey of the Production of Tars and Oils From Coal. Jour. Junior Inst. Eng. (London), vol. 54, 1944, pp. 225–244; Jour. Inst. Fuel, vol. 17, 1944, pp. 192–196; Engineering, vol. 158, 1944, pp. 236, 318–320, 337–338; Chem. Abs., vol. 38, 1944, p. 5381.

This is a discussion of carbonization industries (creosote-pitch fuel, pulverized pitch, tar diesel oil, motor benzene), coal-oil suspensions (colloidal fuel), the hydrogenation of coal (catalysts, products, development, hydrogenation of tars and tar oils), indirect production of oil from coal (processes, efficiency and yields, lubricating oils), new processes (C_2H_4 and C_3H_6, CH_4 from coal measures and sewage, CaC_2, cannel tar), and direct replacement of oils in motor fuels.

1764. ———. Work of the Gas Research Board. Report of the Director. Synthesis of Methane. Gas Research Board Pub. 8; Gas Jour., 1944, pp. 623–624, 660–661, 689, 691; Gas World, vol. 120, 1944, p. 6245; vol. 121, 1944, p. 18; Chem. Abs., vol. 38, 1944, p. 4775.

In experiments on the synthesis of CH_4, with a granular Ni catalyst and with passage of the gas at atmospheric pressure, a low reaction temperature (350°–500°) led to loss of catalyst activity and deposition of C, as the result of the development of a high surface temperature where the reaction gases first come into contact with the catalyst. The rate of loss of activity is increased by a decrease in the ratio H_2: CO; in practice, it may be necessary to employ a ratio above 1.2. The addition of steam counteracts the tendency to form C from the CO and also under certain circumstances prevents the loss of catalyst activity caused by sintering. The surface temperature also can be controlled by recirculation and by use of a shaped or rod catalyst arranged to lose heat rapidly by radiation. By use of these expedients it is possible to operate the simple Ni catalyst at any temperature within the range 350°–800° and at any pressure within the range 1–50 atm. In the synthesis from water gas with high H_2: CO ratios the most suitable catalyst for work at a relatively low temperature is Ni promoted by ThO_2 and supported on kieselguhr. The S in the gas is kept below 0.1 grain per 100 cu. ft. by using an Fe oxide–Na_2CO_3 contact material at 180°–230°. With purified water gas, the catalyst life was 77 days, during which time the CH_4 content of the CO_2-free gas varied from 80 down to 30% with an average of 65%. In order to prevent undue deposition of C, the H_2: CO ratio must be kept above 1.5. Other factors affecting the formation of C are the rise in temperature of the catalyst, its size, and a rise in pressure above atmospheric. The gas should be passed downward through the catalyst. Under these conditions and with an exit temperature of 350°, the process gas can be treated at the rate of 3,700 vol. per vol. of catalyst per hr. Difficulties were encountered in developing these results to a semiscale apparatus possessing 5,000 cu. ft. of gas per day.

1765. ———. Better Utilization of Coal for the Production of Oil and Petrol. Gas and Oil Power, vol. 40, March 1945, pp. 99–101; Gas Abs., Inst. Gas Technol., vol. 1, No. 4, July 1945, pp. 6–7.

Brief review of modern methods for converting coal, both directly and indirectly, into motor fuels, oils, and other products is given. In the Fischer-Tropsch process the purified gases from the gasification of coal or coke are passed through Ni and Co oxide catalysts at atmospheric pressure and about 400° F. High-quality lubricating oils may be made from the primary product by the thermal cracking of the middle oil and polymerization of the olefinic products with $AlCl_3$ catalyst. Yields of about 35%, by weight, have been claimed, although these may be considerably higher if Fischer's claims are justified for the direct production of unsaturated oils by the use of an Fe catalyst at 15–20 atm. pressure.

1766. ———. Complete Gasification of Coal—Thermal Considerations. Gas World, vol. 122, 1945, pp. 220–226; Gas Jour., vol. 245, 1945, pp. 342, 344; Am. Gas Jour., vol. 163, No. 3, 1945, pp. 16–20, 60; Chem. Abs., vol. 39, 1945, p. 2191.

Discusses outstanding processes, with special reference to those conditions that affect thermal efficiency. The over-all thermal efficiency of a process is defined as the % that the thermal value of the products bear

to the sum of the thermal values of the raw materials used and of the heat and power consumed. It is apparent that complete conversion of coal to gas in a water-gas plant, which has had some application in the United States, must be thermally more efficient than the separate production of coal gas and water gas. It may be calculated that the advantage is about 12%. The Fuel Research Station, by adopting a special cycle, has gasified bituminous and sub-bituminous coals in a water-gas generator at a thermal efficiency of 64%. Data are given for several processes. The Tully, Humphreys-Glasgow (thermal efficiency 57% including the fuel for steam raising), Travers-Clark, and Broadhead (62% excluding power and steam) processes exemplify the type of combination carbonization and water-gas plant. The German processes for complete gasification have received more intensive development for 3 reasons: To utilize brown coal, to produce $CO:H_2$ mixtures for synthesis gas, and to make use of industrial O_2. They fall into 3 classes: (a) Those that involve heating by the recirculation of hot gases, for example, Pintsch-Hillebrand, Koppers, and Wintershall-Schmalfeld, which gasify brown coal at an over-all thermal efficiency of 50%; (b) those that involve an externally heated reaction chamber, for example, Heller, Ahrens (78.2% efficiency), Strache, and Didier-Bubiag (68.7% efficiency), have had industrial success as a flexible means of making synthesis gas at a $CO:H_2$ ratio of 2); (c) those that involve the use of O_2, for example, Winkler (77% excluding O_2 production), Lurgi-Drawe (62.2%, this process has probably reached the peak of efficiency under present operating conditions), Thyssen-Galoczy (80% including O_2 production). The special advance of this last group has been brought about by the use of O_2 made available from synthetic NH_3 plants. If O_2 were made specially for the purpose, the cost would be much higher. The development of a fairly cheap O_2 plant for application in the gas industry is one of the pressing problems.

1767. ———. Synthesis of Methane. Gas World, vol. 122, 1945, pp. 196–200, 209; Gas Times, vol. 42, Supp., 1945, pp. 1–4; Chem. Abs., vol. 39, 1945, p. 2189.

Review of research and a discussion of the reactions involved in synthesizing CH_4 from water gas and the application of these reactions to the production of city gas. With a high $H_2:CO$ ratio and when the main reaction at a low temperature and atmospheric pressure is

$$CO+3H_2 \rightleftharpoons CH_4+H_2O, \quad (1),$$

the water-gas-shift reaction must be satisfied:

$$CO+H_2O \rightleftharpoons CO_2+H_2. \quad (4)$$

If the $H_2:CO$ ratio is reduced, reaction (4) becomes more effective and more CO_2 appears in the final gas. When the ratio reaches unity, the reaction is:

$$2CO+2H_2 \rightleftharpoons CH_4+CO_2. \quad (2)$$

The effect of increase of temperature is to favor the water-gas reaction (4) at a high ratio and the CH_4 reaction (1) at a low ratio. A constant $CO_2:CH_4$ ratio independent of the $H_2:CO$ ratio is suggested at a temperature of about 750° C. The effect of pressure up to 25 atm. is nil at 300° but reduces the effect of increasing temperature. At 300° and 1 atm., the percentage of CH_4 obtainable in the dry CO_2-free gas rises from 83 to 98% as the $H_2:CO$ ratio falls from 3:1. With increase of temperature the % of CH_4 falls until it is less than 10% at 700°; a gas containing 50% CH_4 is obtained at 500° when the pressure is 1 atm. and at 700° when the pressure is 25 atm. In operating a technical process, assuming the use of a catalyst active enough to bring reactions (1) and (4) to completion at a high space velocity, the most favorable conditions for obtaining a gas of high CH_4 content would be low temperature and atmospheric pressure whatever the $H_2:CO$ ratio. At a higher temperature, however, the CH_4 content would be maintained and catalyst activity preserved only by increasing the working pressure. Care must be taken to prevent deterioration of the catalyst by surface overheating and bringing on reaction:

$$2CO \rightleftharpoons CO_2+C. \quad (5)$$

The deposition of C can be suppressed by using a high $H_2:CO$ ratio, which favors reaction (1). To obtain a ratio of 3:1, it may be necessary to treat part of the water gas with steam

$$H_2+CO+H_2O \rightleftharpoons CO_2+2H_2 \quad (6)$$

and to remove the CO_2 by washing under pressure, thus increasing the H_2 content of the original gas to the desired figure. Ni catalysts have been developed that can be operated at a high space velocity and that have an initial activity many times greater than is necessary to carry the main reactions to equilibrium. The reactions have been subjected to close study, and the knowledge collected is being applied to the control of the reaction on a larger scale looking towards the development of a pilot plant to operate under the proved conditions.

1768. ———. Control of Chemical Reactions on a Large Scale. Gas Times, vol. 51, 1947, pp. 369–372; Inst. Gas. Eng., Commun. and Repts., Commun. 315; Gas World, vol. 126, 1947, pp. 779–786, 808; vol. 127, pp. 93–98; Chem. Abs., vol. 41, 1947, p. 7015.

A presentation of the principles of the fluidized technique and a review of its development in the fields of petroleum refining, hydrocarbon synthesis, and coal gasification. Several advantages are evident: (1) The constant uniformity of temperature control obtainable; (2) the elimination of undesirable hot-spots in catalyzed reactions by the rapid mixing and turbulence of particles; (3) the achievement at high efficiency of high rates of heat transfer; (4) the high reaction rates obtainable because of the large surface available, the scrubbing action of gases in reducing protective layers, and the maintenance of deep reaction beds under uniform conditions; and (5) the convenient and cheap method of movement of large quantities of solids.

———. *See* abs. **451, 452, 453, 1466, 1467, 3198.**

1769. KINGMAN, F. E. T. Adsorption of Hydrogen by a Zinc Oxide–Chromium Oxide Catalyst. Trans. Faraday Soc., vol. 27, 1931, pp. 654–661; Chem. Abs., vol. 26, 1932, p. 355.

Adsorption of H_2 on a $ZnO–Cr_2O_3$ catalyst was studied at −80°, 0° and 100°. 3 types of adsorption probably occur, 1 at low temperature, involving a low energy of activation, another at higher temperatures involving a high energy of activation but not leading to the reduction of the catalyst, and a 3d at high temperature, leading to reduction of the catalyst.

———. *See* abs. **450, 1144, 1145.**

1770. KINGMAN, F. E. T., AND CAWLEY, C. M. Cracking of Middle Oil From the Fischer-Tropsch Process. Petroleum (London), vol. 9, 1946, pp. 126–128; Chem. Abs., vol. 40, 1946, p. 5903.

Experiments were carried out on the thermal cracking of the middle oil fraction, boiling at 200°–300°, from Fischer-Tropsch product, using a vertical, electrically heated, Pyrex tube with a 35-ml. reaction space. The cracking temperature varied from 570°–635°, the throughput from 40–110 gm. per hr., and the reaction time from 30–10 sec. At 635° and a throughput of 90 gm. per hr., the total yield of liquid product was 67.6 wt. % of the original oil, with a yield of gasoline to 200° of 20.4%. Recycling the oil boiling above 200° gave a total yield of 37.8% of gasoline to 200°, Br No. 130, and a yield of gas of 39.3 l. per 100 gm. of raw material. The gasoline to 170° had a Br number of 148, and contained approximately 80–90% olefins

with less than 2% aromatics. The gaseous product from thermal cracking contained only a small proportion of H_2; the olefins, which increased from 57% at 570° to 63% at 635°, consisted mainly of C_2H_4 and C_3H_6 with a smaller proportion of C_4H_8 and a very small amount of butadiene. With a catalyst of mixed alumina and silica, the yield of gas increased and the nature of the products was noticeably affected. The gasoline had a lower olefin content and a higher content of both aromatic and saturated hydrocarbons. The gas contained a greater proportion of H_2; the proportion of total olefins was not greatly changed, but the catalyst favored the production of C_3H_6 and C_4H_8 in place of C_2H_4, and the formation of butadiene was completely suppressed.

1771. KINGTON, G. L., BEEBE, R. A., POLLEY, M. H., AND SMITH, W. R. Entropy of Adsorbed Molecules. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 1775–1781; Chem. Abs., vol. 44, 1950, p. 6228.

Differential heats of adsorption of N_2 and O_2 on TiO_2 were determined calorimetrically at 78.5° K. The TiO_2 used in both cases was a sample of anatase with a Brunauer, Emmett, and Teller (abs. **389**) surface area of 13.9 $m.^2$ per gm. The magnitude of the heat in both cases indicates that the adsorption is van der Waals in nature. The initial increments of N_2 showed a heat of adsorption approximately 1 kcal. per mol. higher than the initial O_2 values. The partial molal entropy of the adsorbed gas was determined from experimental data for both N_2 and O_2 adsorbed on C black and TiO_2 (anatase) at 78.5° K. The results show that the partial molal entropy of the adsorbed gas is less than the partial molal entropy of the bulk 3-dimensional liquid or solid phases, at coverages less than a monolayer, as defined by B. E. T. v_m, for all the systems investigated. At coverages greater than a monolayer, the partial molal entropy approaches the entropy of the 3-dimensional liquid or solid. The entropy requirements of the B. E. T. theory are shown to be incompatible with experimental evidence at coverages less than a monolayer.

KINI, K. A. *See* abs. **1192, 1193, 1193a.**

1771a. KINI, K. A., BASAK, N. G., AND LAHIRI, A. Adsorption of Hydrogen and of Carbon Monoxide on an Iron–Copper–Magnesia Catalyst. Jour. Sci. Ind. Research (India), vol. 10B, No. 10, 1951, pp. 243–245; Chim. et ind., vol. 67, 1952, p. 790.

Adsorption of H_2 and CO on a Fischer-Tropsch catalyst (Fe–Cu–MgO, 80:5:15) was determined between 99° and 249°. The results show that synthesis of hydrocarbons is realized by chemical adsorption. In order for the synthesis to occur under the best conditions, it is essential that chemical adsorption of CO should exceed that of H_2.

1772. KINNEY, C. R. Nonfuel Uses of Bituminous Coal. Proc. Coal Min. Inst. America, 58th Ann. Rept., Dec. 7, 1944, pp. 1–11.

Brief mention of the use of coal for makng water gas from which MeOH and synthetic gasoline can be made by the Fischer-Tropsch process.

KIPERMAN, S. *See* abs. **3367, 3369.**

1773. KIPERMAN, S., AND TEMKIN, M. [Kinetics of Ammonia Synthesis on Molybdenum Catalyst.] Acta Physicochem. U. R. S. S. vol. 11, 1946, pp. 267–282; Jour. Phys. Chem. (U. S. S. R.), vol. 20, 1946, pp. 369–378; Chem. Abs., vol. 40, 1946, p. 6950.

Experimental data confirm the work of Temkin and Pyzhev on the synthesis of NH_3 on promoted Fe catalyst and extend the results to a Mo catalyst. A flow system was used with 2 cc. of catalyst. The Mo catalyst was prepared by reducing ammonium molybdate in NH_3 for 20 hr. at 600°–650°. X-ray diffraction patterns indicate that the catalysts operate in the form of metallic Fe and Mo_2N. The data for both catalysts support the kinetic equation suggested by Temkin and Pyzhev, the value of α for both catalysts is 0.5. The apparent activation energy of NH_3 decomposition on Mo catalyst as calculated from the synthesis rate is 42.5 kcal. per mol. The NH_3 synthesis on Fe and Mo is considered to have the same mechanism.

1774. KIPNIS, F. Separation of Catalysts from Hydrogenation Reaction Mixtures. Ind. Eng. Chem., anal. ed., vol. 16, 1944, p. 637; Chem. Abs., vol. 39, 1945, p. 3.

A filter aid, such as Dicalite 4200, is used with a Büchner funnel to give a clear filtrate.

1775. KIRKBY, W. A. Oil From Coal in Japan. Fuel, vol. 23, 1944, pp. 32–33.

Notes on recent developments in fuel technology.

1775a. KIRKPATRICK, W. J. Nickel Sulfide Catalysts. Advances in Catalysis, Academic Press, Inc., New York, vol. 3, 1951, pp. 329–339.

A number of reactions catalyzed by Ni sulfide are given and the conditions under which Ni sulfide acts as catalyst are mentioned. The 2 Ni sulfides, Ni_3S_2 and NiS, which can exist under conditions prevailing in some catalytic systems, are catalysts for some reactions also catalyzed by metallic Ni and for other reactions not yet found to be catalyzed by the metal. Explanations of this behavior in terms of bond theory or Brillouin zones can be expected in the near future. 19 refs. are given.

1776. KIRSCHFELD, L. [Water-Gas Equilibrium in Homogeneous and Heterogeneous Reactions.] Chem. Tech., vol. 18, 1945, pp. 52–59.

Graphic methods are used for determining the water-gas equilibrium (1) for constant C content, (2) for constant O_2 content, and (3) for interaction of the gas with Fe and Fe oxides.

KIRSCHT, P. H. *See* abs. **3057, 3059.**

KISTIAKOWSKY, G. B. *See* abs. **1419, 3336.**

1777. KITA, G. Catalyst for Production of Synthetic Gasoline. Jour. Fuel Soc. Japan, vol. 16, 1937, pp. 497–511, in English, pp. 60–62; Jour. Inst. Petrol. Technol., vol. 23, 1937, p. 362A; British Chem. Abs., 1937, B, p. 1005; Chem. Abs., vol. 31, 1937, p. 6858.

Further discussion is presented on the suitabilities of different types of catalysts used in the production of synthetic gasoline in the Fischer process. Co catalysts with accelerators, particularly ThO_2 and U_3O_8, give good yields, the quantity required being reduced to 1/6 if pumice is used as the carrier. Increased yields are given by the addition of sucrose which increases the porosity by decomposition of $Co(NO_3)_2$ at high temperatures. Ni catalysts are highly susceptible to manufacturing conditions and should be prepared by settling with the addition of alkali carbonate, and reduction should be carried out at 450° C., while the Ni should not contain more than 0.5%, and must contain an irreducible oxide accelerator plus a small quantity of alkali. The substitution of Al_2O_3 or acid clay for ThO_2 as an accelerator gave improved results. Alloy catalysts made from Ni–Co–Al–Si alloy from which Al or Si is extracted with alkali have the advantage of small volume, high thermal conductivity, and granular form. Ni–Co catalysts of composition 50% Co–50% Ni+15% Mn+3% ThO_2+5% U_3O_8+125% diatomaceous earth gave the highest yield of gasoline obtained in these tests, 166 cc./$m.^3$ of gas. Fe catalysts are of low activity, producing about 1/3 of the yield of gasoline given by more effective catalysts.

1778. ———. Artificial Petroleum. Chem. Rev. (Japan), vol. 4, 1938, pp. 436–449; Chem. Abs., vol. 35, 1941, p. 7679.

Lecture.

1779. ———. Synthetic Petroleum From Water Gas by Iron Catalyst. Chem. Rev. (Japan), vol. 7, 1941, pp. 203–208; Chem. Abs., vol. 35, 1941, p. 7679.

A lecture with figs.

KLAPCHUK, S. V. *See* abs. **1267.**

1780. KLAR, M. [Technical Preparation of Formaldehyde.] Chem.-Ztg., vol. 59, 1935, pp. 741–744; Chem. Abs., vol. 29, 1935, p. 7277.

World production of HCHO, 40 vol. %, amounts to about 75,000 tons/yr., almost wholly from MeOH, 85% of which is produced synthetically from water gas.

KLAS, H. *See* abs. **3056.**

1781. KLEINSCHMIDT, R. V. Handling High Pressures in Chemical Synthesis. Chem. and Met. Eng., vol. 40, 1933, pp. 361–364; British Chem. Abs., 1933, B, p. 815.

Soft Fe and Cu are suitable gasket materials for high-pressure joints, but Cu cannot be used where temperature variations are encountered. The use of soft Fe in grooves is indicated. Joints in which rubber packing is pressed outward by the fluid pressure against the gasket are satisfactory, but not at higher temperature. The use of 2 valves in series enables the second valve to be closed under favorable circumstances. Flow control valves are often fitted with a coil of small high-resistance tubing to dissipate the energy of expansion. The use of valves utilizing the principle of the labyrinth packing gland is suggested. Compressors should be designed for the particular gas with which they have to deal. In the design of converters provision should be made for (1) an outer curtain of incoming gas to act as an insulating medium, (2) a countercurrent heat exchanger with preferably small tubes of considerable length, (3) generally concurrent heat transfer from the catalyst bed to render the bed thermally stable and to prevent too great a range of temperature in the bed.

———. *See* abs. **1080.**

1782. KLEMENC, A., AND RUPP, J. [Behavior of Iron Catalysts in the Temperature Range of 250°–450° Toward Illuminating Gas and Other Similar Gases.] Angew. Chem., vol. 47, 1934, pp. 182–184; Chem. Abs., vol. 28, 1934, p. 3221.

Behavior of commercial illuminating gas was investigated in the presence of the following Fe catalysts: (1) Fe precipitated from $Fe(CO)_5$, (2) Fe powder, (3) Fe powder activated by treatment with $AlCl_3$ and NH_4OH or NaOH solutions and (4) synthetic catalysts, for example, Fe oxides from various sources. A reduction of the CO content and an increase of the CH_4 content take place. The most effective temperature range for the experimental conditions was found at 280°–450°. A greater retort length results in greater CO conversion, while increasing gas velocity results in smaller CO conversion. The catalyst surface undergoes a continual change, and the progress of the reaction dilutes the catalyst. As side reactions the decomposition of heavier hydrocarbons and reactions with H_2O vapor were encountered, but it was found that temperatures can be chosen low enough to avoid the decomposition of the heavier components; however, larger quantities of H_2O vapor act disturbingly upon CH_4 formation. Attempts to regenerate the catalysts by simple processes failed, and it was found that a mixture of 21–22% C and 32–34% Fe, with a ratio of Fe : O_2=3 : 4.1, becomes inactive. At a gas velocity of 500 l. per hr. (area=81.6 $cm.^2$), a consumption of 10 gm. catalyst per $m.^3$ of converted gas was determined, after a passage of 140 $m.^3$ of gas, and the catalyst was still in a decidedly active condition.

1783. KLEMM, H. [Type of Structure in the Iron-Carbon System.] Arch. Metallkunde, vol. 3, 1949, pp. 265–271; Chem. Abs., vol. 44, 1950, p. 507.

Fe–C diagram is analyzed and photomicrographs show the various transition and equilibrium phases as they accur. Typical structures resulting from the method of production and as a result of segregation are shown.

1784. KLEMM, R. [Fused-Iron Catalysts for Carbon Monoxide–Hydrogen Synthesis.] TOM Reel 278, item 2, 44 pp.; PB 82,353; FIAT Rept. 1267, Supp., 1949, 39 pp.; PB 97,368 S.

Summary of observations and experience gained during 8 years of experimentation with the development of fused Fe catalysts used in CO–H_2 synthesis under high pressure and temperature. The catalysts discussed were produced by fusing Fe and the additives in a stream of O_2. Microscopic examination is described in detail. The effect of basic and acidic additives and of lattice displacement and disturbance on the effectiveness and yield of the catalysts is studied. The most advantageous location of the additive in the lattice is given. The results obtained with various catalysts of this type are presented.

1785. KLEMPT, W. [Contact Furnaces and Contact Equipment in the Chemical Industry.] Ztschr. Ver. deut. Ing., Beih. Verfahrenstech., vol. 83, 1939, pp. 122–127; Chem. Abs., vol. 34, 1940, p. 4.

Discussion of most-important types of equipment for catalytic gas reactions with figures and 12 refs.

———. *See* abs. **1724.**

1786. KLEMPT, W., AND BRODKORB, F. [Methane-Steam Equilibrium and Its Control.] Ber. Gesell. Kohlentech., vol. 3, 1930, pp. 220–229; British Chem. Abs., 1931, B, p. 325.

Theoretically, at high temperatures the reaction between CH_4 and steam takes place according to the equation (1) $CH_4+H_2O=CO+3H_2-48.9$ kcal., while at lower temperatures it takes the form (2) $CH_4+2H_2O=CO_2+4H_2-38.5$ kcal. The equilibrium constants for these two reactions have been determined only for a few temperatures, but it is possible to calculate their values from those obtained in the reactions $CH_4=C+2H_2$; $C+CO_2=2CO$; and $CO+H_2O=CO_2+H_2$, which are known over the range 450°–1,200°. The constants $K'_p={}_pCH_4\cdot pH_2O/pCO\cdot pH_2$ and $K''_p=pCH_4\cdot pH_2O^2/pCO_2\cdot pH_2^4$ are tabulated over the same range, but it is emphasized that the values of K'_p can only be strictly accurate at very high temperatures, while the applicability of those of K''_p is limited to lower temperatures. Calculation of the equilibrium condition shows that at 500° the cracked gas contains CH_4, 33.3%; H_2O, 33.3%; CO, 8.33%; and H_2, 25.0%; while at 940° the composition is CH_4, 0.505%; H_2O, 0.505%; CO, 24.8%; and H_2, 74.1%; when reaction (1) takes place. A similar table is given in connection with equation (2). Since in practice an excess of steam would be used, calculations have been made to find the effect of 2-fold and 6-fold excess of steam on the equilibrium when pure CH_4 is used. The influence is considered of the other constituents on the equilibrium amount of CH_4 present in a gas of the following composition: 10% ($CO+CO_2$), 30% ($CH_4+C_nH_m$) 50% H_2, 10% N_2. Temperature-composition graphs are given for both reactions (1) and (2) with this mixture. At about 820° the CH_4 decomposes to give at equilibrium a gas containing equal proportions of CO and CO_2.

1787. ———. [Water-Gas Equilibrium and Its Control.] Ber. Gesell. Kohlentech., vol. 3, 1930, pp. 261–274; British Chem. Abs., 1931, B, p. 325.

Theoretically, the known values for the equilibrium constant of the reaction $CO+H_2O=CO_2+H_2$ over the range 327°–2,090° indicate that at higher temperatures the equilibrium is in favor of CO-steam. To favor the production of H_2, as low a temperature as is compatible with suitable reaction velocity must be chosen. The

use of catalysts alone does not materially assist in the complete removal of CO from the gas at temperatures at which it is practicable to work. The theory is discussed of the disturbance of the equilibrium by use of excess of steam and by removal of the CO_2 formed simultaneously with the H_2 by absorbents such as lime. The pressure of CO_2 in the system $CaCO_3$–CaO–CO_2 limits the temperature at which the latter method of disturbing the water-gas equilibrium can be used to an extreme of 600°. In practice, lower temperatures would have to be used. This theoretical study leaves no doubt that the removal of CO_2 is the more practicable method of achieving a good conversion of the CO. Thus, at 550°, to reduce the steam- and CO_2-free gas to the same CO content as that produced by the passage over lime, using 1 vol. of steam, requires a volume of steam 20 times that of the CO. By using a slight excess of steam in conjunction with CO_2 removed at this temperature, the CO can be reduced to a mere trace. The foregoing considerations are applied to the gas resulting (abs. **1724**) from the action of steam and air on CH_4.

1788. KLEPPA, O. J. [Equilibrium $CoO+H_2=Co+H_2O$. The Molar Entropy of Cobaltic Oxide.] Svensk Kem. Tid., vol. 55, 1943, pp. 18–25; Chem. Zentralb., 1943, I, p. 1970; Chem. Abs., vol. 38, 1944, p. 4855.

Equilibrium was studied by the stream method, and values were obtained that agree with the static method. For the constant $K_p=pH_2O/pH_2$ the heterogeneous equilibrium gives $K_p^{598}=39.35$, $K_p^{849}=44.2$, $K_p^{793}=51.3$, $K_p^{738}=56.8$ (temperature in degrees Kelvin). According to $\Delta F=-RT \log K_p$, the change in free enthalpy (reaction-work) can be calculated, and also the heat content by means of van't Hoff's equation, which then can be determined at other temperatures with the help of molecular heat. The normal values $\Delta F^{298}=-3461$ cal. per mol., and $W_p^{298}=859$ cal. per mol., are obtained, from which it follows that $\Delta S^{298}=8.73$ cal. per mol. per degree. From the known normal entropies of H_2O, Co, and H_2 it follows that S^{298} Co$=11.94\pm0.2$ cal. per deg. mol.

1789. KLIMOV, B. K., LANIN, V. A., AND TIKHONOVA, Z. T. [Formation of Methane in the Preparation of Water Gas From Peat Coke.] Jour. Chem. Ind. (U. S. S. R.), vol. 11, 1934, No. 7, pp. 50–52; Chem. Abs., vol. 29, 1935, p. 321.

CH_4 is formed from CO and H_2 owing to the great catalytic activity of the peat coke.

1790. KLING, A. [Production of Fatty Acids From Paraffins.] Parfumerie, vol. 1, 1943, pp. 185–188, 213–216; Chem. Abs., vol. 40, 1946, p. 5269.

Address briefly reviewing the general processes for synthesizing paraffins and for their controlled oxidation for the production of industrial, and even edible, fatty acids. A major part of the address is devoted to the Fischer-Tropsch process and to the work of Arditti.

KLINGER, P. *See* abs. **1498.**

1791. KLYUKVIN, N. A. AND KLYUKVINA, S. S. [Conversion of Methane. I.] Jour. Chem. Ind., U. S. S. R., vol. 7, 1930, pp. 743–752; Chem. Abs., vol. 25, 1931, p. 4520.

Investigation deals with conversion of CH_4, industrially available in great quantities as a waste product, into commercial products. Catalytic conversion of CH_4 can be used industrially for the production of H_2. CH_4 and mixtures of CH_4 with CO_2 and with H_2O were passed through porcelain tubes 50 cm. long and 16 mm. in diameter, or Fe tubes 100 cm. long and 22 mm. in diameter heated in an electric oven 28 cm. long. The temperature was measured with a pyrometer provided with a Pt thermocouple and inserted in a quartz tube. The gases were conducted at the rate of 3,000 cc./hr., or 38 sec. of contact. With reduced NiO as catalyst in a porcelain tube only 1.6% CH_4 remained unchanged at 850°, while without a catalyst 69.8% at 850° and 57.2% of CH_4 at 1,000° were recovered. The gas contained also H_2 94.3 and N_2 4.1% and showed 99.6% increase in vol. The thermal decomposition of CH_4 may be complicated by side reactions with formation of CO and CO_2, and, when no Ni is used, with unsaturated compounds. A mixture of CH_4 and CO_2 (1 : 1) produced with Ni at 1,000° 97.6% conversion (95% increase in vol.); the reaction is based on the formula: $CH_4+CO_2=2\ CO+2\ H_2$. The gas was composed of CO 47, H_2 48.6, N_2 2.6% and no byproducts. The formation of CO begins at 700°. An addition of Al_2O_3 to Ni (2 : 1) does not change the general character of the reaction but retards somewhat the progress of conversion. This experiment repeated without a catalyst gave in a porcelain tube at 1,000° only 43% conversion of CH_4, and in Fe tubes 58%. Under equal conditions, the conversion of CH_4 is in direct proportion to the speed with which the gas is passed through the reaction tube, and at the velocity of 9 l./hr., instead of 3 l./hr., is reduced by 10%.

1792. ———. [Conversion of Methane. II.] Jour. Chem. Ind., U. S. S. R., vol. 7, 1930, pp. 877–885; Chem. Abs., vol. 25, 1931, pp. 4520–4521.

Conversion of CH_4 with H_2O was carried out in an Fe tube 100 cm. long and 22 mm. in diameter. As catalysts reduced NiO (16 gm.) and NiO (24 gm.) were used. The gas mixture consisted of 1 vol. of CH_4 and 4 vol. of steam and was passed with a velocity of 6 liter/hr. The conversion is based on the formula $CH_4+H_2O=CO+3H_2$, which at low temperature may be modified to: $CH_4+2H_2O=CO_2+4H_2$, while the interaction of the reaction products may be as follows: $CH_4+CO_2=2CO+2H_2$ and $H_2O+CO=CO_2+H_2$, all of which is substantiated by the composition of the resulting gas. The best result obtained is 98.4% conversion of CH_4 with 218% increase in volume, the gas containing CO_2 5.8, CO 12.6, H_2 80, O_2 0.4, N_2 0.7, CH_4 0.5% and no unsaturated compounds. A substitution even in part of Al_2O_3 or reduced Fe for Ni produced unsatisfactory results. Activated vegetable C gives 100% conversion of CH_4 at 800° with 142% increase in volume, while the respective figures for reduced Ni at 800° are 33.3 and 100%. At lower temperature (500°–700°) both catalysts give about equal conversion of CH_4, but the quantity of gases obtained is higher with C; this indicates that the conversion of CH_4 is accompanied by decomposition of water: $C+2H_2O\rightarrow CO_2+2H_2$. At 700° the resulting gas mixtures contain 1.2% of CO_2 with Ni and 10.4% with C. It must be noted, however, that the increase in vol. is 142% with C and 218% with Ni. The conversion of CH_4 with C catalyst without H_2O results at 800° in 26.9% and at 900°–950° in 100% conversion of CH_4 with 100% increase in vol. The gas is of exceptional purity, containing CO_2 0.2, CO 0.8, H_2 93.1, N_2 5.9% and no O_2, CH_4 or unsaturated compounds. To investigate more closely the catalytic action of activated C in the thermal conversion of CH_4, the last 2 experiments were repeated with C in porcelain tubes instead of Fe tubes, thereby eliminating any possibility of the catalytic action by Fe. Since the velocity of the gas was 6 l./hr. instead of 3 l./hr. as in the experiments with Ni, it can be concluded from the results that C is a less active catalyst than Ni. With Ni the reaction begins at 300° and reaches a complete conversion of CH_4 at 850°, while with C it starts only at 500°–600°, and ends with only 62.4% of conversion at 1,000°. The test with inactivated birch C under these conditions produced at 1,000° 47.1% conversion of CH_4 in a porcelain tube, and 100% conversion with 100% increase in vol. at 900° when conducted in an Fe tube; that is, equal in its activity to activated C. From 27 gm. of the C used 26.8 gm. were recovered after 8

experiments. A catalyst containing 9 gm. of inactivated birch C and 72 gm. of Fe filings produced in a porcelain tube at 1,000° 100% conversion of CH_4 with 100% increase in vol., the gas containing H_2 97.5, N_2 2.5% and no other products. The results are similar to those obtained with Ni and with C in an Fe tube. No decrease in weight of the catalyst was observed after 9 experiments.

1793. ———. [Chemical Treatment of Natural Gases. I.] Prirodnuie Gazui, vol. 2, 1931, pp. 91–128; Chem. Abs., vol. 26, 1932, p. 1416.

CH_4 containing 8% N_2 was passed through a porcelain tube in the presence of reduced Ni and heated at various temperatures; the highest conversion to H_2, amounting to 94.3%, was attained at 850°, the balance being 1.6% CH_4 and 4.1% N_2, while under the above condition with a temperature of 1,000° 57.2% of CH_4 still remained unchanged when the reaction was carried out without a catalyst. Equal volumes of CH_4 and CO_2 require a 100° higher temperature. In the conversion of CH_4 and H_2O vapor in the presence of a mixture of Ni and NiO catalysts the highest yields (increase of volume by 205%) were obtained at 900° and a CH_4 : H_2O ratio of 1 : 4 and 1 : 5. When activated wood charcoal was substituted for the Ni catalyst, a complete conversion was obtained at 750°–800°, but the yield of H_2 amounted to only 55.9%, while 37.7% CO was present in the final gas mixture. This is probably due to the reaction $C+H_2O \rightarrow CO+H_2$, favored by temperatures exceeding 750°. Conclusion: The conversion of gases containing CH_4 is commercially feasible. The process temperature is of the magnitude of 800°–950°. Reduced Ni may be used as catalyst. Semicoke prepared from brown coal as well as coke from hard coal are catalysts equivalent to Ni. An excess of H_2O favors the formation of H_2. The thermal decomposition of CH_4 in the presence of water vapors is insignificant above 800°, and a complete conversion is obtained at about 900°.

1794. ———. [Preparation of Mixtures of Carbon Monoxide and Hydrogen for the Synthesis of Alcohol.] Natural Gases, U. S. S. R., vol. 8, 1934, pp. 52–58; Chem. Abs., vol. 31, 1937, p. 3642.

Of 16 Ni catalysts tested, Ni–Th–Mg on kieselguhr and Ni–Fe on kieselguhr were best. In the presence of Ni–Fe on kieselguhr, with an excess of water vapor (CH_4 : H_2=1 : 1.5) and a concentrate of natural gas (CH_4, 60 and N_2, 40%), containing CH_4, 91, and N_2 9%, yielded at 750° CO_2, 1, CO, 20, and H_2 75%. The gas mixture obtained used in alcohol synthesis in the Patart apparatus at 350° under an initial pressure of 150–125 atm., in the presence of a Zn–C catalyst and a velocity of 18,000 l./hr., yielded 113–187 cc. of condensate boiling at 65°–75°, 17.9–18.8; 75°–85°, 69.9–65.7; and 85°–95°, 2.2–2.6%. Activation of the Fe catalyst with a 1% admixture of Ni promotes formation of water gas at 900°, whereas a 5% admixture of Ni reduces the CO formed to C. Activation of the catalyst with a 5% admixture of Mg yields satisfactory results at 900°.

1795. KLYUKVIN, N. A., AND VOL'NOV, Y. N. [Synthetic Hydrocarbons From Water Gas.] Khim, Tverdogo Topliva, vol. 4, 1933, pp. 355–362; Chem. Zentralb., 1934, II, p. 3464; Chem. Abs., vol. 28, 1934, p. 6279.

Catalysts Ni–Th, Ni–Th–Hg, and Ni–Mg were best for the production of gasoline from CO and H_2, yielding under the most favorable conditions 0.1 gm. of gasoline per l. gas passed, that is, 30–40% on the converted CO, this yield being raised to 98–100% on recycling. By the proper selection of the catalysts and the process conditions, a product high in unsaturated compounds can be obtained. 26 refs.

1796. KLYUKVIN, N. A., VOL'NOV, Y. N. AND KARPINSKIĬ, M. N. [Ethanol Synthesis. I.] Khim. Tverdogo Topliva, vol. 3, 1932, pp. 829–837; Chem. Abs., vol. 28, 1934, p. 5806.

Feasibility of various methods for the preparation of EtOH is discussed. The experiments were carried out with a gas containing CO 33.4, H_2 66.2 and CO_2 0.4%. After the experiments the composition of the gas was changed; it contained CO_2 up to 12, CH_4 11, CO about 33.4 and the amount of H_2 decreased to 45–50%. The condensate contained fractions boiling 60°–70°, 76°–80° and above 80°. The highest yield, 39%, of EtOH was attained at 320°–330°, 120 atm. and in the presence of ZnO : CoO : : 3 : 1, catalysts. A series of alcohols from Me to Am were traced in addition to EtOH. The experiments are described and the effect of changes in the experimental conditions is shown on diagrams.

KLYUKVINA, S. S. *See* abs. **1791, 1792, 1793, 1794.**

KNAPP, B. *See* abs. **166.**

1797. KNEULE, F. [Tendency to Carbonization of Diesel Fuel.] Ztschr. Ver. deut. Ing., vol. 86, 1942, pp. 76–78; Brennstoff-Chem., vol. 23, p. 285; Chem. Abs., vol. 37, 1943, p. 3903.

Experiments showed that the Conradson carbonization test is a reliable indication of the tendency of a fuel to deposit C on the fuel-inlet nozzles. Addition of relatively small amounts of Fischer-Tropsch products can lower the coking tendency of many fuels.

———. *See* abs. **3093.**

1798. KNIEL, L. Propane Recovery by Absorption. Petrol. Processing, vol. 3, No. 11, 1948, pp. 1066–1072; Petrol. Refiner, vol. 27, No. 11, 1948, pp. 588–593.

Presented at meeting of the California Natural Gasoline Association. Increased extraction of propane of the required purity in absorption-gasoline plants may be achieved through changes in the fractionating absorber and its important adjuncts, the gas cooler and partial condenser. Design formulas are presented for the absorber, for the determination of liquid and vapor traffic, key temperatures, and other factors that relate to retention in the absorber and to rejection in the stripper with overall recovery. Plant design based on the formulas is applied to the recovery of 90% propane from a wet gas of specified composition, as an example. Product costs are shown lower than in most conventional plants handling an equal volume of gas and recovering gasoline and butanes only. The direct cost of production is calculated at $0.705 per gal. of total liquid products recovered.

———. *See* abs. **3227.**

1799. KOBAYASHI, K. Production Methods of Synthetic Fuels and Oils. Trans. World Power Conf., Tokyo Sectional Meeting, vol. 1, 1929, pp. 574–576; Chem. Abs., vol. 26, 1932, p. 2298.

1800. ———. Recent Investigations on the Synthesis of Petroleum. Jour. Fuel Soc. Japan., vol. 12, 1933, pp. 436–446; Chem. Abs., vol. 27, 1933, p. 3808.

Brief review of progress in Japan.

1801. KOBAYASHI, K. AND YAMAMOTO, K. Synthesis of Petroleum Hydrocarbons From Hydrogen and Carbon Monoxide at Ordinary Pressure. I. Jour. Soc. Chem. Ind. (Japan), vol. 32, 1929, p. 54; Suppl. 32, 1929, p. 23B; Chem. Abs., vol. 23, 1929, p. 5035.

Experiments are described in which petroleum hydrocarbons were obtained by passing a mixture of 3 vol. of H_2 and 2 vol. of CO over a catalyst consisting of Co, Cu and Mn at about 300° under atmospheric pressure.

1802. KOBAYASHI, K., YAMAMOTO, K., AND ISHIKAWA, H. Synthesis of Petroleum Hydrocarbons From Hydrogen and Carbon Monoxide at Ordinary Pressure. II. Mem. Faculty Sci. Eng. Waseda Univ. (Tokyo), No. 7, 1930, pp. 26–27; Chem. Abs., vol. 25, 1931, p. 2840.

Nine catalysts composed of Co, MnO and Cu were used in the synthesis of oil from CO and H_2. Active C formed from the decomposition of the CO is considered the basic material for subsequent hydrogenation and polymerization to oils. CH_4 was formed simultaneously.

1803. ———. Synthetic Petroleum From Carbon Monoxide and Hydrogen. Jour. Fuel Soc. Japan, vol. 9, 1930, p. 40.

Paper presented at the 33d annual meeting of the Society of Chemical Industry, Japan. In the synthesis of petroleum, it is necessary, first of all, to explain the mechanism of the reaction, which can be divided into the following 4 stages: (1) Decomposition of CO into CO_2 and C, the latter in a nascent state; (2) the reaction between CO and H_2 with CH_4 and H_2O as the products; (3) production of C_2H_4 and C_2H_2 from C liberated in stage 1; (4) condensation of C_2H_4 and C_2H_2 into petroleum. To obtain the maximum yield of petroleum, it is important to accelerate reactions 1 and 3 and depress 2 as far as possible. For this purpose, the reactions must be carried out separately in the production of C_2H_4 and C_2H_2 on the one hand and the condensation of those products on the other.

KOBE, K. A. *See* abs. **2759.**

1804. KOBOZEV, N. I. [Mechanism of the Inhibiting Effect of Promoters on the Reduction of Iron-Ammonia Catalysts.] Acta Physicochim. U. R. S. S., vol. 4, 1936, pp. 829–840; Chem. Abs., vol. 30, 1936, p. 7987.

Theoretical discussion based on the results of Natanson (abs. **2370**) and Dubrovskaya and Kobozev (abs. **749**).

1805. ———. [Mechanism of the Retarding Effect of Promoters on the Reduction of Iron-Ammonia Catalysts.] Jour. Phys. Chem. (U. S. S. R.), vol. 8, 1936, pp. 226–233; Chem. Abs., vol. 31, 1937, p. 1559.

Data are given for the retarding effects of K_2O, BeO, KF, and Al_2O_3 on the reduction of Fe_2O_3 by H_2 and of MgO on that of FeO. Promoter action of the catalyst results when the added substance is surface-active and reduces the rate of reduction of the Fe oxide.

———. *See* abs. **749.**

1806. KOBOZEV, N. I., EROFEEV, B. V., KAVERIN, I. B., AND BOGOYAVLENSKAYA, A. N. [Mechanism of the Promotion Action of Iron Ammonia Catalysts.] Acta Physiochim. U. R. S. S., vol. 1, 1934, pp. 483–492; Chem. Abs., vol. 29, 1935, p. 7774.

Promoting action of Al_2O_3 and MgO on FeO was studied from the viewpoint of mixed crystals between the promoter and the initial Fe oxide. The formation of mixed crystals is not enough, in itself, to cause the promoting action. It was proposed that it was necessary for a promoter to be surface-active with regard to the initial mass of the catalyst. A pronounced difference between the surface tension of Fe_3O_4 and $Fe_3O_4+Al_2O_3$ and an absence of such a difference between FeO and FeO+MgO as confirmed by the catalytic activity of Fe reduced from these oxides was experimentally shown.

1807. KOCH, H. [Synthesis of Benzine From Carbon Monoxide and Hydrogen Under Atmospheric Pressure by the Method of F. Fischer and H. Tropsch.] Glückauf, vol. 71, 1935, pp. 85–90; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 577–587; Chem. Abs., vol. 29, 1935, p. 6401.

Fundamental principles of the synthesis with reference to mechanism of reactions, preparation of catalysts, and reacting gases and properties of primary and secondary products. The best gas mix contained 29% CO and 58% H_2, which with a Co catalyst yielded an oil, 62% boiling at 30°–200°, containing 30% olefins. Other products were 4% boiling at <30°, 23% boiling at >200°, and 14% solid paraffin. A Co–Th catalyst precipitated on kieselguhr gave a yield of 110 gm. of oil for 60 days, after which the efficiency began to decrease. The motor-spirit fraction must be rendered anti-knocking, for example, by blending with C_6H_6. Heavy oils lend themselves to preparation of synthetic alcohols and motor spirit through cracking and subsequent treatment of cracked residues. Lubricating oils of superior quality are prepared from the olefins by condensation in the presence of $AlCl_3$ or from the paraffins by chlorination and condensation with aromatic hydrocarbons, for example, xylene. The mechanism of the reactions by which liquid hydrocarbons are formed involves formation of metallic carbides; these react with H_2, forming CH_2, which condenses.

1808. ———. [Synthetic Lubricating Oils.] Ztschr. Ver. deut. Ing., vol. 80, 1936, pp. 49–50; Coal Carbonisation, vol. 2, 1936, p. 63; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 588–592; Mech. Eng., vol. 58, 1936, pp. 248–249; Chem. Abs., vol. 30, 1936, p. 2741.

Good yield of lubricating oil can be obtained by polymerization of the olefin hydrocarbons in the Kogasin product of the Fischer-Tropsch synthesis. It is desirable that the monoolefin content should be as high as possible and can be brought about by using a 1:1 ratio of CO to H_2 instead of the usual 1:2 ratio whereby a Kogasin is obtained with 50% of reactive olefins. Polymerization is effected by $AlCl_3$ catalyst in about 8 hr. at 100° C. Synthetic lubricants from the olefin fractons of boiling point 125°–250° C. are equal in viscosity to the best Pennsylvania oils, their specific gravity is only 0.84–0.85, and their coking tendency is very low. They are quite free from S and have very low setting points (—30° C. for an aviation lubricant of 123 Engler viscosity at 20° C.). With the present development of the process, the yield of thick oils is about 60% of the weight of olefins treated; most of the remaining 40% is converted to comparatively thin oils, which can be combined with the gas-oil fraction. For a further increase in total yield, the paraffin hydrocarbons of the Kogasin can be processed by chlorination and catalysis, yielding another series of lubricating oils of excellent quality.

1809. ———. [Some Properties of Synthetic Lubricants From Kogasin.] Brennstoff-Chem., vol. 18, 1937, pp. 121–127; British Chem. Abs., 1937, B, p. 408; Chem. Abs., vol. 32, 1938, p. 8756.

Previous work reviewed briefly. Essential differences from petroleum lubricants such as higher H_2 content and lower specific gravity are discussed. Various Kogasin products, a number of American and European petroleum products, and a polymerization product of 2-pentene are compared for specific gravity, average molecular weight, kinematic viscosity at 20° and 50°, and viscosity-temperature index. The first named with viscosity-temperature characteristics improved over those previously reported are residual distillation fractions boiling >200° and 250° at 15 mm. Hg. The 2-pentene product gave a very steep viscosity-temperature curve. At corresponding viscosities, Kogasin molecular weights are higher than those of the petroleum products. A wide range, 355–1,029, of average molecular weights is encountered. The Wijs I numbers increase with viscosity and for the better lubricating fractions are similar to those of petroleum products. Mild and strong hydrogenations of Kogasin lubricants with Co and Ni catalysts beginning with 100 atm. at 180° show corresponding decrease in I number with increase in absolute viscosity but with slight increase in viscosity-temperature index. Comparisons of two Pennsylvania oils, three Kogasin oils (one hydrogenated), and a commercial transformer

oil for aging effects, light, and air treatment, showed sludge in the last after 8 days, considerable sludge in the winter-grade motor oil, but none in the summer-grade or Kogasin products even after 8 mo. Acid and saponification numbers show somewhat less increase in the synthetic products. Aging was greatly accelerated in the parallel tests by the presence of H_2O, even the summer oil formed sludge. Asphalt could not be precipitated from aged Kogasin oils by addition of petroleum ether, in contrast to the natural oils; S is absent in the former. Subjected to the British Air Ministry test (2 6-hr. periods at 200° in air current) the aged Kogasin oils remained clear but colored, free from asphalt, doubled in viscosity (fourfold for the hydrogenated oil). In contrast, the aged petroleum oils became darker, cloudy, contained much asphalt, and increased to 8 times in viscosity. For both types of oils, the viscosity-temperature indexes increased slightly, the average molecular weight increased 10%, and Conradson C increased but remained lower in the Kogasin oils. Hydrogenation at 190°–200° with Ni catalyst after aging by this method restored the original properties of the Kogasin products. Practical motor tests showed 10% increase in viscosity after 3,800 km. acid and saponification numbers increased to 2.5 times, Conradson C increased from 0.125 to 0.22%, viscosity-temperature index changed from 1.85 to 1.83. Tests of low-viscosity oils, as transformer oils, show no depreciation in properties, the original Kogasin oil falling far within tolerances as to saponification and acid numbers, H_2SO_4 test, and with electrical breakdown of 180 kv. per cm. 15 refs.

1810. ———. [Newer Investigations of Lubricating Oils Prepared From the Synthesis Product (Kogasin) of the Fischer-Tropsch Process.] Brennstoff-Chem., vol. 19, 1938, pp. 337–343; Proc. Pure Applied Chem., Rome, 10th Intern. Congr., 1938; British Chem. Abs., 1938, B, p. 1385; Chem. Abs., vol. 32, 1938, p. 9466.

Viscometric properties, chemical composition, aging characteristics, influence of hydrogenation, and behavior in use of monoolefins prepared from Kogasin are described and discussed with comparative data and references. More recent work shows the dependence of the viscosity-temperature behavior not only on the boiling range of the Kogasin fractions used in preparation of the oils, but on the olefin content of the fractions. Studies in determination of the I number of Kogasin lubricants by various methods show the importance of controlling time, concentration, and excess reagent in the tests. Ring analyses show approximately 1 naphthene ring per mol. regardless of viscosity-temperature characteristics. Similarly, extraction with acetone indicates that the proportion of the ring is the same in fractions of all viscosities. Aging tests of oil for transformer use by the method of Weiss and Salomon showed no sludge formation in 11 days. Exhaustive hydrogenation increased oil stability to light and air progressively to low acid and saponification numbers after 6-mo. storage tests.

1811. ———. [Artificial Production of Lubricating Oils.] Arch. Eisenhüttenw., vol. 12, 1939, pp. 533–537; Umschau, vol. 43, 1939, pp. 195–197; Chem. Abs., vol. 33, 1939, p. 5639.

Trend to produce more and more synthetic lubricating oils instead of using the natural oils with their widely varying properties is justified by the much greater uniformity that can be obtained in the synthetic oils. The various methods of producing synthetic oils are discussed. 10 refs.

1812. ———. [Catalytic Aromatization of Aliphatic Hydrocarbons. Literature Review and Verification.] Brennstoff-Chem., vol. 20, 1939, pp. 1–9; Chem. Abs., vol. 33, 1939, p. 9280.

Procedure of Italian Patents 351,078 and 352,747 was used in treating the C_7 Kogasin fraction at 500° with V and Cr oxides on Al_2O_3 for catalysts. Treatment of the fraction boiling at 92°–95° and containing 68% heptene was attempted at 400°–530°; toluene was formed as the main constituent in an aromatic yield of 55% with 1 pass. Dehydration, cyclization, and cracking also occurred, and the action of their products required frequent reoxidation of the catalyst. In comparison, the reaction yield was much smaller when platinized C at 310°–350° was used. With gasoline boiling >100° and prepared by the activated-C process, d. was increased from 0.710 to 0.742 and n_D from 1.404 to 1.422 without the formation of low-boiling hydrocarbons in 5 sec. contact time at 520° with V oxide on Al_2O_3. From a Kogasin fraction boiling 150°–300° passed over Cr oxide on Al_2O_3 for 3–4 sec. at 500°–510°, 15% low-boiling material was produced in which benzene, toluene, xylene, and PhEt were identified. Gaseous products, depending upon the conditions and starting material, consisted of 5–10% unsaturated and 10–20% saturated compounds. 10 refs.

1813. ———. [Synthetic Lubricating Oil.] Umschau, vol. 43, 1939, pp. 195–197; Arch. Eisenhüttenw., vol. 12, 1939, pp. 533–537; Chem. Abs., vol. 33, 1939, p. 7086.

Discussion of what has been realized to date commercially in the synthesis of improved lubricating oils from raw materials, such as coal, animal oils, and petroleum products.

1814. ———. [Alkylation of Aliphatic Hydrocarbons, Particularly With Regard to Kogasin.] Reichsamt Wirtschaftsausbau, Prüf-Nr. 102, 1940, pp. 49–57; PB 52,004; Chem. Abs., vol. 41, 1947, p. 6698.

By alkylation in the presence of anhydrous HF the products of Kogasin (heavy oil from the Fischer-Tropsch process) synthesis can be converted into high-antiknock fuels similar to isooctane. The HF catalyst gives few side reactions, has a long life, and when activated by BF_3, also can be used for the conversion of C_2H_4 or ethylenic mixtures. Fractions of Kogasin not useful elsewhere are either isomerized and split with $AlCl_3$ or pyrolized, to give an olefin mixture suitable for the alkylation reaction.

1815. ———. [Quantitative Separations of Hydrocarbons by Distillation at Various Temperatures and Separation of Olefins and Paraffins.] Reichsamt Wirtschaftsausbau, Prüf-Nr. 43, 1940, pp. 93–102, PB 52,003; Chem. Abs., vol. 41, 1947, p. 6492.

Separation and identification of some of the components of Kogasin are described. For studying the lower hydrocarbons, a low-temperature column was designed that consisted of a 6-m. spiral of glass tubing of 5 mm. inside diameter surrounded by a vacuum jacket. The head of this column works on the thermosiphoning principle. With a test mixture of *n*-heptane and methylcyclohexane, this column showed 20 theoretical plates. A chart of the separation of C_3H_8, *n*- and iso-C_4H_{10}, and iso-C_5H_{12}, is shown. A high-temperature column was developed in which a heated oil was circulated around the column to maintain adiabatic conditions. A review of the results obtained in I number methods for olefins is described. The Kaufmann and Gross-Oetringhaus thiocyanogen method using CCl_4 gave the best results for the 5 olefin types. The Hg(OAc)2–MeOH method was used for separating olefins from paraffins. An olefin-paraffin mixture was extracted with $Hg(OAc)_2$–MeOH reagent, and the paraffin was removed from the reaction mixture by reduced-pressure distillation. The olefins were recovered in pure form by hydrolyzing the $Hg(OAc)_2$, olefin complex with a strong mineral acid such as HCl. Of the paraffins in a lower Kogasin fraction, 2-methylbutane, *n*-C_5H_{12}, 2-methylpentane, 3-methylpentane,

n–C_6H_{14}, 2–methylhexane, 3–methylhexane, and n–C_7H_{16} have been isolated. Of the monöolefins 3–methyl–1–butene, 1–pentene, cis-and trans-2-pentene, 3–methyl, 1–pentene, 4–methyl, 1–pentene, 1–hexene, cis-and trans-2–hexene, 3–methyl–1–hexene, 5–methyl–1–hexene, 4–methyl–1–hexene, 1–heptene, and cis-and trans-2–heptene have been isolated.

1816. ———. [Decomposition of Synthetic Paraffin by Hydrogenation.] Erdöl u. Kohle, vol. 3, No. 1, 1950, p. 9.

Paper presented at the 1949 meeting of the Deutsche Gesellschaft Mineralölwissenschaft u. Kohlechemie. Synthesis paraffin was subjected in a stream of water at about 200° to selective demethylation. In the gasoline fractions obtained from the decomposition products, the degree of branching was ascertained, and conclusions were drawn as to the content of isohydrocarbons in the synthesis paraffins.

1817. ———. [Development of the Fischer-Tropsch Hydrocarbon Synthesis Process.] Chem.-Ztg., vol. 74, No. 8, 1950, pp. 103–106.

Reviews progress.

———. *See* abs. **983, 984, 985, 986, 1032, 1033, 1034, 1048, 1362, 3458.**

1818. Koch, H., and Billig, R. [Investigation of the Solid Paraffin Hydrocarbons Produced in the Benzine Synthesis of F. Fischer and H. Tropsch Atmospheric Pressure Synthesis.] Brennstoff-Chem., vol. 21, 1940, pp. 157–167; Chem. Abs., vol. 35, 1941, p. 3803.

Previous work reviewed briefly. By use of apparatus previously described, the solid products recovered with the liquid hydrocarbons in the train beyond the catalyst tube and the high-melting ceresins extracted from the catalyst itself after prolonged use have been investigated. Similarly, quantitative relations between molecular weight and melting point of products solid at room temperature, establishment of isoparaffins by physical and chemical data, and conversion of fractionated extracts into lubricants have been studied. Appreciable increase of extracted ceresin, accompanied by decreased yield of other products and the elevation of average boiling range of condensates, followed the alkalization of the Co–Th on kieselguhr catalyst with 0.25–2% Na_2CO_3 and 0.5–1% K_2CO_3 in 4-l.-per-hr. tests with 29% CO–59% H_2 gas mixtures at 190°–200°. As much as 50% more solid paraffins were found in the fraction boiling >300°. Paraffin precipitation was carried out over the range +5° to −20°, with 1:5 to 1:100 oil:solvent ratios. Between certain limits, the amounts of solid paraffins decreased steadily with increasing melting point. The regularity of the relation was found also in products of Fe–Cu and technical-scale syntheses. By fractional extraction of a Kogasin paraffin with 3:2 ether-alcohol mixture and of the ceresins with ether, 13 and 15 close fractions were obtained, respectively. The synthetic ceresin and several fractions thereof, treated with HSO_3Cl, decreased 1.3°–1.9° and increased 1°, respectively, in melting point, and their average molecular weights increased by 10–40. The reaction was preferential for isoparaffins. Hydrogenation under 80 atm. pressure around 190° with Ni catalyst gave colorless products, increases of 0.0002 in n_D, and 1° in melting point. In solidification curves, the ceresin fractions exhibited definite points of heat of crystallization as compared to the perfectly smooth-cooling curve of the whole ceresin. 15 refs.

1819. ———. [Preparation of Lubricants From Solid Paraffin Hydrocarbons of the Fischer-Tropsch Atmospheric Pressure Synthesis by Way of Their Olefinic Cracked Distillates.] Brennstoff-Chem., vol. 21, 1940, pp. 169–177; Chem. Abs., vol. 35, 1941, p. 3803.

Method used by Sullivan and others, with natural solid and paraffin-wax fractions of petroleum, has been applied to fractional extracts from Kogasin paraffin and from synthetic ceresin. Repeated passes gave 40–50% yields of nearly pure olefins boiling >250°, with 35–45% cracked gas containing 60% of unsaturated hydrocarbons. The distillate boiling >250° was converted to lubricants with 5% anhydrous $AlCl_3$ in a 7-hr. reaction to 60°, with 65–75% yields of oils of good viscosity-temperature relations, poles of 1.57–1.83 abs. viscosity of 240–820 centistokes[50] or 32°–108° E. Yield of a diesel oil was 5–14%. However, close fractions obtained from the cracked distillates of the ceresins produced lubricants whose viscosity behavior depended upon the boiling ranges of the corresponding fractions. Viscosity poles decreased with increasing boiling range, for example, for the 230°–250° fraction, the lubricant pole was 1.31. Lubricants from 5 of these fractions were hydrogenated with Ni catalyst at 250°–260° at 80 atm. subsequently, and complete physical examination generally showed no appreciable change in viscosity-temperature relation. However, viscosity increased around 10% without great change in average molecular weight n_D averaged 0.0004 lower, solid point increased 1°–2°, and aniline point increased 4°–5°. Ring analyses showed 1.51–2.88 naphthalene rings per mol. and on the basis of molecular weight were parallel to viscosity poles. 11 refs.

1820. Koch, H., and Gilfert, W. [Synthesis of Lubricating Oils From Olefins of Kogasin. I.] Brennstoff-Chem., vol. 20, 1939, pp. 413–420; Chem. Abs., vol. 34, 1940, p. 8240.

Kogasin fraction was treated with 5% (calculated on olefin content) of anhydrous $AlCl_3$ with vigorous stirring (1 hr. at 0°, 3 hr. warming to room temperature, 1 hr. heating to 50°, 3 hr. at 50°). The polymerization product was separated from the $AlCl_3$ compound, treated with fuller's earth and freed from the lower boiling constituents by distillation to 200° per 15 mm. Fractions from (I) Kogasin from water gas ($1CO:1H_2$) and from (II) Kogasin from synthesis gas ($1CO:2H_2$) were used. Fractions from (I) corresponding approximately with C_5, C_6 and C_7 hydrocarbons, respectively (olefin content 70–75%), gave about 65% (calculated on olefin content) of lubricating oil having a viscosity of 1,110–1,550 centistokes at 20° and viscosity-pole heights of 1.88–2.33; the corresponding fractions from (II) (olefin content 43–55%) gave lower yields (37–55%) of oils having a viscosity of 473–585 centistokes at 20° and viscosity–pole heights of 2.23–3.10. The lower yields from (II) were due, not to the lower olefin content of the starting material, but to a difference in constitution of the olefins. When the olefin content of (I) was reduced by partial hydrogenation lower yields of an inferior oil were produced by polymerization of the remaining olefins. The C_6 and C_7 fractions were refractionated into narrow cuts, from each of which a lubricating oil was synthesized. The properties of the products varied considerably with the boiling point of the starting material; for example, the viscosity of the oils from the C_6 fractions varied from 22,777 (from fraction 57.0°–61.0°) to 476 (from fraction 67.5°–9.0°) centistokes at 20°; the flattest viscosity-temperature curve (viscosity-pole height 1.77) was given by oil from the fraction 63.0°–3.5° (principally 1–hexene) and the steepest (viscosity-pole height 2.53) by the oil from the fraction 67.5–9.0 (2–hexene). The products from the C_7 fractions showed similar but somewhat less marked variations in properties. In neither case was there any apparent relation between the absolute viscosity of the oils and the viscosity-pole height. The mean molecular weight of the lubricating oils varied 550–1,240.

1821. ———. [Synthesis of Lubricating Oils From Olefins of Kogasin. II.] Brennstoff-Chem., vol. 21, 1940, pp. 1–7; Chem. Abs., vol. 34, 1940, p. 8240.

By lowering the temperature of polymerization of a C_5 Kogasin fraction (in presence of anhydrous $AlCl_3$) from 20° to 0° a more viscous lubricating oil was obtained; its viscosity–temperature behavior was not appreciably affected. At —80° no polymerization occurred. All the lubricating oils produced by polymerization of Kogasin fractions had 1 double bond per mol. Saturation of this bond by hydrogenation caused some increase in the viscosity of the oil, but had little effect on the viscosity–temperature coefficient. Examination of the oils by Waterman's method indicated the presence of 1 naphthene ring per mol., even for oils of considerably different viscosity-pole heights. The relation between viscosity and the mean molecular weight of the oils is discussed; in this respect some differences are observed between the synthetic oils and petroleum lubricating oils.

1822. ———. [Breaking Down and Building Up of Hydrocarbons Under Hydrogenating Conditions Over the Cobalt Catalyst Used in Fischer-Tropsch Syntheses.] Brennstoff-Chem., vol. 30, 1949, pp. 213–218; Chem. Zentralb., 1950 I, p. 1302; Chem. Abs., vol. 43, 1949, p. 7663.

Various hydrocarbons in vapor form mixed with H_2 and CH_4 were recirculated at 200° over a reduced Co catalyst used for Fischer-Tropsch syntheses. The paraffin hydrocarbons *n*–C_6H_{14}, *n*–C_7H_{16}, *n*–C_8H_{18}, and 2–methylpentane in a current of H_2 were broken down by demethylation, about half of the hydrocarbon being converted. In addition to shortening the C chain, there was also a distinct building up to the next higher homolog. Isomerization also occurred to a slight extent, and some aromatization occurred with 2–methylpentane. With *n*–C_6H_{14} mixed with the circulating gas containing CH_4 considerable chain lengthening to C_7H_{16} took place, presumably because of combination with CH_4. In CH_4 without H_2, the *n*–C_6H_{14} remained unchanged. Toluene was formed to a surprising extent by the conversion of cyclohexane in a stream of H_2. At the same time, C_6H_6 was formed by dehydrogenation and cyclopentane, by way of isomerization, to methylcyclopentane followed by demethylation. Benzene reacted with H_2 to form toluene, but this conversion was relatively slow. No increase of the toluene yield was produced by adding CH_4 to the circulating gas.

1823. Koch, H., and Hilberath, F. [Literature Review and Comparative Investigations of Methods for Determining the Iodine Number of Hydrocarbons.] Brennstoff-Chem., vol. 21, 1940, pp. 185–194; Chem. Abs., vol. 35, 1941, p. 7319.

Reviews 62 papers published since 1884. The Wijs, Kaufmann, and iodo-thiocyanate methods and the procedures of Hanus, Francis, and Grosse-Oetringhaus have been compared for 17 simple olefin hydrocarbons. For the exact determination of the I number of aliphatic monoolefins and hydrocarbon mixtures, the methods of Kaufmann and Grosse-Oetringhaus alone are suitable. For approximations, the KBr-KBO_3 method of Francis is suitable. The use of the Wijs, Hanus, and Kaufmann methods involves large substitution errors with tertiary or ditertiary olefins. These 3 methods can be used with olefins not branched at the double bond, as with the Kogasins. No general conclusions were reached for the determination of cyclic monoolefins because of few data: Cyclopentene and cyclohexene can be analyzed by the methods named, but side reactions were observed with certain unsaturated cyclic terpenes. Conjugated double bonds in dienes can be considered as having the I consumption of single double bonds with the iodo-thiocyanate, Wijs, and Hanus methods. On the other hand, the method of Francis, as modified by Cortese, produces complete saturation, and the method can be used in combination with the other methods to determine the content of conjugated double bonds in mixtures by difference. Few tests were made with acetylenes; the methods of Wijs and Hanus give 50% of the theoretical I-consumption; the method of Lucas and Pressman gives complete saturation in the absence of substitutable olefins. With synthetic Kogasin lubricating oils, the suitability of the iodo-thiocyanate method for the exact determination of double bonds and the Wijs method (limited to 2–3 min. reaction time) for approximations was shown.

1824. ———. [Suitable Apparatus for Fractional Distillation at Low Temperature.] Brennstoff-Chem., vol. 21, 1940, pp. 197–203; Chem. Abs., vol. 35, 1941, p. 7239.

Previously proposed apparatus are described briefly with reference data. The fact that the new column, which is described in detail, employs complete condensation permits recovery of distillates of ether liquid or gas at will. Arrangement of the column head and accessories allows desired reflux conditions and the maintenance of constant operating adjustments. The possibility of overheating or overcooling of the temperature indicators is prevented, and progress of the fractionation is followed easily by true temperature measurement with thermometer or thermocouple. Manipulation of the column, with a glass tube spiral as exchanger, is described. Efficiency is demonstrated by separation of mixtures of propene-propane, isobutane-butane, and motor-fuel oil. In addition to the form of column for preparation purposes, an analytical arrangement also is described. Illustrated.

1825.———. [Hydrocarbons Boiling Below 100° in Synthetic Gasoline From Carbon Monoxide and Hydrogen (Kogasin).] Brennstoff-Chem., vol. 22, 1941, pp. 135–139, 145–152; Chem. Abs., vol. 36, 1942, p. 5331.

Olefins were separated from paraffins by means of the $Hg(OAc)_2$ method. Tests showed that this method also can be used for ditertiary olefins; for example, C_2Me_4. The 2 hydrocarbon groups were further split up by fractional distillation. For this purpose a packed column (23 in. high, heated by oil circulation) and several glass spiral columns (80, 160, and 320 cm. high) were made. The applicability of the semimicrofractionating column with a rotating metal band of Lesesne and Lochte type (Chem. Abs., vol. 32, 1938, p. 7310) was extended by various additions. The paraffin mixture was separated into its individual components by 58 fractional distillations, most of which occupied several days. Besides the predominant *n*-paraffins, *n*–C_5H_{12}, –C_6H_{14}, and –C_7H_{16}, the following pure isoparaffins were isolated: $MePr^B$, β– and γ–methyl–pentane and –hexane, and the presence of $CHEt_3$ was proved. Multibranched paraffins were present only in traces, if at all. The olefin mixture was separated by 134 fractional distillations into the following: $\Delta\alpha$– and $\Delta\beta$–pentene, –hexene, and –heptene, as well as $CHPr\beta$. CH_2, ξ–methyl–$\Delta\alpha$, hexene, a mixture of γ– and ξ–methyl–Δ^{α}–pentene, and a mixture of γ– and ϵ–methyl–Δ^{α}–hexene. The olefins were identified by their physical properties and partly by hydrogenation reactions. The olefins consisted mainly of unbranched α– and β–olefins. Besides these, small quantities of α–olefins singly methylated outside the double linking were found. The presence of other types of olefins can be assumed but quantitatively they are negligible. Appreciable amounts of tertiary but no quaternary C were found in the products from Co catalysts.

1826. ———. [Polymerization of Monoolefins to Viscous Oils.] Brennstoff-Chem., vol. 23, 1942, pp. 67–73; Chem. Abs., vol. 36, 1942, p. 4701.

Properties of polymer lubricating oils, having the structure of the olefins charged to the polymerization process, were investigated. Most of the olefins used were obtained from the gasol and the light gasoline of the Kogasin process. The olefins with 5–7 C atoms, liquid at room temperature, were polymerized at 0° and 15°, respectively, under comparable conditions. Viscosities and yields of the resulting products vary greatly. It appears that these differences are due to the olefins belonging to different groups, of which the following four were noted: (1) Straight-chain α–olefins; (2) Branched α–olefins, the branch not starting on one of the double-bond C atoms; (3) Straight-chain β–olefins; (4) Branched β–olefins, with the branch starting on one of the double-bond C atoms. The reaction temperature is critical for the polymerization of the isobutene, while it is not critical when polymerizing olefins belonging to 1 of the groups 1–3.

1827. KOCH, H., AND HORN, O. [Comparative Investigation of Motor Behavior of a Synthetic Naphtha (Kogasin I) by Fischer–Tropsch and a Petroleum Naphtha.] Brennstoff-Chem., vol. 13, 1932, pp. 164–167; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 530–536; Chem. Abs., vol. 26, 1932, p. 3657.

Various 10° fractions of the 2 naphthas have been examined and compared for density, unsaturated hydrocarbons, I number, C_6H_6 number and octane number. With increasing boiling point of the fractions, unsaturated hydrocarbons decrease from 46–23% in the synthetic product but increase from 16.5–29% with the petroleum fuel. Antiknock rating decreases from 85–41.5 octane no. with the synthetic, and from 77–54.5 with the petroleum fuel.

1828. KOCH, H., AND IBING, G. [Composition of Hard Paraffins Produced in the Naphtha Synthesis of F. Fischer and H. Tropsch.] Brennstoff-Chem., vol. 16, 1935, pp. 141–148; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 402–419; Petrol. Refiner, vol. 22, 1943, pp. 279–286; Chem. Abs., vol. 29, 1935, p. 5642.

Separation of the high-molecular hydrocarbons by various methods has been studied, and the extraction and reduced pressure-distillation methods have been investigated. Extraction with ether, dichloroethylene, and $CHCl_3$ indicates possible separation into groups of similar molecular weight and properties. Repeated distillation at 10^{-5} mm. Hg did not greatly concentrate individual hydrocarbons. Molecular weights increased uniformly with melting point. *n*-Paraffins to as high as $C_{150}H_{302}$ are indicated; they melt at 117° and have a molecular weight of 2,000.

1829. ———. [Diesel Oil Obtained in the Benzine Synthesis of F. Fischer and H. Tropsch. Isolation and Chlorination of Symmetrical Paraffin Hydrocarbons.] Brennstoff-Chem., vol. 16, 1935, pp. 185–190; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 420–433; Chem. Abs., vol. 30, 1936, p. 1984.

Diesel oil, in part dewaxed Kogasin II, was subjected to vacuum distillation. Normal paraffins from decane to octane were isolated. The remaining 60–70% of the paraffins consisted of isoparaffins. The *n*-paraffins were chlorinated and fractionated by vacuum distillation. Bibliography is given.

1830. ———. [Constitution of Lubricants Prepared From Kogasin II.] Brennstoff-Chem., vol. 16, 1935, pp. 261–268; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 465–481; Chem. Abs., vol. 30, 1936, p. 1985.

Alkyl chlorides previously prepared were condensed in the presence of active Al or condensed with aromatic hydrocarbons in the presence of $AlCl_3$. Reaction products were separated by distillation and the composition of the fractions was determined. Viscosities and viscosity-temperature curves are given.

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1831. KOCH, H., AND KÜSTER, H. [Catalytic Reduction of Carbon Dioxide With Hydrogen.] Brennstoff-Chem., vol. 14, 1933, pp. 245–251; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 249–262; British Chem. Abs., 1933, B, p. 737; Chem. Abs., vol. 27, 1933, p. 5154.

Catalyst of Co and Ni for the synthesis of benzine is very effective at 150° in the production of CH_4. Traces of CO- and O_2-containing compounds were found in a few cases. With a large excess of CO_2, complete equilibrium is reached, which at 150°–400° is almost completely toward the CH_4 side. Adding steam at the start strongly retards the reaction by increasing the H_2 concentration. When blast-furnace gas treated with steam is used, a N_2-diluted CO_2–H_2 mixture is obtained, which, passed over CO, gives CH_4. CH_4 is obtained quantitatively from a similar CO_2–H_2–N_2 mixture passed over Ni. Passing CO and steam over Ni gives 3 : 1 CO_2 and CH_4. MeOH, a possible intermediate compound, is completely decomposed in the presence of CO_2 over Ni at >200°. S compounds poison the catalysts.

1832. KOCH, H., AND RICHTER, H. [Isomerism Equilibrium of Hexane.] Ber. deut. chem. Gesell., vol. 77, 1944, B, pp. 127–132; Chem. Abs., vol. 39, 1945, p. 903.

1833. ———. [Isomerization of Butene.] Oel u. Kohle, vol. 40, 1944, pp. 231–241; British Abs., 1948, B, II, p. 285; Chem. Abs., vol. 44, 1950, p. 5307.

When *n*–C_4H_8 is isomerized at 190° on a Fischer-Tropsch catalyst, a shifting of the ethylenic linking and cis-trans-conversion takes place, yielding an equilibrium mixture that accords with that calculated by Frost from free energies of the isomers. At higher temperature and pressure, slight cracking occurs and a red polymer is formed as a byproduct. Active C catalyzes the shift of the ethylenic linking at 325°, the main reaction being a redistribution of H_2, with formation of C_4H_{10} and higher unsaturated hydrocarbons. Al_2O_3 catalyzes this shift at 190°, but at 400° iso-C_4H_8 is formed accompanied by cracking, which gives C_3H_6 and polymerization leading to C_5H_{10} as main product. In presence of H_2 phosphates of Cd as catalyst formation of iso-C_4H_8 occurs at a lower temperature and is accompanied by polymerization; at a higher temperature polymerization is reduced, but the catalyst soon loses its activity. If in the Fischer-Tropsch synthesis, C_4H_8–isomers are added to the reactant gases, besides hydrogenation, shift of the ethylenic linking occurs, by which the composition of the residual C_4H_8 approaches the equilibrium for *n*–C_4H_8; C_5 hydrocarbons are not produced from C_4H_8 in this reaction.

1834. KOCH, H., AND STEINBRINK, H. [Synthesis and Hydrogenation of Polyalkylated Benzenes.] Brennstoff-Chemie, vol. 19, 1938, pp. 277–285; Chem. Abs., vol. 33, 1939, p. 150.

Preparation of hydrocarbons with lubricating properties has been attempted in the preparation of alkylated benzenes of high molecular weight, similar to the Kogasin products, and their hydrogenation to the corresponding cyclohexane derivatives.

1835. ———. [Cracking of Paraffin Wax by Action of Aluminum Chloride Formed in Situ.] Brennstoff-Chem., vol. 20, 1939, pp. 147–152; Chem. Abs., vol. 34, 1940, p. 6053.

By treating a natural or a Kogasin paraffin wax with activated Al (5–10% of the wax)+HCl at 210°–260° (15–120 hr.), yields of 40–60% of gasoline and 10–15% of gasol were obtained. The gasoline contained no detectable quantities of C_6H_6 or toluene. It consisted principally of paraffin hydrocarbons but contained also some alkyl chlorides. Part of the latter decomposed on distillation; olefins were formed.

1836. KOCH, H., AND TITZENTHALER, E. [Determination of the Degree of Branching in Synthetic and Natural Solid Paraffins With the Help of Hydrogenating Decomposition on a Cobalt Catalyst.] Brennstoff-Chem., vol. 31, 1950, pp. 212–221; Chem. Abs., vol. 44, 1950, p. 9335.

Various synthetic and natural solid paraffins were decomposed by hydrogenation on a Fischer-Tropsch Co catalyst within the temperature range 180°–230°. The liquid hydrocarbons obtained with the main product CH_4 were analyzed in the boiling range 30°–170° by close fractionation. Since by demethylation splitting, branching is preferably maintained in the same positions, quantitative conclusions can be drawn from the amount of isocompounds in the decomposition product as to the original isocontent of the initial paraffin. Taking a straight-chain paraffin, *n*–octadecane, for example, it can be shown that even with careful decomposition a limited amount (about 4%) of branched hydrocarbons formed through isomerization must be reckoned with. A synthetic gatch fraction obtained on a Co or Fe catalyst yielded about 30% of isoparaffin, while a synthetic hard paraffin gave an average proportion of branched compounds of 38%. A soft paraffin from the spindle-oil fraction of an Emsland crude oil yielded 8% and a hard paraffin separated from the machine oil fraction 24% of isocompounds. A Tief-Temperatur Hydrierung brown-coal paraffin showed about 11% of branched hydrocarbons. The hydrogenating decomposition also was accompanied to a limited extent by aromatization whereby the methylated aromatics appeared to a large extent as benzol. Tests on the splitting hydrogenation of paraffin on active Fe catalysts did not produce the desired results at the temperatures employed up to 350°. It was further discovered that Co catalysts temporarily lose their ability to split hydrocarbons by hydrogenation when small amounts of NH_3 are added to the H_2.

1836a. KOCH, H., AND VAN RAAY, H. [Individual Branched Hexenes and Their Isomerization Equilibria.] Brennstoff-Chem., vol. 32, 1951, pp. 161–174; Chem. Abs., vol. 45, 1951, p. 8238.

During the war, catalytic isomerization reactions were of importance in increasing the octane number of synthetic gasoline; such reactions are also of importance in preparing a variety of products from the alcohols obtained in the oxo synthesis by varying the position of the double bond. The reaction mechanisms of the isomerization of olefins and isomerization dehydration of alcohols are reviewed. A Co gasoline-synthesis catalyst permitted equilibrium to take place smoothly in an autoclave at 190° between 2, 3–dimethyl–l–butene and 2, 3– dimethyl–2–butene while the isomerization of the 2–methylpentenes did not progress under similar conditions.

1837. KOCH, H., PICHLER, H., AND KÖLBEL, H. [Fatty Acids Obtained in Small Amounts in the Benzine Synthesis of F. Fischer and H. Tropsch.] Brennstoff-Chem., vol. 16, 1935, pp. 382–387; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 433–443; Chem. Abs., vol. 30, 1936, p. 3970.

Formic, acetic, propionic, and butyric acids were identified in the 0.35% yield obtained with Co catalysts in the synthesis. These acids are found in the reaction liquor, of which 2/3 is acetic. No unsaturated acids were found. Acids dissolved in Kogasin were 0.06% of the latter, mostly of 5–10 C atoms and a small amount still higher.

KOCH, H. W. *See* abs. **1233.**

1838. KOCH, W. [Electrolytic Separation of Carbides in Alloy and Carbon Steels.] Stahl u. Eisen, vol. 69, 1949, pp. 1–8; Chem. Abs., vol. 43, 1949, p. 5718.

It is possible to isolate carbides in ferritic-pearlitic steels without breaking them down. When performing the separation in heat-treated steels in the transition or martensite phase, the C remains in the residue. The investigation of these carbides is difficult because of the surface activity of these materials. Electron microscopy was used, and photographs are shown.

1839. KODAMA, S. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. I. Studies by the Heating-Curve Method of the Catalytic Activity of a Few Metals. Bull. Inst. Phys. Chem. Research (Tokyo), vol. 8, 1929, pp. 277–283; abstract sec. 2, 1929, pp. 35–36; Jour. Soc. Chem. Ind. (Japan), vol. 32, suppl., 1929, pp. 4, 6, 23; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 12, 1930, pp. 193–204; Chem. Abs., vol. 23, 1929, p. 3844; vol. 24, 1930, p. 2663.

Ni, Co and Fe are reduced at various temperatures, and their catalytic activity in the reduction of CO by H_2 under atmospheric pressure is measured. The mixture of 1 mol. H_2+1 mol. CO is passed through 2 tubes, 1 with, and 1 without catalyst and heated progressively to 400°. A differential thermocouple records the exothermic reaction. After the reaction, the Ni dissolved in the HCl without leaving any residue, while Co left a residue of C. The activity of Ni is thus independent of the temperature of reduction, while the opposite is true with Co. In the absence of H_2, both Ni and Co catalyze the decomposition of CO. Fe reduced at 350° and 450° shows an exothermic reaction around 300° which is caused principally by the oxidation of Fe. The Fe catalyst is then no longer active, and is found to be a mixture of FeO and C. Furthermore, the heating curve with CO alone is virtually identical with that of CO+H_2.

1840. ———. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. II. Study by the Heating-Curve Method of the Influence of a Few Substances on the Catalytic Activity of Cobalt. Bull. Inst. Phys. Chem. Research (Tokyo), vol. 8, 1929, pp. 284–287; abs. sec. 2, 1929, pp. 36–37; Jour. Soc. Chem. Ind. (Japan), vol. 32, suppl., 1929, pp. 4, 6, 23; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 12, 1930, pp. 205–210; Chem. Abs., vol. 23, 1929, p. 3844; vol. 24, 1930, p. 2663.

Influence of K_2CO_3, Cu, ThO_2, Al_2O_3 and MnO on the activity of a Co catalyst was studied by the method described above. The decomposition of CO with separation of C is not evident when ThO_2 or Cu is added to the Co catalyst, while the addition of K_2CO_3 decreases it. ThO_2 and Cu to a less degree increase the activity of Co toward the reduction of CO and the formation of hydrocarbons. Al_2O_3 and MnO are detrimental to the activity of Co.

1841. ———. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. III. Preparation of Liquid Hydrocarbons With a Cobalt-Copper-Thoria Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 32, suppl., 1929, pp. 285–286; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 12, 1930, pp. 211–224; Chem. Age, vol. 27, 1929, p. 406; Chem. Abs., vol. 24, 1930, p. 2036.

Reaction begins at 160°; liquid products were observed. The best temperature is 252°; at higher temperature the greater part of the CO decomposed becomes CO_2 and CH_4 hydrocarbons, and there is little oil formation. The reaction temperature is lower than that given in the literature. At 248°, 84.4 l. of the gas mixture at a velocity of 5 l. per hr. gave 3.85 cm.^{3} H_2O, 0.45 cm.^{3} petroleum, and 0.4 cm.^{3} benzine.

1842. ———. Catalytic Reduction of Carbon Oxides Under Ordinary Pressure. IV. Influence of Beryllium Oxide, Magnesium Oxide, Zinc Oxide and Cadmium on the Cobalt-Copper Catalyzer. Jour. Soc. Chem. Ind. (Japan), vol. 33, suppl., 1930, p. 60; Sci. Papers Inst. Phys. Chem. Research (Tokyo),

vol. 13, 1930, pp. 93–105; British Chem. Abs., 1930, A, p. 551; Chem. Abs., vol. 24, 1930, p. 2979.

Study of the influence of BeO, MgO, ZnO and Cd on the Co–Cu catalyst for the synthesis of petroleum hydrocarbons from water gas at atmospheric pressure has shown that MgO is the best accelerator, being most active at 240° and giving the highest yields. BeO is most active at 260°; however, the yields are small. ZnO is the poorest accelerator, the reaction starting at 260°. Cd completely destroys the activity of Co.

1843. ———. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. V. Influence of Titanium Oxide, Zirconium Oxide and Cerium Oxide. Jour. Soc. Chem. Ind. (Japan), vol. 33, suppl., 1930, pp. 202–203; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 14, 1930, pp. 13–25; Chem. Abs., vol. 24, 1930, p. 4376.

To determine the most effective catalyst for synthesizing petroleum from water gas the influence of TiO_2, CeO_2 and ZrO_2 was examined. The catalyst containing 3 parts Co, 1 part Cu, and the above oxides was reduced at 300° from the oxides derived from the nitrates. The gas mixture contained equal parts of CO and H_2 and was passed over 30 gm. of catalyst at 5 liter per hr. Catalysts containing TiO_2, ZrO_2 or CeO_2 give liquid products at 180°–200° and all show similar gas contractions. With TiO_2 gas contraction diminishes to 26.1% after 12 hr., then gradually to 40.7% after 39 hr., forming mainly gaseous hydrocarbons. ZrO_2 is the best, but not as good as MgO. CeO_2 is the poorest accelerator.

1844. ———. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. VI. The Hydrocarbon-Forming Action of Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 33, suppl., 1930, pp. 399–400; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 14, 1930, pp. 169–183; Chem. Abs., vol. 25, 1931, pp. 496, 1039.

Fe catalysts for synthetic hydrocarbons are of greater commercial importance than those containing Co. No experimental details on Fe catalysts have yet appeared. Fe catalysts produce no H_2O; Co catalysts always, sometimes several times as much as hydrocarbon. The CO_2 content of the reaction gas is about 20% when using Fe catalysts; with Co 5–10%. The unconverted reaction gas with Fe catalyst contains more CO than H_2; with Co the opposite. Fe catalysts give a colored oil; Co seldom a yellow, never a colored benzine. Fe catalysts require higher temperature than Co. Catalysts containing mostly Fe withdraw O of the CO in the form of CO_2. Since CO is more decomposed than H_2, the H_2 content of the final gas is always greater than the CO content; with Co, vice versa. A catalyst containing Fe 1, Cu 1, Na_2CO_3 0.02, gives the best yield, 1.8 cm.^{3} kerosine and 1.4 cm.^{3} benzine from 157.0 l. of gas, which is lower than that from Co–Cu catalysts containing MgO or ZrO_2. Addition of MgO to the Fe catalyst injured it. Without addition of alkali an Fe–Cu catalyst forms only lower hydrocarbons.

1845. KODAMA, S. AND FUJIMURA, K. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. VII. Effect of Alkalies on Iron-Copper Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 34, suppl., 1931, pp. 14–16; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 29, 1936, pp. 272–279; Chem. Abs., vol. 25, 1931, p. 1952; vol. 30, 1936, p. 8570.

With a Cu–Fe catalyst prepared from the nitrates, 3.0 cm.^{3} of oil containing a small quantity of a substance like vaseline was obtained at 270° from 141 l. of water gas. Addition of 0.0005–0.05 mol. of Na_2CO_3 to the above catalyst increased its initial activity and favored formation of higher hydrocarbons. With catalysts containing alkalies there is a high gas contraction at first, the activity diminishing gradually. The catalyst may become coated with the higher hydrocarbon. No diminution of activity occurs with alkali-free catalysts. The best catalyst contains Fe 1 atom, Cu 1 atom, Na_2CO_3 0.005 mol.

1846. FUJIMURA, K. Catalytic Reduction of Carbon Monoxide at Ordinary Pressure. VIII. Iron-Copper Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 34, suppl., 1931, pp. 136–138; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 29, 1936, pp. 280–284; Chem. Abs., vol. 25, 1931, p. 4173.

Three catalysts in which the ratio of Fe to Cu was 5:1, 3:1 and 1:2 were studied in the formation of hydrocarbons from water gas at about 275° and atmospheric pressure. The 1st catalyst was most reactive, and the other 2 had approximately the same reactivity. About 3.3 cm.^{3} of liquid hydrocarbon was produced from 140 l. of gas with each catalyst.

1847. ———. Catalytic Reduction of Carbon Monoxide under Ordinary Pressure. IX. Additional Tests With a Co–Cu–MgO Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 34, suppl. 7, 1931, pp. 227–229; Chem. Abs., vol. 25, 1931, p. 5341.

Tests were made to determine the relation between catalyst activity and volume; a pumice support is used in 1 case and a light-sugar charcoal support in the other. With the first catalyst the gas contraction was about 40%, and 38.4–46.6 cm.^{3} of oil was produced from 68.7–75.3 l. of gas, solid paraffin appearing in 1 case. With the voluminous catalyst the gas contractions were 60 and 34.5%, and the oil yields 36.6 and 27.0 cm.^{3} from 75.1 and 68.7 l. of gas respectively.

1848. ———. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. X. Influence of Certain Materials on the Catalytic Action of Cobalt–Copper–Magnesium Oxide Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 34, suppl., 1931, pp. 384–386; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 17, Nos. 333–338, pp. 11–15, 16–21; Chem. Abs., vol. 26, 1932, p. 900.

Under the conditions of previous tests Co–Cu–Mg–Th, 8:1:2:0.4, or Co–Cu–Mg–U, 8:1:2:0.4, were most effective; the yield of liquid products was 81.5 cc. per m.^{3} in 1 case. Addition of W, Mo or Cr oxide was not as good as addition of Th or U. The above catalysts were less effective when supported on voluminous sugar charcoal.

1849. ———. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressures. XI. Jour. Soc. Chem. Ind. (Japan), vol. 35, suppl., 1932, pp. 179–182; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 22, 1933, pp. 189–197; Chem. Abs., vol. 26, 1932, p. 4444.

Catalyst of Co–Cu–Th–U, 8:1:0.15:0.15, mixed with equal quantities of starch and carried on kieselguhr proved most satisfactory. The physical condition of the catalysts is as important as the chemical composition.

1850. FUJIMURA, K. AND TSUNEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressures. XII. Jour. Soc. Chem. Ind. (Japan), vol. 35, suppl., 1932, pp. 415–416; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 22, 1933, pp. 198–201; Chem. Abs., vol. 27, 1933, p. 16.

Irradiation of catalysts with 50-kv. x-rays was tried but without success. With a Cu–Co–Th–U catalyst 1 : 8 : 0.2 : 0.1 there was obtained 145 cc. benzine/m.^{3} gas in 1 passage. Changing the proportions of Th and U has no effect.

1851. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XIII, XIV. Nickel Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 36, suppl., 1933, pp. 119–121; Sci. Papers

Inst. Phys. Chem. Research (Tokyo), vol. 22, 1933, pp. 242–247, 248–253; British Chem. Abs., 1933, B, p. 452; Chem. Abs., vol. 27, 1933, p. 3133.

Most effective temperatures were 190°–220°. A catalyst of Ni+18% ThO_2 gave 108 cc. liquid/m.^{3} of gas mixture. Mn can be substituted for Th. Small amounts of alkali carbonates were effective as promoters. A catalyst of Ni+18% Mn+15 cc. Rb_2CO_3 (N/1400) also gave 108 cc. liquid.

1852. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressures. XV, XVI. Nickel Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 36, suppl., 1933, pp. 413–416; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 22, 1933, pp. 254–258, 259–263; Chem. Abs. vol. 27, 1933, p. 4997.

Ni catalysts with additions of Mn, Cr, Mo, W, U_3S_8, ThO_2, Al_2O_3 and fuller's earth as well as Ni, Mn and Cu combinations were tested. Best results were obtained with ThO_2, Al_2O_3 and fuller's earth additions. A catalyst consisting of Ni and 15% Mn and 0.5% Cu gave good results also.

1853. ———. Synthesis of Benzine From Carbon Monoxide and Hydrogen under Ordinary Pressure. XVII. The General Properties and Chemical Composition of the Reaction Products. Jour. Soc. Chem. Ind. (Japan), vol. 37, suppl., 1934, pp. 395–400; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 24, 1934, pp. 79–92; Brennstoff-Chem., vol. 15, 1934, p. 412; British Chem. Abs., 1934, B, p. 662; Chem. Abs., vol. 28, 1934, p. 4655.

Products of the reaction were gases, oils and an aqueous solution. Composition of the gases varied widely. With a Co catalyst there was a little CO_2 and some hydrocarbons together with unchanged CO and H_2 but with Ni catalysts the hydrocarbons varied 6–35%. 80% of the oils distilled below 200° and the normal paraffins from C_5 to C_{11} were identified. The use of Ni catalysts gave over 90% saturated hydrocarbons while Co gave up to 57% olefins. No aromatic hydrocarbons or naphthenes could be detected. The higher the boiling point of a fraction the less olefin it contained. Investigation of the aqueous solution showed small amounts of aldehydes, alcohols, acids, and ketones.

1854. FUJIMURA, K., TSUNEOKA, S., AND KAWAMICHI, K. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XVIII. Effect of Sulfur Compounds on the Nickel Catalyzers. Jour. Soc. Chem. Ind. (Japan), vol. 37, suppl., 1934, pp. 395–400; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 24, 1934, pp. 93–102; Brennstoff-Chem., vol. 15, 1934, p. 412; British Chem. Abs., 1934, B, p. 662; Chem. Abs., vol. 28, 1934, p. 4655.

Action of H_2S and CS_2 was studied. Small amounts of either increased the activity of a Ni–Mn–(15%) Al_2O_3 (3%) (1) catalyzer but larger amounts poisoned it. They had no preliminary activating effect on a Ni–Mn(15%)–ThO_2(3%) (2) catalyzer and this was more easily poisoned.. From 16–28 mg. H_2S or approximately 50 mg. CS_2/gm. Ni were required to halve the activity of (2) and 54 mg. H_2S/gm. Ni was required for (1). The poisoning power of the CS_2 increased directly the amount of CS_2, but that of the H_2S increased directly with the logarithm of the amount of H_2S. When a large amount of (1) was used H_2S had no effect on it up to a certain point, after which it poisoned it in the usual way. It was shown that excess catalyst had no effect on the reaction and that the necessary and sufficient quantity of catalyst was 2 gm. Ni when the oven temperature was 200°, the gas flow was 4 l./hr. and the volume ratio CO : H_2 was approximately 1 : 2. Under these conditions there was produced 135 cc. benzine/m.^{3} of gases used and 3.5% of the Ni was in an active condition.

1855. FUJIMURA, K. AND TSUNEOKA, S. Synthesis of Benzine From Carbon Monoxide and Hydrogen Under Ordinary Pressure. XIX. Composition of the Initial Gas Mixture (1). Jour. Soc. Chem. Ind. (Japan), vol. 37, suppl., 1934, pp. 395–400; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 24, 1934, pp. 103–112; Brennstoff-Chem., vol. 15, 1934, p. 412; British Chem. Abs., 1934, B, p. 662; Chem. Abs., vol. 28, 1934, p. 4655.

It was theoretically deduced and proved by experiment that a volume ratio of CO : H_2 of 1 : 2–1 : 2.1 was the best for benzine synthesis. An excess of CO had little effect but excess H_2 caused an excessive production of CH_4.

1856. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen Under Ordinary Pressure. XX. Composition of the Initial Gas Mixture (2). Jour. Soc. Chem. Ind. (Japan), vol. 37, suppl., 1934, pp. 704–711; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 25, 1934, pp. 127–136; British Chem. Abs., 1935, B, p. 132; Chem. Abs., vol. 29, 1935, p. 1230.

When a mixture (I) of 32.8% CO, 65% H_2 and 2.2% N_2 was passed at the rate of 4 l./hr. over a 27-cm. contact layer of catalyzer (Ni+15% Mn+3% ThO_2+125% kieselguhr) containing 2.5 gm. Ni at 200°, 117 cc. of liquid benzine per m.^{3} of pure CO+2H_2 was obtained. Under the same conditions (I) containing approximately 10% N_2 gave 115 cc., 10% CH_4 120 cc., 10% CO_2 111 cc., 20% N_2 112 cc., 20% CH_4 106 cc., 20% CO_2 91 cc., 40% N_2 95 cc., 40% CH_4 85 cc. and 40% CO_2 90 cc. Thus less than 20% of inert gas did not seriously affect the reaction but 40% cut the yield considerably. Also the more the mixture was diluted, the lighter and more volatile was the oil produced. After removing the S compound and CO_2 from a commercial gas it was passed over a 47-cm. layer of catalyzer containing 3.5 gm. Ni under the above conditions. This gas (30.2% CO, 54% H_2, 4.7% CH_4, 10.9% N_2), containing 81% usable CO+2H, gave 98 cc. benzine/m.^{3} of gas or 121 cc./m.^{3} of pure CO+2H. Under like conditions (I) gave 137 cc./m.^{3} of pure CO+2H.

1857. TSUNEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXI. Relations of the Gas Composition to the Working Temperature and to the Degree of Saturation of the Benzine Respectively. Jour. Soc. Chem. Ind. (Japan), vol. 37, suppl., 1933, pp. 711–716; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 25, 1934, pp. 137–143; British Chem. Abs., 1935, B, p. 132; Chem. Abs., vol. 29, 1935, p. 1231.

Ni–Mn–Al_2O_3 catalyst is used. With the ratio of CO : H_2 in the initial gas above 1 : 2.0–1 : 2.1 the yield of benzine and the reaction velocity can be increased by raising the temperature. No CH_4 is formed if the temperature is kept below 200°–210°. If the H_2 content of the initial gas is increased, the temperature must be lowered to suppress the CH_4–synthesis reaction. There is a linear relationship between the H_2 content of the outlet gas and the I number of the benzine. The higher the H_2 content, the greater the saturation of the benzine. The volatility of the benzine increases with higher working temperatures.

1858. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXII. Usefulness of a New Alloy Catalyzer. Jour. Soc. Chem. Ind. (Japan), vol. 37, suppl., 1933, pp. 738–744; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 25, 1934, pp. 144–151; British Chem. Abs., 1935, B, p. 132; Chem. Abs., vol. 29, 1935, p. 1231.

Porous catalyzer of good thermal condition is obtained by dissolving out the Si from a Ni–Co–Si (1:1:2) alloy. With this catalyst, a benzine yield of

108 cc. per m.^{3} is obtained at 180° by a single pass of the theoretical gas mixture. Increasing the temperature decreases the degree of saturation of benzine. Increasing the amount of the catalyst increases the benzine yield and lowers the working temperature.

1859. TSUNEOKA, S., AND MURATA, Y. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXIII. The Extraction and Leaching Treatment of Alloy Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 38, suppl., 1935, pp. 199–206; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 27, 1935, pp. 13–22; Chem. Abs., vol. 29, 1935, p. 4551.

Experiments were carried out on the methods of preparation of Ni–Co–Si (1:1:2) catalyst to improve the activity of alloy catalysts. The extraction of Si from the alloy is an essential operation and the most favorable procedure consists in boiling 24 hr. with the theoretical amount of NaOH. Any residual alkali in the extracted catalyst exerts a detrimental influence upon its activity, and as complete a removal of alkali as possible is indicated. The residual alkali increases the power of CH_4 formation of the catalyst. The experiments with the Ni–Co–Si catalyst did not show any relation between the gas contraction and the benzine yield. The activity of the benzine catalyst becomes greater as the most favorable reaction temperature is lowered. With 25 gm. of Ni–Co alloy catalyst a maximum benzine yield of 120 cc. per m.^{3} was obtained in a single-pass operation with an initial gas composition of 33.5% CO, 65.6% H_2 and 0.9% N_2. Increase in quantity of catalyst resulted in a less volatile and more saturated benzine.

1860. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXIV. The Influence of the Particle Size and the Hydrogen Treatment or Oxidation Conditions of the Alloy Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 38, suppl., 1935, pp. 206–212; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 27, 1935, pp. 23–31; Chem. Abs., vol. 29, 1935, p. 4551.

Activity of the catalyst became less with a decrease in particle size. The H_2 pretreatment of the Ni–Co–Si alloy catalyst is unimportant, almost no increase in activity being obtained by H_2 pretreatment at 220°. A H_2 treatment at 350°–450° is detrimental and at 450° it results in complete inactivation of the catalyst. Oxidation of the catalyst before and after H_2 treatment is likewise considered unfavorable.

1861. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXV. General Properties and Constituents of the Benzine Prepared With an Alloy Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 38, suppl., 1935, pp. 212–217; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 27, 1935, pp. 32–38; Chem. Abs., vol. 29, 1935, p. 4551.

Catalyst used was of the composition Ni : Co : Si = 1 : 1 : 2. Double fractionation with a Widmer column gave distillates at 30°–40°, 60°–70°, 90°–100°, 120°–130° and 140°–150°. About 75 vol. % were found to be distillable at 220°. The contents of unsaturated hydrocarbons were determined by the observation of density, n and I number; they are lower for a higher boiling point. The method of Garner gave 90.5% paraffins and 9.5% olefins. The product was water white, had good volatility, did not contain any S compounds and diolefins, refining was not necessary and it had a high heating value.

1862. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXVI. Gas Contraction and Benzine Synthesis. Jour. Soc. Chem. Ind. (Japan), vol. 38, suppl., 1935, pp. 569–575; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 28, 1935, pp. 48–56; Chem. Abs., vol. 30, 1936, p. 270.

No relation appears to exist between the total gas contraction and yield of benzine.

1863. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXVII. Cobalt-Alloy Catalysts. Jour. Soc. Chem. Ind. (Japan), vol 39, suppl., 1936, pp. 267–273; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 30, 1936, pp. 1–14; British Chem. Abs., 1936, B, p. 1028; Chem. Abs., vol. 30, 1936, p. 8570.

Activity of Ni–Co–Si, Ni–Co–Mn–Si and Co–Si alloys has been improved by melting the original alloy in a high-frequency furnace. With 10 gm. Ni–Co–Si (1:1:2) alloy catalyst a maximum benzine yield of 130 cc. per m.^{3} was obtained from 1 m.^{3} of initial gas (33.6% CO and 65.4% H_2). A small addition of Mn to Ni–Co–Si alloy catalyst appears harmful. Mn checks hydrogenation of the catalyst and accelerates polymerization. The activity of Co–Si catalyst increases with decrease in particle size. H_2 treatment of Co–Si catalyst is detrimental. The optimum temperature for Co–Si catalyst is 230°. The activity is lower than that of Ni–Co–Si alloy catalysts.

1864. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXVIII. Nickel Alloy Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 39, suppl., 1936, pp. 273–278; Sci. Papers Inst. Phys. Chem. Research (Tokyo). vol. 30, 1936, pp. 15–29; British Chem. Abs., 1936, B, p. 1028; Chem. Abs., vol. 30, 1936, p. 8570.

Activity of Ni–Al catalyst increases with a decrease of particle size. A H_2 treatment at 350° increases the activity, but at 450° complete inactivation results. CH_4 formation is most favorable at 240°–250°. The activity of Ni–Si catalyst increases with the decrease of particle size. No H_2 treatment is necessary for this catalyst. Though the optimum temperature of Ni–Si catalyst is lower than Co–Si, it has a lower activity. The addition of Mn to Ni–Si catalyst influences the activity unfavorably. The activity of Ni–Fe–Al (1:1:2) catalyst increases with decrease in particle size. H_2 treatment is unnecessary for this catalyst.

1865. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXIX. Influence of Bore and Length of the Reaction Tube. Jour. Soc. Chem. Ind. (Japan), vol. 39, suppl., 1936, pp. 294–298; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 3, 1936, pp. 30–39; British Chem. Abs., 1936, B, p. 1028; Chem. Abs., vol. 30, 1936, p. 8570.

With 10 gm. of Ni–Co catalyst a bore of 13 mm. is most favorable. The smaller the bore the greater is the formation of gaseous hydrocarbons. The volatility of the benzine formed is dependent upon the bore and length of the reaction tube. The best length of reaction tube for a bore of 13 mm. or less is approximately 30 cm. A 20-mm. reaction tube must be longer than 50 cm. With constant bore the decrease of reaction tube length promotes the formation of gaseous hydrocarbons. With decrease in tube length the most favorable reaction temperature decreases. The volatility of the benzine formed is increased.

1866. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXX. Influence of Catalyst Concentration. Jour. Soc. Chem. Ind. (Japan), vol. 39, suppl., 1936, pp. 325–329; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 30, 1936, pp. 40–51; British Chem. Abs., 1936, B, p. 1028; Chem. Abs., vol. 30, 1936, p. 8570.

If more than a certain amount of catalyst is used, constant velocity being assumed, the reaction reaches a condition of equilibrium independently of the amount of catalyst used. This limiting value depends on the quality of the catalyst and the conditions of the experiment. Polymerization, hydrogenation, heavy hy-

drocarbon formation and CO_2 formation are promoted by the use of too large a quantity of catalyst. When the most favorable amount of catalyst is used the formation of gaseous hydrocarbons is at a minimum.

1867. MURATA, Y., ISHIKAWA, S., AND TSUNEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXI. Influence of Current Velocity. Jour. Soc. Chem. Ind. (Japan), vol. 39, suppl., 1936, pp. 329–333; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 30, suppl., 1936, pp. 52–59; British Chem. Abs., 1936, B, p. 1028; Chem. Abs., vol. 30, 1936, p. 8570.

Most favorable velocity for a 13-mm. bore is 4 l. per hr., corresponding to a mass velocity of 500. Wide variations in velocity do not markedly affect the most favorable reaction temperature, but marked changes occur in the composition of the benzine, the formation of CO_2, C_nH_{2n+2} and heavy hydrocarbons.

1868. TSUNEOKA, S., AND MURATA, Y. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXII. Studies on the Material of the Reaction Furnace. Jour. Soc. Chem. Ind. (Japan), vol. 40, No. 11, suppl., 1937, pp. 438–441; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 33, 1937, pp. 305–312; Chem. Abs., vol. 32, 1938, p. 1426.

Probable effect of using Fe, Ni, Cu, Al and brass furnaces on the yield of benzine has been studied by mixing small pieces of these metals with the alloy catalyst, Ni–Co–Si (1 : 1 : 2), and carrying out the synthesis in the normal manner (see abs. **1859**). The metals used did not effect the yield and exerted no catalytic effect. It is suggested that Fe furnaces can probably be used most practicably for large-scale production.

1869. MURATA, Y., AND TSUNEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXIII. Relation of Free Space in the Reaction Tube and the Reaction Rate of the Initial Gas, and Also the Influence of Materials Mixed With the Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 40, No. 11, suppl., 1937, pp. 438–441; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 33, 1937, pp. 313–332; Chem. Abs., vol. 32, 1938, p. 1426.

With a horizontal contact tube the contact between the incoming gas and the catalyst becomes insufficient when the free space above the catalyst goes above a certain limiting value. With a catalyst layer length of 30 cm. and a gas flow of 4 l. per hr. this maximum value is 13 mm. For a given gas-volume velocity and catalyst layer length this value decreases as the diameter of the tube is increased. Natural silica and Fe are useful as packing materials. Active charcoal and silica gel are unsuitable. The I-number of the generated benzine decreases if the catalyst is mixed with other substances; that is, if the free space in the reaction tube is decreased. When the catalyst is to be used with other substances complete mixing is necessary.

1870. TSUNEOKA, S., AND KURODA, R. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXIV. Analytical Studies of Alloy Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 40, No. 11, suppl., 1937, pp. 449–451, 451–454; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 33, 1937, pp. 333–338, 339–346; Chem. Abs., vol. 32, 1938, p. 1426.

Ni–Co–Si (1 : 1 : 2) alloy catalyst prepared in a high-frequency furnace gave Ni 23.9, Co 22.6 and Si 50.5%.

1871. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXV. Microscopic Study of Alloy Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 40, No. 11, suppl., 1937, pp. 449–451, 451–454. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 33, 1937, pp. 339–346; Chem. Abs., vol. 32, 1938, p. 1426.

Shows photomicrographs of the following alloy catalysts: Co–Si (1:1); Ni–Si (1:1); Ni–Co–Si (1:1:2); Ni–Co–Si (1:1:2) after treatment with enough NaOH solution theoretically to remove 20% Si; Ni–Co–Si (1:1:2) after treatment with 50% of the amount of NaOH necessary for complete removal of Si; Ni–Co–Mg (1:1:2) after complete removal of Mg with $(NH_4)_2CO_3$.

1872. TSUNEOKA, S., AND MURATA, Y. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXVI. Relation of the Activity of the Catalyst to the Synthesis Requirements at Too High a Temperature. Jour. Soc. Chem. Ind. (Japan), vol. 40, No. 12, suppl., 1937, pp. 478–484, Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1937, pp. 68–82; Chem. Abs., vol. 32, 1938, p. 2715.

Influence of raising the optimum temperature of 195° to 300° has been studied. In the range 240°–250° no synthesis of benzine takes place; CH_4 and some H_2CO_3 are formed. At 270° benzine is again formed, but in small quantity. If the reaction is carried on at a temperature above the optimum and then brought back again to the optimum the catalyst loses its characteristic activity, depending on the amount of treatment at the high temperature. When the reaction has been carried on at a temperature higher than the optimum, any benzine subsequently formed at the optimum temperature will have a higher I number proportionate to the increase in temperature used in the previous treatment.

1873. TSUNEOKA, S., AND NISHIO, A. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXVII. Volume Velocity of the Gas. Jour. Soc. Chem. Ind. (Japan), vol. 41, suppl., 1938, pp. 11–16; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1937, pp. 83–98; Chem. Abs., vol. 32, 1938, p. 3592.

For given amounts of catalyst and fixed layer lengths, the yield of benzine decreases if the velocity of the current of gas is increased. With a fixed-gas volume velocity and catalyst-layer length, the yield of benzine obtained during an increasing velocity of the current of gas after it once reaches a maximum decreases gradually. The amount of unsaturation has a tendency to rise with the larger values of gas-volume velocity. In a reaction tube of 20 mm. width, with a constant gas-volume velocity (500), the unsaturation increases as the velocity of the current of a gas becomes larger. If the volume velocity of the gas is not large, the rate of production of CO_2 tends to increase with the amount of catalyst.

1874. MURATA, Y., AND TSUNEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXVIII. Relation Between Conditions of Synthesis and the Unsaturation of the Benzine Produced. Jour. Soc. Chem. Ind. (Japan), vol. 41, suppl., 1938, pp. 16–22; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1937, pp. 99–115; Chem. Zentralb, 1938, II, p. 2874; Chem. Abs., vol. 32, 1938, p. 3592.

Following are the I nos. of the benzines produced with different catalysts: Fe–Cu–Na_2CO_3 150, Ni–Mn–Th_2O 7.5, Ni–Mn–Al_2O_3 11.8, Ni–Si (1:1) 18.0, Co–Cu–U_3O_8 82.2, Co–Cu–U_3O_8–Mn 98.9, Co–Cu–Th–U 100.0, Co–Si 88.3, Ni–Co 20.0 and Ni–Fe 51.8. Silica added to the catalyst decreases the I number. The highest I number is obtained with a reaction tube 13 mm. in diameter. It is possible to increase the content of

unsaturated hydrocarbons by increasing the CO in the original gas. The I number increases as the gas volume velocity and also the velocity of the current of gas increases. The temperature at which the benzine is synthesized may increase or decrease the I number, depending on the catalyst used.

1875. TSUNEOKA, S., AND MURATA, Y. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXIX. Properties of a Precipitated Nickel-Cobalt Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 41, suppl., 1938, pp. 52–57; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1938, pp. 280–294; Chem. Abs., vol. 32, 1938, p. 3945.

Precipitated Ni–Co catalyst (I), without the addition of an accelerator, is useless for the production of benzine. With ThO_2 (II), Al_2O_3 or Cr_2O_3 as accelerators the optimum temperature of reaction is comparable to that of U_3O_8 (III). (II) and (III) are excellent accelerators while Mn is not very effective. With (I) the optimum amount of Mn is 15–20%. The optimum reduction temperature of a Ni–Co–Mn catalyst is at 350°, while if (II) or (III) is added, the reduction is more successful at 400°. The most suitable mixing proportions of Co and Ni are 1 : 1.

1876. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XL. Proportions of Nickel and Cobalt, and the Influence of the Addition of Copper to the Precipitated Nickel–Cobalt Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 41, suppl., 1938, pp. 57–59; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1938, pp. 295–300; Chem. Abs., vol. 32, 1938, p. 3945.

Optimum reduction temperature decreases from 400° to 300° if 10% Cu is added to Ni–Co, 1 : 1, catalyst. The activity of (I), however, is decreased.

1877. KATAYAMA, I., MURATA, Y., KOIDE, H., AND TSUNEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLI. Activation of Catalysts by Slow Oxidation With Atmospheric Oxygen. Jour. Soc. Chem. Ind. (Japan), vol. 41, suppl., 1938, pp. 393–399; Sci Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1938, pp. 1181–1196; Chem. Abs., vol. 33, 1939, p. 1261.

Catalyst (I) used in the work was a mixture of (50% Ni+50% Co)+15% Mn+5% U_3O_8+3% ThO_2+125% kieselguhr (*see* abs. **1875**). A study was made of the change in activity of (I) caused by slow oxidation with air and the possibility of its storage in air as a result of exposing a sample, freshly reduced with H_2, with and without a subsequent exposure to CO_2, to the oxidizing action of varying amounts of air at room temperature. In the experiments an amount of (I) was taken such that it contained 1.5 gm. each of Ni and Co, and which had a volume of about 30 cc. The reaction tube was hard glass of about 20 mm. diameter. Freshly reduced (I) showed an increase in activity when directly oxidized with 1,700–2,600 vol. of air at a velocity of 50–80 l. per hr. and with a maximum increase in activity of 10% with 130 vol. at 4 l. per hr. The oxidation of (I), previously treated with CO_2, with 4,500 vol. of air at a velocity of 140 l. per hr. increased the activity, and with 3,300 vol. at 4 l. per hr. the increase was about 8%. A freshly reduced (I), which had been treated first with CO_2 and then partly oxidized with air, is much less susceptible to further oxidation than is a freshly reduced (I) which has been partially oxidized with air but without the CO_2 treatment. (I) which has been activated by slow oxidation with air and then used in a benzine synthesis cannot be further activated by a subsequent oxidation. Samples of (I) which have received a slow and weak oxidation with air are stable to further exposure to the air, whereas (I), when freshly prepared by reduction with H_2, is rapidly oxidized on direct exposure to the air with evolution of much heat, even to redness.

1878. TSUNEOKA, S., AND FUNASAKA, W. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLII. Purification of the Gaseous Raw Material Used for Benzine Synthesis. 1. Removal of Organic Sulfur Compounds at Low Temperature. Jour. Soc. Chem. Ind. (Japan), vol. 41, suppl., 1938, pp. 43–47; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1938, pp. 301–309; Chem. Abs., vol. 32, 1938, p. 3577.

Researches were undertaken to find a satisfactory method of S removal, with known or new materials, from a gas to be used further for the synthesis of benzine, its S content to be less than 0.2 gm. S per 100 m.^{3} City gas, with a total S content of 24.0 gm. S per 100 m.^{3} of which 22.6 gm. S is organic, was freed of CO_2 and H_2S and as such used over adsorbent materials, dry purificants and H_2S extraction materials at room temperature. As adsorbent materials were used active C, SiO_2 gel, Japanese acidic-earths and Adosol. Active C was found the most efficient but not active enough to produce a highly purified gas. As dry purificants Fe_2O_3 on a pumice support and Luxmasse were used, as H_2S scrubbing materials Thylox solution and $(C_2H_5)_3N$ to which Fe_2O_3 was added were used. 80% S removal was obtained with the dry purificants. Thylox failed to extract the organic S, while with $(C_2H_5)_3N$, 67.7% S removal was obtained; it was further improved by addition of Fe_2O_3.

1879. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLIII. Purification of the Gaseous Raw Material Used for Benzine Synthesis. 2. Removal of Organic Sulfur Compounds at High Temperature. Jour. Soc. Chem. Ind. (Japan), vol. 41, suppl., 1938, pp. 47–51; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1938, pp. 310–320; Chem. Abs., vol. 32, 1938, p. 3577.

Same city gas was used for S removal at high temperature by passing the gas through heated pipes without and in the presence of catalysts. Fe, Cu and V2A–steel pipes were used. At 500°, Fe pipe gave the best results but desulfuration is only 77%. Ag catalysts (1% Ag by wt.), CuO–CrO_4Pb, Ni, Fe–Cu, Ag catalysts (10% metal) and active C were used in an effort to eliminate the organic S by transforming it into H_2S, by contact. With CuO–CrO_4 Pb, Ni, Fe–Cu catalysts (10% metal), at temperatures 450°, 350°, 300°, 330 cm.^{3} per hr. per cm.^{3} contact (*see* abs. **1026**) in each case, the organic S content was reduced to less than 0.2 gm. S per 100 m.^{3} of gas. The amount of organic S changed into H_2S was very small, the major part of it being fixed on the catalyst. A preliminary extraction of H_2S from the gas is necessary, otherwise the amounts of total S, remaining in gas, are 0.66, 3.12, 0.82 gm. per 100 m.^{3} respectively. With Fe_2O_3 on a pumice support (30% Fe_2O_3) and Luxmasse, at 350° and 330 m.^{3} per hr. per cm.^{3} contact, the organic S was completely removed from the gas. No preliminary extraction of H_2S is necessary and the S is economically removed to less than 0.2 gm. S per 100 m.^{3} (organic S less than 0.07 gm. per 100 m.^{3}, total S less than 0.07 gm. per 100 m.^{3} or 99.7% S removed). The Luxmasse used by the authors was a by-product obtained in the manufacture of Al ("red mud"), often used in city-gas plants for H_2S removal, which in muddy form contained 38.2% of H_2O. The material was dried for 12 hr. at 105° and then crushed to 3–5 mm. granules.

1880. FUNASAKA, W. AND KATAYAMA, I. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLIV. Purification of the Gaseous Raw Material Used for Benzine Synthesis. 3. Removal of Organic Sulfur by Means of Luxmasse and Admixtures. Jour. Soc. Chem. Ind. (Japan), vol.

42, suppl., 1939, pp. 9, 12; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1938, pp. 32–38; British Chem. Abs., 1939, B, p. 688; Chem. Abs., vol. 33, 1939, p. 3559.

Use of various addition agents to Luxmasse for the removal of organic S from a gas containing 30.1 gm. S per 100 m.^{3} of which 28.4 gm. S is organic was investigated. The addition of 1 wt. % of ThO_2, UO_2 or NaOH to Luxmasse had little effect. The addition of 10% NaOH, $Ba(OH)_2$, ThO_2, Cr_2O_3, Al_2O_3 or K_2CrO_4 improved the efficiency and the life of the Luxmasse. For the greatest efficiency Luxmasse containing 10% NaOH and 10% ThO_2 was used. At 400°, this mixture removed 98.9% of the S. The addition of Na_2CO_3 was not very promising.

1881. ———. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLV. Purification of the Gaseous Raw Material Used for Benzine Synthesis. 4. Removal of Organic Sulfur by Means of Synthetic Agents. Jour. Soc. Chem. Ind. (Japan), vol. 42, suppl., 1939, pp. 9, 12; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1938, pp. 39–46; British Chem. Abs., 1939, B, p. 688; Chem. Abs., vol. 33, 1939, p. 3559.

With the same gas many synthetic masses were used for the removal of organic S. A mixture of Fe_2O_3–Al_2O_3–brimstone and NaOH (Fe 10%, Fe_2O_3: Al_2O_3= 1 : 1 and 1% NaOH) at 450° and a gas rate of 330 l. per hr. reduced the S to 0.19 gm. per 100 m.^{3} A 7 : 3 mixture of Luxmasse and diatomaceous earth with 30% NaOH at 350° and a gas rate of 330 l. per hr. reduced the S to 0.07 gm. per 100 m.^{3} A mixture of Fe_2O_3–bentonite–NaOH containing 10% Fe and 10% NaOH at 400° and a gas rate of 790 l. per hr. reduced the S to 0.16 gm. per 100 m.^{3} With the Fe_2O_3–Al_2O_3–diatomaceous earth–NaOH mass, the presence of CO_2 was harmful. Diatomaceous earth is the best carrier and materially increases the life of the purification mass.

1882. Tsuneoka, S., Murata, Y., and Makino, S. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLVI. Preparation of New Iron Catalysts and Their Superior Properties. Jour. Soc. Chem. Ind. (Japan), vol. 42, suppl., 1939, pp. 107–112. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1939, pp. 330–336; Chem. Abs., vol. 33, 1939, p. 4761.

Two new catalysts of Fe base were prepared: (I) is composed of Fe 4, Cu 1, kieselguhr 5 and K_2CO_3 0.09. (II) consists of Fe 4, Cu 1, Mn 0.08, kieselguhr 5 and K_2CO_3 0.09. Solutions of $Fe(NO_3)_3$, $Cu(NO_3)_2$ and accelerator were mixed with unpurified kieselguhr and precipitated with an equivalent solution of alkali carbonate in the cold. The precipitate was filtered on a porcelain filter, washed with warm H_2O, impregnated with a small amount of alkali, dried in air at 100° and pulverized. With (I) a gasoline yield of 83 cc. per m.^{3} and I number 141.0 is possible. (II) produced a yield of 88 cc. per m.^{3} of gasoline having an I number of 132. The Fe catalyst is cheaper than Co and Ni catalysts, and with it water gas can be used directly as a starting material. A reaction temperature of 250° is required as compared with 200° for Co and Ni catalysts, and its durability is slightly lower.

1883. ———. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLVII. Composition of Starting Gases With New Iron Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 42, suppl., 1939, pp. 107–112; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1939, pp. 337–347; Chem. Abs., vol. 33, 1939, p. 4761.

Tabular results are given for experiments with CO and H_2 in the following ratios: 4 : 1, 3 : 1, 2 : 1, 1 : 1 and 1 : 2. With a catalyst consisting of Fe+25% Cu (by weight of Fe)+125% kieselguhr+3% K_2CO_3, highest gasoline yields resulted from an initial gas mixture ratio of $CO : H_2$=1 : 1–1 : 2. An initial gas ratio of 1 : 2 was found most conducive to high yields with a catalyst comprising: Fe+5%Ni+25% Cu+125% kieselguhr+3% K_2CO_3. The larger the CO content of the gas the greater the degree of unsaturation of the gasoline. Excess H_2 produces no deleterious effects on the synthesis. The gasoline resulting from the synthesis employing the new Fe catalysts is colorless and clear. Water hinders the progress of the reaction. Volatility and degree of unsaturation increase with higher reaction temperatures. H_2 reduction increases the activity of the catalysts.

1884. Murata, Y., Makino, S., and Tsuneoka, S. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLVIII. Influence of Addition of Copper and Alkali on New Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 42, suppl., 1939, pp. 107–112; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1939, pp. 348–355; Chem. Abs., vol. 33, 1939, p. 4761.

Experiments carried out with a catalyst containing Fe+125% kieselguhr +3% K_2CO_3 (% based on weight of Fe) to which various amounts of Cu were added show that best gasoline yields were obtained by addition of Cu in amounts of 20–40% of the weight of Fe. The addition of 2–3% of alkali carbonate (K_2CO_3) to catalysts of composition Fe+25% Cu+125% kieselguhr, and Fe+5% Ni+25% Cu+125% kieselguhr increases the yield for $CO : H_2$ ratios both of 1 : 1 and 1 : 2. In general, however, the larger the CO content of the gases the smaller should be the addition of alkali. Degree of unsaturation increases with increasing amounts of alkali.

1885. ———. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLIX. Influence of Various Metals, Metal Oxides and Precipitants on Fe–Cu–Kieselguhr Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 42, suppl., 1939, pp. 107–112; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1939, pp. 356–364; Chem. Abs., vol. 33, 1939, p. 4762.

Addition of U_3O_8, ThO_2, Al_2O_3 and Cr_2O_3 to Fe–Cu–kieselguhr catalysts brings about very poor gasoline yields, especially with the last 2 oxides. The addition of 2% Mn or MgO to a catalyst consisting of Fe+25% Cu+125% kieselguhr+2% K_2CO_3 produces a yield of 88 cc. per m.^{3} The presence of Ni accelerates the reaction provided the $CO : H_2$ is 1 : 2. Co is less harmful than Ni. H_2O formation is noticed if the catalyst contains more than 2.5% Ni. Gasolines produced with Ni catalysts also have a low I number. Addition of ThO_2, U_3O_8, etc., to an Fe catalyst containing 10% Ni proved ineffectual. Na_2CO_3 is the most suitable precipitant for producing the catalyst. Replacing the carbonate with caustic soda proved damaging.

1886. Funasaka, W. Benzine Synthesis From Carbon Monoxide and Hydrogen. L. Removal of Organic Sulfur Compounds From Water Gas. Jour. Soc. Chem. Ind. (Japan), vol. 43, suppl., 1940, pp. 200–203; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 37, 1940, pp. 323–330; Chem. Zentralb., 1941, I, p. 849; Chem. Abs., vol. 34, 1940, p. 6796.

In contrast to the previously tested city gas, water gas containing 11.7 gm. total S per 100 m.^{3} and 11.0 gm. organic S per 100 m.^{3}, from which the H_2S had been removed by treatment with Thylox solution (1.5% Na_2CO_3; 0.7% As_2O_3), could not be freed sufficiently from S compounds to be suitable for use in the benzine synthesis, which requires less than 0.2% S per 100 m.^{3}, by treatment at 250° with Luxmasse, Luxmasse+10% NaOH, Luxmasse+Na_2CO_3 (2 : 1), ignited Fe_2O_3–Al_2O_3–diatomaceous earth–NaOH (1 : 1 : 2 with 10% NaOH),

ignited Fe_2O_3–Al_2O_3–pumice–NaOH (1:1:2 with 10% NaOH, Luxmasse–diatomaceous earth–NaOH (7:3 with 30% NaOH) or ignited Fe_2O_3–bentonite (containing 10% Fe), with a total of 150 l. of gas, a gas velocity of 30 l. per hr., a space velocity of 400, and a 25 cm. layer of treating agent. Total S contents of the treated gas samples (gm. S per 100 m.^{3}) were 1.72, 1.88, 1.90, 1.30, 9.30, 3.68, and 4.05, respectively. 10% of an equimolecular mixture of Fe and Cu on pumice and of Ni on pumice lowered the S content of the water gas to 0.43 and 0.85 gm. S per 100 m.^{3}, respectively. Temperatures above 250° resulted in C formation from the CO of the water gas; thus at 350°, although the S content of the gas was reduced to less than 0.07 gm. per 100 m.^{3}, the Luxmasse+10% NaOH contained much C from energetic decomposition of CO.

1887. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen. LI. Highly Active Sulfur-Fixation Agent Which Purifies Water Gas to the Highest Degree at Comparatively Low Temperatures, Such as 200°–250°. Jour. Soc. Chem. Ind. (Japan), vol. 43, suppl., 1940, pp. 203–206; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 37, 1940, pp. 331–337; Chem. Zentralb., 1941, I, p. 849; Chem. Abs., vol. 34, 1940, p. 6796.

At 250° under the conditions mentioned previously, water gas containing 18 gm. total S per 100 m.^{3} and 14.6 gm. organic S per 100 m.^{3} showed the following total S content after treatment with the agent mentioned: Luxmasse, 1.72; Luxmasse+10% Ni hydroxide (precipitated by addition of NaOH solution to hot $NiSO_4$ solution), 0.35 (0.30 with 900 l. gas; 0.97 at 200°, 250 space velocity, 40 cm. layer of treating agent and 30 l. per hr. gas stream velocity); Luxmasse+20% Ni hydroxide, 0.34; Luxmasse+10% Ni hydroxide+10% NaOH, 0.50 (0.44 with 900 l. gas); Luxmasse+10% Cu hydroxide (prepared similarly to Ni hydroxide), 0.30 (0.42 at 200° with 150 l. gas; 0.75 at 200° with 900 l. gas); Luxmasse +10% Cu hydroxide+10% NaOH, 0.18 (0.77 for 900 l. gas; 0.54 and 1.05 at 200° for 150 and 900 l. gas, with 250 space velocity and 40 cm. layer of agent; 0.26 and 0.14 at 200° for 160 and 100 space velocity and 60 and 45 cm. layer of agent, respectively); Luxmasse +20% Cu hydroxide+10% NaOH, 0.16; Luxmasse+ 10% commercial CuO+10% NaOH, 1.24; Luxmasse+ 20% commercial CuO+10% NaAH, 0.58; Luxmasse+ 30% commercial CuO+10% NaOH, 0.21; and Luxmasse +10%Cu hydroxide+10%NaOH (2 successive treats), 0.21. The efficiency of each fixation agent containing Cu rapidly decreased with use.

1888. Murata, Y., and Makino, S. Benzine Synthesis From Carbon Monoxide and Hydrogen. LII. Influence of the Initial Materials, Carriers and Filling Agents Upon the Iron Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 43, suppl., 1940, pp. 210–215; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 37, 1940, pp. 338–349; Chem. Zentralb., 1941, I, p. 849; Brennstoff-Chem., vol. 24, 1943, p. 9; Chem. Abs., vol. 34, 1940, p. 6796.

In the benzine synthesis at 257° from gas containing approximately equal proportions of H_2 and CO, with catalyst having the composition Fe+25% Cu+125% kieselguhr+2% K_2CO_3, best results were obtained with the catalyst precipitated from the nitrate solution (by K_2CO_3 solution), inferior results with that from chloride solution, and no reaction at all where precipitation was made from sulfate solution. The best carrier for the catalyst Fe+25% Cu+2% Mn+2% KOH (Na_2CO_3 precipitation agent) was 125 wt. % of kieselguhr (based on Fe present), Mn being somewhat inferior and A–carbon giving no yield of benzine. When used with Fe+25% Cu+125% kieselguhr+2% KOH (K_2CO_3 precipitation agent) and pumice, soda-lime, Mn, CaO and BaO were all good filling agents. With Fe+25% Cu+125% kieselguhr (K_2CO_3 precipitation agent) the following catalyst addition agents (2% based on Fe present) are arranged in the order of decreasing effect on the catalyst; Rb_2CO_3 (additional 2% Mn) >KOH >KNO_3 >Rb_2CO_3 >$KMnO_4$ >K_2CO_3 >Na_2CO_3 >KCl, the benzine yield being much lower when KCl was present than when either of the other catalyst addition agents was present. Optimum quantities of K_2CO_3, KOH, Rb_2CO_3 and $KMnO_4$ for use as catalyst addition agents (with respect to quantity of Fe present) were 2%, 2%, 2–3% and 2–5% respectively. The use of Fe+25% Cu+2% Mn+125% kieselguhr +2% Rb_2CO_3 catalyst at 257° resulted in a benzine yield of 90 cc. per m.^{3}

1889. Makino, S., Koide, H., and Murata, Y. Benzine Synthesis From Carbon Monoxide and Hydrogen. LIII. Influence of Aluminum Oxide, Silver, and Other Addition Agents Upon the Iron Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 43, suppl., 1940, pp. 235–241; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 37, 1940, pp. 350–365; Chem. Zentralb., 1940, I, p. 2842; Brennstoff-Chem., vol. 24, 1943, p. 9; Chem. Abs., vol. 34, 1940, p. 6797.

When precipitated with Fe+25% Cu+2% Mn+125% kieselguhr+2% KOH catalyst or when Al_2O_3 was added before precipitation, Al_2O_3 decreased the yield of benzine at 250° from gas containing approximately equal amounts of CO and H_2. When 1–3% Al_2O_3 was added (based on Fe present) after precipitation of the catalyst, the benzine yield was increased (94 cm.^{3} per m.^{3} with 3% Al_2O_3). Addition of the following Al compounds (2–5% with respect to Fe present) to the above catalyst resulted in decreasing yields of benzine in the order shown: $AlPO_4$>Al acetate >Al silicate>Al $(OH)_3$ >"$Al_2(CO_3)_3$." The yield of benzine was 0 when $Al_2(SO_4)_3$ of $AlCl_3$ was added to the catalyst. Acid–clay (containing approximately 15% Al_2O_3) added to the above catalyst in quantities up to 25% (based on Fe present) increased the benzine yield, but when the acid clay was substituted for a portion of the kieselguhr of the catalyst, inferior yields were obtained. Coprecipitation of Ag (3–30%, based on Fe content) with the above catalyst or addition of 3–10% Ag_2O to the catalyst resulted in unchanged or diminshed yields of benzine. Substitution of the Cu of the catalyst by 10, 20 or 30% Ag (based on Fe present) resulted in very inferior yields of benzine and the formation of some paraffin wax. Precipitation of 2–5% (based on Fe present) of Ba, Ca, Cd, Bi, Pb, Sn or W with the above catalyst resulted in inferior yields of benzine, Bi, Pb and W giving especially low benzine yields.

1890. Murata, Y., and Yamada, T. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. LIV. Influence of Carbon Dioxide in the Initial Gas Upon the Iron Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 44, suppl., 1941, pp. 33–38. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 38, 1940, pp. 118–131; Chem. Zentralb., 1941, I, p. 2203; Brennstoff-Chem., vol. 24, 1943, p. 9; Chem. Abs., vol. 35, 1941, p. 2297.

When a gas mixture containing varying quantities of CO_2 and approximately equal volumes of CO and H_2 was passed over a catalyst consisting of Fe+25% Cu +125% kieselguhr+2% KOH at 253° at a rate of 3.8–4.3 l. per hr., the yield of liquid product and the I number of the liquid product decreased rapidly with increase in the CO_2 content of the gas charged, the effect being much greater than a simple diluent effect. Experiments with catalysts composed of Fe+25% Cu+2% Mn+125% kieselguhr and 0–5% KOH at 254° showed that the yield of liquid product and the C : H_2 ratio of the gas resulting from the reaction increased with increase in alkali content of the catalyst; with a catalyst composed of Fe+25% Cu+2% Mn+125% kieselguhr+2% KOH at 254° the yield of liquid prod-

uct increased with a decrease of gas velocity to 2.6 l. per hr., when the gas charge contained approximately 20% CO_2. When the catalyst was pretreated with CO_2, the yield of liquid products from CO and H_2 decreased with the increase in length of the CO_2 pretreatment; the CO_2 apparently decreased the activating effect of alkali on the catalyst. At 253° there was very little reaction between CO_2 and H_2 in the presence of Fe+25% Cu+125% kieselguhr+2% KOH.

1891. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. LV. Influence of Nitrogen, Methane, Oxygen, and Ammonia in the Initial Gas Upon the Iron Catalyst. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 38, 1941, pp. 218–229; Brennstoff-Chem., vol. 24, 1943, p. 10; Chem. Abs., vol. 35, 1941, p. 5284.

When a mixture of approximate molecular proportions of CO and H_2 is diluted with N_2 and passed at 253° over catalyst having the composition Fe+25% Cu+125% kieselguhr+2% KOH and at a gas velocity of 3.4–4.1 l. per hr., the yield of liquid product decreases, with respect to CO and H_2, with increasing amount of N_2 in the initial gas mixture, and the I number of the liquid product increases. This effect of N_2 in the initial gas mixture is observed when the catalyst has high activity. When the initial gas is diluted with CH_4, the effect is similar but much less (very little effect when the initial gas contains less than 10% CH_4) than when either N_2 or CO_2 is used as a diluent. Oxygen strongly decreases the yield of liquid products (initial gas containing 12.6% O_2 decreased the yield 83.3%, based on the CO and H_2 present) and the I number of the liquid produce increases moderately with increasing O_2 content of the initial gas. When the initial gas mixture contained 5% and 15% respectively of NH_2, the yields of liquid product were decreased 19.5% and 93%, based on the CO and H_2 present.

1892. KODAMA, S., TARAMA, K., OSHIMA, T., AND FUJITA, K. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Atmospheric Pressure. LVI. Analysis of the Synthetic Oil by Precision Distillation. Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, suppl. binding, pp. 270–272; Chem. Abs., vol. 44, 1950, p. 7509.

Analytical distillations over a Podbielniak column were carried out on the gasoline fraction (obtained by sorption on activated C), naphtha fraction, hydrogenated naphtha fraction and the C_6–H_9 portion of the latter, all derived from the product obtained at 245°–250° from a synthesis gas of approximately equal parts of CO and H_2 with an Fe catalyst containing Cu 25, Mn 2, kieselguhr 125, H_3BO_3 20, and K_2CO_3 3%. The same type of distillation was applied to the naphtha fraction and the hydrogenated naphtha fraction from the oil obtained at 210°–212° from 1 part CO and 2 of H_2 with a Co catalyst containing Cu 10, Th 5, U 2.5, kieselguhr 125%. The C_5 and C_6 fractions each contained the following % by volume of *n*– and iso–hydrocarbons, respectively : Gasoline from Fe catalyst 61.8, 38.2; 58.3, 41.3; naphtha fraction from Fe catalyst 59.4, 40.6; 56.3, 43.7; hydrogenated oil from Fe catalyst 61.1, 38.9; 53.8, 46.2; naphtha fraction from Co catalyst 63.0, 37.0; the same, hydrogenated 72.0, 28.0; 57.0, 43.0.

1893. MURATA, Y., TATSUKI, Y., YAMADA, H., AND SAWADA, Y. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LVII. Effect of Some Added Substances on Iron–Copper Catalysts. Jour. Soc. Chem. Ind (Japan), vol. 45, 1942, pp. 557–560, suppl., pp. 229–232; Chem. Abs., vol. 43, 1949, p. 2399.

Effect of organic acids and other compounds on Fe–Cu catalysts was studied. With Fe catalysts the results were as follows: (1) $K_2C_2O_4$, HCO_2K, KOH, K_2CO_3, and KNO_3 accelerated the action, and the optimum amount of each is about 1.5% as K. (2) Organic acids were injurious. (3) $Cr(NO_3)_3$, CrF_3, $Cr_2(CO_3)_3$, and $Cr(OAc)_3$ were injurious to the catalyst but Cr_2O_3 was not. (4) $Zn(NO_3)_2$, ZnO, $Z_3(PO_4)_2$, $Zn(OAc)_2$, and Zn stearate were injurious, but $Zn(OH)_2$ was not. Because of the action of H_3BO_3 Zn borate had an accelerating action.

1894. MURATA, Y., SAWADA, Y. AND TAKEZAKI, Y. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LVIII. Mutual Influence of Boric Acid and Alkali in Promoting Activities of Iron–Copper Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 670–675; Chem. Abs., vol. 43, 1949, p. 2399.

Mutual influence of diatomaceous earth, H_3BO_3, and alkali on Fe–Cu catalysts was investigated. The activating action of H_3BO_3 is very weak for Fe catalysts with no alkali; it increases with the addition of alkali. H_3BO_3 prevents the formation of high molecular hydrocarbons, such as solid paraffins, and promotes the formation of saturated hydrocarbons. With increases in the amount of H_3BO_3 added the durability of the catalyst increases.

1895. MURATA, Y., AND YASUDA, M. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LIX. Activation of Iron–Copper Catalysts by Boron. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 675–677; Chem. Abs., vol. 43, 1949, p. 2400.

Various B compounds were added to Fe catalysts, and their influence was studied. Mn and Mg borates have the same action as H_3BO_3. The addition of B compounds is effective even by mechanical mixing, while alkali has no effect by the same treatment.

1896. MURATA, Y., YASHIRO, R., AND TASHIRO, E. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LX. Effect of Copper on Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1117–1121; Chem. Abs., vol. 43, 1949, p. 2400.

Cu has excellent accelerating action on the activity of Fe catalyst, and the optimum amount of Cu is different for catalysts of different compositions. When H_3BO_3 and alkali are added, the optimum amount of Cu is about 10%. Cu has no effect on the durability of Fe catalysts. The composition of the feed gas has no effect on the optimum amount of Cu. The amount of Cu has no effect on the optimum reaction temperature. The effect of alkali on the Fe catalyst is not affected by the amount of Cu present.

1897. MURATA, Y., YOSHIOKA, Y., OJI, G., AND SAITO, S. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXI. Reaction Temperature and Durability of Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1271–1286; Chem. Abs., vol. 43, 1949, p. 2400.

Durability of Fe catalysts on the composition Fe : Cu : Mn : kieselguhr : H_3BO_3 : K_2CO_3=100 : 25 : 2 : 125 : x : y, where x=0 or 20 and y=1, 2, 3 or 4 in powdered form, and x=20 and y=4 in tablet form, used in the Fischer synthesis with a gas mixture (CO : H_2=1 : 1) at 200°–270° was studied. The optimum value of y is 2 to 4 when x=0 or 20, respectively, regardless of the reaction temperature, and an increase in y diminishes the durability of the catalyst. The promoting effect of H_3BO_3 is not noticeable below 220°, and the optimum reaction temperature is not affected by the addition of H_3BO_3. On the whole an Fe catalyst is active at 230°–260°, and its durability can be greatly increased by choosing a lower reaction temperature. The optimum reaction temperature can be lowered more when the catalyst is used in the form of tablets than when used in powdered form, probably because of the rise in temperature of the catalyst layer. The lower the activity of the catalyst, the higher is its durability.

1898. ———. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXII. Durability of Iron Catalysts and the Composition of Gas Used in the Synthesis. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1271–1286; Chem. Abs., vol. 43, 1949, p. 2400.

Fischer synthesis was carried out with catalysts similar in composition to those used in preceding experiments with mixtures of composition CO : H_2=1 : 2, 1 : 3 and 1 : 5. With increase in H_2 content the most suitable reaction temperature was lowered, and the durability of Fe catalyst was remarkably increased. Thus with a mixture of CO : H_2=1 : 2 or 1 : 3 the same catalyst can be used continuously for about 1 month at a suitably fixed reaction temperature. With a mixture of CO : H_2=1 : 2, the highest yield of oil was 102 cc./m.^{3} of gas used, which decreased in proportion to dilution of the gas with more H_2. In these cases a small amount of H_2O was produced along with the oil. The property of H_3BO_3 in promoting the catalytic activity decreased with increases in H_2 content. With gas of composition CO : H_2=1 : 2 the addition of H_3BO_3 increased the durability of the catalyst, but with gas containing more H_2 it showed no effect.

1899. ———. Synthesis of Benzine From Carbon Monoxde and Hydrogen. LXIII. Iron Catalysts and the Composition of Gas Used in the Synthesis. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1271–1286; Chem. Abs., vol. 43, 1949, p. 2400.

Fischer synthesis was carried out with a gas mixture of composition CO : H_2=2 : 1 with an Fe catalyst of high activity containing H_3BO_3. The yield of oil was much smaller with gas of composition CO : H_2= 2 : 1 than with composition 1 : 1. The durability of the catalyst was also reduced. Further, the relations between the composition of gas mixture after the reaction, the ratio of consumption of CO to H_2, properties of the oil obtained, the composition of the feed gas, etc., were summarized.

1900. MURATA, Y., NAKAGAWA, M., TASHIRO, E., AND UMEMURA, T. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXIV. Methods of Preparing Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 52–68; Chem. Abs., vol. 43, 1949, p. 2400.

In the preparation of Fe catalysts the effect of the precipitating method and temperature, the method of washing the precipitate, the concentration at the time of precipitation, the quality and preliminary treatment of kieselguhr, the purity of reagents, the amount of alkali used in precipitation, the method of adding alkali as promoter, etc., on the activity of the catalyst was studied. The catalyst containing Fe 100, Cu 25, kieselguhr 125, and K_2CO_3 2 parts by weight was used with a gas mixture of CO : H_2=1 : 1 at 253°. The results show: (a) It is desirable in the precipitation that alkali should be added as quickly as possible with sufficient agitation and the time of adding kieselguhr has no marked effect, (b) the temperature at the time of precipitation has little influence, (c) washing the precipitate requires special care but less than with Co or Ni catalysts, (d) the concentration of the reagents has no marked influence, but it is desirable that the alkali solution be concentrated and the solutions of metallic salts be rather dilute, (e) the quality of the kieselguhr has a marked effect, and kieselguhr previously treated with acid produces a catalyst of inferior quality, (f) Fe and Na_2CO_3 need not be especially pure (g) 5–15% excess of the precipitating reagent should be used, (h) it is necessary that the alkaline promoter be uniformly spread over the surface of the catalyst.

1901. ———. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXV. Reduction by Hydrogen and Heat Treatment of Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 52–68; Chem. Abs., vol. 43, 1949, p. 2401.

Effect on the activity of Fe catalysts of various compositions by reducing with H_2, reoxidizing with air, and heating (without reduction) in a current of air was studied. Fe catalysts lose their activity when reduced with H_2 according to the temperature and time; thus they totally lose their catalytic power when reduced in H_2 4–8 hr. at 450°, while those reduced at 250° for 4–10 hr. regain their activity in the course of 1–2 days of normal operation. The activity of the catalysts reduced with H_2 is not recovered by oxidation with air at 250°–450°. Fe catalysts slightly increase their activity when heated in an air current at 100°–400°, but when the temperature is above 400°, the activity is gradually reduced with the elevation of temperature until at 600° it is completely lost.

1902. ———. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXVI. Reduction of Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 52–68; Chem. Abs., vol. 43, 1949, p. 2401.

Effect on the activity of the catalyst of reducing with various gas mixtures was studied in detail. The activity of the catalyst is increased when it is reduced by H_2 to which a small amount of CO is added. The effect of adding CO is nearly linear up to CO : H_2=1 : 2 and diminishes gradually when more CO is added. When the ratio of CO : H_2 exceeds that of the gas mixture used in the synthesis, the activity of catalyst is greatly reduced. When the catalyst is reduced with a gas mixture rich in H_2 and used in the synthesis with gas of composition CO : H_2=1 : 2, the durability of the catalyst is greatly increased. Dilution of H_2 with N_2 shows no advantage, and the reduction with mixtures of CO and N_2 is unfavorable.

1903. FUNASAKA, W., AND TOJO, T. Synthesis of Gasoline From Carbon Monoxide and Hydrogen. LXVII. Desulfurizing Ability of Various Metal Hydroxides. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 402–403; Chem. Abs., vol. 43, 1949, p. 2401.

To remove the organic S in water gas the mixtures of hydroxides of Fe, Ni, Co, Cu, Mn, or Cd with kieselguhr were very effective. To remove the organic S in water gas by transforming into H_2S, mixtures of $Al(OH)_3$, $Mg(OH)_2$, and kieselguhr were effective.

1904. TARAMA, K., TATSUKI, Y., KASAI, K., AND TAKEGAMI, Y. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXVIII. Analysis of the Synthetic Oil by Fractional Distillation. (2). Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 533–535; Chem. Abs., vol. 43, 1949, p. 2401.

Fractional distillation of oil synthesized with Fe catalyst confirmed that the synthetic oil consists mainly of aliphatic hydrocarbons and does not contain the aromatic hydrocarbons.

1905. KODAMA, S., MURATA, Y., AND HARA, I. Gasoline Synthesis From Carbon Monoxide and Hydrogen. LXXI. Activity and Deactivation of Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 50, 1947, pp. 119–120; Chem. Abs., vol. 44, 1950, p. 9135.

Gasoline was synthesized 29 hr. from CO and H_2 in a molecular ratio of 1 : 1 at 250° with (*A*) Fe+12.8% Cu or (*B*) Fe+25% Cu+152% kieselguhr. The addition of K_2CO_3 and H_3BO_3 increased the activity of these catalysts. The optimum amount of K_2CO_3 was 1% for (*A*) and 2% for (*B*).

1906. MURATA, Y. Gasoline Synthesis From Carbon Monoxide and Hydrogen. LXXII. Composition of Gases and Flow Velocity. Jour. Soc. Chem.

Ind. (Japan), 1947, vol. 50, pp. 120–121; Chem. Abs. vol. 44, 1950, p. 9135.

In the synthesis of gasoline with Fe catalysts, carbides and free C were formed by the activation of CO. The use of a gas mixture with a high H_2 content prevented this and the velocity of gas flow could be increased.

1906a. MURATA, Y., MATSUMOTO, E., AND HOSHINO, S. Gasoline Synthesis From Carbon Monoxide and Hydrogen. LXXIII. Action of Carbon Monoxide on Iron Catalysts. Jour. Chem. Soc. Japan, ind. chem. sec., vol. 53, 1950, pp. 298–300; Chem. Abs., vol. 46, 1952, p. 11,632.

Influence of the pretreatment with pure CO on the activity of Fe catalysts was studied. The longer the time of pretreatment the smaller the gas velocity and the higher the temperature. The effect of pretreatment can be enhanced by adding alcohol.

1906b. MURATA, Y. AND HARA, I. Gasoline Synthesis From Carbon Monoxide and Hydrogen. LXXIV. Influence of Water Vapor on Iron Catalysts. Jour. Chem. Soc. Japan, Ind. Chem. sec., vol. 53, 1950, pp. 338–340; Chem. Abs., vol. 46, 1952, p. 11,632.

Influence of water vapor on the activity of Fe catalysts has been studied under various conditions. Moisture contained in reacting component gases, however small the quantity may be, spoils the activity of Fe catalysts in almost all cases.

KODAMA, S. *See* abs. **2196, 3315, 3316. 3317.**

KODAMA, S. AND FUJIMURA, K. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. VII. Effect of Alkalies on Iron–Copper Catalysts. *See* abs. **1845.**

1907. KODAMA, S., AND TAHARA, H. X-ray Investigation of Iron Catalyst Used in the Synthesis of Gasoline. I. Preliminary Report. Jour. Soc. Chem. Ind., Japan, vol. 45, 1942, pp. 1260–1262; Chem. Abs., vol. 42, 1948, p. 6082.

Freshly prepared catalyst for the hydrogenation of CO, consisting of Fe 100, Cu 25, Mn 2, kieselguhr 125, and K_2CO_3 2 parts was amorphous. Heating at 700° for 6 hours destroyed the catalytic power and produced α Fe_2O_3. Reduction in H_2 at 450° also destroyed the catalytic power and produced α Fe. After use in the synthesis of gasoline at 255° for 2 hours the catalyst had a spinel structure with lattice constant 8.4 A. As the catalytic activity diminished from too long use or from use at too high temperature, the X-ray lines corresponding to spinel disappeared, and new lines appeared corresponding to a face-centered lattice of constant 3.6 A. These results cannot yet be interpreted.

KODAMA, S., HONGO, M., AND TAHARA, H. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Elevated Pressures. XII. Catalyst Carrier. *See* abs. **1914.**

KODAMA, S., MATSUMURA, S., AND ANDO, T. Physicochemical Investigations on Gasoline Synthesis. V. Velocity of Adsorption of Hydrogen by a Catalyst of Cobalt and Infusorial Earth. *See* abs. **2198.**

———. Physicochemical Investigations on Gasoline Synthesis. VI. Velocity of Adsorption of Hydrogen by Cobalt–Thoria–Infusorial Earth Cataylst. *See* abs. **2199.**

KODAMA, S., MATSUMARA, S., AND TARAMA, K. Physicochemical Investigations on Coal Synthesis. IV. Velocity of Adsorbing Hydrogen by Cobalt. *See* abs. **2197.**

KODAMA, S., MURATA, Y., AND HARA, I. Gasoline Synthesis From Carbon Monoxide and Hydrogen. LXXI. Activity and Deactivation of Iron Catalysts. *See* abs. **1905.**

1908. KODAMA, S., TSUNEOKA, S., AND FUJITA, T. Fischer Process—Japan. Jour. Fuel Soc. Japan, vol. 18, 1939, p. a7.

Two synthetic-gasoline plants of the Fischer process are being hastily constructed by the Mitsui Mining Co. at Miike and by the Manchurian Synthetic Fuel Co. at Chinchou. Both plants are of a similar capacity—30,000 tons of synthetic gasoline per yr.—and it is reported that they are nearly completed. Recently the Hokkaidō Artificial Petroleum Co. was established in cooperation with the Imperial Fuel Industry Co., with a capital of 70 million yen. The plant to be constructed by this concern will have a production of 140,000 tons of synthetic oil per yr. and will be erected by the end of 1940. As a semi-industrial test of the synthesis under pressure, continuous investigations are being carried out by the Imperial Fuel Research Institute on 3 types of reaction chambers made of 4 Fe tubes 25 mm. inside diameter and 560 mm. long, 2 tubes 35 mm. inside diameter and 510 mm. long, and 1 tube 55 mm. inside diameter and 520 mm. long were constructed and tested. The reaction chamber was heated by circulating outside the chamber machine oil of high flash point, heated to the desired temperature. The catalyst used was Co–Cu–Th–U–kieselguhr, 100 : 12.5 : 2.5 : 1.25 : 125, prepared by the precipitation method and formed in tablets. The gas velocity was 100 l. per hr. in all cases. Where the inside diameter of the reaction tube was 25 mm. and 35 mm., the yield of gasoline was 98 cc. per $m.^3$ and 78 cc. per $m.^3$, as compared with 110 cc. per $m.^3$ and 101 cc. per $m.^3$ in the small-scale experiments, but it decreased rapidly to 40 cc. per $m.^3$ in the case of the 55-mm. tube. It was concluded that the use of such a large-diameter tube is difficult. Based on the results of the investigation, the capacity of the reaction chamber was enlarged so as to be able to treat 10 $m.^3$ of raw gas per hr. A mixture of water gas and electrolytic H_2 was used, the average organic S content of which was reduced to 1.05 gm. S per 100 $m.^3$ with a Luxmasse–NaOH–$Cu(OH)_2$ (100 : 10 : 10) at about 200° C. The test was continued for about 10 days. The average gasoline yield was 81–85 $cm.^3$ per $m.^3$ (100 $cm.^3$ per $m.^3$ pure base), compared with 120 $cm.^3$ per $m.^3$ in the small-scale experiment.

KODAMA, S., TAHARA, H., HONGO, M., AND FUJITA, H. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Elevated Pressures. XI. Alkalines Used in the Preparation of the Iron Catalyst and Chlorine as a Poison. *See* abs. **1913.**

1909. KODAMA, S., TAHARA, H., IMAI, O., AND YAMADA, T. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Moderately High Pressure. V. Effect of the Increase of Reaction Pressure. Jour. Soc. Chem. Ind. (Japan), vol. 50, 1947, p. 121; Chem. Abs., vol. 44, 1950, p. 9135.

In gasoline synthesis at moderately high pressure with Fe catalysts the maximum yield of oil was obtained at 15 kg. per $cm.^2$ With an increase of pressure the amount of K_2CO_3 added must be increased.

1910. KODAMA, S., TAHARA, H., TAKIGUCHI, K., TOSHIMA, S., AND IHARA, K. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Moderately High Pressure. VI. Promoter Action of Various Oxides. Jour. Soc. Chem. Ind. (Japan), vol. 50, 1947, pp. 121–122; Chem. Abs., vol. 44, 1950, p. 9135.

Various promoters were tried. The optimum conditions were found with an Fe catalyst with Cu 25, Mg 5, kieselguhr 125 and K_2CO_3 6%. At a pressure of 10 kg./$cm.^2$ and 210° with a molecular ratio of CO : H_2 of 1 : 1 yield of oil was 111 gm. per $m.^3$

1911. KODAMA, S., TAHARA, H., NAKBAYASHI, T., AND HONGO, M. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Elevated Pressures. IX. Influence of the Composition of the Raw Gas on the

Reaction. Jour. Chem. Soc. Japan, ind. chem., sec., vol. 51, 1948, pp. 23–24; Chem. Abs., vol. 44, 1950, p. 9135.

With H_2: CO ratios in the raw gas of 1.1, 2.0, or 2.7 oil yields are 61, 57, or 50 gm. per $m.^3$, respectively, with H_2: CO consumption ratios of 0.7, 1.0, or 1.4 respectively with a catalyst of Fe+Cu 25+kieselguhr 125+K_2CO_3% at 10 kg. per $cm.^2$ pressure and 210°. Under similar conditions the addition of 16% CO_2 ($CO:H_2=1:1$) decreases the oil yield, but 5% CO_2 does not. A determination of N($CO:H_2=1:2$) up to 33.4% does not affect the yield for practical purposes.

1912. ———. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Elevated Pressures. X. Dependence of the Oil Yields on the Gas Flow. Jour. Chem. Soc. Japan, ind. chem. sec., vol. 51, 1948, p. 24; Chem. Abs., vol. 44, 1950, p. 9135.

With catalyst containing Fe+Cu 25+kieselguhr 125+K_2CO_3 6% at 10 kg. per $cm.^2$ an increase in the flow rate from the standard value, 4 liter (N. T. P.) per hr., decreases the yield per unit volume and increases the yield per unit time at 210° and 230°, while a decrease of the flow rate decreases the yield per unit volume only slightly at 190° and 210°.

1913. KODAMA, S., TAHARA, H., HONGO, M., AND FUJITA, H. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Elevated Pressures. XI. Alkalies Used in the Preparation of the Iron Catalyst and Chlorine as a Poison. Jour. Chem. Soc. Japan, ind. chem. sec., vol. 51, 1948, pp. 24–25; Chem. Abs., vol. 44, 1950, p. 9135.

To conduct the reaction with a catalyst containing Fe+Cu 25+kieselguhr 125% at 10 kg. per $cm.^2$ and 210° with a gas ratio $CO:H_2=1:1$ Na_2CO_3 is the best precipitating agent and addition of 6% K_2CO_3 to the catalyst is necessary. Cl in large amounts lowers the yield.

1914. KODAMA, S., HONGO, M., AND TAHARA, H. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Elevated Pressures. XII. Catalyst Carrier. Jour. Chem. Soc. Japan, ind. chem. sec., vol. 51, 1948, pp. 25–26. Chem. Abs., vol. 44, 1950, p. 9136.

In the synthesis at 210° and 10 kg. per $cm.^2$ several carriers (125% of the Fe) are substituted for kieselguhr with different amounts of alkaline salt. The oil yields decrease in the order: kaolin>active earth>acid earth>bentonite, their maximum yields being 70, 50, 40 and 25 gm. per $m.^3$ respectively, with 4, 6, 8 and 6% K_2CO_3, respectively. As much as 90 gm. per $m.^3$ oil can be obtained by the most favorable composition. (Fe+Cu 25+kaolin 150+K_2CO_3 4%).

KODAMA, S., TAHARA, H., NAKBAYASHI, T., AND HONGO, M. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Elevated Pressures. IX. Influence of the Composition of the Raw Gas on the Reaction. *See* abs. **1911.**

KODAMA, S., TAHARA, H., NAKBAYASHI, T., AND HONGO, M. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Elevated Pressures. X. Dependence of the Oil Yields on the Gas Flow. *See* abs. 1912.

1915. KODAMA, S., TARAMA, K., OSHIMA, T., AND FUJITA, K. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. I. Effect of Temperature With the Iron Catalyst. II. Effect of Rate of Flow of the Starting Gases With the Iron Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 44, suppl. binding, 1941, pp. 272–274, 274–275; Chem. Abs., vol. 44, 1950, p. 7507.

In order to synthesize predominantly C_4 hydrocarbons, a synthesis gas composed of equal parts of CO and H_2 was passed at temperatures varying from 242°–299° over an Fe catalyst containing Cu, 25; Mn, 2; kieselguhr, 125; H_3BO_3, 20; K_2CO_3, 3%. Increase in temperature resulted in a decrease in CH_4 formation and a decrease in reaction velocity. The maximum yield of gasoline was reached at 250°, while the yield of C_4 hydrocarbons increased up to 270° and remained virtually constant above this temperature. Operation at 251°–253° with varying space velocities indicated that a space velocity of 180–200 represents the optimum for C_4 hydrocarbon production.

1916. KODAMA, S., TARAMA, K., MISHIMA, A., FUJITA, K., AND YASUDA, M. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. III. Influence of Copper, Manganese, Potassium Carbonate and Boric Acid on Iron Catalysts. IV. Influence of the Temperature of the Synthesis on Various Promoters in the Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 69–77; Chem. Abs., vol. 43, 1949, p. 2398.

K_2CO_3 greatly increased the mean molecular weight of the product, as did Cu to a lesser degree. The effect of adding H_3BO_3 and Mn was the reverse. However, the effect of these substances on the production of gasol (mixture of C_2H_6, C_3H_8 and C_4H_{10}) was not very marked, so that it was not possible to improve the production of gasol by the addition of these substances alone. On the contrary, the elevation of the temperatures of the synthesis had a remarkable effect in increasing the yield of gasol. Of the various catalysts used 100 Fe+125 kieselguhr gave the best results, yielding a product containing 78% gasol, although this catalyst had less power of causing CO and H_2 to react.

1917. KODAMA, S., TARAMA, K., MISHIMA, A., FUJITA, K., AND YASUDA, M. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. V. Influence of Potassium Carbonate on Iron Catalyst. VI. Influence of Boric Acid on the Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 404–408; Chem. Abs., vol. 43, 1949, p. 2398.

Addition of K_2CO_3 increased the mean molecular weight of the hydrocarbons produced and decreased the formation of CH_4, while the addition of H_3BO_3 decreased the mean molecular weight.

1918. KODAMA, S., TARAMA, K., TAKAZAWA, T., FUJITA, K., TEJIMA, T., ITO, S., AND YOKOMAKU, Y. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. VII. Effect of Temperature on Synthesis With Cobalt Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949, p. 2398.

Hydrocarbons were prepared from a 1:2 mixture of CO and H_2 by means of Co, 100; Cu, 12.5, ThO_2, 2.5; U_3O_8, 1.25; and diatomaceous earth 125 parts, a reaction temperature of 180°–290°, and a period of operation of 24 hr. Temperature elevation increased the yield of the lower hydrocarbons but did not increase the relative yield of CH_4, as was the case with the Fe catalysts. Usually with a Co catalyst a small elevation of temperature caused a remarkable increase in the yield of CH_4, but, from the results of these experiments, it was observed otherwise, although an increase in the relative yield of the gaseous hydrocarbons (CH_4, gasol) was noticeable. In short, it may be impossible to produce the gasol without the other components by elevating the temperature. In these experiments, the maximum yield of gasol was 18.9 l. per $m.^3$ at 270°. In comparing Co and Fe catalysts, the difference is explained by evaporation of hydrocarbons from the surface of the catalyst and a decrease in adsorbed H atoms.

1919. ———. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. VIII. Effect of Composition of the Synthesis Gas on Iron

Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949, p. 2398.

Catalysts of Fe, 100; Cu, 25; diatomaceous earth, 125, and K_2CO_3, 2 parts was used at 270° over a period of 6 hr. For the gasol synthesis the optimum $CO : H_2$ ratio is 50–60 : 50–40. For the least CH_4 production the ratio is 1 : 1. For maximum gasol production with least CH_4 the ratio is 1 : 1.5. In view of the life of catalyst the optimum ratio is 1 : 1.5.

1920. ———. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. IX. Effect of Addition of Diatomaceous Earth on Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949, p. 2398.

Catalysts of Fe 100+Cu 25 parts was used with CO and H_2 (1 : 1) at 270° over a period of 16 hr. The addition of diatomaceous earth improves the life of the catalyst; 125% diatomaceous earth is most suitable for gasol synthesis.

1921. ———. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. X. Effect of Various Carriers on the Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949, p. 2398.

Catalysts of Fe 100, Cu 25, and K_2CO_3 2 parts was used with CO and H_2 (1 : 1.5). With active C, Murata reported that hardly any oil was produced but the authors found an increase in the volatile fractions. With white clay the gasol yield is very small, but its composition is unusual; it is high in C_4 and C_3 hydrocarbons, and the degree of unsaturation is high, 70–85%. Japanese acid clay increases the yield of gaseous hydrocarbons, 125% giving maximum gasol, 27.4 l. per $m.^3$.

1922. ———. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XI. Comparative Study of the Synthesis Under Normal Pressure and Other Pressures. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949, p. 2399.

With a catalyst of Fe 100 and diatomaceous earth 125 parts, and CO and H_2 (1 : 1) at 270°–275° for a period of 2–4 hr., pressure increases the life of the catalyst and improves the yield of gasol, and especially the yield of oil.

1923. ———. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XII. Effect of Pressure. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949, p. 2399.

On use of a catalyst of Fe+25% Cu on 125% diatomaceous earth at 5–20 kg. per $cm.^2$ the yield of gasol and the rate of reaction show maximum values at 15 kg. per $cm.^2$ With the same catalyst+2% K_2CO_3 on 125% white clay at 5–40 kg. per $cm.^2$ there was no change in the yield of oil. The gasol yield and rate of reaction were maximum at 15 kg. per $cm.^2$ No satisfactory explanation of the effect of pressure was made. The optimum pressure range was approximately 15–20 kg. per $cm.^2$ with a gasol yield of 30 l. per $m.^3$

1924. ———. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XIII. Effect of Temperature at Constant Pressure. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949, p. 2399.

Elevation of temperature increases the yield of lower hydrocarbons and therefore increases the yield of gasol, but increased yields of CH_4 also occur because of the increase in the reactivity of H_2. Thus an increase in gasol by the elevation of temperature without an increase in CH_4 cannot be expected. The optimum temperature range for gasol synthesis is 270°–320°.

1925. ———. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XIV. Effect of Various Carriers and Promoters. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949, p. 2399.

Effect of white clay and active C as carriers for Fe+25% Cu+2% K_2CO_3 was studied. White clay increased the yield of hydrocarbons and decreased the reactivity of H_2. Active C increased the reactivity. The effect of K_2CO_3 on the following catalysts were studied: Fe+25% Cu+250% white clay, Fe+25% Cu +125% active C, and Fe+25% Cu+125% Japanese acid clay. K_2CO_3 increased the yield of higher hydrocarbons, decreased the reactivity of H_2, and increased the unsaturated content of the gasol.

1926. ———. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XV. Summary of the Studies on the Synthesis Under Pressure. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949, p. 2399.

With Fe catalysts pressure increases the life of catalyst, and increases the total rate of reaction; the yield of gasol approaches 30 l. per $m.^3$ Increase in the gasol yield is not attainable by greater elevation of temperature. The optimum temperature is 270°–320°. The effect of pressure is comparatively complex. Raising the pressure increases the tendency to form higher hydrocarbons as well as lower hydrocarbons, especially CH_4 and C_2H_6, because of an increase in the reactivity of H_2. This fact is interpreted to be a peculiarity in the mechanism of the synthesis under pressure. Therefore, gasol synthesis in which a high degree of unsaturation is desired should be carried out with a catalyst containing white clay as the carrier or by adding K_2CO_3 to a catalyst containing acid clay or active clay to promote the adsorption of CO. By raising the temperature it is impossible to increase the yield of gasol without also raising the yield of CH_4, as is the case at ordinary pressure.

KODAMA, S., TARAMA, K., OSHIMA, T., AND FUJITA, K. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Atmospheric Pressure. LVI. Analysis of the Synthetic Oil by Precision Distillation. *See* abs. **1892.**

KODAMA, S., MATSUMURA, S., TARAMA, K., ANDO, T., AND YOSHIMORI, K. Physicochemical Research on Gasoline Synthesis. VII. Velocity of Adsorption of Hydrogen by Iron. *See* abs. **2200.**

KODAMA, S., MATSUMURA, S., TARAMA, K., ANDO, T., AND YOSHIMORI, K. Physicochemical Research on Gasoline Synthesis. VIII. Velocity of Adsorption of Hydrogen by Iron on Infusorial Earth. *See* abs. **2201.**

KODAMA, S., MATSUMURA, S., TARAMA, K., ANDO, T., AND YOSHIMORI, K. Physicochemical Research on Gasoline Synthesis. IX. Velocity of Adsorption of Hydrogen by a Composite Iron Catalyst. *See* abs. **2202.**

KODAMA, S., MATSUMURA, S., TARAMA, K., ANDO, T., AND YOSHIMORI, K. Physicochemical Research on Gasoline Synthesis. X. Adsorption of Carbon Monoxide on Cobalt, Cobalt–Kieselguhr and Cobalt–Kieselguhr–Thoria Catalysts. *See* abs. **2203.**

KODAMA, S., MATSUMURA, S., TARAMA, K., ANDO, T.,AND YOSHIMORI, K. Physicochemical Research on Gasoline Synthesis. XII. Adsorption of Carbon Monoxide on Iron, Iron–Kieselguhr, Iron–Kieselgush–Copper–Manganese Catalysts. *See* abs. **2204.**

KODAMA, S., TAHARA, H., TAKIGUCHI, K., TOSHIMA, S., AND IHARA, K. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Moderately High Pressure. VI. Promoter Action of Various Oxides. *See* abs. **1910.**

KODAMA, S., TARAMA, K., MISHIMA, A., FUJITA, K., AND YASUDA, M. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. III. Influence of Copper, Manganese, Potassium Carbonate and Boric Acid on Iron Catalysts. IV. Influence of the Temperature of the Synthesis on Various Promoters in the Catalyst. *See* abs. **1916.**

KODAMA, S., TARAMA, K., MISHIMA, A., FUJITA, K., AND YASUDA, M. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. V. Influence of Potassium Carbonate on Iron Catalyst. VI. Influence of Boric Acid on the Iron Catalysts. *See* abs. **1917.**

KODAMA, S., MATSUMURA, S., YOSHIMORI, K., NISHIBAYASHI, Y., KADOTA, N., AND IWAMURA, E. Physicochemical Studies on Gasoline Synthesis. XIII. XV. Influence of Potassium Carbonate and Boric Acid on the Activated Adsorption of Hydrogen and Carbon Monoxide on Iron Catalysts. *See* abs. **2205.**

1927. KODAMA, S., TAHARA, H., FUKUSHIMA, I., IAWO, M., KOMAZAWA, S., AND KIMURA, K. Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen under Medium Pressure. II. Characteristics of Hydrocarbon Synthesis under Medium Pressures With an Iron Catalyst. Durability of the Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1263–1271; Chem. Abs., vol. 43, 1949, p. 2397.

Petroleum synthesis was carried out at 230°–260° under a pressure of 10 kg./cm.^{2} with an equimolecular mixture of CO and H_2; 40 cc. of Fe catalyst of composition Fe : Cu : Mn : kieselguhr : H_3BO_3 : K_2CO_3=100 : 25 : 2 : 125 : 20 : 7 and a gas velocity of 6 m.^{3} at standard conditions/hr. were used continuously for 180 days to determine the durability of the catalyst. Catalyst durability under such conditions was excellent, and the rate of oil production of about 90 gm./m.^{3} could be maintained for 6 months by merely raising the temperature slightly. As the durability of the catalyst is very great even at higher reaction temperatures, Fe catalysts presumably have greater durability than Co catalysts under high pressure. Other characteristics of the medium-pressure process are the production of water with consequent diminution of CO_2 content in the waste gas and an increased need of solid paraffins in comparison with the synthesis carried out under atmospheric pressure. The production of CH_4 did not increase even when the activity of catalyst was increased by raising the temperature.

1928. ———. Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen Under Medium Pressure. III. Effect of Adding Alkali and Changes in the Reaction Temperature on the Activity of Fe–Cu–Mn–H_3BO_3 Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1263–1271. Chem. Abs., vol. 43, 1949, p. 2397.

Catalysts with 7–20 parts K_2CO_3 and other components, as given above, were compared in medium-pressure petroleum synthesis to determine the optimum composition. The catalysts containing 7–10 parts K_2CO_3 gave the best yield of oil. The rate of consumption of CO compared to H_2, the amount of solid paraffin produced, and the degree of unsaturation of oil produced all increased with the increase in the amount of K_2CO_3 added. By trial, the best reaction temperature was found to be 230°–250°.

1929. ———. Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen Under Medium Pressure. IV. Effect of Changing Alkali, Boric Acid, and Kieselguhr Contents on the Activity of Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1263–1271; Chem. Abs., vol. 43, 1949, pp. 2397–2398.

To determine the best composition of Fe catalysts to be used in medium-pressure petroleum synthesis, the effect of varying amounts of K_2CO_3, H_3BO_3, Cu and kieselguhr was studied. The addition of H_3BO_3 lowers the activity of Fe catalyst. The optimum amount of alkali is 4–5 parts when no H_3BO_3 is used. In this case, however, rate of oil production changes very sharply with the alkali content of the catalyst. A catalyst containing 4 parts K_2CO_3 and a catalyst containing no H_3BO_3 have high activities even at lower temperatures, with rates of oil production of 116 gm. per m.^{3} and 84 gm. per m.^{3}, respectively, at 220°. The optimum amounts of Cu and kieselguhr to be added are 25 parts and 50–125 parts, respectively.

KODAMA, S., TARAMA, K., TAKAZAWA, T., FUJITA, K., TEJIMA, T., ITO, S., AND YOKOMAKU, Y. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. VII. Effect of Temperature on Synthesis with Cobalt Catalysts. *See* abs. **1918.**

———. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. VIII. Effect of Composition of the Synthesis Gas on Iron Catalysts. *See* abs. **1919.**

———. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. IX. Effect of Addition of Diatomaceous Earth on Iron Catalysts. *See* abs. **1920.**

———. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. X. Effect of Various Carriers on the Iron Catalysts. *See* abs. **1921.**

———. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XI. Comparative Study of the Synthesis Under Normal Pressure and Other Pressures. *See* abs. **1922.**

———. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XII. Effect of Pressure. *See* abs. **1923.**

———. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XIII. Effect of Temperature at Constant Pressure. *See* abs. **1924.**

———. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XIV. Effect of Various Carriers and Promoters. *See* abs. **1925.**

———. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XV. Summary of the Studies on the Synthesis Under Pressure. *See* abs. **1926.**

1930. KODAMA, A., FUNABASHI, W., HASHIMOTO, G., HIRAO, T., TAHARA, H., MATSUMURA, A., KATO, J., AND TARAMA, Y. Process Development in the Hydrocarbon Synthesis to 1941. Bureau of Mines Inf. Circ. 7593, 1951, 41 pp.

Report compiled from Japanese documents on the investigation of the Fischer-Tropsch process. Some of the results are summarized as follows. (Experiment 17.) Using a Co catalyst in a water-cooled converter (designed for synthesis gas throughput of 100 m.^{3} per hr.), a 2-week run was carried out successfully. Over a reaction temperature range 200°–215° and at an average gas throughput of 79.6 m.^{3} per hr., the following average yields were obtained at an average apparent contraction of 56.2%: 168 ml. H_2O, 86 ml. of primary liquid products (oil), and 7 l. of gasol per m.^{3} of synthesis gas. Correcting these results for the 15.5% of inerts in the synthesis gas, an actual contraction of 66.5% was obtained and the yields were increased to 199 ml. H_2O, 102 ml. oil, and 8 l. gasol per m.^{3} of pure 2 H_2 : 1 CO synthesis gas. The catalyst was constituted as follows: 100 Co : 10 Cu : 5 ThO_2 : 2.5 U_3O_8 : 125 diatomaceous earth. The results suggest that commercial synthesis of gasoline and hydrocarbon oils in a water-

cooled converter may be economically feasible. Preparation and purification of synthesis gas is described. Using the same converter and an Fe catalyst (experiment 18) (a mixture of two catalysts of different Cu contents—100 Fe : 25 Cu (12.5 Cu) : 2 Mn : 20 H_3BO_3 : 4 K_2CO_3 : 125 kieselguhr), a 1-month run was made. The average operating results compared favorably with that using Co catalyst:

	Cobalt	*Iron*
Operating time, days	14	25
Initial temp., °C	202	235
Final temp., °C	211	238
Synthesis gas used, m.³	26, 729	56, 255
Total oil formed, l	2, 288	4, 203
cc. per m.³ synthesis gas	86	75
cc. per m.³ useful gas	102	86
cc. per m.³ H_2+CO	139	180

1931. KOENIG, A., AND WEINIG, R. [Formation of Formaldehyde From Water Gas in the Electric Glow Discharge.] Festschrift 100-Jähr. Bestehen Tech. Hochschule zu Karlsruhe, 1925, pp. 525–530; Chem. Zentralb., 1926, II, p. 2134; Chem. Abs., vol. 21, 1927, p. 3834.

Treatment of mixtures of CO and H_2 by the glow current leads to gaseous, liquid, and solid products of varying composition, among which H_2O, CO_2, HCO_2H, HCHO, and glycolaldehyde were identified (*see* abs. **2130**). In attempts to determine the optimum conditions for HCHO formation, it was proved that, with a current of gas, the products are adsorbed and adhere to the walls as a result of electrophoresis. To avoid their enrichment with undesirable reaction products, the walls of the Siemens tube were continuously or periodically rinsed with water. In this way it became possible to obtain HCHO as the chief product of the action of the glow discharge on water gas, so that up to 77% of the gas treated was recovered as HCHO. The maximum yield of HCHO was obtained when the incoming gas contained 46% CO by volume. Calculated on a basis of the electric energy consumed, the yield was 2 gm. of HCHO per kw.-hr.

1932. KOETSCHAU, R. [Nature and Occurrence of Natural Petroleums, Their Chemical Relationship to Each Other and to the Distillation Products of Coal.] Brennstoff-Chem., vol. 8, 1927, pp. 273–288; Chem. Abs., vol. 22, 1928, p. 1464.

Review of the literature on chemical composition of petroleum and a discussion of the theories on its origin. A possible connection is assumed between the formation of natural petroleum and of synthetic petroleum from gas by the Fischer-Tropsch process.

1933. KOHLE UND ERZ. [Diesel Fuel From Coal.] Vol. 36, May 4, 1939, p. 278.

1934. ———. [Oils and Fats From Coal in Germany.] Vol. 36, No. 23, 1939, pp. 640–641; Coke Smokeless-Fuel Age, vol. 2, 1940, p. 71.

From the standpoint of oil and fat production, the Fischer-Tropsch synthesis is important. The paraffin-bearing intermediate product gatsch coming between Diesel oils and solid paraffin is an excellent material from which to start the synthesis of fatty acids. Catalytic oxidation is effected at low temperatures, up to 120° C, and fatty acids are derived from which a whole series of soaps can be prepared. The fatty acids production of Germany is now about 30,000–40,000 ton per yr. and is increasing.

KÖHLER, G. *See* abs. **2435.**

1935. KOHLHAAS, R., AND MEYER, W. F. [Formation, Stability and Structure of Nickel Carbide.] Metallwirtschaft, vol. 17, 1938, pp. 786–790; Chem. Abs., vol. 32, 1938, p. 7870.

Addition of C to Co-free Ni, in the form of powder or wire from benzene vapor, water gas, or illuminating gas at temperatures ranging 230°–730° shows that only Ni_3C is observable, which is formed from 240° up to 530°–580°. Tempering experiments in a vacuum show the Ni_3C formed above 420°–500° to be metastable. The separation of C increases very much with increasing temperature; probably it is due to the diffusion equilibrium of the gases used and their decomposition products. X-ray pictures show that Ni_3C can have no hezagonal symmetry but that a rhombic structure of the compound and hence its isomorphy with Fe_3C and Co_3C is very likely.

1936. KOHLSCHÜTTER, H. W., AND LOHNES, K. [Preparation and Transformation of Iron Nitride.] Ztschr. anorg. Chem., vol. 255, 1947, pp. 73–78; Chem. Abs., vol. 43, 1949, p. 2744.

Preparation of the nitrides of Fe by reaction of Fe with NH_3 and the catalytic decomposition of NH_3 with the intermediate formation of Fe_2N.

1937. KOHLSCHÜTTER, V., AND NÄGELI, A. [Topochemical Reactions. Formation of Carbon on Contact Substances.] Helv. Chim. Acta, vol. 4, 1921, pp. 45–76; Chem. Abs., vol. 15, 1921, p. 2767.

Study was made of the nature of the C deposited upon electrolytic films of Co, Ni, Fe, and Ag and upon powders of these metals by the reaction $2\ CO=C+CO_2$, at about 500°. The supporting metal upon which the catalytic metals are electrolytically deposited influences the amount of C formed, it being greater when the support is Pt, and less when it is Ag or Cu. The nature of the catalytic metal determines specifically the method of deposition and the amount and the characteristics of the C. In the case of smooth Co, Ni, and Ag deposits, the C is not deposited visibly upon the surface but in the interior of the metallic film and appears as an unweighable film when the metal is dissolved in acid. In the case of Fe, however, the C forms a deep-black surface deposit. Co affords the largest C deposit, then Ni, Fe, and Ag. The C deposited on Co is strongly graphitic; on Ni also graphitic, but somewhat more easily oxidizable; on Fe more sooty, and still more easily oxidizable; and on Ag very small in amount and difficult to oxidize. On dark, lusterless deposits the C is deposited visibly on the surface, as was the case with smooth deposits of Fe; and it is more easily oxidized than C deposited within the metallic layer. The amount of C produced by metallic powders was large and almost inseparably associated with fine particles of the metal.

1938. KOHN, S. Theory of the Water-Gas Process. Jour. Ind. Eng. Chem., vol. 14, 1922, pp. 69–72; Chem. Abs., vol. 16, 1922, p. 634.

Kohn discusses the 10 possible and the 3 probable combinations of reactions that can be used to explain the water-gas process. Demonstration is made of a possibility of drawing conclusions from the composition of the resulting gases to the actual procedure of the reactions. The applicability of the principles outlined is tested on a series of 9 observations published by Bunte and Harries, and their application to catalytic observations is discussed.

KOIDE, H. *See* abs. **1877, 1889.**

1939. KÖLBEL, —. [Hydrocarbon Synthesis With an Iron Catalyst.] TOM Reel 178, Sept. 13, 1940, frames 2,627–2,642; Bureau of Mines Transl. T–468, Dec. 28, 1948, 21 pp.; PB 97330t2.

Lecture pointing out advantages in substituting Fe as the catalytic element in place of Co. Brief discussion of the problems met during the development of the Fe catalyst, and some results of the investigation. Some suggestions are made for carrying out the synthesis with powdered-Fe catalyst in the liquid phase.

1940. KÖLBEL, H. [Content of Cobalt and Diatomaceous Earth in Gasoline Synthesis Catalysts.] FIAT Reel K–30, frames 7454–7467, Mar. 9, 1938; PB 73,587.

Test results on the influence of the Co and diatomaceous earth content on the efficiency of gasoline synthesis catalysts are discussed. It was found that a reduction of the Co and its replacement by a correspondingly larger quantity of diatomaceous earth exceeding the ratio 1 : 1 diminishes the yield of liquid products. Furthermore, with a constant quantity of CO and a constant flow velocity of the gas, an increase of the Co : diatomaceous earth ratio beyond 1 : 1 up to 1 : 1.2 does not improve the catalyst. By the use of catalysts poorer in diatomaceous earth the capacity of the catalyst space increases by 40–60%, as compared with catalysts now in use.

1941. ———. [Diesel-Fuel Mixtures From Bituminous-Coal Tar Oil.] Oel u. Kohle Erdoel Teer, vol. 14, 1938, pp. 1042–1049; Brennstoff-Chem., vol. 20, 1939, p. 92; Chem. Abs., vol. 33, 1939, p. 7989.

By heat pretreatment with and without pressure and catalyst (abs. **2301**) mixtures of tar oil and Kogasin II yield fuels suited for high-speed use, with desired ignitability, carbonization, storage stability, and miscibility characteristics in motor and road tests.

1942. ———. [Importance of the Fischer-Tropsch Synthesis for the Production of Domestic Diesel Fuels. I.] Brennstoff-Chem., vol. 20, 1939, pp. 352–355; Chem. Abs., vol. 34, 1940, p. 7573.

Properties of Kogasin II and the possibilities of motor uses, particularly in diesel mixtures.

1943. ———. [Importance of the Fischer-Tropsch Synthesis for the Production of Domestic Diesel Fuels. II.] Brennstoff-Chem., vol. 20, 1939, pp. 365–369; Chem. Abs., vol. 34, 1940, p. 7573.

Mixtures of Kogasin II with bituminous coal-tar oil, especially tar oils obtained from carbonization processes employing offtake from within the coal charge, and high-pressure hydrogenated oils prepared from coal, coal tar, and coal extracts are discussed. Depending upon ignition characteristics, 40–55% Kogasin II can be used to make fuel mixtures of 65–85 cetene no. and equal to the petroleum fuels in ignitability, resistance to coke formation, and completeness of combustion. Unrefined tar oils destroy the storage stability of the mixtures, as well as their motor values.

1944. ———. [Synthesis of Lubricating Oil Through Alkylation of Naphthalene.] Erdöl u Kohle, vol. 1, 1948, pp. 308–318; Chem. Abs., vol. 43, 1949, p. 4454.

Method is based on the condensation of chlorinated paraffin hydrocarbons obtained from the Fischer-Tropsch synthesis with naphthalene by means of the Friedel-Crafts reaction. Kogasin $d_{20}=0.77$; boiling point, 280°–320°; Cl 20.9% was superior to a similar petroleum fraction as base stock. Physical properties of various synthetic oils are given; d_{20} of synthetic motor oil is approximately 0.925, in contrast to petroleum oils, density has no significance as a criterion of quality for synthetic oils. Gasoline- Diesel- and steam-engine tests showed a superiority of the synthetic oils over good quality natural oils. Includes a plant diagram.

———. *See* abs. **409, 1040, 1041, 1336, 1837.**

1945. KÖLBEL, H., AND ACKERMANN, P. [Hydrogenation of Carbon Monoxide in Liquid Medium.] Angew. Chem., vol. 61, 1949, p. 38.

Carrying out of the Fischer-Tropsch synthesis in a liquid medium is claimed to offer considerable advantages.

1946. ———. Hydrogenation of Carbon Monoxide in a Liquid Medium. Bureau of Mines Transl. K–10, 1949, 19 pp.

Paper read at a meeting of German Chemical Society, September 1948. Synthesis in the liquid phase with a suspended catalyst eliminates completely the disadvantages of synthesis in the vapor phase, such as local overheating of the catalyst, CH_4 formation, hydrocarbon deposition, plugging of the reactors, nonuniform utilization of the catalyst, imperfect cooling, complicated filling and emptying of the reactors, and limitations upon the reactor capacity. The process has been studied chiefly with Fe catalyst and has been developed to the industrial stage and results in higher yields than obtained in the vapor phase with the same CO conversion of up to 175 gm. of hydrocarbons per $m.^3$ $CO+H_2$ because of the suppression of CH_4 formation. H_2O is formed as a primary product of the reaction upon the Fe catalyst as well as upon the Co catalyst and is converted to CO_2 and H_2 with the CO of the synthesis gas. It is possible to conduct the synthesis over Fe catalyst entirely by way of formation of water and over Co catalyst completely by way of CO_2 formation. It is therefore possible to obtain good yields with CO-rich gases, water gas, or H_2-rich gases with Fe catalyst by properly adjusting the operating conditions. It is shown for the first time that during CO hydrogenation the chain length of the higher molecular weight saturated and unsaturated aliphatic hydrocarbons can be increased. Operating in liquid phase permits the conversion up to 73% of the paraffin hydrocarbons to solid paraffins, so that 1 $m.^3$ of $CO+H_2$ will produce 152 gm. of paraffin boiling above 320°, of which 95 gm. are formed during CO hydrogenation, and 57 gm. by the lengthening of the C chain.

1946a. ———. Hydrogenation of Carbon Monoxide in Liquid Phase. Proc. 3d World Petrol. Cong., The Hague, May–June 1951.

Using a finely-divided Fe catalyst in the fluidized state, certain advantages were obtained which were claimed to largely meet economy requirements for the Fischer-Tropsch process. Advantages over fixed-bed operation included faster removal of reaction heat, reduction of CH_4 formation and C deposition, reduction of reactor choking, and utilization of a gas space velocity 4–8 times higher. Using larger reactors and smaller cooling surfaces the relative weight of the synthesis furnace as well as capital service charge were said to be reduced to ¼.

———. Reaction Mechanism of the Fischer-Tropsch Synthesis. IV. Molecular Size of the Aliphatic Hydrocarbons From the Catalytic Hydrogenation of Carbon Monoxide. *See* abs. **1950.**

1947. KÖLBEL, H., AND ENGELHARDT, F. [Reaction Mechanism of the Fischer-Tropsch Synthesis. I.] Erdöl u. Kohle, vol. 2, 1949, pp. 52–59; Chem. Abs., vol. 43, 1949, p. 4828.

Proposed mechanisms explaining the formation of CO_2 and H_2O by Fe and Co catalysts, respectively, are reviewed and the action of these catalysts in the water-gas reaction is studied. An Fe catalyst of composition 100, Fe; 0.5, Cu; 0.25, K_2CO_3 was used. Initial experiments were conducted with four different contact conditions: Carbidic, 24-hr. treatment with CO at 270° (I); metallic, 24-hr. treatment of (I) with electrolytic H_2 at 270° (II); oxidic, reduction of catalyst with H_2 at 270° (III); synthesis, treatment for 100 hr. at 1 atm. at 230°, $CO:H_2O=1:2$, space velocity 100 (IV). A graph of time, total 24 hr., versus conversion of CO at 240°, $CO:H_2=1:1$, space velocity=100, gives almost a straight line for (II) near equilibrium; (IV) runs parallel to (II) at a lower level; (III) is inactive at this temperature; and (I) is rapidly approaching (IV). Results at 240°, $CO:H_2O=3:1$ and space velocity=100, show that (I) and (II) have approached each other within the first 100 hr. and then run concurrently for more than 400 hr. Analysis of (I) for total C, elemental C, carbidic C, and unoxidized Fe, respectively, before test; 14.2, 7.35, 6.85, 62.7: after; 16.2, 12.0, 4.2, 57.3. Similar

results for (II) are before; 7.0, 7.0, 0.0, 67.1: after; 19.0, 14.2, 4.8, 56.9. Results indicate that initially (II) is more active than (I), but that finally both attain the same activity and carbide concentration. Method for analysis is based on the fact that the velocity of ion exchange is a function of the carbide–C content in such a way that with increasing carbide–C the permutation velocity decreases; Hg^{++} ions were used. Carbide–C was determined by difference of total C before and after treatment with H_2 at 270°. A highly reactive, commercial Co–Th–Mg catalyst with 100% kieselguhr was treated as follows: By reduction of a precipitated catalyst with H_2 at 450° (V); 24-hr. treatment of (V) with CO at 270° (VI); active use for 150 hr. (VII). (V) is by far the best, conversion close to equilibrium; (VI) is the poorest; (VII) midway between the two. For $CO:H_2O=1:1$ and space velocity=100, 180° was the lower limit of conversion for both Fe and Co catalysts. This is important in connection with the fact that the optimum synthesis for the Co catalyst is below 180° while that for Fe is considerably higher, which may explain that in the former O_2 from CO can escape in the form of H_2O. Experiments with a Co catalyst showed that lowering the space velocity from 100 to 10 at 180° and changing the $H_2:CO$ ratio from 2:1 to 2:3.55, H_2O concentration decreased progressively and an almost parallel increase of CO_2 resulted. Division of the Fe catalyst into four portions separated by layers of $CaCl_2$ (230°, space velocity 100) resulted in a progressive increase of H_2O formation and a parallel decrease of CO_2 concentration. These results are in disagreement with the opinion advanced by Craxford (*see* abs. **638**). A working hypothesis for the mechanism is proposed.

1948. KÖLBEL, H., ACKERMANN, P., JUZA, R., AND TENTSCHERT, H. [Reaction Mechanism of the Fischer-Tropsch Synthesis. II. Investigation of Iron Catalysts in the Hydrogenation of Carbon Monoxide.] Erdöl u. Kohle, vol. 2, 1949, pp. 278–285; Chem. Abs., vol. 43, 1949, p. 8117.

Fe catalysts prepared from Fe $(NO_3)_3$, initially α–Fe_2O_3, promoted with Cu (0.001–0.16%), K_2CO_3 (0.0–0.25%), and $BaCO_3$ were investigated analytically, catalytically, magnetically, thermomagnetically, by means of X-rays, and by adsorption measurements. It was found that the milder the treatment during preparation, the more imperfect the α–Fe_2O_3 lattice and the greater the surface development. Promotion with Cu or alkali had no influence on the state of crystallization. After exposure to synthesis, the catalyst consisted principally of magnetite (Fe_3O_4) and always contained Fe carbide. No free Fe was present. Whether Cu or K was built into the magnetite lattice could not be decided. Below 5%, Cu could not be detected by means of X-ray analysis. Above 5% it was present in the elementary state. In active catalysts, the system Fe–C is a function of the original composition and the conditions of catalysis (CO–H_2). A labile carbide (Curie temperature, 220°) appears initially during synthesis and is stable only to about 290°. After longer synthesis exposure, a second thermally stable carbide (Curie temperature between that of cementite Fe_3C and that of Fe_2C) either replaces the first or is formed in addition. High alkali content, higher gas pressures, and CO content in combination with longer synthesis exposure favor the formation of Fe_2C (Curie temperature 250°) stable up to 400°. Since even the most labile of the 3 carbides had virtually no influence on the catalyst activity, it is concluded that Fe carbide is not the important intermediary it was thought to be previously. For confirmation, *see* abs. **2009.**

1949. KÖLBEL, H., AND LANGHEIM, R. [Reaction Mechanism of the Fischer-Tropsch Synthesis. III. Investigation of the Carbides Formed in the Hydrogenation of Carbon Monoxide on Iron Catalysts.] Erdöl u. Kohle, vol. 2, 1949, pp. 544–550; Chem. Abs., vol. 44, 1950, p. 3235.

Purpose of the work reported in this paper was to examine the carbide theory of CO hydrogenation and to explain the carbide found by thermalmagnetic examination on used Fe catalysts. Of further interest was the effect of the promoters of Fe catalyst, alkali and Cu, on carbide formation. A review of the work of other investigators on the formation of Fe carbides is presented. In the treatment of pure, paramagnetic γ–Fe_2O_3 with CO at 265° a carbide Fe_2C is obtained. Beside this there is a separation of elementary C. The stability of the Fe_2C, which results in a certain manner from the speed of hydrogenation of the carbide–C, depends upon the raw material and its previous history as well as upon the conditions surrounding its preparation. Alkali hastens the formation of carbide- and elementary C. Cu accelerates the formation of carbide- but exerts a negative effect on the formation of elementary C. It also hastens the reduction of the Fe catalyst in carbide formation and CO hydrogenation. In the presence of both alkali and Cu, the speed of formation of carbide- and of elementary C undergoes a further, quite considerable increase. The X-ray diagram of Fe_2C agrees well with that found by G. Hägg, and the Curie point lies at about 240°–250°. The formation of a well-defined carbide and the synthesis reaction are not 2 consecutive but 2 parallel occurring reactions, which have their common starting point in the activation of the CO, which in one case leads to carbide formation and in the other to hydrocarbons. Alkali catalyzes both reactions directly, Cu catalyzes indirectly through the acceleration of the reduction of Fe_2O_3.

1950. KÖLBEL, H., AND ACKERMANN, P. [Reaction Mechanism of the Fischer-Tropsch Synthesis. IV. Molecular Size of the Aliphatic Hydrocarbons From the Catalytic Hydrogenation of Carbon Monoxide.] Brennstoff Chem., vol. 31, 1950, pp. 10–14; Chem. Abs., vol. 44, 1950, p. 3697.

When higher-molecular liquid aliphatic hydrocarbons (C_{15}–C_{19} hydrocarbons from Kogasin) are introduced into the Fischer-Tropsch synthesis, they form solid hydrocarbons by chain lengthening under synthesis conditions that normally lead to the predominant formation of high molecular hydrocarbons, solid at normal temperatures. The rate of this chain lengthening is directly related to the building up activity of the catalyst. As regards the synthesis-gas mixture (used along with the higher hydrocarbons), 45–57 gm. of solid hydrocarbons are formed per $m.^3$ of the CO–H_2 mixture. Two different Kogasin fractions were used, containing 2 and 11% of olefins, respectively. No difference could be noted as to their reactivity. Reviews theories as to the reaction mechanism.

1951. KÖLBEL, H., AND ENGLEHARDT, F. [Reaction Mechanism of the Fischer-Tropsch Synthesis. V.] Angew. Chem., vol. 61, 1949, p. 448; Chemie-Ing. Tech., vol. 22, 1950, pp. 97–104; Chem. Abs., vol. 44, 1950, p. 5566.

Paper presented at the annual meeting of the German Chemical Society in September 1949. After a brief review of the empirical development of the synthesis, the carbide theory of Fischer is thoroughly examined. The composition of the catalyst in respect to operating conditions as well as to the synthesis of higher hydrocarbons is discussed both from the standpoint of previous work and from more recent conceptions. It is shown that the carbide theory no longer stands up against experimental proof. Activated adsorption is put forward as the basis for a new working hypothesis, and the possibility of a uniform method

of examination of all CO hydrogenation processes is discussed.

1952. ———. [Reaction Mechanism of the Fischer-Tropsch Synthesis. VI. Function of Water Vapor in the Hydrogenation of Carbon Monoxide.] Erdöl u. Kohle, vol. 3, 1950, pp. 529–533; Chem. Abs., vol. 45, 1951, p. 2177.

This paper was presented at the 3d meeting of Die Deutsche Gesellschaft für Mineralölwissenschaft und Kohlechemie, September 1950. CO_2 formation on the Fischer-Tropsch catalysts results from a secondary reaction of CO with primarily formed H_2O vapor. The result of this conversion reaction is important in the choice of synthesis conditions. The effect of temperature upon the reaction has been previously determined, and now proof is made of the influence of space velocity on the conversion of CO with water vapor, especially in the presence of Fe catalyst. The results obtained permit of predicting the $CO:H_2$ ratio for the synthesis and the space velocity to be chosen for obtaining satisfactory yields; they offer further some criterion for the most favorable synthesis gas composition for a given space velocity and temperature. Determination of the speed of reaction of the CO conversion in a static system at temperatures down to 85° supposes a reaction of the first order, which may rest upon the dissolution of the adsorption complex of CO with H_2O on the catalyst surface. By using a H_2--rich gas and space velocities of about 100, at normal pressure above 180° an oxidation of the catalyst by the water vapor formed during the synthesis occurs, in case a definite relation is maintained between the partial pressures of the CO and H_2O in the reaction gas. Under these conditions the outer catalyst layers deteriorate through oxidation by water vapor. The CO conversion is then to be considered not only as a troublesome side reaction, but it acts under certain conditions as a protector of the Fe catalyst against oxidation. In the hydrocarbon synthesis on Fe catalysts under normal pressure, the space velocity must either be chosen so high and the temperature so low that neither CO conversion nor catalyst oxidation occurs or the CO content of the synthesis gas must be so high that even in the outer catalyst layers enough CO is present to react with the water vapor with satisfactory velocity. In practice these conditions should exist in proper combination.

1953. ———. [Synthesis of Hydrocarbons and Oxygen-Containing Compounds From Carbon Monoxide and Water Vapor.] Brennstoff-Chem., vol. 32, 1951, p. 150; Chem. Abs., vol. 45, 1951, p. 7333.

In addition to the usual reaction of CO and H_2 to form hydrocarbons, the reaction $3\ CO+H_2O\rightarrow(CH_2)+2\ CO_2$ is important in forming hydrocarbons. While this reaction proceeds at normal pressure under suitable conditions, it is favored by high pressure and a temperature 200°–300° in presence of a highly active catalyst. Yields of 195 gm. (theoretical 208 gm.) hydrocarbons per standard cu. m. of CO were secured, and a wide variety of O-containing compounds was formed, including aldehydes, alcohols, acids, oxy acids, etc., CO-containing gases can be used, as well as pure CO.

1953a. ———. [Synthesis of Hydrocarbons and Oxygenated Compounds From Steam and Carbon Monoxide.] Brennstoff Chem., vol. 33, 1952, pp. 13–21; Erdöl u. Kohle, vol. 5, 1952, pp. 1–9; Angew. Chem., vol. 64, 1952, pp. 54–58; Chem. Age, vol. 66, 1952, pp. 375–376.

CO and H_2O can be converted in a single step to paraffin hydrocarbons and oxygenated compounds using catalysts of group 8 and either standard or high pressures and temperatures 210°–260°, space velocity 1,000 or more. $H_2O:CO<0.5$. Conversion of H_2O and CO were both over 90%. Yields up to 216 gm. hydrocarbons and oxygenated compounds per $m.^3$ CO were obtained. The reacting elements must be in strictly definite and somewhat narrowly defined limits. Thus, for hydrocarbons: $H_2O+3\ CO\rightarrow(-CH_2-)+2\ CO_2$ and for alcohols (ethyl): $3\ H_2O+6\ CO\rightarrow C_2H_5OH+4\ CO_2$. Another important factor in maximum efficiency is the space velocity which is governed by reaction rate at the catalyst surface and involves the duration of contact by the reacting elements. Effect of pressure is discussed with pressures up to 100 atm. Temperature must be adjusted for maximum catalyst activity, but not so high as to cause undesirable side reactions. With a freshly reduced Fe catalyst and normal pressure at 200°, the water gas reaction predominated; yet even with a slight rise to 210° the CO conversion was 90%, and rose to 93–97% at 250° after which it slowly declined with further increase of temperature. CH_4 formation increased beyond 240°, and from this point production of hydrocarbons was no longer parallel with CO conversion. Cheap industrial gases with low CO content, such as generator and furnace gases, can be used without serious inconvenience. Products are mainly saturated and unsaturated paraffins with olefins ranging 35–60% and up to solids in the homologous series. Alcohols may also be produced, especially at pressures >30 atm., with minor amounts of aldehydes, fatty acids and esters. EtOH predominates. The % compositions of the products obtained at 0 and 100 atm. at 235°–238° are tabulated. (*See also* abs. **1953.**)

———. [Reaction Mechanism of the Fischer-Tropsch Synthesis. V.] *See* abs. **1951.**

———. [Reaction Mechanism of the Fischer-Tropsch Synthesis. VI. Function of Water Vapor in the Hydrogenation of Carbon Monoxide.] *See* abs. **1952.**

KÖLBEL, H., AND LANGHEIM, R. [Raction Mechanism of the Fischer-Tropsch Synthesis. III. Investigation of the Carbides Formed in the Hydrogenation of Carbon Monoxide on Iron Catalysts.] *See* abs. **1949.**

1954. KÖLBEL, H., AND ULLMANN, D. [Greases From the Initial and Final Fatty Acid Fractions of Paraffin Oxidation.] Erdöl u. Kohle, vol. 3, 1950, pp. 16–21; Chem. Abs., vol. 44, 1950, p. 4234.

Initial (4–9 C atoms, equivalent weight 110–130) and final (more than 20 C atoms, equivalent weight 310–360) fatty acid fractions from the paraffin oxidation of the Fischer-Tropsch fraction of 320°–450°, ordinarily waste products, formed superior Ca and Na greases when mixed in a 40:60 ratio. The low-molecular fraction contributed greatly to better storage stability (no change after 8–10 years) and in combination with Na was responsible for increase in drip point of the mixture. Substitution of Na acetate and Na formate for the low-molecular acids produced an increase in drip point similar to that obtained by the low-molecular fraction. A theoretical explanation of this behavior is attempted. Bearing-test results were satisfactory.

KÖLBEL, H., ACKERMANN, P., JUZA, R., AND TENTSCHART, H. [Reaction Mechanism of the Fischer-Tropsch Synthesis. II. Investigation of Iron Catalysts in the Hydrogenation of Carbon Monoxide.] *See* abs. **1948.**

1955. KÖLBEL, H., ACKERMANN, P., RUSCHENBURG, E., LANGHEIM, R., AND ENGELHARDT, F. [Fischer-Tropsch Synthesis on Iron Catalysts. I., II. Induction of Iron Catalysts, Behavior During Synthesis, and Results Obtained in Various Synthesis Processes.] Chemie–Ing. Tech., vol. 23, No. 7–8, 1951, pp. 153–157, 183–189.

Comprehensive review of previous investigations. Discusses influence of surface improvement and com-

position as well as the role of promoters and of Fe carbides on the activity of the catalyst, the preparation of precipitated catalysts, the induction of the catalyst, its reaction mechanism and behavior in the synthesis, and the results of various synthesis processes. Fixed-bed vapor-phase and liquid-phase operation is considered also.

KOLLWITZ, J. *See* abs. **711.**

1956. KOMAREWSKY, V. I. Production of Synthetic Liquid Fuel From Natural Gas. Petrol. Refiner, vol. 24, No. 5, 1945, pp. 96–98; Petrol. Eng., vol. 16, No. 12, 1945, pp. 202, 204, 206.

Fischer-Tropsch synthesis is reviewed with brief description of the products—gasoline, diesel oil, paraffins, and lubricants. The progress of the process was accelerated by the discovery of the middle-pressure synthesis in 1936. At pressures of 75–220 p. s. i., an optimum yield of solid plus liquid hydrocarbons was obtained. The chief advantage was that loss in catalyst activity was decreased. Whereas the yield dropped from 7.7 to 5.9 lb. per 1,000 cu. ft. in normal-pressure synthesis in 4 weeks, the middle pressure synthesis produced 8.9 lb. initially, and still was above 5.9 lb. after 26 weeks of operation. This synthesis has been performed with Co and Fe catalysts; Ni catalysts deteriorate rapidly owing to formation of Ni carbonyl. In 1938 it was found that Ru catalyst at high pressure produced solid hydrocarbons more effectively than any other metal of the 8th group. At 1,500 p. s. i. pressure and 383° F., 5.9 lb. of paraffin wax and 3 lb. of oil were obtained per 1,000 cu. ft. of synthesis gas with no appreciable change in the activity of the catalyst in a 6 months test. By solvent extraction of a solid paraffin obtained in this way, a wax was obtained with a melting point of 270°–273° F. and with a molecular weight of 23,000. Recently 2 new syntheses have been announced, naphthene synthesis and isosynthesis; details, however, have not been disclosed. It is implied that gasoline of higher octane numbers is produced; naphthenes and aromatics and isoparaffins, respectively, are produced. In the latter case the C_4 fraction from the process contains 90% of isobutane. Future developments in the Fischer-Tropsch process must proceed in the following directions: (a) Development of a S-resisting catalyst; (b) utilization of CO–H_2 mixtures of various composition; (c) synthesis of branched-chain hydrocarbons. The last can probably be attained by developing a complexaction catalyst combining the hydrogenation, polymerizing, and isomerizing ability.

———. *See* abs. **2824.**

1957. KOMAREWSKY, V. I., AND RIESZ, C. H. Fischer-Tropsch Synthesis and the Gas Industry. Petrol. Refiner, vol. 23, No. 11, 1944, pp. 415–422.

Reviews of the development of the process from the beginning to the present. A reaction mechanism is proposed, which postulates that the function of the catalyst is to provide a hydrogenating-polymerizing surface whereby CO is converted to CH_2 at the catalyst surface, and this is polymerized to hydrocarbons containing more than 1 C atom. Poisoning of the catalyst by S is explained on the basis of this mechanism. The process is of potential value to the gas industry, since it offers the possibility of converting off-peak gas production to valuable products. The costs of the process must however first be lowered to make it economical. Research should be directed toward the following objectives: Develop more active catalysts, which will operate at shorter contact periods; produce a catalyst capable of directing the reaction toward a specific product, for example, iso-paraffins; obtain a S-resistant catalyst having a tolerance of at least 2–4 grains of S per 100 cu. ft.; develop a process that will utilize a 1 : 1 mixture of $CO : H_2$.

1958. ———. Fischer-Tropsch Synthesis and the Petroleum Industry. Nat. Petrol. News, Tech. sec., vol. 37, 1945, pp. R–97–104.

Review of historical development and various theories of the mechanism of the reaction.

1959. KOMAREWSKY, V. I., RIESZ, C. H., AND THODOS, G. Aromatization of Fatty Alcohols. **Jour. Am.** Chem. Soc., vol. 61, 1939, pp. 2525–2527; Chem. Abs., vol. 33, 1939, p. 8580.

Under the action of a mixed CrO_3–Al_2O_3 catalyst, fatty alcohols undergo a complex reaction involving dehydration, Al_2O_3, dehydrogenation and cyclization, CrO_3, producing aromatic hydrocarbons. It is proposed to name this type of mixed catalysts complex-action catalysts. The reaction of aromatization is of the first order and formula, $\kappa = 2.303/t \log a1, a-x$, where t is time, a the amount taken into the reaction and x the amount of product in %, can be applied. The energies of activation are calculated. Heptyl alcohol at 450° gives 7.8% of PhMe and at 500° 58–66% PhMe, calculated from n_D^{25} and from H_2 of the gases evolved, Pr_2CHOH at 468° gives about 7% and at 480° about 13% PhMe; hexyl alcohol at 467° gives 38% and at 500° 38% PhMe; octyl alcohol at 475° gives 3% PhMe, 4.5% PhEt, 7% of the xylenes, and 32.7% of higher boiling aromatics. The gases evolved consist of O_2, CO, CO_2, and H_2. A table gives the amount of alcohol dehydrated, dehydrogenated, and cyclized.

1959a. KOMATSU, S., AND KURAKU, H. Catalytic Action of Nickel–Magnesium on the Reaction Between Methane and Steam. Jour. Chem. Soc. Japan, vol. 63, 1942, pp. 1,551–1,554; Chem. Abs., vol. 41, 1947, p. 3,267.

It is found that 91–95% CH_4 is decomposed by steam at 650°–700° in the presence of Ni–Mg catalyst. The best catalyst is prepared as follows: $Ni(NO_3)_2$ and $Mg(No_3)_2$ are dissolved in H_2O (Ni : Mg = 9 : 1). The solution is absorbed by the grains of pumice stone and calcined at 400° and reduced by H_2.

KOMAZAWA, S. *See* abs. **1927, 1928, 1929.**

KOMIYAMA, D. *See* abs. **3314, 3315.**

1960. KÖNIG, E. [Synthetic Oils From Coal Gasification Products at Ordinary Pressure.] Teer, vol. 24, 1926, pp. 385–387; Brennstoff-u. Wärmewirt., vol. 8, 1926, pp. 228–229; Chem. Abs., vol. 20, 1926, p. 3557.

Noncritical review of Fischer's recent work on oils from water gas. (*See* abs. **1021.**)

1961. KÖNIG, H. [Smallest Ferromagnetic Elementary Size of Iron.] Naturwissenschaften, vol. 33, 1946, pp. 71–75; Chem. Abs., vol. 41, 1947, p. 7177.

Review in some detail of history of ferromagnetism and various methods used to determine the size of the elementary Fe magnet. The author's method, in which a collodion film with attached Fe layer is brought between the poles of a magnet and the magnetism determined by Farraday effect, rotation of polarized light, is described more specifically. Differences were found for different types of Fe precipitates. From 20 different Fe films it was found that the smallest mean crystal size to give measurable rotation; that is, ferromagnetism, is 10–12 Å. With γ–Fe_2O_3, ferromagnetism does not begin until the particles are 30–40 Å. In both cases, this indicates the presence of at least 64 elementary cell units.

1962. KONOBEYEVSKI, S. [Solid Solution of Iron in Graphite.] Ztschr. Krist., vol. 72, 1929, pp. 381–397; Chem. Abs., vol. 24, 1930, p. 1011.

Diffraction patterns from some natural graphites were duplicated in samples of graphite heated with Fe. Solid solution of Fe in the graphite occurs with the probable formation of Fe_2C. The presence of

superstructure lines in the pattern indicates a regular distribution of the Fe atoms.

1963. KOPPENBERG, H. [Mineral Oil From Coal.] Vierjahresplan, vol. 1, 1937, pp. 271–277.

Technical and economic aspects of the production of synthetic motor fuels are discussed, with special reference to the Bergius high-pressure and the Fischer-Tropsch synthetic processes by means of which Germany is to be made independent of foreign oil supplies.

———. *See* abs. **3088.**

1964. KOPPERS REVIEW. Chemistry and Economics of the Fischer-Tropsch Process. Vol. 2, No. 3, 1937, pp. 99–139.

Describes the process and its products. Gives analyses of the lubricants obtained from olefins produced in the process and results of engine trials with Fischer-Tropsch diesel oils are reported. Compares Fischer-Tropsch and coal-hydrogenation processes and discusses the economics of the former.

1965. KÖRBER, F., AND OELSEN, W. [Thermodynamic Considerations on Some of the Equilibrium Curves in the Iron-Carbon Condition Diagram.] Arch. Eisenhüttenw., vol. 5, 1932, pp. 569–578; Chem. Abs., vol. 26, 1932, p. 5483.

Because of the uncertainty existing, the shape and coordinates of the saturation lines of γ–mixed crystals in α– and β–Fe (*GOS*) and in cementite (*SE*) were calculated thermodynamically from the heat-content curves of pure Fe given in the literature. The calculated *GOS*–line is convex to the concentration axis and the *SE*–line is straight, in agreement with numerous experimental results. Similar calculations, with the heat of fusion of γ–Fe for the beginning (*BC*) and the end (*JE*) of the separation of γ–mixed crystals from the melt, show that the *JE*–line is straight. These also show that in the melt, C is dissolved principally as Fe_3C molecules, and to a smaller extent as C atoms. On the basis of *JE*– and *BC*–lines, no definite statement can be made as to the molecular form of C in the γ–mixed crystals. The heat of solution of 1 gm. Fe_3C in γ–mixed crystals is −30.2 cal., the heat of transformation at 731° of 1 gm. of pearlite 20.5 cal., and the heat of formation of cementite −5 to −7 kcal. per mol. Bibliography.

1966. KÖRBER, F., WIEMER, H., AND FISCHER, W. A. [Thermal Disintegration of CO on Fe and Its Alloys and in Mixtures With Carbon.] Arch. Eisenhüttenw., vol. 17, 1943, pp. 43–52; Chem. Abs., vol. 38, 1944, p. 5769.

Catalytic bodies of pure Fe cause a stronger disintegration of CO at about 900° which, however, if compared with the equilibrium concentrations of Boudouard's curve, cannot be ascribed to catalytic effects but probably to chemical reactions between the Fe and CO. Admixtures of graphite up to 1.5% do not affect this action of soft-Fe basic bodies. If, however, the basic body contains cementite a very pronounced maximum of CO_2 formation is observed between 500° and 600° at 0.4% C as cementite. This maximum is equal or even higher than the value for soft Fe around 900° depending on the quantity of basic body, and can be observed, though weaker, even at lower cementite contents. Increasing the cementite content increases the maximum value between 500° and 600°, while at 900° it becomes smaller and is hardly noticeable at 1.2–1.5% C. Steel has much less disintegrating action on CO than powdered basic catalytic bodies. Magnetic measurements showed that in passing CO over Fe powder up to 500° the latter is transformed entirely into cementite; the velocity of the transformation depends on the fineness of the Fe powder. Simultaneous formation of higher carbides or any other oxides could not be observed at this temperature.

1967. KOREVAAR, A. [Influence of Water Vapor in Gas Generators.] Chem. Weekblad, vol. 22, 1925, pp. 66–73; Chem. Abs., vol. 19, 1925, p. 1622.

Earlier work is critically reviewed. It is concluded that the water-gas equilibrium $H_2O+CO=CO_2+H_2$ plays a very unimportant role; it is virtually never reached. The reactions taking place are solely determined by the equilibrium conditions for (I) $C+H_2O=CO+H_2$ (Lang) and (II) $2CO=C+CO_2$ (Boudouard). It is not yet possible to give a complete calculation of the reactions involved. From a technical point of view, Bone and Wheeler's result that only a limited amount of H_2O can be completely utilized, is very important. A partial calculation shows that at a lower temperature of the combustion zone more H_2O vapor can be decomposed.

1968. KORNETZKI, M. [Curie Temperature and Hydrostatic Pressure.] Ztschr. Physik, vol. 124, 1948, pp. 566–569; Chem. Abs., vol. 43, 1949, p. 8783.

Change in Curie temperature with hydrostatic pressure is estimated on the basis of the relation between Curie temperature and the lattice constants for the halides of the metals from V to Cu. The dependence of the Curie temperature of Fe on its lattice constant is an approximate agreement with previous theoretically estimated values.

KORNIĬCHUK, G. P. *See* abs. **1751.**

KORTENGRABER, A. *See* abs. **3059.**

1969. KOSTELITZ, O., AND HENSINGER, G. [Catalytic Dissociation and Synthesis of Methanol.] Chim. et ind., vol. 42, 1939, pp. 757–773; Chem. Abs., vol. 34, 1940, p. 3572.

Activities of some ZnO preparations obtained by different processes and treated in various ways were studied in the synthesis of MeOH from CO and H_2, and the catalytic action of these preparations after they had been used for the synthesis were studied on the dissociation of MeOH to see what changes were undergone during the high-pressure synthesis tests. When Merck's pure $ZnCO_3$ is pressed and then decomposed at 300° in an atmosphere of MeOH, the catalytic power per unit vol. of catalyst increases during dissociation of MeOH with the rate of compression; when the $ZnCO_3$ is first converted to ZnO by heating at 300° in air and is then pressed, the catalytic power per unit vol. of catalyst at first increases with the degree of compression to a maximum at 1,000 atm., and then decreases at higher pressures. If the activity of the preparations is calculated with reference to the values of total dissociation, the following degrees of activity (activity scale) during the dissociation of MeOH are obtained: ZnO pressed under 1,000 atm. has about the same activity as $ZnCO_3$ pressed under 2,000 atm.; smithsonite (natural $ZnCO_3$) has a much lower activity. If the numerical values of CO formed by dissociation of MeOH are chosen as a basis for comparison, ZnO pressed under 1,000 atm. is slightly more active than smithsonite, followed by $ZnCO_3$ pressed under 2,000 atm. The tests on the synthesis of MeOH showed that smithsonite is the most active catalyst, followed in order by ZnO pressed under 1,000 atm. and by $ZnCO_3$ pressed under 2,000 atm. and subjected to preliminary treatment in an atmosphere of MeOH vapor at 300°. Smithsonite is a good catalyst without having undergone any preliminary treatment, whereas hydrated $ZnCO_3$ requires special precautions (preliminary treatment in MeOH vapor at 300°). With smithsonite increase in the velocity of circulation of the gases increases the catalytic power per unit vol. of catalyst; with ZnO the reverse is the case. Tests on the dissociation of MeOH with catalysts that had been used for synthesis showed a considerable decrease in the catalytic power, and the specific activity of these catalysts also seemed to have undergone considerable

modifications. ZnO preparations produce chiefly a strong dissociation of MeOH (80–90%) into CO and H_2 and a slight decomposition (10–20%) of the MeOH into secondary products; but, after they had been used for the synthesis of MeOH, they produce little decomposition into CO and H_2 (20–50%), and most of the MeOH is decomposed into secondary products, especially Me formate (15–37% of the initial MeOH). The activity of the catalysts during dissociation of MeOH on the one hand and during synthesis of MeOH on the other is not the same. The study of the catalytic dissociation of MeOH is not a reliable method for determining the most efficient catalysts for the high-pressure synthesis of MeOH. The dissociation reaction seems to be useful merely for furnishing, by means of relatively simple apparatus, a few qualitative data relative to the activity of catalysts for the synthesis of MeOH; to determine the most suitable catalysts it is preferable to carry out synthesis tests under varying conditions of pressure, temperature and quantity of reactants.

1970. KOSTER, W. [Effect of Heat Treatment Below the A_1 Point on the Properties of Technical Iron.] Arch. Eisenhüttenw., vol. 2, 1929, pp. 503–522.

KOTH, A. W. *See* abs. **2576, 2577.**

1971. KOTZSCHMAR, —. [Production of Paraffin From Carbon Monoxide and Hydrogen. Experiments to Explain the Unfavorable Outcome of a Large-Scale Experiment at Leuna.] FIAT Reel R–20, frames 7552–7561, Oct. 20, 1939; PB 73,564.

Experiments were carried out in the I. G. Farbenindustrie Ammonia Laboratory, Oppau, in an attempt to explain the failure of a large-scale experiment at Leuna on the production of paraffin from CO and H_2 in the presence of a Co catalyst. After elimination of several possible factors, it was concluded that the conditions of reduction of the catalyst were responsible for the failure of the Leuna experiment. The failure was due to the swift rise in the reduction temperature of the catalyst. Heating for 4 hr. yielded satisfactory catalysts, whereas heating for 15 min. gave poor catalysts.

KOVACS, S. *See* abs. **3374.**

1972. KOWALSKI, J., AND GONDZIK, J. [Cracking of Higher-Boiling Benzene Hydrocarbons to Motor Fuel.] Przeglad Gorniczy., vol. 6, 1950, pp. 203–208; Chem. Abs., vol. 44, 1950, p. 10307.

Synthetic fraction b. 200°–300° from the Fischer-Tropsch process was cracked at 550° and 5–25 atm. with a contact time of 0.5 sec. to produce 71% of gasoline of 61 octane no. without C formation. Contrary to expectations, a mixture of 71.6% of the synthetic oil and 28.4% of the aromatic fraction from coke-oven-gas manufacture (initial b. p., 156°, 95% up to 193°) will crack at the relatively low optimum temperature of 660° and 25 atm. pressure to yield 65% of gasoline of 78.7 octane no. without any C formation. It is calculated that conversion of the aromatics in the mixture to gasoline was 80% greater than in cracking the aromatic fraction alone. The feasibility of the process on a large scale was confirmed by cracking of mixtures of the synthetic oil and the aromatic fraction in different proportions in a Carburol-type unit of 110-ton-per-day capacity, at a recycle ratio of 5:1.

KOZHENOVA, K. T. *See* abs. **1662.**

1973. KOZHINA, N. K. [Behavior of Fe_3C in a Stream of CO_2.] Stal, vol. 1, No. 7/8, 1941, pp. 78–79; Chem. Abs., vol. 38, 1944, p. 3582.

Interaction between Fe_3C and CO_2 was investigated by X-rays. There were 2 series of experiments: In the first powdered pure Fe_3C was heated at various temperatures 200°–800° for 5–60 min. in a stream of pure CO_2; in the 2d the Fe_3C was heated at 400° for 30 min. in a stream of CO_2; then the CO_2 was cut off, and the heating continued to 800°–1,200°. In the 1st series, the results were divided into 3 groups: Samples heated at 200°, 300°, and 400° had a predominance of Fe_3C. The predominant phase of samples heated at 500° and 570° was hard to determine. The predominant phase of samples heated at 600°–800° was Fe_3O_4. Lines of FeO appeared on all röntgenograms. In the second series the predominant phase was α–Fe.

KOZLOV, L. I. *See* abs. **1589, 1590.**

KRAEBER, L. *See* abs. **2151.**

1974. KRAFT, J. [Artificial Motor Fuels.] Bányász. Kohász. Lapok, vol. 70, 1937, pp. 366–370; Chem. Abs., vol. 32, 1938, p. 1425.

General account is given. The method of Fischer-Tropsch is proposed for working up Hungarian coal occurrences in the Mecsek Mountains.

KRÄGELOH, F. *See* abs. **3051.**

1975. KRASE, N. W. High-Pressure Gas Research at the University of Illinois. Chem. and Met. Eng., vol. 35, 1928, pp. 463–465; Chem. Abs., vol. 22, 1928, p. 4284.

1976. ———. High-Pressure High-Temperature Technology. Chem. and Met. Eng., vol. 37, 1930, pp. 530–533; Chem. Abs., vol. 24, 1930, p. 5394.

Synthetic NH_3 industry, synthetic MeOH industry, and the hydrogenation of pertoleum industry are the ones using high pressures and temperatures. Flexibility of the hydrogenation process permits refineries to adjust their output in accordance with demands of consuming market, producing gasoline, kerosene, gas oils, or lubricants in the proportions desired. The process permits 100% conversion of crude oils into gasoline of excellent quality, while but 70% is obtained; for example, S as H_2S passes out of the picture. Plants are virtually ready to go into operation to produce higher alcohols from CO and H_2 by pressure-catalytic processes. Fischer's Synthol process and methanation of CO also are high-pressure high-temperature processes of interest to the petroleum industry.

1977. ———. Carbon Monoxide as a Raw Material for Chemical Synthesis. Trans. Am. Inst. Chem. Eng., vol. 32, 1936, pp. 493–510; Chem. and Met. Eng., vol. 43, 1936, pp. 590–595; Chem. Abs., vol. 31, 1937, p. 6763.

Review covering the production, properties, and reactions of CO and its utilization in CO–H_2 mixtures for production of MeOH and higher alcohols and liquid organic compounds.

———. *See* abs. **3195.**

KRATZER, M. B. *See* abs. **2341.**

1978. KRAUCH, C. [Technical and Economic Considerations on Coal Refining, With Special Reference to High-Pressure Processes.] Stahl u. Eisen, vol. 47, No. 27, 1927, pp. 1118–1126; Jour. Inst. Petrol. Technol., vol. 13, 1927, pp. 347–352A; Erdöl u. Teer, vol. 3, 1927, pp. 455–457; Petrol. Times, vol. 18, 1927, p. 679; Petroleum, vol. 23, 1927, p. 1213; Chem. Abs., vol. 21, 1927, p. 4047.

General discussion.

1979. ———. Catalysis Applied to the Conversion of Hydrocarbons. Proc. Internat. Conf. Bituminous Coal, 2d Conf., 1928, pp. 32–48; Brennstoff-Chem., vol. 10, 1929, p. 9.

General discussion of catalysis with some application to coal hydrogenation and the oxidation of paraffin hydrocarbons to obtain fatty acids. No specific mention of special catalysts.

1980. KRAUT, H., WEISCHER, A., AND HUGEL, R. [Suitability of Fats Synthetized From Fatty Acids or From 6 to 12 C Atoms. I. Preparation of the Synthetic Fats and Their Hydrolysis by Pancreatic

Lipase.] Biochem. Ztshr., vol. 316, 1943, pp. 96–107; Chem. Abs., vol. 38, 1944, pp. 4626–4627.

Experiments were made with fats from various lower fat acids to determine the lipase action in alkaline or acid medium and in a medium of variable *p*H. The hydrolysis is greater the smaller the molecular weight of the triglyceride, but no appreciable difference was found between fat acids with even or odd C numbers.

1981. KRAUTWALD, A. [Synthetic Fat as a Foodstuff.] Deut. Gesundheitsw., vol. 3, 1948, pp. 354–356; Chem. Abs., vol. 42, 1948, p. 7898.

Synthetic fat consisted of glycerides of saturated fatty acids, of which 50% had an odd number of C atoms. Analysis showed the following ester composition: Lauric acid 18%, undecanoic acid 18%, tridecanoic acid 20%, myristic acid 8%, palmitic acid 15%, margaric acid 7%, and stearic, nonadecanoic, arachidic, and capric acids totaled 3%. The remaining 11% were high boiling point esters. Synthetic fat looked like butterfat, was solid at room temperature and was virtually without taste or odor. Its melting point was 36.5°, saponification no. 235, I no. 11. It could be stored for 2 years without apparent change in taste or odor. Persons in good health were able to digest 100 gm./day. It was well tolerated even by patients with liver or stomach ailments in amounts up to 50 gm./day. It was absorbed from the intestines and easily metabolized. Ingestion of a 50-gm. dose produced a fall in respiratory quotient in a mannere similar to butter. Experimentally induced ketosis in healthy persons could be reduced by administration of synthetic fat.

1982. KREBS, R. W. Development of Synthetic Fuels From Natural Gas. Petrol. Refiner, vol. 26, No. 10, 1947, p. 171.

Paper at the Southwest Louisiana Sec. meeting, American Chemical Society, discusses the reserves of liquid fuel that can be made available from our resources of natural gas, coal, and oil shale at varying gasoline price levels, and presents simplified diagrams of some of the process equipment that will be utilized.

1983. KREULEN, D. J. W. [Physical and Chemical Constants of Two Completely Hydrogenated Oils Prepared by the Fischer–Tropsch Gasoline Synthesis.] Chem. Weekblad. vol. 35, 1938, pp. 410–411; Chem. Abs., vol. 32, 1938, pp. 7252.

These lubricating oils differ markedly from natural petroleum products in that the aliphatic side chains are very much branched. The molecular weights (774 and 457, d. 0.8580 and 0.8453) are different, but the molecular constitutions are parallel; in both cases the viscosity poleheights are identical, although the viscosity time indexes are different. The Ubbelohde law that oils of the same origin have the same pole height is confirmed.

1984. ———. [The Chemism of the Fischer-Tropsch Synthesis.]. Chem. en Pharm. Tech., vol. 3, No. 12, 1948, pp. 205–206; Chim. et ind., vol. 61, No. 2, 1949, p. 151.

Standard catalyst for this synthesis is composed of Co : Th : Mg : kieselguhr in the proportion of 100 : 5 : 8 : 200. The Th may be omitted and the quantity of Mg decreased. The kieselguhr has a double role; it insures a very fine division of the Co and renders the catalyst porous. It is very improbable that Co carbide is formed as an intermediate product. The mechanism of the polymerization reaction has not yet been clarified.

1985. KRICHEVSKII, I. R., AND KHAZANOVA, N. E. [The ϵ–Phase of Iron Nitride.] Doklady Akad. Nauk S. S. S. R., vol. 71, 1950, pp. 677–680; Chem. Abs., vol. 45, 1951, p. 1410.

Equilibrium constant K_1 of the reaction $[2m/(n-m)]\ Fe_mN = [2m/(n-m)]\ Fe_nN + N_2$ where Fe_mN is the ϵ-phase and Fe_nN is the γ-phase, was calculated from existing data for the synthesis of NH_3 and for the reaction of Fe nitrides with H_2. The values obtained for log K_1 were: 400° 5.616, 450° 5.555, 500° 5.491, 550° 5.433, and 600° 5.382. By combining these values with data on the fugacity of N_2, the N_2 pressure in equilibrium with the ϵ– and γ–phases at 400°–600° was calculated at approximately 12,000–13,600 atm.

1986. ———. [Nitriding of Iron.] Doklady Akad. Nauk. S. S. S. R., vol. 71, 1950, pp. 481–484; Chem. Abs., vol. 44, 1950, p. 10,631.

Specimens of Fe were nitrided at 375°, 400°, 450°, and 500° at atmospheric pressure in NH_3–H_2 mixtures, the NH_3 content ranging 35–65%. The nitriding reaction stopped almost completely as a limiting N_2 content in the Fe was approached, the final N_2 content increasing with increase in temperature or NH_3 concentration. Nitriding is the result of 2 opposing reactions: (1) $2\ NH_3 + 2x\text{Fe} \rightarrow 2\ \text{Fe}x\text{N} + 3\ H_2$, and (2) $2\ \text{Fe}x\text{N} \rightarrow 2x\text{Fe} + N_2$. Reaction (1) is limited by rate of diffusion of N_2 through Fe and Fe nitrides, and because of the low rate of diffusion through Fe nitrides, the reaction slows down as the nitrides increase until equilibrium between the 2 reactions is attained.

KRIEG, A. *See* abs. **43a, 44, 46, 48, 49.**

1987. KRIEG, A., DUDASH, A. P., AND ANDERSON, R. B. Improved Caustic Scrubber. Ind. Eng. Chem., vol. 41, No. 7, 1949, p. 1508.

Description of small laboratory scrubber for removing CO_2 from the exit gas of the Fischer-Tropsch synthesis.

1988. KRINGS, W., AND KEMPKENS, J. [Solubility of Oxygen in Solid Iron. I.] Ztschr. anorg. Chem., vol. 183, 1929, pp. 225–250; Chem. Abs., vol. 24, 1930, p. 44.

Fe used was prepared by reduction of pure Fe_2O_3 in dry H_2 at 720°–750°. The solubility of O_2 in this Fe was determined by means of equilibrium experiments in a current of H_2–H_2O vapor at 715° and was found to be $0.11 \pm 0.015\%$. The same experiments served for a study of the equilibrium $FeO + H_2 \rightleftharpoons Fe + H_2O$.

1989. ———. [Solubility of Oxygen in Solid Iron. II.] Ztschr. anorg. Chem., vol. 190, 1930, pp. 313–320; Chem. Abs., vol. 24, 1930, p. 3974.

By measurement of the O_2 pressure of Fe–O mixed crystals with H_2O–H_2 mixtures, the solubility of O_2 in solid Fe at 800° was found to be $0.095 \pm 0.01\%$. At 715° the value of $0.11 \pm 0.015\%$ had been previously determined. These results were confirmed by the decomposition of freshly prepared Fe_2O_3 in the same gas mixture.

1990. KROEPELIN, H. [Heat Transfer in the Fischer-Tropsch Synthesis, Especially in Lamella Furnaces.] Erdöl u. Kohle, vol. 3, No. 1, 1950, p. 10.

Paper presented at the 1949 meeting of the Deutsche Gesellschaft Mineralöelwissenschaft u. Kohlechemie. The transfer of the reaction heat set free in the Fischer-Tropsch synthesis is traced from the middle of the catalyst bed to the H_2O space of the catalyst furnace. The problem is divided into 4 parts: (*a*) From the middle of the catalyst bed to the lamella, (*b*) from the lamella to the cooling space, (*c*) from the tube wall to the cooling H_2O, (*d*) from the path of the steam in the cooling tube to the steam accumulator. The heat transfer within the catalyst bed as in the lamella is calculated by the same formula, which shows a quadratic dependence between temperature and path. For the main reaction zone, in which 86,000 kcal. per hr. are generated in 1 $m.^3$ of catalyst, the following temperature differences are shown: (*a*) In the catalyst bed about 8°; (*b*) in the lamella, 3°; (*c*) in the water-tube wall, 1°. Experimental and operating tem-

perature measurements are presented for an active catalyst. Measurements of H_2O circulation in a synthesis furnace as well as its calculation is given briefly.

1991. KROEPELIN, H., OPITZ, W., AND FREISS, W. [Sulfochlorination of Kogasin in the Dark.] Erdöl u. Kohle, vol. 2, 1949, pp. 498–500; Fuel Abs., vol. 7, 1950, abs. 3133.

Tests on the reaction of Kogasin (b. 225°–305°) with Cl_2 and SO_2 were made using Kogasin of 3 grades of purity, technical, refined (olefin-free), and a superrefined material (olefin-free vacuum-distilled over Na in N_2). Using the refined material, chlorination was the main reaction at 25°–38° and sulfochlorination at 38°–68° (temperature measured in reaction vessel). The best ratio between chlorination and sulfochlorination was at 68°. Technical Kogasin reacted similarly but somewhat more energetically. Using the highly refined Kogasin, reaction with Cl_2+SO_2 could not be obtained. In the course of analyses of the Kogasins, marked sensitivity of the refined olefin-free material to O_2 was observed in the temperature range 100°–130°. Tests with the most highly refined material to which 0.5% of chain initiators (dodecylene–1, benzoyl peroxide) had been added showed strong combination with Cl_2 and SO_2 at 71°–77°, the products containing approximately 16% Cl and 9% S. Inhibitors of the reaction (alcohols, pyridine) also were tested. In the case of pyridine the inhibitory action is due to a pyridine-chlorine compound. Smooth sulfochlorination of petroleum fractions from crude oil was not obtained, presumably owing to the presence of natural inhibitors. The experiments confirm that, even in the dark, sulfochlorination is a chain reaction.

1992. KRÖGER, C. [Action of Inorganic Polycatalysts in the Water-Gas Process.] Ztschr. Elektrochem., vol. 44, 1938, pp. 577–578; Chem. Abs., vol. 32, 1938, p. 9446.

Oxides of Cu, Ni, Co, Fe, U, and Mn, or alkali carbonates promote the water-gas reaction when mixed with coke, graphite, lampblack, or wood charcoal. The catalytic activity of K_2CO_3 is promoted by CuO, Co_3O_4, Ag_2O, or ZnO when added to graphite. Low-temperature coke or wood charcoal is activated by Li_2CO_3. The addition of K_2CO_3–Co_3O_4 or K_2CO^3–CuO to lignite coke or wood charcoal gives a lower yield than when these substances are added to graphite. The action of the catalysts depends upon the fixation of the free alkali metal on the surface of the C and its infiltration into the graphite lattice. When steam reacts the lattice is destroyed.

———. *See* abs. **2436.**

1993. KRÖGER, C., AND MELHORN, G. [Action of Inorganic Additions as Single and Multiple Catalysts in the Water-Gas Reaction.] Brennstoff-Chem., vol. 19, 1938, pp. 157–169; Chem. Abs., vol. 32, 1938, p. 8744.

In apparatus and procedure previously described the action of various metal oxides on the gasification of graphite with steam at 600°–800° has been studied. Oxides with medium heats of formation were found most active. None, however, surpassed CuO, which gave 22% steam decomposition at 700°, graphite alone, only 6%. Next, in order of decreasing activity, were oxides of Cr, Ni, Fe, U, Tl, Mn, Co, and Al. Combinations of these did not increase effects. With alkaline carbonates, the order was K and Na, 32% decomposition at 660°, Rb, Cs, and least, Li. Greatest steam decompositions, 65% at 650°, were obtained with K_2CO_3 combined with CuO and Co_3O_4; these and NiO also gave results above the additive expectations. A ternary K–Ni–Co mixture gave results similar to K_2CO_3. The electronegative position of K is offered in explanation of its superior effect in reaction mechanisms offered. Formation of unsaturated hydrocarbons was observed in the reaction when additions of Hg, Te, Th, and U oxides, Li_2CO_3, and mixtures with K_2CO_3, were made to the graphite, ThO_2 producing 2.1% at 711°. Composition of the reaction gas showed that equilibrium is established beginning at 570° with activated graphite. No establishment of the Boudouard equilibrium was found. The literature is reviewed briefly, with 72 ref.

KRONIG, W. *See* abs. **3459.**

1994. KRONSTEN, J. A. Poland's Oil Position Today. Synthetic and Substitute Products. Petrol. Times, vol. 51, 1947, pp. 159–160.

Of the 3 German-built synthetic plants on Polish territory, not one is in a fit condition to be rebuilt. They will, therefore, be combined at the site of the Oswiecim synthetic oil works, which will be equipped with plant allocated to Poland under the German reparation scheme and coming from the Fischer-Tropsch plant at Schwarzheide near Dresden. Also, a certain amount of salvaged equipment will be transferred from the works at Blachownia-Blechhammer, formerly the Schlesische Hydrierwerke A.-G. and from Kedzierzyn in Silesia. The new works at Oswiecim will have an output of 40,000 tons per yr. of intermediates for further processing into motor fuel and other products, but plant completion is unlikely before 18–24 months.

1995. KROUPA, G. [Profitableness of Obtaining Oil From Water Gas.] Petrol. Ztschr., vol. 23, 1927, pp. 1524–1525; Chem. Abs., vol. 22, 1928, p. 1464.

Synthetic production of oil from water gas is uneconomical at the present time as compared with the hydrogenation of coal, and even though the process proves to produce the greatest yield of products, the cost of production will remain prohibitive. The water-gas process is slow and uneconomical because of the several additional steps that must be introduced including distillation, gasification, chemical gas purification, and the synthetic operation.

KRSEK, G. *See* abs. **3, 4.**

1996. KRUG, J. A. Report of the Secretary of the Interior on the Synthetic Liquid Fuels Act, 1946. 1947, 82 pp.

Report covers the work of the Bureau of Mines for 1946. It is divided into 2 parts; the 1st summarizing the major progress and developments of the year, and the 2d giving a detailed account of the engineering and scientific achievements. As the result of the research in the field of synthetic fuels, it is concluded that gasoline may be produced from coal or oil shale at a cost of $0.075–$0.095 per gal., and from natural gas at $0.055–$0.07 per gal., exclusive of any profit or interest on the investment. Construction is far advanced at 2 of the major Bureau projects for the small-scale investigation of coal hydrogenation by the Bergius process and the production of synthetic gasoline by the Fischer-Tropsch reaction. Furthermore the oil-shale demonstration plant in Colorado is expected to start operation soon. In this project fundamental data on the design of oil-shale and pilot-plant units have been worked out. A thermal-solution process is being developed for shale oil recovery, which shows more oil obtained than the shale assay has indicated. Two shale mines will supply the demonstration plant with shale and will determine commercial mining costs; these are expected to be about $0.50 per ton of shale. Underground gasification of coal is undergoing experimental tests in Alabama to determine the possibilities for the production of synthesis gas. A coal liquefaction plant is being prepared at Louisiana, Mo., from a Government-owned NH_3 plant to produce up to 200 bbl. of oil per day. Laboratory studies are being made at Morgantown, W. Va. to develop cheaper and better methods for producing CO and H_2 for synthesis gas

and for coal hydrogenation. Lower pressures, lighter equipment, minimum H_2 consumption, and the use of dry coal without a vehicle or with one readily flashed off are indicated in the coal-hydrogenation process as contributing greatly to the reduction of production costs, while in the synthesis process production rates 3–5 times those of German plants have been indicated through use of a new type of internally cooled converter embodying an improved cooling method consisting in dripping a cooling oil directly over the catalyst preferably in cocurrent flow at high space-velocities of the synthesis gas. Besides the increased production reported, there are the further advantages of a lower content of gaseous hydrocarbons in the product, the possibility of greatly enlarged reaction chambers, and the use of a wider range of catalysts in comparison with fluidized types. Still other methods of cooling are under investigation such as liquid-phase suspended catalyst and hot-gas recycle.

1997. ———. Report of the Secretary of the Interior on the Synthetic Liquid Fuels Act from January 1, 1947, to December 31, 1948, 128 pp. Combustion, vol. 19, February 1948, pp. 49–51; Petrol. Processing, vol. 3, 1948, pp. 207–208; Chem. and Eng. News, vol. 26, 1948, pp. 610–611.

Progress made in the development of industrial methods for the production of synthetic liquid fuels is reported. Projects under way include both demonstration plants and laboratory and pilot-plant investigations of shale oil, coal hydrogenation, synthesis gas by complete gasification of coal in presence of O_2 and steam, the Fischer-Tropsch process, and subterranean gasification of coal. In addition, experimental work is being carried on in connection with the production of liquid fuels from agricultural wastes. Operations in oil shale are concerned with both mining and processing. The use of large-scale equipment in the mining of shale has reduced the mining cost to $0.70 per ton and it is expected to reduce this to $0.50 per ton. The best figure obtained thus far in preparing the shale for retorting is $0.16 per ton and for retorting $0.096 per gal. of liquid crude shale oil. It is believed the ultimate figure will be $0.05 per gal. A coal hydrogenation plant with a capacity of 250 bbl. gasoline per day will be completed in 1948. Economic studies have shown that by using coke-oven gas as the source of process gas, fuel oil can be made for approximately $0.07–$0.11 per gal. The cost of high-pressure H_2 is approximately 40–50% of the total cost of producing fuel oil. Dry hydrogenation is being investigated as indicating a lower content of asphaltic material in the product. Two types of coal solvents also are being investigated toward development of a liquefaction process operating at moderate temperatures and low H_2 pressure. One type, such as o-cyclohexylphenol, effects chemical dissociation and H_2 transfer to the coal molecule, and the other, such as phenanthrene, acts as a dispersing agent for the coal. Initial tests are being made on the gasification of powdered coal with O_2 and steam in a reactor of the vortex type with a capacity of approximately 100 lb. of coal per hr. A complete Fischer-Tropsch synthesis plant of about 80-bbl.-per-day capacity is being designed to provide engineering and cost information. The plant will be erected at Louisiana, Mo. Research is being continued on the liquid-phase catalyst suspension process as well as internal oil cooling of the catalyst. Encouraging results are being obtained in the gasification of pulverized coal entrained in superheated steam and O_2, and promise is made of considerable cost reductions for synthesis gas under that achieved in standard water-gas sets. The favorable results obtained with underground coal-gasification tests warrants further study and investigation will be continued. The cost of the Gorgas, Ala., project is reported as $2.33 per ton of coal gasified, and a gas is obtained of calorific value 125 B. t. u. per cu. ft.

1998. ———. Synthetic Liquid Fuels. 1948 Annual Report of the Secretary of the Interior. I. Oil From Coal. II. Oil From Oil Shale. III. Liquid Fuels From Agricultural Residues. IV. Secondary Recovery and Petroleum Chemistry and Refining Research. Bureau of Mines Repts. of Investigations 4456, pp. xviii, 1–62; 4457, pp. xviii, 1–57; 4458, pp. xviii, 1–25, January 1949.

Comprehensive review of all of the phases of the Government's synthetic liquid fuels development program. Detailed engineering studies and cost estimates of the various processes.

KRYUKOV, Y. B. *See* abs. **152**, **152a**.

1999. KUBELKA, P., AND WENZEL, W. [Equilibrium Relations Involved in the Interaction of Water Vapor and Methane. I.] Metallbörse, vol. 21, 1931, pp. 1227–1228; Brennstoff-Chem., vol. 12, 1931, p. 380; Chem. Abs., vol. 25, 1931, p. 5612.

Develops equilibrium constants for all the steps and for the complete reaction of H_2O vapor and CH_4 for the production of H_2 under isobaric conditions. Mathematical expressions for evaluating the partial pressure of each of the gases, CH_4, CO_2, and CO, in terms of equilibrium constants and the partial pressure of the other components.

2000. ———. [Equilibrium Relations Involved in the Interaction of Water Vapor and Methane. II.] Metallbörse, vol. 21, 1931, pp. 1275–1276; Brennstoff-Chem., vol. 12, 1931, p. 380; Chem. Abs., vol. 25, 1931, p. 5612.

Mathematical expressions are modified to give actual weight and vol. % ratios, and tables are compiled for temperatures 550°, 650°, 750°, 850°, and 1,000° or above (1,200°) showing the effect of varying the H_2O vapor 0.5–4 mol. per mol. CH_4, both with and without H_2 introduced with the CH_4.

2001. ———. [Equilibrium Relations Involved in the Interaction of Water Vapor and Methane. III.] Metallbörse, vol. 21, 1931, pp. 1372–1373; Brennstoff-Chem., vol. 12, 1931, p. 380; Chem. Abs., vol. 25, 1931, p. 5612.

Further tables showing equilibrium relations at the temperatures shown in pt. II (*see* abs. **2000**).

2002. ———. [Equilibrium Relations Involved in the Interaction of Water Vapor and Methane. IV.] Metallbörse, vol. 21, 1931, pp. 1421–1422; Brennstoff-Chem., vol. 12, 1931, p. 380; Chem. Abs., vol. 25, 1931, p. 5612.

Above 850° from a general consideration of tables and graphs it was shown that (1) when excess water vapor is avoided the reaction is virtually according to the equation $CH_4+H_2O \rightarrow CO+3\ H_2$; (2) with an excess of water vapor at intermediate temperatures around 750° the CH_4 is most effectively decomposed for the production of H_2 virtually according to the equation $CH_4+2H_2O=CO_2+4H_2$.

2003. KUBOKAWA, M. Activated Adsorption of Methane on Reduced Nickel. Proc. Imper. Acad. (Tokyo), vol. 14, 1938, pp. 61–66; Rev. Phys. Chem. Japan, vol. 12, 1938, pp. 157–167; Chem. Abs., vol. 32, 1938, p. 5678.

Adsorption of CH_4 on Ni was studied at pressures $5–10^{-3}$ mm. Between —112° and 20° adsorption is due to van der Waals' forces. The heat of adsorption is 1 kg.-cal. per mol. Above 40°, activated adsorption takes place. Isotherms were obtained up to 250°. The mechanism is assumed to be: $CH_4 \rightarrow CH_3+H \rightarrow CH_2+2H \rightarrow CH+3H \rightarrow C+4H$. The desorption process consists in the formation of CH_4 by the hydrogenation of CH radicals. The heat of activated adsorption of CH_4 on

Ni is calculated to be 12 kg.-cal. per mol. if the difference between the 0-point energy of the CH and the CD bond is taken as O.

2004. ———. [Decomposition of Methane on Reduced Nickel.] Rev. Phys. Chem. Japan, vol. 12, 1938, pp. 90–104; Chem. Abs., vol. 33, 1939, p. 1579.

Equilibrium constant and the reaction velocity of the catalytic decomposition of CH_4 on reduced Ni were measured in the temperature range 420°–500° below 30 mm. pressure. The reaction velocity in the initial stage is given by: $dx/dt=k(a-x)/x^n$, where a is the initial amount of CH_4, x the decomposed amount at time t, k, and n constants. The retardation exponent, n, was always larger than unity when the catalyst was activated by reduction with H_2, and it became smaller than 1 when the catalyst was used repeatedly without being reduced and also when temperature was lowered. No effect of added H_2 was observed. These results agree with those for Pt catalyst.

2005. KUCHINKA, R. [Synthesis of Edible Fats From Coal by Fischer-Tropsch Products and Air by Paraffin Oxidation.] Pharmazie, vol. 3, 1948, pp. 439–444; Chem. Abs., vol. 43, 1949, p. 5878.

Survey of methods of synthesis, especially of the higher fatty acids and technical processes developed. Points out need for further study of the physiological action of the synthetic fats, especially of the nonsaponifiable fractions.

———. *See* abs. **2566.**

KÜHN, J. *See* abs. **425.**

KUMMER, J. T. *See* abs. **831, 831a, 2718.**

2006. KUMMER, J. T., AND EMMETT, P. H. Chemisorption of Carbon Monoxide and the Heterogeneity of the Surface of Iron Catalysts. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 2886–2889.

Radioactive and nonradioactive samples of CO have been added in succession as two separate fractions to a reduced Fe synthetic NH_3 catalyst at —195° or —78°. The chemisorbed CO layer has then been removed by pumping and analyzed for $C^{14}O$. The results show that the 2d fraction of added CO tends to desorb first. However, the results also show that a partial rapid exchange equivalent to a coverage of about 50% of the Fe surface occurs between the 2 added fractions of chemisorbed CO even if both fractions are added at —195°.

2007. ———. Study of the Amount of Hydrogen Left on the Surface of a Reduced and Evacuated Iron Synthetic Ammonia Catalyst. Jour. Phys. and Colloid Chem., vol. 55, 1951, pp. 337–345.

To remove one of the uncertainties in measuring the adsorption of H_2 on metal catalysts, it is necessary to determine the amount of H on the catalyst at the start of the adsorption run. To determine the amount of residual H present on samples of pure and of promoted iron synthetic ammonia catalysts use was made of H isotopes after the catalysts had been degassed for a number of hours at 500°. The procedure is described. It was found that promoted iron synthetic ammonia catalysts, but not pure iron catalysts, retain enough H after 24-hr. evacuation at high temperature (about 500°) to be equivalent to the covering of 5–35% of the metallic surface, or 1–10% of the part of the surface covered with promoter. Accordingly, due account should be taken of this residual H in any adsorption measurements on promoted iron catalysts.

2008. KUMMER, J. T., BROWNING, L. C., AND EMMETT, P. H. Thermodynamic Calculations Concerning the Possible Participation of the Carbides of Iron as Intermediate in Fischer-Tropsch Synthesis. Jour. Chem. Phys., vol. 16, No. 7, 1948, pp. 739–740; Chem. Abs., vol. 42, 1948, p. 6623.

It is concluded from thermodynamic considerations that neither n–mono–olefins nor the higher n–paraffins can be formed from CO and H_2 by reduction of the bulk or the hexagonal Fe_2C or Fe_3C by H_2 It is indicated, however, that the lower normal paraffins with n as high as 6 could, as far as thermodynamic limitations are concerned, be formed under Fischer-Tropsch synthesis conditions by reduction of bulk Fe_2C by H_2.

2009. KUMMER, J. T., DEWITT, T. W., AND EMMETT, P. H. Some Mechanism Studies on the Fischer-Tropsch Synthesis Using C^{14}. Jour. Am. Chem. Soc., vol. 70, 1948, pp. 3632–3643; Chem. Abs., vol 43, 1949, p. 2081.

Fischer-Tropsch synthesis experiments using C^{14} as a tracer show that the greater part of the product of synthesis is formed by some process other than by the reduction of carbide as an intermediate. Only about 10% of the hydrocarbon product appears to have been formed through the carbide for Fe catalysts at or below 260° and for Co at 200°; at 300° the part of the reaction occurring through the carbide reduction mechanism seems to average about 16%. The % formed through the adsorbed phase is not critically dependent on the H_2: CO ratio in the range 1 : 1–3 : 1, on the total pressure of the synthesis, within the limits 150–800 mm. pressure; or on the % Fe_2C initially present in the range 4–100%. The exchange of the C in the gases, CH_4, CH_4H_{10}, butene–1, and C_2H_2, with an Fe carbide surface at 250° is found to be very low; CO exchange with the C in the carbide is only about 5% in 30 min. at 250°, but is as high as 29% in 7 min. at 322°. The mechanism of carbiding has been investigated and has been shown to be complicated by the possibility of a nonuniformly reacting surface. No completely satisfactory picture of the mechanism of carbiding has been formulated.

2010. KUMMER, J. T., PODGURSKI, H. H., SPENCER, W. B., AND EMMETT, P. H. Mechanism Studies of the Fischer-Tropsch Synthesis. Addition of Radioactive Alcohol. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 564–569; Chem. Abs., vol. 45, 1951, p. 4907.

To help elucidate the mechanism of Fischer-Tropsch synthesis, methyl-labeled and methylene-labeled radioactive EtOH were added to a $1:1=CO:H_2$ synthesis gas passed at 1 atm. pressure over an Fe catalyst at about 230°. Measurement of the radioactivity of the hydrocarbon products shows negligibly small activity for all CH_4 formed and an approximately constant activity of $2{,}150\pm100$ counts per minute per cc. S. T. P. for the C_5–C_{10} hydrocarbons. The C_2, C_3, and C_4 hydrocarbons have activities of about 1,825, 1,850, and 2,000 counts per minute per cc. Degradation experiments on the C_3 hydrocarbons show that about 90% of the added C atoms are attached to the α–C atom of the alcohol adsorption complex, whereas 10% are attached to the β–C. These results suggest that either EtOH or some surface complex formed by the adsorption of EtOH behaves like an intermediate in hydrocarbon synthesis over Fe Fischer-Tropsch catalysts and that at least the 1st of the added C atoms attaches itself principally to the α–C atom of the surface complex.

KUNG, K. M. *See* abs. **1508.**

KURAKU, H. *See* abs. **1959a.**

2011. KURDYUMOV, G. [X-Ray Investigation of the Structure of Tempered Carbon Steel.] Ztschr. Physik, vol. 55, 1929, pp. 187–198; Chem. Abs., vol. 23, 1929, p. 4658.

Steel sample containing 1.44% C was studied by the Debye-Scherrer powder method. The changes in property of hardened steel on annealing in the temperature range of 100°–150° depend upon the destruction of the tetragonal form, which tends to go into the cubical lattice. The 2d change is due to the decomposition of austenite and the 3d change is connected with the formation of the mixture of α–Fe and

cementite. These 3 changes have been found previously by a study of thermal expansion and electrical conductivity by G. Kurdjumov, and E. Kaminskii.

———. *See* abs. **70.**

2012. KURDYUMOV, G., AND LYSSAK, L. Application of Single Crystals to the Study of Tempered Martensite. Jour. Iron Steel Inst. (London), vol. 156, 1947, pp. 29–36; Chem. Abs., vol. 42, 1948, p. 82.

Martensite tempered at 125–150 hr. has a tetragonal lattice with an axial ratio of about 1.012 and represents the partly decomposed solid solution of the C in α–Fe. After tempering at 150° a certain amount of C, 0.3–0.5%, remains in solid solution and decreases as the tempering temperature rises until after tempering at temperatures above 300° less than 0.1% C remains in solution. 15 refs.

2013. KURDYUMOV, G., AND SACHS, G. [Mechanism of Steel Hardening.] Naturwissenschaften, vol. 18, 1930, p. 534; Chem. Abs., vol. 24, 1930, p. 4746.

Mixture of austenite and martensite crystals from slow solidification and subsequent chilling of a 1.5% C steel was studied for crystal nature and orientation. The (011) plane of the tetragonal crystallites always was parallel to the (111) planes of austenite, also (111) direction to (101), giving an 8° angle between tetragonal axis and austenite axis. This position repeats itself 24-fold in agreement with general cubical symmetry. It can be derived from a superposition of 2 simple slip motions.

2014. ———. [The Mechanism of Hardening Steel.] Ztschr. Physik, vol. 64, 1930, pp. 325–343; Chem. Abs., vol. 25, 1931, p. 271.

Austenite, γ–iron, chilled from 1,100° to room temperature is partly converted into a tetragonal modification, as shown by X-ray diagrams, Debye-Scherrer, from a rotating rod of the material. The dark ground of the films points to considerable irregularities in the arrangement of the atoms of the crystal lattice. Tempering leads to formation of martensite. The lattice distortion (continuous ground) diminishes with increasing temperature and time of tempering. The relative orientation of the crystals of the austenite modification, the tetragonal phase and the γ–iron has been found and the possible course of the rearrangement is discussed.

2015. KURIN, N. P. [Investigations of the Activities of the ZnS–CuS Methanol Catalysts.] Nauch. Tekh. Konferentsiya v Svyazi s Sorokaletnim Yubileem Uchebno-Nauch. Deyatel–nosti Tomsk. Ind. Inst., Tezisy Dokladov, 1940, pp. 108–110; Khim. Referat. Zuhr., vol. 4, No. 4, 1941, p. 100; Chem. Abs., vol. 37, 1943, p. 5306.

ZnS–CuS catalysts were obtained by the separate precipitation of ZnS and CuS, and they contained various amounts of CuS. Pure CuS and ZnS also were studied. The activities of the catalysts were determined by the decomposition of MeOH vapors at volume velocities 420–2,100 (vol. of vapor/unit vol. of catalyst/unit vol. of catalyst/hr.) and at temperatures 250°–450°. Data for catalysts possessing a maximum activity are given. H_2S poisoned the catalysts, but their activities were restored by the passage of MeOH vapors. The decomposition velocity constants of MeOH were calculated. The relation between log k and $1/T$ indicated that the decomposition process of MeOH took place through two stages. The 1st stage presumably was the decomposition of MeOH into HCHO and H_2 and the second stage the decomposition of HCHO into CO and H_2. The activation energies of these reactions were determined.

2016. ———. [Investigation of the Activity of Ammonia Catalysts Reduced by Pure Hydrogen.] Nauch.–Tekh. Konferentsiya v Svyazi s Sorokaletnim Yubileem Uchebno–Nauch. Deyatel–nosti Tomsk. Ind. Inst., Tezisy Dokladov, 1940, pp. 112–113; Kim. Referat. Zhur., vol. 4, No. 4, 1941, p. 88; Chem. Abs., vol. 37, 1943, p. 5560.

Remelted NH_3 catalyst containing Fe_3O_4, Al_2O_3, and K_2O was used for investigating the reduction process and the activity of the catalyst by the dynamic method at atmospheric pressures, at various temperatures, and various volume velocities. At constant volume velocities, the reduction velocity of the catalyst by H_2 increased with the increase in temperature. The use of H_2 for the reduction (instead of the H_2+N_2 mixture) increased the activity of the catalyst. The optimum conditions for the reduction were obtained at large volume velocities and at temperatures equal to approximately 450°.

KURODA, R. *See* abs. **1870, 1871.**

2017. KUROKAWA, M., AND TAKENAKA, Y. [Thermal Effect on the Catalyst of the Water–Gas Reaction.] Jour. Soc. Chem. Ind. (Japan), vol. 40, 1937, B, p. 347; Chem. Abs., vol. 32, 1938, p. 1554.

Fe_2O_3 catalyst generally used for the conversion of CO and H_2O to H_2 and CO_2 is impaired by the heat of the exothermic reaction. The conversion at 450° was measured with promoted Fe_2O_3 catalysts before and after heating to 850°. The resistance of the catalyst to heat was greatly improved by additions of Cr_2O_3 and MgO. The optimum ratio Fe_2O_3 : Cr_2O_3 : MgO was 1 : 0.1 : 0.03. The catalyst obtained by precipitation with KOH was better than that with NH_3.

2018. ———. Hydrogen by Water–Gas Reaction. Repts. Imperial Fuel Research Inst. Japan, No. 41, 1939; Jour. Fuel Soc. Japan, vol. 19, 1940, pp. a21–26; Fuel, vol. 19, 1940, pp. 146–149; Chem. Abs., vol. 34, 1940, p. 5603.

Activity of the catalyst under standard testing conditions and the effect of temperature and S compounds on the activity of the catalyst are shown. The results with a semicommercial plant are given. It is concluded that the Fe_2O_3+10% Cr_2O_3+3% MgO catalyst can be efficiently used in the practical application of the water-gas reaction for the manufacture of H_2.

2018a. KUROSAWA, K. Pulverized–Coal Gas Producer. Jour. Fuel Soc. Japan, vol. 30, 1951, pp. 7–13; Chem. Abs., vol. 46, 1952, p. 3,237.

Problems relating to this subject are analyzed from the standpoint of low-grade domestic coal. When compared with the Winkler producer, the plant for gasification of pulverized coal for synthesis gas has the advantage that any kind of coal can be gasified, the capacity is large, the construction is simple, the elasticity of capacity is good, and the danger of clinker formation is small. Fine coal used in the plant contained 75% of powders under 4,900 mesh. The rate of gasification is 155–200 kg. per m^3 per hr. The utility of C is 95%. The gasification chamber must be constructed almost spherically for efficient use of radiating heat. As the temperature in the chamber is very high, special attention must be paid to the selection of firebrick and to heat recovery, but the higher construction expenses can be sufficiently compensated by the greater rate of gasification. The minimum economic unit of this plant is about 10,000 $m.^3$ per hr. According to the heat balance, the synthetic heat efficiency is 78% when the sensible heat of gas produced is recovered by the waste heat boiler. The necessary equipment for a 10,000 $m.^3$ per hr. plant is briefly described, and the construction costs and gas production cost are estimated; the possibility of cheap synthesis–gas production with log-grade domestic coals is suggested.

KURZEN, F. *See* abs. **3067, 3069.**

2019. KUSAMA, T., AND YUKIO, U. Thermal Decomposition of Methane. Bull. Inst. Phys. Chem. Research, vol. 8, 1929, pp. 1–11; abs., vol. 2, p. 1; Chem. Abs., vol. 23, 1929, p. 1866.

CH_4 has been pyrolyzed on several catalyzers: (a) Pure Ni, (b) Ni+kieselguhr, (c) same as (b) but deprived of its activity by being used to reduce $C_{10}H_8$, and (d) reduced Fe: (b) and (c) are equally suitable. X-ray spectrograms show that C thus obtained is graphite, which was also proved by the graphitic acid method. This graphite has catalytic properties, which are due to the presence of small amounts of Ni from the catalyzer. By determining the S content of the catalyzer before and after a run, it was ascertained that natural gas contains a certain quantity of S but only a negligible amount. HCl is better than HNO_3 to recover the catalyst, and a new catalyzer produced by the reduction of $NiCl_2$ is as active as one obtained from $Ni(NO_3)_2$. H_2 obtained by the pyrolysis of CH_4 always contained some CH_4 that could not be removed, but the mixture can be used very satisfactorily to reduce $C_{10}H_8$.

2020. KUSS, E. [Decomposition Mechanism of Methanol.] Angew. Chem., vol. 49, 1936, pp. 483–486; Chem. Abs., vol. 30, 1936, p. 6321.

Experiments were carried out in a modified Stock apparatus, which is described. The reaction products were: CH_2O, Me_2O, H_2, H_2O, CH_4, CO, CO_2, and C. The quantitative findings could be expressed by the following equations:

(1) $MeOH \rightleftarrows CH_2O + H_2$
(2) $2MeOH \rightleftarrows Me_2O + H_2O$ } Primary
(3a) $Me_2O \rightleftarrows CH_4 + CH_2O$
(3b) $Me_2O \rightleftarrows CO + C + 3H_2$
(4) $CH_2O \rightleftarrows CO + H_2$
(5) $2CO \rightleftarrows CO_2 + C$
(6) the CH_4 equilibrium

With quartz glass, in opaque pieces, the decomposition did not begin below about 600°, and quartz tubes were therefore used as contact tubes in further experiments. With Ag, as Ag wool (analysis: 0.0544% Cu, traces of Pb, and 0.0085% Fe), decomposition began at 400°, and the reactions (1), (2), (3a), (4), and (5) were involved. Ag is a good catalyst as it accelerated the desired decomposition (1) very strongly. With Pt, as a fine screen, decomposition began at 500°, and the reactions (1), (2), (3a), (3b), (4), and (6) were involved. Pt differed from Ag essentially in accelerating decomposition (4), besides (1), and it is not suitable as contact or material of construction. With Al gravel, surface oxidized, decomposition began below 300°, and the reactions (2), (3a), (3b), and (4) were involved. The decomposition (2) was accelerated almost exclusively, and Al is not suited for use, but it is a good catalyst for the preparation of Me_2O from MeOH, and possibly for the synthesis of Me_2O from CO and H_2. With Cu, as shavings, decomposition began at 450°, and the reactions (1), (2), (3a), (4), and (5) were involved. Cu did not accelerate decomposition (1) selectively, and structural parts in contact with CH_2O formation cannot be made of Cu, but others operating below 400° can be made of Cu. With Fe, as wrought Fe shavings, decomposition began at about 550°, and the reactions (1), (2), (3a), (3b), and (4) were involved. Fe in itself is a good catalyst, accelerating decomposing (1) very strongly, but considerable acceleration of side reactions results in the covering of the Fe with C, and the material is not suitable for construction of an apparatus. With burned lime, decomposition began at about 450° and the reactions (1), (3b), (4), and (5) were involved, and all strongly accelerated. With compressed C, decomposition began at about 450°, and reactions (1) to (5) were all strongly accelerated, making C a very unsuitable material. Experimental results and 5 refs. are given.

———. *See* abs. **2296, 2297.**

2021. KÜSTER, —. [Synthesis of Hydrocarbons From Carbon Monoxide at Atmospheric Pressure Under the Influence of Catalysts of the Iron Group.] Génie civil, vol. 109, 1936, pp. 438–439.

2022. KÜSTER, H. [Literature Review of the Synthesis of Formaldehyde From Water Gas.] Brennstoff-Chem., vol. 17, 1936, pp. 103–109; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 298–310.

43 literature and 30 patent refs.

2023. ———. [Reduction of Carbon Dioxide to Higher Hydrocarbons at Atmospheric Pressures by Catalysts of the Iron Group.] Brennstoff-Chem., vol. 17, 1936, pp. 221–228; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 277–292; Chem. Abs., vol. 31, 1937, p. 1581.

Conversion with CO_2–H_2 mixtures has been effected at 200°–300° in one stage. Hydrocarbons formed are similar to those obtained in the benzine synthesis with CO and H_2. The intermediate formation of CO is indicated in the reaction mechanism. The reducing, hydrogenating, and polymerizing effects of the catalyst are influenced by impregnation of the unreduced catalyst with K_2CO_3. Results obtained by various single, double, and triple combinations of Co, Fe, Cu, Ni, Al, and Th are compared. Conversion and products are shown graphically for 20° intervals.

2024. ———. [Reduction of Carbon Dioxide to Methane Upon Iron Catalysts at Ordinary Pressures.] Brennstoff-Chem., vol. 17, 1936, pp. 203–206; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 270–277; Chem. Abs., vol. 30, 1936, p. 7790.

Contrary to Sabatier, pure Fe at temperatures above 300° permitted conversion of CO_2 to CO and CH_4, the last in very small yield. Addition of small amounts of Al or Mn did not affect activity of the Fe. Cu and Co are practical activators. The hydrogenating characteristics of Ni appear evident even with 5%. With Co added, higher gases and liquid hydrocarbons are formed. 12 refs.

———. *See* abs. **987, 1831, 2621.**

KVALNES, H. M. *See* abs. **150.**

2025. KWAN, T. Adsorption of Carbon Monoxide on Platinum Catalyst. Jour. Research Inst. Catalysis, vol. 1, 1949, pp. 110–116; Chem. Abs., vol. 44, 1950, p. 4304.

CO adsorption isotherms were measured at pressures between 0.001 and 1 mm. Hg at 180°, 200°, 280°, and 300°. The differential heat of adsorption is constant for all quantities adsorbed and equals 11 kcal. per mol. By developing, on a statistical-mechanical basis, an expression for the change in heat of adsorption with fraction of surface covered by adsorbent, assuming that adsorption occurs without dissociation or that CO is dissociated to C and O, better agreement was obtained between observed and calculated values for the latter case.

2026. ———. Adsorption of Hydrogen on Nickel, Cobalt and Platinum at Low Pressures. Jour. Research Inst. Catalysis, vol. 1, 1949, pp. 81–94; Chem. Abs., vol. 44, 1950, p. 4304.

Adsorption isotherms of H at pressures between 10^{-3} and 1 mm. Hg on Ni, Pt, and Co powders and 50°–300° were determined with special care for absence of adsorption-desorption hysteresis. Surface areas of the samples were determined by the Brunauer-Emmett-Teller method. Initial H adsorption occurs at constant differential heat of adsorption equal to 26, 18, and 19 kg.-cal. per mol. for Ni. Pt. and Co, respectively, at 300°. After about 0.1 of the sur-

face is covered, there is a gradual decrease in the heat of adsorption. On statistical-mechanical considerations an expression was derived for the relation between the differential heat of adsorption on H and the fraction of the sorbent surface covered. Comparison between observed and calculated data for this relation shows satisfactory agreement and is interpreted to mean that the Brunauer-Emmett-Teller measured surfaces of these materials are homogeneous and completely available for H adsorption.

2027. ———. Research on Pure Iron and Synthetic Ammonia Catalyst by Means of Hydrogen Adsorption. Jour. Research Inst. Catalysis, vol. 1, 1949, pp. 100–109; Chem. Abs., vol. 44, 1950, p. 4304.

Adsorption isotherms of H at pressures between 10^{-4} and 1 mm. Hg on pure Fe and synthetic NH_3 catalyst were determined at 0°, 25°, 50°, and 100°. Differential heats of adsorption diminish continuously from 17.5 kg.-cal. per mol. at the lowest pressure to 5 kg.-cal. per mol. at the highest pressure. Calculations from the rate of decrease of the differential heat of adsorption yield surface areas 70 and 14 times, respectively, the Brunauer-Emmett-Teller area of Fe and synthetic NH_3 catalysts and are in contrast to results on Ni and Co powders. To account for these results it is assumed that 2 different types of crystal planes are involved in the adsorption, and a modified expression is derived for the variation of the heat of adsorption on this basis.

2028. ———. Adsorption of Carbon Dioxide on Reduced Nickel. Jour. Chem. Phys., vol. 18, 1950, pp. 1309–1310; Chem. Abs., vol. 45, 1951, p. 18.

Adsorption isotherms are derived for the adsorption of CO_2 as CO_2, $CO+O_2$, and $C+2$ O. Experimental evaluation was accomplished at 150° and 200°, with equilibrium pressures 0.001–0.1 mm. Hg. The differential heat of adsorption was almost constant at 22 kg.-cal. per mol. The experimental values for fraction of surface covered agreed best with the isotherms for complete dissociation. Experiments on *reduced* Co gave similar results.

KWANTES, A. *See* abs, **1739.**

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2029. LACHINOV, S. S. [Reduction of Iron Catalysts Used in the Synthesis of Ammonia. I. Investigation of the Reduction Process.] Jour. Appl. Chem. (U. S. S. R.), vol. 10, 1937, pp. 19–34 (in German, pp. 34–35); Chem. Abs., vol. 31, 1937, p. 4457.

"L–1" Fe catalyst is not completely reduced by the N–H mixture below 475°, though the reduction process may cease in the presence of O adsorbed by Fe. The velocity of reduction increases with the increase of temperature, according to the Arrhenius law $lnK=C-(A/RT)$, where K is the velocity constant, A is the change of the energy in calories, and C is an integration constant. The following formulas can be used for all practical purposes: (1) $yx^{0.22}=1{,}000$, at $p=100$ atm. and $Cv=15{,}000$ cal. and (2) $yx^{0.117}=805$, at $p=100$ atm. and $Cv=30{,}000$ cal., where y is temperature and x is time in hours; both formulas represent a parabolic relation between temperature and time. The velocity of the reduction of an Fe catalyst also increases with increase of the volume velocity of the stream of N–H mixture and can be represented for the "L–1" catalyst by a straight line at the velocity of 1,000–10,000, by a parabola at 10,000–25,000, and by a hyperbola at 25,000–90,000. The general equation for this catalyst at $p=100$ atm. and $t=375°$–500° is $(15.8x+y-11{,}522)(8.6\times10^{-8}\ x^{2.39}-y)\ (0.6x^2-196x+20{,}120-y)=0$, where x is the time of reduction in hours, and y is the volume velocity. The velocity of reduction increases first with increase of the pressure, but the increase of the pressure inhibits the reduction at the end of the process. 12 refs.

2030. LACHINOV, S. S., VVEDENSKII, A. A., AND TELEGIN, V. G. [Reduction of Iron Catalysts Used in the Synthesis of Ammonia. II. Influence of the Reduction Conditions on the Activity of the Catalyst.] Jour. Appl. Chem. (U. S. S. R.), vol. 10, 1937, pp. 435–455 (in German, p. 456); Chem. Abs., vol. 31, 1937, p. 7201.

High reduction temperature of the "GIVD–L–L" catalyst (containing: FeO, 21.90; Fe_2O_3, 71.48; K_2O, 1.90; Al_2O_3, 4.05; SiO_2, 0.10; MnO, 0.41; S, 0.03; and P, 0.01%) at constant pressure and volume velocity, has a negative influence on the activity of the catalyst. The volume velocity of the H_2–N_2 mixture has a positive influence on the activity of the catalyst. The pressure (within 1–300 atm.) has only slight negative influence upon the activity of the catalyst, which can be neutralized by corresponding increase of the volume velocity. A method of reduction of the catalyst was worked out, consisting of a stepwise increase of the temperature from 360°–500°, keeping the catalyst at 360°, 380°, 400°, 425°, 450°, 475°, and 500° for complete separation of H_2O at each temperature, and maintaining the highest possible partial pressure of H_2 and the best H_2O vapor condensation. Further investigation is required for improvement of the method.

2031. LACHINOV, S. S. [Reduction of Iron Catalysts Used in the Synthesis of Ammonia. III. Duration of the Complete Reduction of the Catalyst and Its Activity in Relation to Its Composition, the Regimen of Smelting and the Conditions of Reduction.] Jour. Appl. Chem. (U. S. S. R.), vol 10, 1937, pp. 1847–1866 (in French, pp. 1866–1867); Chem. Abs., vol. 32, 1938, p. 2298.

All conditions of reduction that lead to the accumulation of H_2O vapor in the gas phase above the catalyst increase the duration of reduction and lower the catalytic activity. The harmful action of H_2O vapor upon the activity of the catalyst is explained by the development of the oxidation-reduction processes, which caused the recrystallization of the contact surface. An increase of the volume velocity of gas mixture decreases the duration of the reduction and increases the activity of catalyst, but only to a certain limit, after which, a further increase of the volume velocity has no effect. The velocity of the reducing-gas stream at which H_2O vapor is removed as fast as formed permits reduction in the shortest time and produces the most active catalyst. An increase of temperature, all other conditions being equal, decreases the duration of complete reduction of catalyst and lowers its activity, but increase of the volume velocity of gas mixture decreases the harmful effect of increased temperature. An increase of pressure during the reduction lowers the activity, but an increase of the volume velocity decreases or completely neutralizes this effect. A slight increase of temperature and duration of smelting of the catalyst increases the duration of reduction. Oxidation of Fe under O_2 pressure with an admixture of activators yields a highly active and stable catalyst, in spite of the presence of 1.5% SiO_2. The Fe–Mo catalyst, prepared from a ferromolybdate by oxidation smelting with the K_2O–Al_2O_3 admixture, is not easily reduced, and has an average activity and high stability. Admixture of oxides of Cu or Ni to this catalyst decreases its activity. 40 refs.

2032. ———. [Conference on Heterogeneous Catalysis. Moscow, May 13–16, 1940. Analysis of the

Process of Reduction of Ammonia Catalysts.] Jour. Phys. Chem. (U. S. S. R.), vol. 14, 1940, pp. 1260–1270; Chem. Abs., vol. 35, 1941, p. 3882.

Various data on the reduction of Fe_2O_3, Fe_3O_4 with 2–5% K_2O and Al_2O_3 at temperatures up to 500° and pressures up to 300 atm. are discussed. The reduction of an activated catalyst proceeds 5–6 times as fast; the activators aid in the formation and stabilization of the active centers. The reduction takes place in an induction, an autocatalytic and a residual-reduction period.

2033. LACHINOV, S. S., AND TELEGIN, V. G. [Activity and Stability of Iron Catalysts for the Synthesis of Ammonia.] Jour. Chem. Ind. (U. S. S. R.), No. 12, 1934, pp. 31–33; Chem. Abs., vol. 29, 1935, p. 2311.

Al_2O_3, MgO, and SiO_2 activate Fe catalysts but do not make them stable. K_2O renders them stable but gives decreased activity. K_2O and SiO_2 together form a good activator, but the catalyst is quite unstable. K_2O and Al_2O_3 or MgO and SiO_2 give a very stable catalyst. Mechanisms of activation are discussed .

2034. LACHINOV, S. S., AND TELEGIN, V. G. [Iron Catalysts for the Synthesis of Ammonia.] Jour. Chem. Ind. (U. S. S. R.), No. 5, 1934, pp. 30–32; Chem. Abs., vol. 28, 1934, p. 5605.

Addition of about 10% K_2O to Fe_3O_4 lowers the activity of this catalyst, though small amounts of both K_2O and MgO increase the activity. These effects are due to the alkalinity of the added compounds, which causes more rapid desorption of the NH_3. Catalysts containing K_2O are easily decomposed by air. Addition of K_2O and Al_2O_3 increases the stability of the catalyst toward heat.

LACHINOV, S. S., VVEDENSKII, A. A., AND TELEGIN, V. G. [Reduction of Iron Catalysts Used in the Synthesis of Ammonia. II. Influence of the Reduction Conditions on the Activity of the Catalyst.] *See* abs. **2030.**

2035. LACY, B. S., DUNNING, R. G., AND STORCH, H. H. Equilibrium in the Synthesis and Decomposition of Methanol. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 926–938; Chem. Abs., vol. 24, 1930, p. 2943.

Average equilibrium constants for the reaction $2H_2+CO=CH_3OH$, measured at 300° and 250° from both sides, and at 200° from the synthesis side, all at 50 atm. pressure, were 1.9×10^{-4}, 1.25×10^{-3} and 3×10^{-2}, respectively, and 1.8×10^{-3} at 250° and 20 atm. from the synthesis side. Similar constants were found by calculations, using the reactions of HCOOMe and H_2 and of MeOH and CO. (See abs. **560, 2448,** and **3209.**)

2036. LAHIRI, A. Synthetic Oil From Coal. I. Jour. Sci. Ind. Research (India), vol. 7A, 1948, pp. 357–361; British Abs., 1949, B, I, p. 29.

Describes production of synthetic oil and gasoline from coal by various hydrogenation processes.

2037. ———. Synthetic Oil From Coal. II. Fischer-Tropsch Process. Jour. Sci. Ind. Research (India), vol. 7, A, 1948, pp. 406–411; British Abs., 1949, B, I, p. 233.

Reviews development of the process and discusses inherent advantages and difficulties. Analyzes recent developments, which have been concentrated on the problem of heat transfer. Catalysts are now introduced at a constant rate in the fluidized condition and plants contain internal heat exchangers. Heat of reaction is removed by evaporating oil introduced with the synthesis gas. The gasification of coal and coke by the Bubiag-Didier, the Thyssen-Galocsy, and the Pintsch–Hillebrand processes are summarized.

2038. ———. Synthetic Oil From Coal. III. Economics of Synthetic Oil Manufacture. Jour. Sci. Ind. Research (India), vol. 7, A, 1948, pp. 442–446; British Abs., 1949, B, I, p. 336.

Discusses in detail products and economics of the hydrogenation and Fischer-Tropsch processes for the manufacture of petroleum from coal; it is stressed that the 2 processes are complementary. Reviews present position regarding raw materials in India, with particular reference to the quality of coal, and considers the economic prospects of the 2 processes.

———. *See* abs. **1771a.**

2039. LAHIRI, D. Liquid Fuels From Water Gas. Sci. and Culture, vol. 3, 1938, pp. 670–673; Chem. Zentralb, 1938, II, p. 1521.

Special attention is paid to synthesis by Fischer-Tropsch process.

2040. LAHUERTA, P. [Literature Referring to Fischer-Tropsch Synthesis.] Combustibles (Zaragoza), vol. 6, September–December 1946, pp. 126–134.

2041. LAIDLER, D. S., AND TAYLOR, J. Study of the Carburization Process With Special Reference to Gas Carburizing. Reduction of the Carbon Dioxide Content of Town Gas. Jour. Iron Steel Inst. (London), vol. 165, 1950, pp. 23–39; Chem. Abs., vol. 44, 1950, p. 9890.

Carburization process with town gas as the carburizing medium has been developed. In purified town gas or in CO, all the atomic C formed at the surface is absorbed into the steel. The rate of diffusion of C in the steel and the rate of graphite formation are the rate-controlling reactions. With town gas containing O_2, moisture, and CO_2 there are 3 important differences: Soot forms at the surface at the expense of atomic C. The soot so deposited restricts further carburization. Formation of graphite from atomic C is rapid and is no longer the rate-controlling reaction. In a gas containing 2.6% CO_2, 0.8% O_2, 2.6% C_n H_m, 24.7% CH_4, 48.3% H_2, and 12.3% N_2, the O_2 and CO_2 contents are decreased by passing the gas over a baryta catalyst. 16 refs.

LAIDLER, K. J. *See* abs. **3180.**

LAMBERT, G. I. *See* abs. **3591.**

2042. LAMBRIS, G. [Deposition of Carbon in the Electrolysis of Nickel From Solutions.] Ztschr. Electrochem, vol. 15, 1909, pp. 973–981; Chem. Abs., vol. 4, 1910, p. 866.

Previous work upon the electrolytic deposition of C is reviewed and the author's experiments are described in detail. Various C-containing baths of Ni were used and the deposited Ni and gases analyzed. The gases in 1 of the experiments were: CO_2, 6%; hydrocarbons (heavy), 1.2%; hydrocarbons (light), 2.6%; air, 4.8%; H_2, 89.9%; total 99.1%. These values are about the same for several experiments. It is shown that the colloidal theory for the deposition of C does not hold good and that C_2H_2 plays a large part in the deposition. The conclusions given are: (1) The absorption of C by the Ni is entirely due to a gas reaction. (2) The gases that will introduce C into the Ni are CO, CO_2, and C_2H_2. Gases reduced beyond C_2H_2 do not introduce any. (3) Oxalic acid is partly reduced to C_2H_2 upon Pt and Ni, but not when Cu, Fe, or Sn cathodes are used. Therefore C_2H_2 is the only carrier of C to metals in electrolysis. (4) The C in electrolytic Ni is present in the form of carbide.

2043. LAMECK, P., AND NIERHAUS, H. [Utilization of Coal.] Stahl u. Eisen, vol. 57, 1937, pp. 1041–1048, 1074–1079; British Chem. Abs. 1937, B, p. 1152.

Discussion of the progress since 1934 in coal preparation, coking, carbonization, hydrogenation, gas purification and utilization, benzine synthesis, etc.

2044. LAMECK, P., AND SCHEER, W. [Coal Improvement—Fischer-Tropsch Process.] Stahl u. Eisen, vol. 61, 1941, pp. 63–66, 86–90, 109–112; Chem. Zentralb. I, 1941, p. 3029.

Report for 1937–39 on statistics on coking, briquetting, gas purification, high-pressure hydrogenation, Fischer-Tropsch, gasification, and low-temperature carbonization.

2045. LAMME, N. [Synthesis of Hydrocarbons According to Fischer-Tropsch.] Thesis, Tech. High School, Delft, Holland, Feb. 20, 1946, 207 pp. (in Dutch); Chim. et ind., vol. 56, 1946, pp. 213–214.

2 catalysts were utilized by the author in his investigations; the Raney skeleton catalyst of Ni–Co and the precipitated Co–ThO_2–kieselguhr catalyst of Fischer. In the synthesis, at atmospheric pressure, the best results were obtained by first reducing the catalyst and then heating it in an atmosphere of CO. The catalyst in any case does not become active until after 5–10 days use, then it maintains its activity for 30–50 days. The yield of product is about 50%; the ratio of oil to gasoline is about 1:1, depending upon the synthesis temperature. The catalyst is regenerated by means of H_2. ⅓ of the reaction gas mixture is transferred into liquid and solid hydrocarbons, ⅓ into gaseous hydrocarbons, and the remainder is not converted. At a higher temperature, a higher transformation takes place but in the form of gaseous hydrocarbons. Under 10 atm. pressure and with the Co–ThO_2–kieselguhr catalyst the average molecular weight of the hydrocarbons formed is the same as that of the hydrocarbons obtained at atmospheric pressure. The synthesis of CH_4 also is increased, and larger amounts of CH_4 and CO are found in the residual gases. In the reduction of CO_2 by H_2 it is found that CO acts as a catalyst poison. The hydrocarbons formed are mostly C_5 and C_6, their amount diminishing as the molecular weight increases; for a hydrocarbon of definite molecular weight, an increase in quantity keeps pace with the diminution in saturation. There is no formation of cyclic compounds in the Fischer-Tropsch process.

2046. LAMP. Synthetic Gasoline. Vol. 29, No. 2, March 1947, pp. 7–11.

Development and present status of the synthesis process for producing gasoline from gas are discussed with special emphasis on the so-called fluid catalyst process of the Standard Oil Development Co. The reduction in the number of reactors for a 10,000-bbl.-per-day plant from 128 in the Fischer-Tropsch process to 4 in the fluid process is considered one of the outstanding achievements in its development. Even so, the heavy initial investment involved and the rigid location requirements will inevitably limit the number of commercially feasible synthesis plants. The commercially available potential reserve of synthetic gasoline from sources other than natural gas, such as coal, tar sands, and oil shales, is pointed out also. Whereas production of synthetic gasoline from these sources is not at present attractive commercially, it will become more competitive as research continues. The quantities of gasoline that could be brought into commercial production from each of the above sources would, of course, depend upon the service station price range per gal. For instance, a price of up to $0.26 would make marketable 300 billion bbl. from coal and 1 billion from tar sands; $0.26–$0.31, 18 billion bbl. from oil shales, 3,500 billion from coal, and 2 billion from tar sands; $0.31–$0.36, 38 billion bbl. from oil shales, and 2 billion from tar sands; and over $0.36, 45 billion bbl. from oil shales.

2047. LANDA, S. Synthetic Fuel in Europe. Petrol. Eng., Refining Gas Processing sec., vol. 21, No. 11, October 1949, p. A–58.

Abstract of a paper presented at United Nations Resources Conference. Review of synthetic-fuel production in Europe, with particular reference to the methods developed in Germany and other central European countries by hydrogenation and synthesis. Discusses factors influencing the economic operation of synthetic fuel plants, and estimates capital requirements and operating costs. Prospects for further development of the industry are considered excellent.

2048. ———. Possibilities and Costs of Synthetic Fuels. Petrol. Eng., vol. 22, January 1950, pp. A53–54, 56.

There are 2 general methods of obtaining synthetic fuels, pressure hydrogenation and complete synthesis from CO and H_2. Coal is given chief consideration for production of synthetic liquid fuels. Several factors influence production costs in producing synthetic fuels, such as the complicated installations, high labor cost, and the preparation of synthesis gas and hydrogen. It is possible, however, to effect economics in operation. Automatic devices have already been introduced, which not only reduce labor costs but insure more efficient operation as well.

2049. LANDER, C. H. Recent Developments in the Science of Coal Utilization. Mech. Eng., vol. 49, 1927, pp. 1–11; Chem. Abs., vol. 21, 1927, p. 811.

Results obtained during the past few years from the scientific researches on coal are reviewed and discussed in relation to their engineering problems and practical applications. Among the subjects treated are: The constitution of coal; low-temperature carbonization; low-temperature coke and tar; metallurgical coke; synthetic fuels from CO and H_2 by the Patart and Fischer-Tropsch processes; hydrogenation of coal; and furnace design.

2050. ———. Treatment of Coal to Produce Liquid Fuels. Bull. Liverpool Eng. Soc., vol. 6, No. 6, 1933, pp. 17–22.

Discusses low-temperature carbonization, direct hydrogenation of coal with flowsheet, and hydrogenation of CO.

2051. ———. Hydrogenation—Review of Early Difficulties. Proc. South Wales Inst. Eng., vol. 53, 1938, pp. 424–447; Chem. Abs., vol. 32, 1938, p. 6833.

11th Menelaus Memorial lecture.

2052. LANDGRAF, —. [Influence of an Increased Rate of Flow on the Olefin Content of Synthetic Gasoline.] FIAT Reel K 29, Frames, 7,172–7,183, 1938, PB 70,218.

Tests establish that an increase in the rate of flow causes a reduction of the olefin content of the gasoline produced and increases the exhaustion of catalysts. The olefin content of the oil produced is not influenced to a noticeable degree. 3 graphs, 1 picture, 2 tables.

2053. LANE, J. C. Fischer-Tropsch Potentialities of Public Utility Gas Companies. Gulf Research & Development Co., Chemistry Division Rept. 259, 1944.

Evaluation of public-utility gas companies of the United States with regard to their potentialities as manufacturers of synthine products. Only 8 of the 118 companies considered appear very likely to enter the field of synthetic liquid fuels.

2054. LANE, J. C., AND WEIL, B. H. Synthine Process. I. Introduction, Synthesis-Gas Production and Purification. Petrol. Refiner, vol. 25, 1946, pp. 355–366; Chem. Abs., vol. 42, 1948, p. 9118.

History and nomenclature of the Synthine (Fischer-Tropsch) process are traced. The ratio of H_2:CO in this process ranges 2:1–<1:1. The important methods for producing the water-gas mixtures are (1) standard manufacture from coke, (2) manufacture from low-volatile coal, (3) manufacture from coal or coke by using O_2 in the steam blast, and (4) conversion

of coke-oven gas with steam, either catalytically or noncatalytically. These methods, with some less conventional methods, are discussed in detail. Underground gasification of coal by (1) the chamber, (2) the stream, and (3) the percolation methods is discussed in some detail. Synthesis gas can be obtained also by means of the reaction: $CH_4+H_2O\rightarrow 3H_2+CO$ or $CH_4+CO_2\rightarrow 2CO+2H_2$. Yields, catalysts, and manufacturing procedures are given for these two reactions. Controlled oxidation of CH_4 to give H_2 and CO also is economical, and catalysts and reaction conditions are discussed. Regardless of its source, synthesis gas must be purified of S and its compounds. The H_2S is removed first by ethanolamine, ferric oxide, or other methods, and then the organic S compounds are catalytically oxidized and removed. Patents and processes for this purpose are reviewed.

2055. ———. Synthine Process. II. Catalytic Synthesis, Including Catalysts and Reaction Mechanisms. Petrol. Refiner, vol. 25, 1946, pp. 423–434; Chem. Abs., vol. 42, 1948, p. 9118.

Two main reactions take place in the synthine process, the predominant one depending chiefly on the ratio of H_2: CO and the type of catalyst used: (1) $n\mathrm{CO}+(2n+1)\mathrm{H_2}\rightarrow \mathrm{C}_n\mathrm{H}_{2n\pm 2}+n\mathrm{H_2O}$; (2) $n\mathrm{CO}+2n\mathrm{H_2}\rightarrow \mathrm{C}_n\mathrm{H}_{2n}+n\mathrm{H_2O}$. Since the reaction is exothermic and involves a reduction in volume, relatively low temperatures and elevated pressures favor the reaction. Temperatures range from 375° with Ni or Co catalysts to 465° with Fe catalysts, and pressures vary from atmospheric pressure to 150 p. s. i. The synthesis gas is passed through reaction chambers in 1 or more stages, with or without recycle of the unconverted portion. The heavier products are condensed from the residual gas, and the lighter products are adsorbed on charcoal or in oil. Most theories of the reaction mechanism stipulate the intermediate formation of carbides of the catalyst metals. By hydrogenation of these unstable carbides, CH_2 groups are produced, but there are various theories as to the method of producing them. Both polymerization and hydrogenation then occur to produce hydrocarbons of higher molecular weight. Catalysts consist of Fe and Co alone, or in mixtures with Ni. They are supported on an inert carrier (kieselguhr), or used as all alloy-skeleton type catalysts, or fluid catalysts. The German commercial operation is described. The various modifications in the process that will produce branched-chain hydrocarbons, alcohols, aromatic hydrocarbons, or CH_4 are all discussed in detail.

2056. ———. Synthine Process. III. Products, Byproducts, and Special Topics. Petrol. Refiner, vol. 25, 1946, pp. 493–504; Chem. Abs., vol. 42, 1948, p. 9119.

Primary products are almost entirely straight-chain paraffinic and monoölefinic hydrocarbons. Aromatic compounds and naphthenes are present in only negligible amounts. The yield of oxygenated compounds ranges from almost zero to several %. The hydrocarbons produced range from CH_4 to hard waxes. CH_4 yield is 10–15%. Medium pressure (150 p. s. i.) yields liquefied petroleum gases, 7; gasoline, 38; diesel oil, 30; and wax, 25%. None of the processes gives any oils with lubricant properties. Light products are recovered by adsorption on charcoal or absorption in oil. Residual gas consists of: CH_4, 30.9; H_2, 18.0; CO, 10.5; CO_2, 20.3; N_2, 18.5; and C_2H_4–C_2H_6, 1.6%. The heating value of this gas is about 395–425 B. t. u. per cu. ft. and is mostly burned as fuel. The C_3–C_4 fraction is used in the synthesis of polymer or alkylate gasolines, synthetic alcohols by sulfonation and hydrolysis, or is burned as fuel. Since gasoline from the Synthine process is low in octane number owing to its straight-chain paraffinic structure, it is upgraded by cracking before use. Diesel-oil fractions have a very high cetane number, but are improved by mixing with petroleum oils. Some of this fraction was used for Mersolate detergents. The paraffin waxes, consisting of a mixture of normal and isoparaffins with no cyclic hydrocarbons, were separated into soft, slab, and hard paraffins by distillation, pressing, and sweating. Lubricants have been made by polymerization of the olefins, alkylation, and condensation. Fatty acids are produced by oxidation of paraffin waxes, and esterification with glycerol gives some edible fats. Heavy synthine oils were sulfochlorinated and saponified to give detergents. Greases were made from oxidized paraffin waxes. Treatment of the Synthine olefins with H_2 and CO gives alcohols and aldehydes, and a small amount occurs as byproducts directly from the process. Miscellaneous chemicals produced in small quantity as byproducts are listed.

2057. ———. Synthine Process. IV. Basic Economics and the Current Situation. Petrol. Refiner, vol. 25, 1946, pp. 587–598; Chem. Abs., vol. 42, 1948, p. 9119.

Discusses economics of the process. It is predicted that the total investment cost for producing gasoline by the Synthine process with coal as the source of gas eventually will be $2,500/bbl./day. Steel requirements are high, and a plant could not be erected speedily in an emergency. With natural gas for the process, it cannot at present compete with refinery methods utilizing crude petroleum. Byproducts will help balance costs, however. A list of companies and organizations and their current situation in the Synthine process field is given. 360 refs.

LANG, A. *See* abs. **2773.**

2058. LANG, W. A. Research in the Coal Industry in Canada. Canadian Min. and Met. Bull. 406; Trans. Canadian Inst. Min and Met., vol. 49, 1946, pp. 51–62.

3 methods are available for converting coal into oil: The Fischer-Tropsch synthesis from water gas; the Bergius direct coal hydrogenation; and the carbonization of coal followed by hydrogenation of the tars and light oils. The first process has become competitive with gasoline from petroleum when based on the utilization of natural gas as the raw material. It is thought, however, that the ultimate source of synthesis gas will be the lower-rank coals or a char produced from them. The use of efficient, continuous water-gas producers, made possible by the use of O_2 instead of air, would be a necessary development. The production of gasoline by direct hydrogenation of coal does not appear as hopeful of success as does the Fischer-Tropsch process because of the very high capital costs owing to the high temperatures and pressures used. Recent modifications, such as the extraction-hydrogenation processes of Pott-Broche and Uhde, which allow the use of lower pressures in the initial stages, may change this outlook. It also appears that partial hydrogenation of coal for the production of crude fuel oils and tar acids and for high-heat-value gas may do much toward solving the economic problem by lowering the costs of production materially. The amount of tar acids produced by this method is roughly 10 times the amount produced by carbonization. Much fundamental research is necessary on the reactions of coal hydrogenation. The production of coking coals from non-coking coals, and the production of CH_4, MeOH, etc. are also visualized as possible developments.

2059. LANGE, H., AND MATHIEU, K. [Progress of Austenite Transformation in the Undercooled State of Iron–Nickel–Carbon Alloys.] Mitt. Kaiser-Wilhelm-Inst. Eisenforsch Düsseldorf, vol. 20, 1938, pp. 125–134; 239–246; Chem. Abs., vol. 32, 1938, p. 7878.

Use of the thermomagnetic method in the study of steels is described. Explains magnetic balance.

2060. LANGER, A., AND FOX, R. E. Mass-Spectrometer Analysis of Some Oxygen-Containing Compounds. Anal. Chem., vol. 21, No. 9, 1949, pp. 1032–1035.

In an attempt to analyze some oxygenated compounds by means of the mass spectrometer, using the same procedures as in the analysis of gaseous and liquid hydrocarbons, several difficulties were encountered. Extremely long evacuation times were necessary to remove some compounds from the tube, and, even more serious, large variations in peak heights occurring in successive scanning of the sample indicated that the instrument was unable to maintain calibration. Some of these difficulties were partly overcome by using a heated tube and a new trap design. Results obtained with mixtures of MeOH, formic acid, methyl formate, and methylal are included. In general, the results do not attain the precision and reproductibility of hydrocarbon analyses.

LANGER, C. *See* abs. **2306.**

LANGHEIM, R. *See* abs. **1949, 1955.**

LANGLEY, W. D. *See* abs. **1488.**

LANIN, V. A. *See* abs. **1789.**

2061. LANNING, H. J., AND CLARK, G. C. Manufacture of Fatty Acids by Oxidation of Paraffins, Hydrogenation of the Fatty Acids at I. G. Farbinindustrie A.-G., Ludwigshafen-Oppau. BIOS Final Rept. 748, September 1946, 21 pp., PB 47,720.

As raw material for the production of fatty acids, synthetic paraffins obtained from hydrogenation of CO or from low-temperature carbonization of lignite were used. The average melting point of the paraffins is 30°–50° and the average chain length C_{18}–C_{30}. Oxidation was carried out with potassium permanganate. Production and labor costs and yields are given; also flowsheets.

LAPSHIN, S. I. *See* abs. **3763, 3764, 3766.**

2062. LARIN, A. Y. [Cracking of Heavy Petroleum Stocks Over Heated Surfaces.] Bull. acad. sci. U. R. S. S., classe sci. tech. 1944, pp. 42–47; U. O. P. Co. Survey Foreign Petroleum Literature, Transl. 495; Nat. Petrol. News, vol. 38, No. 14, pp. R 286, R 288–289, 1946.

Heavy paraffin hydrocarbons obtained from CO and H_2 (Kogasin) are known to decompose under the action of a heated wire spiral immersed in them, forming a gas abundant in olefins. This method was used in cracking heavy-oil distillates containing paraffins, also naphthenes and aromatics, as well as heavy resinous substances. A gas was produced of a composition approximately identical with that obtained from paraffin wax. However, the yields of gas per unit energy consumed are lower, when the charge is richer in compounds with a low H content. An oil distillate consisting essentially of naphthenes gives a yield of gas per kw.-hr. that is half that obtainable from paraffin wax, whereas 1 containing up to 21% aromatics gives about ¼ as much. From fuel oils the yields of gas are still lower and fluctuate greatly depending upon the contents of resins and carboids in the charge.

2063. LARSON, A. T. Ammonia and Methanol Catalysts. Trans. Electrochem. Soc., vol. 71, 1937, pp. 346–351; Chem. Abs., vol. 31, 1937, p. 3644.

MeOH catalysts are reactive at appreciably lower temperatures than NH_3 catalysts. One of the earliest commercial catalysts for NH_3 was Fe to which was added a small % of a promoter such as oxides of the alkaline earths. Generally speaking, most MeOH catalysts have operating temperatures 350°–400°. NH_3 is the only product of the interaction of N_2 with H_2, but the products of the interaction of CO and H_2 are numerous, often depending upon the catalyst used. Thus, for example, a mixture of ZnO and Al_2O_3 as catalyst will produce Me_2O, and a mixture of ZnO and Cr_2O_3 will confine the product to MeOH over a wide range of temperature. S has a serious, poisonous effect on the Fe catalysts for NH_3, but has no effect on the ZnO–CR_2O_3 catalyst for MeOH.

2064. LARSON, A. T., AND BROOKS, A. P. Ammonia Catalysts. Ind. Eng. Chem., vol. 18, 1926, pp. 1305–1307; Chem. Abs., vol. 21, 1927, p. 802.

Fe, Co, Ni, W, and Mo have been studied in the temperature range 450°–550° as NH_3 synthesis catalysts. Ni and Co were found inactive; at 550° W and Mo were the most active, and at 450° Fe and a mixture of Fe and Mo. The studies with Fe included a study of the promoter action of 16 difficultly reducible oxides added singly to the Fe. Only 5 of these oxides of Al, Si, Zr, Tl, and Cl, had any promoter action under the conditions used. Mixing these oxides showed that when the oxides are closely related chemically, the combined effect is about the same as that given by each constituent. If the oxides differ considerably in their basic or acidic properties, the promoter action of the mixture is greater than that of either constituent alone. Promoters of mixtures of potash-alumina, potash-silica, and potash-zircon produced very active Fe catalysts.

2065. LASHAKOV, L. M. [Calculation of the Equilibrium $2H_2+CO=CH_3OH$.] Acta Physiochim, U. R. S. S., vol. 11, 1939, pp. 849–860; Chem. Abs., vol. 34, 1940, p. 4648.

By means of the constants of the Beattie-Bridgeman equation of state, the specific volumes and fugacities of the $2H_2+CO \rightleftharpoons CH_3OH$ system are calculated at temperatures from 250°–350° and pressures from 100–200 atm. By a graphical method, from the Newton-Dodge equation (abs. **2457**) the equilibrium concentrations of CH_3OH are found to be much lower than those obtained on the basis of the ideal gas laws; the values agree well with the experimental data of Newitt, Byrne, and Strong (abs. **2448**) and of Wettberg and Dodge (abs. **3583**).

2066. LATEGAN, P. N. Possibilities of Establishing a Coal-Oil Industry in South Africa. Jour. South African Inst. Eng., vol. 29, 1930, pp. 23–28; Chem. Abs., vol. 26, 1932, p. 1416.

Outline of the Fischer and the Bergius processes. Experiments have shown that South African coals will yield 120–150 gal. of petrol per ton.

2067. ———. Oil From Coal. South African Min. and Eng. Jour., vol. 51, 1940, pp. 625–627; Coke Smokeless-Fuel Age, vol. 2, 1940, pp. 258–259; Chem. Abs., vol. 34, 1940, p. 8218.

In the Fischer-Tropsch process, the yield of gasoline is 1 ton per 5–6 tons of coal processed; the economic unit is much smaller than for hydrogenation, but the thermal efficiency is about ½ that of the hydrogenation process. It is believed that relative costs of production would be about the same in South Africa as in Great Britain, cheaper raw material and labor being offset by higher capital cost. Construction of the smallest economic units in South Africa is recommended to gain data and experience. The Fischer process would involve the lower capital expenditure. Its synthesis gas forms the basis of other chemical industries. Coal mined in conjunction with torbanite is very suitable for the production of synthesis gas.

2068. ———. Production and Distribution of Petrol From Coal and From Imported Crude Petroleum. Jour. Chem. Met. Min. Soc. South Africa, vol. 51, 1951, pp. 297–318; Coke and Gas, vol. 13, 1951, pp. 385–390.

Comparison of the production costs of synthesis gas for the Fischer-Tropsch process by the Koppers suspension method, the Winkler fluidized bed method, and the Lurgi fixed bed method shows that the costs per

1,000 cu. ft. are respectively 15.33 d., 16.74 d., and 18.40 d. (the latter after allowing credit of 3 d. for byproducts). It is found that gasification costs represents 60–70% of the total cost of synthesis gasoline. Capital costs for these 3 types of plants in South Africa capable of producing 300 million cu. ft. of gas per day are, respectively, £8 million, £5.6 million, and £15.3 million, not including £3 million for an O_2 plant. There are 3 methods for carying out the synthesis reaction: The fixed-bed system, the liquid-medium system, and the fluidized system. The total estimated cost for a complete oil-from-coal plant including a Koppers gasification, an O_2 plant, and a synthesis plant of 100 million gal. annual capacity will be £27 million or 1 s. 5 d. per gal. The estimated costs of gasoline from imported crude refined in a Rand refinery of 100 million gal. annual capacity costing £11,500,000, including the cost of a pipe line from the coast to the refinery, is 10.5 d. per gal. Allowing a return of 10% on the total capital investment the selling price amounts to 1 s. 1.25 d. per gal., compared with 1 s. 11.5 d. for synthetic gasoline and 1 s. 10.75 d. for imported gasoline. Refinery gasoline is therefore 10.25 d. cheaper than synthetic gasoline and 9.5 d. cheaper than imported refined gasoline.

2069. LATTA, J. E., AND WALKER, S. W. Commercial Application of Hydrocarbon Synthesis in the United States. Chem. Eng. Progress, vol. 44, No. 2, 1948, pp. 173–176; British Abs., 1948, B I, p. 279.

Some of the problems encountered in the commercial development of the hydrocarbon synthesis are discussed, and a general summary of the lines along which process design and engineering on the proposed plants at Hugoton and Brownsville are proceeding is presented. Pilot-plant operation has disclosed the best reaction system and the knowledge obtained will be applied to the commercial operation of the enlarged plants, although much research work will still be required to determine the operability of the fluid Fe catalyst process and to resolve the many reaction variables involved in the changeover to large-scale operation.

LAUGHREY, P. W. *See* abs. **3311.**

LAUNER, P. J. *See* abs. **420a.**

2070. LAUPICHLER, F. G. Manufacturing Costs of Gases for Ammonia Synthesis. Gas World, vol. 105, 1936, pp. 71–75; British Chem. Abs., 1936, B, p. 883.

Economics of the water-gas shift reaction are discussed.

2071. ———. Catalytic Water-Gas Reaction—Mass Transfer and Catalyst Activity. Ind. Eng. Chem., vol. 30, 1938, pp. 578–586; British Chem. Abs. vol. 32, 1938, p. 4866.

Equations are derived for mass transfer and reaction velocity in the catalytic water-gas reaction at constant temperature, which permit calculation of conversion rate for any given amount of catalyst, or the amount of catalyst required to obtain a given conversion. The equations are then extended to include the effect of gradually increasing temperature as found in commercial processes. The heterogeneous velocity coefficient obtained may be used to compare the activities of different catalysts. The effect of varying the initial temperature, steam : CO ratio, and flow rate were determined. The equations gave calculated values in good agreement with experimental determinations and are useful in determining the optimum conditions for operating catalytic converters.

LAUSCHKE, G. *See* abs. **2928.**

LAWTON, G. *See* abs. **328.**

LAYMANN, A. *See* abs. **3060, 3062.**

2072. LAZIER, W. A. Hydrogenation of Carbon Oxides. 12th Rept., Committee on Catalysis, Nat. Research Council, 1940, pp. 120–130; Chem. Abs., vol. 34, 1940, p. 4968.

Review (83 references) discusses the synthesis of HCHO, MeOH, CH_4, and Kogasin from CO and H_2 and includes a list of recommended catalysts for the last named reaction.

2073. LAZIER, W. A., AND ADKINS, H. Adsorption of Ethylene and Hydrogen by Zinc Oxide, Iron Oxide, Nickel and Copper. Jour. Phys. Chem., vol. 30, 1926, pp. 353–358; Chem. Abs., vol. 20, 1926, p 1545.

Measurements of the adsorption of H_2 and C_2H_4 at 22° and 74 mm. by catalysts were made in the usual constant-pressure adsorption apparatus. The catalysts were Cu, Ni, Fe_2O_3, and ZnO, made by several different methods. The volume of the gas adsorbed was measured by reference to the volume of N_2 required to fill the adsorption apparatus under comparable conditions. The catalytic activity of the catalysts was determined by measuring the decrease in gas volume after exposing the catalyst to equimolecular mixtures of H_2 and C_2H_4. The results of the adsorption and catalytic activity measurements indicate that there is a qualitative agreement between the 2 manifestations of chemical activity, but there is apparently no quantitative relationship between total adsorption and catalytic activity.

LEACH, J. R. *See* abs. **654a.**

LECKY, J. *See* abs. **53b.**

2073a. LECKY, J. A., HALL, W. K., AND ANDERSON, R. B. Adsorption of Water and Methanol on Coal. Nature, vol. 168, 1951, pp. 124–125; Chem. Abs., vol. 46, 1952, p. 11,630.

Results do not agree with a feature of the Ellis's theory of the structure of coal. The true surface area of coal is probably not measured by adsorption of MeOH and H_2O, since these polar compounds are not physically adsorbed in the usual sense, and hence are not amenable to the Brunauer-Emmett-Teller treatment for derivation of surface area.

2074. LE CLERC, G. [Catalytic Activity of Cubic Ferric Oxide in Synthesis of Hydrocarbons by Hydrogenation of Carbon Monoxide at Atmospheric Pressure.] Compt. rend., vol. 207, 1938, pp. 1099–1101; Chem. Abs., vol. 33, 1939, p. 1201.

Under normal conditions the limiting solid solution of K ferrite (formed by mixing K_2CO_3 and $Fe(OH)_3$), catalyzes the mixture $CO+2H_2$, yielding 45 gm. per $m.^3$ of hydrocarbons solid or liquid at 15°. If the catalyst is prepared by adsorbing the K_2CO_3 by the $Fe(OH)_3$ the yield is raised to 80 gm. per $m.^3$. The carbonates of Li, Na, Rb, or Cs give under similar circumstances the same yield and the same thermomagnetic curve. The solid solutions of ferrite in cubic Fe_2O_3 further show, in addition to the Curie point at 575° (that of magnetite), one at 250°. The conclusion that the active substance is the cubic Fe_2O_3 is confirmed by the alteration in yield if the cubic Fe_2O_3 is destroyed by heating above 500°. Thus, the action of the alkaline addition is to stabilize the cubic Fe_2O_3; the optimum temperature for such a catalysis is that of the second Curie point (250°)

———. *See* abs. **2080, 2081, 2276.**

2075. LE CLERC, G., AND LEFEBVRE, H. [Comparison of Catalytic Activity of Allotropic Varieties of Nickel.] Compt. rend., vol. 208, 1939, pp. 1650–1651; Chem. Abs., vol. 33, 1939, p. 5732.

Reduced Ni gradually loses catalytic power when the mixture $CO+2H_2$ is passed over it at 175°, but this is recovered on heating the Ni to 250° in a vacuum or in N_2. A similar loss of catalytic power is shown in the hydrogenation of C_6H_6 to C_6H_{12} or of Me_2CO to Me_2CHOH. This loss of power is accompanied by transformation of the Ni from the ferromagnetic cubic

to the nonmagnetic hexagonal form. No such loss of catalytic or magnetic power is shown in the similar transformation of Co; the change in Ni would, therefore, appear to be connected with a change in its electronic structure.

2076. Le Clerc, G., and Michel, A. [Mineral Chemistry—Preparation and Properties of the Hexagonal Form of Nickel.] Compt. rend., vol. 208, 1939, pp. 1583–1585; Chem. Abs., vol. 33, 1939, p. 5252.

Cubic Ni (I) heated at 170° for several days in CO is converted into the nonmagnetic variety (II). Thermomagnetic analysis of (II) shows a sudden appearance of magnetization at 250° with Curie point at 358°, and on cooling a further increase is shown. X-rays show (II) to be hexagonal with a=2.65 Å., c=4.32 (abs. **340**), and the recovery of magnetization to be accompanied by reversion to the cubic form (I). This change is accompanied by a linear contraction of 5.4% (compared with 5.6% calculated.)

2077. Ledebur, A. Modification of Carbon in Iron. Jour. Iron Steel Inst. (London), vol. 44, II, 1893, pp. 53–76.

2078. Ledoux, E. Avoiding Destructive Velocity Through Absorbent Beds. Chem. Eng., vol. 55, No. 3, 1948, pp. 118–119; Chem. Abs., vol. 42, 1948, p. 3221.

Dimensionless expression is derived for the maximum safe mass velocity of the gas, G which will not cause motion of the adsorbent bed, with attendant reduction in size owing to abrasion. The equation given is $G_2=0.0167\ Dgd_gd_a$, where D is diameter of average particle, g is acceleration of gravity, d_g is density of the gas, and d_a is apparent density of the adsorbent bed. The constant, 0.0167, was determined from industrial experience.

2079. Lee, J. A. Esso's Fluid Catalyst Modifies Fischer–Tropsch. Chem. Eng., vol. 54, No. 10, 1947, pp. 105–107.

This paper describes certain of the modifications that are being made in the Fischer-Tropsch process by the Standard Oil Development Co. in the pilot plants at Baton Rouge. Natural gas is being processed to form liquid fuels and chemicals through use of the fluid cataylst. Results thus far have demonstrated satisfactorily the use of the fluid catalyst technique. It is found to be an excellent tool for securing uniform temperatures and high rates of heat transfer. Conversion and yield have been good. It is estimated that a synthesis plant to produce 8,300 bbl./day of gasoline having an A. S. T. M. unleaded octane no. of about 80 after mild treatment and 1,050 bbl./day of gas oil would cost about $35,000,000, exclusive of the equipment for recovery of oxygenated compounds. The method appears reasonably attractive from an economic standpoint at present.

Lefebvre, H. *See* abs. **2075.**

2080. Lefebvre, H., and LeClerc, G. [Thermomagnetic Study of Iron Catalyzers for Hydrocarbon production by Fischer's Process.] Compt. rend., vol. 203, 1936, pp. 1378–1380; Chem. Abs., vol. 31, 1937, p. 936.

When $CO+H_2$ is passed over the catalyst (A) prepared by reduction in H_2 of the oxide precipitated by NH_3 or NaOH from solution of $Fe(NO_3)_3$, only gasoline is formed; if, however, about 1% K_2CO_3 is added the cataylst so formed (B), after an initial period of a few hours it produces heavy aliphatic hydrocarbons also. Thermomagnetic analysis gives for (A) a curve characteristic of magnetite, but for (B) one indicating a solid solution of $KFeO_2$ in cubic Fe_2O_3 (*see* abs. **2272**). This is confirmed by the fact that K cannot be extracted from (B) by H_2O, but requires acid (for example, acetic) and that pure H_2 at 250° re-forms magnetite.

2081. ———. [Iron Catalysts in the Synthesis of Motor Spirit by Hydrogenation of Carbon Monoxide.] Compt. rend., Cong. chim. ind., 18th Cong., Nancy, September–October 1938, pp. 725–730; Chem. Abs., vol. 33, 1939, p. 6019.

Fischer synthesis can be carried out with Fe cataylsts, those that are most frequently recommended containing small quantities of another metal together with alkali salts. Fe is active under two forms: magnetite and cubical Fe_2O_3, the latter producing much higher yields than the former. The presence of alkali is indispensable for the formation, under the conditions of the catalysis, of cubical Fe_2O_3; in the absence of alkali, only magnetite is stable. The function of the metal other than Fe is to facilitate the reduction that terminates the preparation of the catalyst and to favor the adsorption of a certain amount of the alkali salt during the preparation of the catalyst, thereby aiding indirectly in the formation of cubical Fe_2O_3.

2082. Lefol, J. [Liquid Fuels by Synthesis.] Carburents nat., vol. 4, 1943, pp. 137–141; Usine, vol. 52, 1943, No. 29; Chem. Zentralb., 1943, II, pp. 794 and 1773; Chem. Abs., vol. 38, 1944, p. 6065.

This lecture briefly reviews the possibility of manufacturing liquid fuels by carbonization, synthesis, hydrogenation, and fermentation of sugar from the hydrolysis of wood.

2083. Legrand, C., and Simonovitch, M. [Utilization of Coal With Particular Reference to the Production of Oil.] Publications Assoc. Ing. l'École de Mines de Mons., part 3, No. 62, 1937; Fuel, vol. 17, 1938, pp. 4–10, 41–47, 65–68, 96–104, 145–160, 217–221; Chem. Abs., vol. 32, 1938, p. 8743.

Survey and discussion of the technical development of the processes for the production of oil from coal by high- and low-temperature carbonization, by hydrogenation, and by synthetic processes. The Fischer-Tropsch process works at atmospheric pressure and at a temperature not normally exceeding 200° C. By keeping the temperature constant within limits of about 1° C., no CH_4 is obtained, but a mixture of liquid hydrocarbons and some solid paraffins. The temperature of reaction varies with the catalyst and the composition of the gas mixture; if rich in H_2, lower temperatures must be used. The production of synthetic gasoline from water gas is effected in the following stages:

(1) $C+H_2O=CO+H_2-28.4$ cal. This stage is endothermic.

(2) Removal of H_2S from the crude gas.

(3) Reduction of organic S content to 0.2 gm. per 100 $m.^3$

(4) $CO+2H_2=(CH_2)+H_2O+48$ cal. This stage is exothermic. The catalysts used contain Fe, Ni, or Co, all of which form carbides. Mixed catalysts are more active and robust than single catalyst. The best catalyst is Co, followed by Ni and then Fe; the best mixed catalyst is Co–Th precipitated on kieselguhr. With Co a yield of 130 gm. of synthetic gasoline per $m.^3$ of gas ($CO+2H_2$) can be obtained against a theoretical yield of 180 gm. The hydrogenation yields a mixture of oil and water in proportions varying between 1:1 and 1:2. The nearer the ratio of oil to water is to 1:1, the better is the yield of liquid products. With Co as catalyst the oil obtained contains 62% gasoline, 4% light products, 23% middle oil, and 11% paraffin (7% in the oil and 4% on the catalyst). The gasoline can be used directly in the motor without further purification because of its aliphatic nature. Its antiknock value can be raised in the usual way by adding tetraethyl lead. The middle oil is an excellent Diesel oil or it can be cracked into gasoline or may be used for making alcohol or lubricating oils.

2084. LEHRER, E. [Recording Apparatus for Determining the Magnetic Transition Points of Small Samples.] Ztschr. tech. Physik, vol. 10, 1929, pp. 177–185; Chem. Abs., vol. 23, 1929, p. 5063.

Discusses theory and possibilities of the instrument at some length. Curves are shown for Fe at various field strengths. Of the unusual applications are cited: Quantitative analysis of an Fe-cementite mixture (3% accurate), thermal decomposition of Fe_2N into Fe_4N. Gives preliminary data on the latter process.

2085. ———. [Equilibrium, Iron–Hydrogen–Ammonia.] Ztschr. Elektrochem., vol. 36, 1930, pp. 383–392; Chem. Abs., vol. 24, 1930, p. 4207.

Many experiments in which Fe was vitrified with H_2–NH_3 mixtures were carried out, and the resulting nitrides were examined by magnetic methods (abs. **2084**). The equilibrium diagram of Fe–H_2–NH_3 showed four phases, α, γ, γ' and ϵ representing five divariant equilibria and two univariant with the phases α, γ, γ' or γ, γ' and ϵ as solid phases, 350°–750°. The α phase is a fixed solution of N in α–Fe, 0–0.5% N; the γ phase is a fixed solution of N in γ–Fe, 1–2.7% N; the γ' phase, Fe_4N mixed crystals 5.5%–6% N; ϵ phase 4.5–11% N. The dissociation pressures were calculated from the Haber values for NH_3 equilibrium. The dependence of the results upon the concentration of NH_3 showed that the γ' phase does not form in demonstrable amounts under normal working conditions.

2086. ———. [Magnetic Investigation of the System Iron–Nitrogen.] Ztschr. Elektrochem., vol. 36, 1930, pp. 460–473; Chem. Abs., vol. 24, 1930, p. 5192.

System Fe–N has been investigated and the results reported in numerous magnetism/temperature curves. 2 eutectoids are reported, at 591±4° and 650±4°, with a N content of 2.55±0.1% and 4.55±0.2%, respectively. The diagrams are interpreted.

2087. LEIBU, H. J. [Reduction of Iron Oxides by Hydrogen and Carbon Monoxide.] Schweiz. Arch. angew. Wiss u. Tech., vol. 14, 1948, pp. 1–19, 49–59, 76–85; Ind. Chemist, vol. 24, 1948, p. 267; Chem. Abs., vol. 42, 1948, p. 4881.

This study was carried out in 2 steps: (1) Determination of the best conditions for reduction in which the action of the gases on pure Fe_2O_3 of varying grain size and porosity was examined; (2) the same reduction process in the presence of other oxides forming the gangue and ores with a low % of Fe_2O_3. The action of H_2 is more effective than CO, being endothermic, while the latter is exothermic; it is about 3–4 times greater at 800°, but this ratio decreases at lower temperatures. At temperatures above 800°, CO disintegrates, forming CO_2 and C, so that Fe free from C cannot be obtained. The physical factors are similar in effect with both gases. Confirmation that H_2 eliminates S and O_2 simultaneously was not forthcoming; indeed, the elimination of O_2 is more rapid and that of S (with P) forms a different process. The reaction is influenced by the chemical composition and crystalline structure of the other oxides present, but their effect is only conspicuous if the ore consists of certain mixed crystals before or during the reaction. Under these circumstances the reaction is, thereby, not merely slowed down but is brought to a standstill, products being formed that resist reduction. Proof of this was obtained by spectral analysis. Reduction is virtually total (*a*) for ferrites (for example, 2 CaO. Fe_2O_3) where Fe is the active cation, while in other ferrites it is inactive; (*b*) for ferrites where O_2 is combined mainly or solely with Fe (for example, FeO_4MgFe). Reduction is more or less impossible: (*a*) In the presence of mixed crystals containing ferric or ferrous oxides in small quantities so that the groups (FeO_6), (FeO_4), are surrounded by crystals of alien cations, for example $(Al, Fe)_2O_3$, (Mg, Fe)O; (*b*) in the presence of intermediate crystals (SiO_4Fe_2) or (FeO_4Al_2) where the O_2 belongs not only to (FeO_6) or (FeO_4) groups but to the (SiO_4) or (AlO_6) groups as well.

LEIBUSH, A. G. *See* abs. **1670.**

2088. LEIBUSH, A. G., AND BERGO, G. Y. [Reaction of Methane With Water Vapor. I.] Jour. Chem. Ind. (U. S. S. R.), vol. 15, No. 5, 1938, pp. 41–47; Chem. Abs., vol. 32, 1938, p. 7698.

Dynamic studies show that when a mixture of CH_4 and H_2O is heated for 1–8 sec, no C is formed below 900°, but when the mixture is heated under static conditions for 0.25–6 hr., C begins to form above 750° and disappears again above 950°. Increase in the amount of excess H_2O in the mixture, decrease in pressure, and the addition of O_2 decrease or stop C formation. These facts are explained by assuming that in a chain reaction CH_4 decomposes to CH_2, C_2H_6, C_2H_4, C_2H_2 and finally C, and that each of these compounds reacts to a greater or less degree with H_2O to give the final stable products, H_2, CO, and CO_2.

2089. ———. [Reaction of Methane With Water Vapor. II. Velocity of Reaction Between Methane and Water Vapor.] Jour. Appl. Chem. (U. S. S. R.), vol. 13, 1940, pp. 1003–1013 (in French, p. 1013); U. O. P. Co. Survey Foreign Petroleum Literature Index, Mar. 14, 1941; Chem. Abs., vol. 35, 1941, p. 1967.

Kinetics of the reaction of CH_4 with water vapor was investigated at 700°–1,050°. The initial stage of the process in a quartz vessel proceeded homogeneously and unimolecularly. Refractory clay and, especially, Ni catalytically accelerated the decomposition of CH_4. A decrease of initial partial pressure of CH_4 and an increase of an excess of water vapor also promoted decomposition of CH_4. The velocity of CH_4 decomposition diminished considerably with the formation of H_2. The relation between velocity and temperature is expressed by $K=2.3\times10^9\ e^{-85000/RT}$ per min.

2090. LEIDHEISER, H., JR., AND GWATHMEY, A. T. Selective Deposition of Carbon on the (111) Face of a Nickel Crystal in the Catalytic Decomposition of Carbon Monoxide. Jour. Am. Chem. Soc., vol. 70, 1948, p. 1206.

Single crystal of Ni was carefully machined to a spherical shape and mechanically and electrolytically polished. Previous studies have shown that this treatment produces a smooth, strain-free surface whose crystalline orientation is the same as that of the bulk of the crystal. CO reacts with this surface and deposits C only on the (111) planes. The authors suggest that this specificity of the (111) plane for the reaction is due to the fact that most of the atoms of the basal plane of graphite can be made to coincide with little distortion with those of the (111) plane of Ni.

LEIPUNSKII, O. *See* abs. **65.**

2091. LEITHE, W. [Determination of the Isoparaffin Content in Natural and Synthetic Soft and Hard Paraffins.] I. G. Farbenindustrie A.-G., Ammonia Laboratory Rept. 1615, May 13, 1939; FIAT Reel R 19, frames 6723–6740, PB 73,594; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, 1949, chapter 56, pp. 49–56.

Method has been developed by modifying the Schaarschmidt reaction with $SbCl_5$ that permits determination of content of isoparaffins in soft and hard paraffin (number of C atoms about C_{16}–C_{35}) within an accuracy of 2–5%. The isoparaffin content was determined by the new method in many natural paraffins, as well as in gatsches and paraffins from the Fischer synthesis (at atmospheric and at medium pressure). The paraffins from the medium pressure synthesis showed,

in contrast to Fischer gatsch obtained without pressure, a strikingly lower content of branched hydrocarbons and are, therefore, especially suitable for the preparation of soaps of slight odor by means of oxidation. The method thus offers a definite basis for evaluating paraffins with regard to their suitability for the preparation of soaps and edible fats.

2092. LELCHUK, S. L., BALANDIN, A. A., AND VASKEVICH, D. N. [Skeleton Catalysts and Their Application in Organic Chemistry.] Uspekhi Khim., vol. 14, No. 3, 1945, pp. 185–212; U. O. P. Co. Survey Foreign Petroleum Literature Index, Apr. 26–May 3, 1946, 17 pp.

Detailed study of alloyed and especially the so-called skeleton catalysts is needed, which may indicate new conditions for carrying out known reactions and help in developing catalysts for reactions that have not been effected. In this connection, the literature on the subject is reviewed, quoting 187 refs. The characteristics of these catalysts, methods suitable for their preparation, the connection between their structure and their catalytic activity, and the field of their applicability are discussed. They have been used successfully in hydrogenation of several types, dehydrogenation, H_2 disproportionation, isomerization, cyclization, dehydration, condensation, and oxidation. In the interaction of CO and H_2, formation of CH_4 must be prevented by maintaining conditions under which free CH_2 radicals are formed, which further interact to form hydrocarbons. Research on the methods of preparation by Fischer established that extensive leaching is favorable for the activity of these skeleton catalysts for the process in question and the most active catalysts contain Ni, Co, and Si. Tsuneoka and Murata conclude that when a catalyst of this type retains 4% Si, not removable by alkali, a molecular compound is apparently formed, and the assumption is justified that the compound not affected by leaching in the synthin catalyst is CoSi.

2093. LEMAIRE, E. [Synthesis of Fatty Acids by Catalytic Oxidation of Heavy Hydrocarbons: Their Application to the Manufacture of Soap and Edible Fats.] Génie civil, vol. 115, 1939, pp. 413–417; British Chem. Abs., 1940, B, p. 263.

Manufacture of soap and butter from coal consists of making fatty acids by oxidation of the heavy saturated paraffins obtained in the Fischer synthesis and then saponifying them to yield soap. A general survey is given of the constitution and properties of the fats and acids, and the process is traced by means of a flow diagram. The application of the synthetic fatty acids to the production of edible fats is said to have been accomplished, but no details are given of the method or its cost.

LEONTOWITSCH, W. *See* abs. **1572.**

LEPERSON, M. *See* abs. **2889.**

LEPETIT, G. *See* abs. **3052, 3053.**

LERNER-STEINBERG, B. *See* abs. **3579.**

2094. LE ROSEN, A. L., AND OWENS, M. L. Method for the Estimation of Oxy Compounds, Aromatic Hydrocarbons, and Nonaromatic Hydrocarbons in Certain Petroleum Products. Am. Chem. Soc., 117th Meeting Abs., March–April 1950, B, p. 1.

Rapid chromatographic method is proposed for the analysis of various hydrocarbon synthesis products in terms of the following classes of compounds: Oxygen-containing compounds, aromatic hydrocarbons, and nonaromatic hydrocarbons. A sample volume of 0.5 ml. is required, and the time consumed in an analysis is less than 1 hr.

LESSING, R. *See* abs. **1287.**

2094a. LE THOMAS, A. AND MORLET, E. [Slow Graphitization at Moderate Temperatures.] Bull. assoc. tech, founderie, No. 9, 1932, Suppl. 20–22; Chem. Abs., vol. 27, 1933, p. 691.

Prolonged dilatometric tests were made on Fe containing total C 3.5, Si 1.57, Mn 0.71, S 0.10, P 0.56%. Examination of the structure and mechanical testing shows that this Fe is susceptible to graphitization at 450° after it is maintained for 700 hr. at this temperature, while its properties were noticeably changed. However, a dilatometric test made in the usual way for a short time at temperatures $<690°$ did not modify the sample.

2095. LEVA, M. Heat Transfer to Gases Flowing in Turbulent Motion Through Packed Tubes. Ind. Eng. Chem., vol. 39, 1947, pp. 857–862; Chem. Abs., vol. 41, 1947, p. 4972.

This has been investigated for Reynolds numbers larger than 200. From the data obtained a dimensionally sound equation is developed, which holds very well for pipe diameters ranging from 0.622–3.1 in. Heat-transfer coefficients were measured for air, CO_2, and N_2, and the equation holds true in all cases very satisfactorily. h (film heat transfer coefficient) was differentiated with respect to D_p at D_t (packing diameter at tube diameter) =constant, and a maximum coefficient was predicted and experimentally verified for $D_p/D_t=0.150$. The effect of the Prandtl group upon h is discussed in detail. The effect of voids upon h was studied. It was found that no coordinated relationship between h and voids existed.

2096. ———. Elutriation of Fines From Fluidized Systems. Chem. Eng. Progress, vol. 47, 1951, pp. 39–45.

Some fundamental relationships between operating variables and elutriation from fluidized systems are discussed. Special attention is given to fluidized beds, such as Fischer-Tropsch catalysts. The simplest type of systems was investigated, those essentially composed of one coarse and one fines component. Rates of elutriation could be expressed by way of the law governing 1st-order chemical reactions and typical rate constants could be calculated. It was shown that the rate constants are related to such variables as linear gas velocity, size of coarse and fines constituents, material density, and bed height. The gas velocity was recognized as a system driving force, and an analogy was suggested between a system of fines in coarse particles or solutions. The analogy was extended further, and it appeared that concentration conditions in dense-phase and dilute-phase fluidized systems could be related by a modified form of Henry's law.

———. *See* abs. **3090.**

2097. LEVA, M., AND CROWELL, J. H. Heat Transfer Through Packed Tubes With Chemical Reaction. Am. Chem. Soc., 111th Meeting Abs., 1947, p. 141.

Reviews previous work in field. Actual experimental temperature distribution data through packed tubes give coefficients that agree with those calculated from equations 1 and 2 for heating and cooling, respectively, and in which the use of the logarithmic mean temperature difference is employed. Heat-transfer data observed with a typical strongly exothermic chemical reaction taking place in the catalytic tube are presented and compared with coefficients estimated by means of the cooling correlation given by equation 2. For the range over which the heat-transfer coefficient correlation was meant to apply—that is, for modified Reynolds numbers lying between 200 and 3,500—the agreement between the observed and calculated values is in the neighborhood of 10%, the calculated coefficients being the lower and more conservative values. This agreement is considered to be close enough for design purposes and for the general overall estimation of the over temperatures in catalytic reactors. Several possible explanations are given why the co-

efficients through the catalytic reactor should be somewhat higher than the values estimated by equation 2. A new concept of average distance of heat travel and a criterion for the efficiency of a tube in the removal of heat are introduced. These may perhaps be useful for consideration of heat flow through tubes of shapes other than those of the conventional circular cross section.

2098. LEVA, M., AND GRUMMER, M. Heat Transfer to Gases Through Packed Tubes—Effect of Particle Characteristics. Ind. Eng. Chem., vol. 40, 1948, pp. 415–419; Chem. Abs., vol. 42, 1948, p. 5281.

2099. LEVA, M., WEINTRAUB, M., AND GRUMMER, M. Heat Transmission Through Fluidized Beds of Fine Particles. Chem. Eng. Progress, vol. 45, No. 9, 1949, pp. 563–572.

Equation is derived for the calculation of heat-transfer coefficients through fluidized beds in terms of characteristic fluidization variables. The study was made in tubes of 2- and 4-in. diameter with round sand, sharp sand, and an Fe Fischer–Tropsch catalyst (Fe_3O_4) in the particle size range of 400–100 mesh. In attempting to correlate the data, 3 equations were developed, the last of which, $h=0.35c_p G^{1.15}$, in which h is expressed in B. t. u./hr./sq. ft./F°, C_p in B. t. u./lb./F° and G in lb./sq. ft./hr., represents the data with an accuracy of + or —27.5%. Within the limits of the experimental data, it is shown that the bed height, the concentration of solids in the bed (state of expansion), the density of the solid phase, and the vessel diameter had no effect upon heat transfer. It is concluded also that the tube diameter affects fluidization less than has been believed. Application of the equation to design of reactors utilizing the fluidization technique is discussed. Channeling has a very pronounced effect on heat transfer. Absolute particle size and shape are considerably more important than size distribution in inducing channeling.

2100. LEVA, M., GRUMMER, M., WEINTRAUB, M. AND POLLCHIK, M. Introduction to Fluidization. I. Chem. Eng. Progress, vol. 44, No. 7, 1948, pp. 511–520.

Counterflow and cogravity flow of air, CO_2, and He through beds composed of round and sharp sand have been investigated. Countergravity flow does not differ from cogravity flow as long as no bed expansion is experienced. Correlations have been developed that permit the prediction of the fluid velocity necessary to expand a bed of sand under countergravity flow conditions. Correlations include a shape factor, and typical photographs of the various sizes and shapes of sands are presented to permit comparison of any new materials with those tested. In this way, it is believed the approximate shape factor of new and similar materials may be determined satisfactorily. The equations presented apply also to mixed sizes of sands, provided the effective diameter of the mixture is evaluated, according to the rule suggested. The most-complex mixture investigated was composed of 5 individual components. It is believed that the correlations apply also with good results to more-complex mixtures. Describes typical fluidization phenomena in 2.5- and 4-in. tubes.

2101. ———. Fluidization of Solid Nonvesicular Particles. II. Chem. Eng. Progress, vol. 44, No. 8, 1948, pp. 619–626; Chem. Abs., vol. 42, 1948, p. 7583.

Fundamental correlations for the fluidization of small particles are developed from experimental data. The experimental work was carried out with round and sharp silica sands varying in size from 0.01505–0.00202-in. effective diameter. The flow of air, CO_2, and He through beds of these particles in a 2.5-in. and 4-in. tube was investigated. A distinction is made between expanded and fluidized beds. It was found that a bed of fine particles must have a certain minimum voidage before fluidization sets in. This minimum fluid voidage has been correlated with the effective diameter of the bed particles for the various shapes considered. With the minimum fluid voidage available and the pressure-drop law describing flow of fluids through packed beds, the onset of fluidization may be predicted. Interpretation of the data permitted the definition of a fluidization efficiency, which may perhaps be used as a criterion for the quality of fluidization operations. Correlations have been applied with good results to mixed sizes up to 5 individual components. The slugging behavior of fluidized beds was considered, and an attempt was made to correlate slugging points. 2 typical problems illustrate the applications of the new correlations; 1 demonstrates that the correlations are also valid for the upward flow of liquids through beds of fine particles.

2102. LEVA, M., GRUMMER, M., WEINTRAUB, M., AND STORCH, H. H. Study of Fluidization of an Iron Fischer-Tropsch. Catalyst. III. Chem. Eng. Progress, vol. 44, No. 9, 1948, pp. 707–716; Chem. Abs., vol. 42, 1948, p. 7957.

Earlier fluidization correlations, based on experimental work with silica-sand beds, are briefly reviewed. New data, observed during the fluidization of a typical fused-Fe Fischer-Tropsch catalyst, are presented This material was considerably more irregular than sharp sand. Typical mixtures, comprising components varying in size from 32–325 mesh, were investigated by using air and He as fluids. It appeared that the new data agreed with the correlations based on the experimental work with sand beds when proper allowance was made for the greater irregularity of the particles. The application of the correlations to process design is discussed on the basis of typical Fischer-Tropsch operating data. The importance of correct evaluation of the physical properties of the reaction mixture was stressed in the application of the correlations. In connection with process calculations, a simple semigraphic method for solving problems was proposed.

2103. LEVA, M., WEINTRAUB, M., GRUMMER, M., AND CLARK, E. L. Cooling of Gases Flowing in Turbulent Motion Through Packed Tubes. Ind. Eng. Chem., vol. 40, 1948, pp. 747–752; Chem. Abs., vol. 42, 1948, p. 5277.

Heat-transfer coefficients were determined for the flow of heat from hot air and CO_2 to cooling water. Tests were made with a 2-in. and a ¾-in. standard packed tube. The packing material was of low thermal conductivity, spherical, and smooth. The ratio $D_p : D_t$ varied from about 0.08–0.27. The gas-flow range was characterized by the modified Reynold's number interval 250–3,000. 2 dimensionally homogeneous equations were proposed correlating h (heat-transfer coefficient) and the physical properties of the system. The coefficient of the 1st equation was differentiated with respect to D_p at D_t (packing diameter at tube diameter) and G=constant, and a maximum heat transfer coefficient was predicted for $D_p : D_t = 0.153$ and verified experimentally. The heat-transfer coefficient was determined for CO_2 and correlated with that for air; the check between the two was excellent. The possible inclusion of the Prandtl number is discussed as well as the application of the equations to tube sizes larger than 2 in.

2103a. LEVA, M., WEINTRAUB, M., GRUMMER, M., POLLCHIK, M., AND STORCH, H. H. Fluid Flow Through Packed and Fluidized Systems. Bureau of Mines Bull. 504, 1951, 149 pp.

Correlations were developed that would be suitable for the design of equipment in which fluids are brought into contact with granular materials as in the Fischer-Tropsch process.

2104. LEVESQUE, C. L. Oxo Reactions in Industry. Chem. Eng. News, vol. 28, 1950, No. 45, p. 3881.

Paper presented at the October meeting of the Philadelphia and Wilmington Organic Chemists Clubs. The industrial use of certain Oxo reactions and their mechanism were discussed. Certain rules for the addition of CO and H_2 to unsubstituted olefins were presented: (1) Isomerization of the double bond, if possible, generally accompanies the hydroformylation; (2) straight-chain olefins give 40–60% straight-chain aldehydes, and 60–40% of other isomers, the α–methyl one predominating; (3) addition of an aldehyde group to a tertiary C does not occur, no quaternary C atom is found; (4) addition of an aldehyde group adjacent to a tertiary C atom is strongly hindered, but may occur to a small extent; (5) the tertiary C atom does not hinder seriously if the double bond is in the 1, 2-position; (6) addition of the aldehyde group adjacent to a quaternary C does not occur. Several examples are given of reactions that have been run, together with products and yields obtained. The mechanism of the Oxo reduction is believed to center around Co carbonyl or Co carbonium hydride as the actual catalyst. The reaction mechanism must explain the fact that the formyl group always goes on the least substituted C atom, and, except in the case of styrene, the formyl group always appears on the β carbon of an α, β–unsaturated compound.

2105. ——— Oxo Reaction. Chem. Eng. News, vol. 29, 1951, p. 1830.

Paper presented at the National Capital Section meeting of the American Institute of Chemical Engineers. The Oxo reaction shows important possibilities for the production of long-chain alcohols for use in detergents, synthetic lubricants, and plasticizers. It is also of great value as a method for synthesizing aldehydes. The method has been principally used in the United States to synthesize alcohols from petroleum hydrocarbons by hydrogenation of the aldehyde formed in the initial reaction. Standard Oil Co. of New Jersey is operating a plant to produce isooctyl alcohol from a mixture of heptenes. It is reported that Standard Oil Co. of Indiana will erect an Oxo plant soon. The Rohm and Haas Co. is operating a pilot plant to produce several derivatives of 3,5,5-trimethylhexaldehyde from diisobutylene. Use of the Oxo reaction to produce C_8 alcohols has already helped materially to relieve the shortage of 2–ethylhexanol, a prime raw material for the production of plasticizers.

———. *See* abs. **3670.**

2106. LEVI, M. G., PADOVANI, C., AND BUSI, M. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen at Ordinary Pressure.] Atti cong. nazl. chim. pura applicata, 3d Cong., 1930, pp. 718–729; Studi ric. comb., vol. 2, 1927–1929, p. 213; Chem. Zentralb., 1931, I, p. 3632; Chem. Abs., vol. 25, 1931, p. 3309.

Experiments were carried out with a carefully prepared mixture of H_2 and CO under well-controlled conditions. Following Fischer's suggestions (abs. **950** and **1021**), mixed catalysts were used such as Fe, Co with oxides of Mn or Cr. The yields of liquid hydrocarbon obtained at 257°–285° are of the order of magnitude of those reported by Fischer. The predominant formation of low-boiling hydrocarbons is emphasized. No solid products and comparatively small quantities of gaseous hydrocarbons are formed. The catalysts become less active if reused in several consecutive runs. If the unreacted gas mixture of previous experiments is used for a new run, only liquid hydrocarbons are formed.

LEVIN, H. *See* abs. **3392.**

LEVINE, R. *See* abs. **3652, 3653.**

2107. LEWIS, W. K. Replaceability of Natural Gas. Gas Age, vol. 98, No. 5, 1946, pp. 29–30; 62, 64.

Emphasizes significance of the possibility of generating both gas and oil from coal by synthetic means. The complete replaceability of natural gas by synthesis gas at a cost that might easily be brought below the delivered cost of natural gas in many areas of the country is thought to be perfectly feasible. It is the opinion that it is not unreasonable to look for considerable commercial development of these synthesis processes within the next 10 yr. The production of synthetic natural gas from coal by the Bergius and Fischer-Tropsch processes is in no sense economically out of the question in the not distant future.

2108. ———. Kinetics of the Reactions of Steam and Carbon Dioxide With Carbon. Chem. and Eng. News, vol. 25, No. 39, 1947, pp. 2815–2818.

New fluidized powder technique for the efficient combustion and gasification of coal is described in the Priestley medal address. In this method, finely powdered coal, actually suspended by a stream of air entering at the bottom of the retort, is subjected to air and steam and converted into a mixture of CO and H_2 gases. Combining with O_2 in the air, CO_2 is formed, and heat is evolved. In the upper part of the retort the CO_2 and heat encounter more C, in the form of powdered coal and steam. 3 important reactions then take place, during which heat is absorbed, while the CO_2 is transformed into CO and H_2. Rapid and even heat distribution is the basis for the success of the method, compared with the older processes in which heat is difficult to control. A great advantage of fluidized powder technique is that all grades of coal can be used. Other advantages are the reduction of operating difficulties owing to elimination of excessive temperatures; prevention of slag formation; reduction of unburned fuel in the refuse and in handling both the coal fed and the ash removed by the fluidized powder technique; high conversion with low CO_2 and undecomposed steam in the product; a definite, though limited, improvement in thermal efficiency; and the reduction in tar formation and its complete utilization. The most serious limitation of the operation is its relatively low capacity; this limit is set by the gas velocity, which cannot be allowed to rise to levels above those necessary for good fluidization. Fluctuations in the gas velocity must also be kept to a minimum. One of its first uses probably will be in the manufacturing of better and cheaper producer gas for industrial purposes. The production of synthesis gas for the Fischer-Tropsch reaction will also be carried out by some modification of this method. The same applies to the synthesis of combustion gases of high heating value.

———. *See* abs. **1097.**

2109. LEWIS, W. K., AND FROLICH, P. K. Synthesis of Methanol From Carbon Monoxide and Hydrogen. Ind. Eng. Chem., vol. 20, 1928, pp. 285–290; Chem. Abs., vol. 22, 1928, p. 1324.

Study has been made of some of the factors governing the synthesis of MeOH from CO and H_2 under high pressure and in the presence of a catalyst. MeOH of high purity may readily be prepared by passing a mixture of CO and H_2, preferably at a pressure of several hundred atm. and at temperatures of 300°–350°, over a catalyst composed of metallic oxides. Working with a catalyst of medium activity prepared from the oxides of Cu, Zn, and Al, it is possible to reach nearly theoretical conversion depending upon the pressure, temperature and rate of gas flow employed. CO_2, H_2O and CH_4 may form, but the amount of CO consumed in these side reactions is small under the conditions most favorable to MeOH formation. The catalyst in question appears to be most active at lower temperature and suffers a permanent decrease in activity when exposed to higher temperatures. Also the catalyst is sensitive to poisons.

2110. LEWIS, W. K., GILLILAND, E. R., AND REED, W. A. Reaction of Methane With Copper Oxide in a Fluidized Bed. Ind. Eng. Chem., vol. 41, 1949, pp. 1227–1237; Chem. Abs., vol. 43, 1949, p. 7199.

Reaction between CH_4 and CuO deposited on silica gel, when stoichiometrically controlled to give a molal O_2: C ratio of 1.0 or slightly greater, is an effective means of producing CO and H_2 in a molal ratio of about 1:2. Reaction rates are high enough so that there is no reason for temperatures to be far in excess of those required by equilibrium. In a fluidization unit with a 4-ft. bed at 1,640° F. and 1 atm., 94% CH_4 decomposition was obtained with a selectivity of 92%. Higher conversions could be obtained with a higher temperature or a greater bed depth. The data were correlated on the assumption that the limiting factor is the reaction of CO_2 and water vapor with CH_4. The CH_4–CuO reaction occurs in 2 steps: An initial step that results in the rapid reduction of Cu and the simultaneous complete oxidation of part of the CH_4 and a 2d step that is rate-controlling and consists of the reforming of the remaining CH_4 with CO_2 and H_2O produced by the 1st step to form CO and H_2. The rates of the reforming reactions over Cu on silica gel are controlled by chemical reaction and not by gaseous diffusion.

2111. LEYE, A. R. [Gasification With Steam and Oxygen. Method for Calculating Results and Extent of Re-forming.] Gas- u. Wasserfach, vol. 83, 1940, pp. 669–672, 688–691; Chem. Abs., vol. 35, 1941, p. 3062.

Method has been developed for calculating the volumetric composition of a generator or re-formed gas, based on the knowledge of the fuel composition and the gasification mediums, such as steam or air, with the help of dimensionless factors for the fuel, gasification mediums, etc. Formulas are set up that permit calculation of the water-gas composition and requirements for fuel, gasification mediums, and efficiency. The effect of changes in fuel or gasification mediums, and other variables can be followed, and one can secure a picture of the effect of all factors on the gasification or reforming results. Examples are given for coke water gas, continuous gasification with steam and O_2 and the re-forming of CH_4 and hydrogenation gas, as well as the production of gas for synthetic purposes. Calculated values agree with those found in practice.

2112. LI, C. H. [Decomposition of Carbon Monoxide on Nickel.] Rev. Phys. Chem. Japan, vol. 2, 1929, p. 11; vol. 4, 1931, p. 118; vol. 5, 1932, p. 41; Jour. Soc. Chem. Ind. (Japan), vol. 43, 1940, B, p. 177.

Decomposition of CO on Ni takes place according to the active points of Ni in the following 3 steps: $2\,CO + 3\,Ni = Ni_3C + CO_2$; $2\,CO + Ni = NiC + CO_2$; $2\,CO = C + CO_2$. Reaction (1) takes place on the most active points of the catalyst and the C of the CO is unreversibly held as Ni_3C in the Ni atom so that the Ni is poisoned. Reaction (2) occurs on the surface with the next-strongest activity on which the CO is adsorbed as NiC, which is reversibly again decomposed into C and Ni. Reaction (3) is the simple catalytic decomposition of CO on the least-active centers.

2113. LIANDER, H. Utilization of Natural Gases for the Ammonia Process. Trans. Faraday Soc., vol. 25, 1929, pp. 462–472; Chem. Abs., vol. 23, 1929, p. 4779.

Possible reactions of CH_4 with O_2, H_2O, and CO_2 were calculated from the Nernst heat theorem. Experiments were made by heating CH_4 and O_2, with and without Ni catalysts, to 550°–850°. With no catalyst the products are CO_2 and H_2O; with catalyst H_2, CO, and CO_2. Conclusion: Natural gas, air, and steam passed over a suitable catalyst at 1,000° would yield gas that could be used as a source of H_2 and N_2 for NH_3 synthesis.

LIANG, S. C. *See* abs. **3337, 3338.**

LIBERMAN, A. L. *See* abs. **1706.**

LILLE, R. *See* abs. **1058.**

2114. LINDE, R. [Progress in Large-Scale Production of Oxygen.] Glückauf, vol. 72, 1936, pp. 114–118; Chem. Abs., vol. 30, 1936, p. 6142.

Methods of fractionating liquid air for O_2 are discussed. The Fränkl method employing intermittent regenerators in heat exchange, instead of countercurrent exchanges, has proved most efficient. 98% O_2 can now be produced at 1.5 pf. per $m.^3$

LINGH, A. E. *See* abs. **3668.**

2115. LINZ, B. F. Plans for Huge Synthetic Plants Fantastic. Oil Gas Jour., vol. 46, No. 40, 1948, p. 38.

B. K. Brown, in a recent appearance before a congressional subcommittee, declared that Government proposals for the initiation of a construction program to supply 2,000,000 bbl. of synthetic oil per day has no justification either from the standpoint of military security or the cost in money, men, and steel. The costs have not yet been determined, but a study is expected to be made by fuel experts from industry and Government. The coal industry would need to be revolutionized to produce the required 468,000,000 tons or more than ⅔ of our highest annual production; to provide 2,000,000 bbl. of oil per day. To produce even 500,000 bbl. per day from natural gas would require the consumption of ½ the gas produced in 1946. To erect the required plants to produce the proposed quantity of oil would require huge amounts of steel—34 tons per ton of oil from shale per day, 49 tons from natural gas, and 70 tons from coal, not including the steel for the production of the raw material—whereas it takes only 26 tons to produce a ton of oil from petroleum at a new refinery in a new field. Furthermore, it is known that gas or coal can be used more economically as such than converted into oil. It is his conviction that more oil can be produced quicker by making steel available to the petroleum industry than by any other method and that the production of liquid fuels from crude petroleum should be given the preference. He appears to be in favor of developing synthetic fuel production, but less painfully and more soundly over a period of years, rather than by forced development.

2116. ———. Synthetic Fuels Program. Oil Gas Jour., vol. 46, No. 44, 1948, pp. 38–39.

In a hearing before a House Armed Services Subcommittee, it was brought out by E. V. Murphree, Standard Oil Development Co., that the cost of producing 2,000,000 bbl. per day of synthetic fuel by Secretary Krug's plan would be 17 billion dollars instead of 9 billion, and that it would be much cheaper either to allow the industry to develop synthetic fuels as rapidly as economic factors dictate or to stockpile petroleum oil at the rate of 500,000 bbl. per day over a period of 5 yrs. Taking oil products at $4.20 per bbl. and tankage at $1.30, the cost of the 5-yr. program would be 5 billion dollars. Discussing the question of costs, it requires for production, transportation, refining, and delivery of Gulf coast oil to New York, 5.7 ton of steel per bbl. of products per day for maximum distillate yield from crude oil and 7.8 tons for maximum gasoline yield. Comparable figures for natural gas products delivered at New York are 7.1 and 7.9 tons respectively, for coal products consumed locally 4.6 and 5.2 tons respectively, and for oil shale products refined and consumed on the Pacific coast 5.7 and 7.4 tons respectively. The capital investment for the above would be $4,300 and $6,500 for petroleum, $7,400 and $8,200 for natural gas, $7,600 and $8,500 for coal, and $6,100 and $8,400 for shale. Allowing costs of $2.78 per bbl. for crude, $0.10 per 1,000 cu. ft. for natural gas, $3.20 per ton for coal, and $1.00 per ton for shale, 5% for amortization and 10% for return on the investment, gasoline from crude, allowing credit for by-products, costs $0.141 per gal., as against $0.128 for gasoline from natural gas, $0.166 from coal, and $0.16 from shale. The figures are based on a gasoline with

an octane-no. level to satisfy a 10:1 compression ratio engine capable of giving about 30% more miles per gal. than present engines.

2117. ———. Bureau of Mines Modified Fischer-Tropsch Plant. Oil Gas Jour., vol. 49, No. 17, 1950, pp. 42–43.

Bureau of Mines 80–100-bbl.-per-day plant for converting coal to oil by a modified Fischer-Tropsch process will be tested this fall with a view to beginning integrated operations next year. The plant will consist of 5 units, respectively for O_2 production, coal gasification, gas purification, hydrocarbon synthesis, and distillation. The gasification unit has been developed by Koppers Co.; it converts pulverized coal under pressure into synthesis gas by the aid of steam and O_2 The gasifier uses about 28 tons of coal, 24 of O_2, and 35 of superheated steam to produce some 2,000,000 cu. ft. of raw synthesis gas daily. The converter will be of the internally cooled type having a fluidized bed of granular, synthetic-NH_3 type catalyst suspended in a constantly flowing body of coolant oil. The anticipated daily production of the gas-synthesis demonstration plant will include 55–60 bbl. of 75-octane-no. gasoline, 10–12 bbl. of 80 cetane diesel oil, and approximately 12 bbl. of heavy oils and waxes suitable for cracking stock.

2118. ———. Fuels Investigation. Oil Gas Jour., vol. 49, No. 45, 1951, pp. 46–47.

Senate Interior Affairs Committee began its investigation of the present and future fuel situation last week with a discussion of all energy resources. It was believed that the reserves of coal and oil would be enough to last for many years at the present rate of consumption. It was agreed that research on synthetic liquid fuels should be vigorously prosecuted but that no commercial plants should be built until production is economically feasible. The forecast was made that when synthetic fuels come into the picture the network of oil and natural-gas pipe lines now spreading over the country will provide a ready-made transportation system for the new fuels.

LIPKA, H. *See* abs. **2479.**

2119. LIPSON, H., AND PARKER, A. M. B. Structure of Martensite. Jour. Iron Steel Inst. (London), vol. 149, 1944, pp. 123–141; Chem. Abs., vol. 38, 1944, p. 1195.

Martensite may be regarded as a deformed supersaturated solid solution of C in α–Fe, formed by very rapid quenching of a solid solution of C in γ–Fe. It is very reactive, decomposing to cementite and α–Fe at temperatures below 300° and as low as 100°–200°. The structure is body-centered tetragonal. Martensite would probably behave like cementite, forming H_2 and hydrocarbons with acids and hydrocarbons only with H_2. The method of formation almost certainly precludes any possibility that it is involved in the Fischer-Tropsch reaction.

2120. LIPSON, H., AND PETCH, N. J. Crystal Structure of Cementite (Fe_3C). Jour. Iron Steel Inst. (London), vol. 142, 1940, pp. 95–106; Chem. Abs., vol. 34, 1940, p. 6501.

Specimen of fine powder (through 380-mesh) was prepared by passing CO over Fe_2O_3 at 550°. Annealing at 600° resulted in partial decomposition (into a structure, probably Fe_2C) and sharpening of the cementite lines. Intensities were measured from the unannealed specimens, and spacings from one annealed at 600° for 17 hr. The structure is an almost close-packing of Fe atoms with C atoms in the interstices. The environment of the C atoms consists of 6 Fe atoms arranged at the corners of a triangular prism. The average Fe–C distance is 2.03 Å. 2 other Fe atoms are only 2.31 Å from each C. The relation of the structure to either the ferrite or austenite structures is not very obvious.

LISTER, F. *See* abs. **2824.**

2121. LITKENHOUS, E. E. Hydrogenation of Nickel Carbonyl. Ind. Eng. Chem., vol. 31, 1939, p. 1060; Chem. Abs., vol. 33, 1939, p. 7498.

In reply to abs. **456**, Litkenhous supports the hypothesis that the principal reaction is $2C+2H_2O=CH_4+CO_4$.

2122. LITKENHOUS, E. E., AND MANN, C. A. Hydrogenation of Nickel Carbonyl. Ind. Eng. Chem., vol. 29, 1937, pp. 934–938; Brennstoff-Chem., vol. 18, 1937, p. 468; Chem. Abs., vol. 31, 1937, p. 6830.

According to the opinion of various investigators, $Ni(CO)_4$ is the intermediate product in the hydrogenation of CO over Ni as catalyst. In order to explain this reaction mechanism and to determine the equilibrium of the ensuing reaction, $Ni(CO)_4$ was reacted with H_2 in the ratio of 1:4. The tests were performed 25°–400° and 1–75 atm. in a Ni tube 61 cm. long. The end gas was analyzed; and, on the basis of the analysis, the equilibrium constants were determined and compared with the data in the literature; at 1 atm. $Ni(CO)_4$ is stable at about 100°, but shortly above, it decomposes completely into Ni and 4 CO. Above 200° the formation of H_2O, CH_4, and CO_2 begins. At 250°, 58–60% of the end gas consists of H_2O, which then decreases with further rise in temperature. Likewise CH_4 and CO_2 are at a maximum at about 350° with 20% of the end gas. The diagrams of 5–75 atm. are basically the same as at 1 atm. except that the stable limit of $Ni(CO)_4$ with rising pressure varies at higher temperatures. For example, at 75 atm. $Ni(CO)_4$ is stable up to about 220°. In contrast, an increase in pressure up to 75 atm. is virtually without influence above 250° on the composition; H_2O, CH_4, and CO_2 maintain almost the same ratio. A fairly large amount of C deposits in the reaction tube but disappears with rising temperature. The end products CO_2, CH_4, and H_2O obtained in the hydrogenation of $Ni(CO)_4$ are identical with those that Sabatier and Senderens found in the hydrogenation of CO. It is seen that the reaction $2C+2H_2O\rightarrow CO_2+CH_4$ gave constant values over the whole reaction range, whereas other possible reactions did not. The reaction can, naturally, first occur whenever C and H_2O have formed, which occurs at 250°. Normally free C does not react with H_2O at 250°, yet the reaction sets in in the presence of the Ni formed from the $Ni(CO)_4$.

2123. LITTLE, A. D. Research—and a Greater Gas Industry. Am. Gas. Assoc. Monthly, vol. 10, 1928, pp. 661–665, 682; Chem. Abs., vol. 23, 1929, p. 2272.

Possibilities in the use of water gas for the synthesis of gaseous, liquid, and solid hydrocarbons.

LITTLE, A. T. *See* abs. **1517.**

LITVIN, M. Z. *See* abs. **1652.**

LIU, C. L. *See* abs. **3753.**

2124. LIVINGSTON, J. W. Report on Leuna Works Near Merseberg. CIOS Rept. XXVIII–27, 1945, 11 pp.; PB 6682.

This report describes briefly the synthesis of MeOH and higher alcohols from CO and H_2; the production of synthetic detergents from the sulfonchlorides produced by the hydrogenation of Kogasin and treatment with SO_2 and Cl_2 with ultraviolet light as catalyst; the production of C_2H_4 by dehydrogenation of C_2H_6 and its polymerization to lubricating oil; the hydrogenation of coal; and the dehydrogenation of butane to butene, which is used for alkylation with H_2SO_4 as the catalyst.

LIVSHITZ, V. D. *See* abs. **1659, 1660, 1661, 1662.**

2125. LOBO, W. E. Report on Oxygen Plant Development. PB 9381, 1945, 564 pp.

Comprehensive report on the design and development by the M. W. Kellogg Co. of O_2 units for the mechanical separation of O_2 from the air. The report contains extensive technical data on the properties of air and its constitutents, and presents comprehensive functional and operative data on the process in many statistical graphs and tables.

2126. ———. Oxygen by Fractionation at Low Pressures. Chem. Inds., vol. 59, No. 1, 1946, pp. 53–56; Chem. Abs., vol. 40, 1946, p. 5888.

1st successful low-pressure unit for liquid air fractionation built by the M. W. Kellogg Co. is described. The M–7 unit produces O_2 by liquefaction and fractionation of air, operating at a maximum pressure of about 100 p. s. i. g. The unit was designed to produce 1,000 std. c. f. h. of gaseous O_2 of 99.5% purity under the extreme atmospheric conditions of 120° F. ambient and 90° F. dew point, and to deliver the O_2, dry, in cylinders at 2,200 p. s. i. g. The complete removal of the CO_2 and H_2O from the inlet air is accomplished without chemical treatment by condensation in a special reversing exchanger. A diagrammatic flow sheet of the unit shows the 4 typical operating systems: Air compression, refrigeration and air purification, fractionation, and O_2 compression. Typical performance data also are plotted.

2127. ———. Production of Oxygen for Industrial Purposes. Chem. Eng. Progress, vol. 1, 1947, pp. 21–26; Petrol Eng., vol. 18, No. 8, 1947, pp. 120, 123, 126, 128; Chem. Abs., vol. 41, 1947, p. 2213.

Basic theory of the Kellogg low-pressure O_2 process is discussed, and a description is given of the unique temperature unbalance system. It is illustrated by means of a flowsheet. Tentative costs of a plant for producing 350 tons per day of 90% O_2 should be about $5,000 per ton of product per day. The total cost of producing O_2 in a plant of this size may be as low as $3.50 per ton, including 3% of plant cost for maintenance, 1.5% for taxes and insurance, 10% for depreciation, and all utilities and labor charges. This is equivalent to about $0.15 per 1,000 cu. ft.

2128. LOBO, W. E., AND SKAPERDAS, G. T. Air Purification in the Reversing Exchanger. Chem. Eng. Progress, vol. 1, No. 2; Trans. Am. Inst. Chem. Eng., vol. 43, 1947, pp. 69–74; Chem. Abs., vol. 41, 1947, p. 1504.

Theory, a description, and the operation of the reversing exchanger developed as a part of the Collins low-pressure O_2 producer. Also described is the so-called unbalance-flow method for temperature control by means of an internal recycle system, developed by Trumpler, as a means of heat exchange and scavenging.

2128a. LOCICERO, J. C., AND JOHNSON, R. T. Oxo Reaction of Camphene. Structure of the Aldehyde and Derivatives. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 2,094–2,097.

Camphene is found to undergo the Oxo reaction smoothly when diluted with an equal volume of benzene using dicobalt octacarbonyl as catalyst. It gives liquid aldehyde of constant boiling point in 65% yield. It undergoes the Oxo reaction without rearrangement giving an aldehyde which is structurally related to isocamphenilanaldehyde by several methods of degradation. Oxidation of the aldehyde with air or O_2 gives a simple acid m. p. 56°–57° of the same chain length.

LOCQUIN, R. *See* abs. **1260.**

2129. LOEB, W. [Assimilation of Carbon Dioxide.] Ztschr. Elektrochem., vol. 11, 1905, pp. 745–752; Jour. Chem. Soc., vol. 90, II, 1906, p. 43.

In the silent electric discharge, moist CO_2 yields CO and O_2 first, HCOOH and H_2O_2 are formed slowly as secondary products. In moist CO, the main reactions are $CO+H_2=CH_2O$ and $CO+H_2O=CO_2+H_2$. HCOOH also is formed. A moist mixture of CO_2 and H_2 gives CH_2O and HCOOH; CO and H_2 give the same products with CH_2O present in greater quantities, as also CO_2. Moist CH_2O vapor decomposes mainly into CO and H_2 with small quantities of CH_4; HCOOH and H_2O vapor behave similarly. From CH_4 and CO_2, it is almost certain that alcohol can be synthesized, and alcohol is very probably one of the intermediate products of the natural synthesis.

2130. ———. [Chemical Action of Silent Discharge.] Ztschr. Electrochem., vol. 12, 1906, pp. 282–312; Jour. Chem. Soc. vol. 90, II, 1906, p. 324.

CH_2O always is formed in small amount by the interaction of H_2 and CO, the H_2 being formed by the reaction $CO+H_2O=CO_2+H_2$. By starting with a mixture of moist CO and H_2, much larger quantities of CH_2O are obtained and also glycolaldehyde $OH.CH_2.CHO$. CH_4 is always formed from mixtures of CO and H_2. CH_4 and CO give acetaldehyde, $CO+CH_4=CH_3.CHO$, but the reduction of acetaldehyde to alcohol by combination with H_2 has not yet been realized in the silent discharge.

2131. ———. [Action of the Silent Electric Discharge on Moist Methane.] Ber. deut. chem. Gesell., vol. 41, 1908, pp. 87–90; Chem. Abs., vol. 2, 1908, p. 1122.

Moist CH_4 was subjected under ordinary pressure to the silent electric discharge and obtained gaseous products consisting of CO_2, C_nH_{2n}, CO, C_nH_{2n+2}, and about 35–45% of H_2, and a colorless, insoluble, solid compound of composition $C_9H_{15}O$. On decomposition with concentrated H_2SO_4 traces of fatty acids were detected.

2132. LOEW, O. [Organic Substances in Primitive Times.] Ztschr. angew. Chem., vol. 40, 1927, pp. 1548–1549; Chem. Abs., vol. 22, 1928, p. 2361.

It would be interesting to ascertain the 1st organic compounds that existed on the earth. Moissan, working with carbides, concluded that they must have been hydrocarbons. Metal carbides were probably formed as the nebular mass cooled. In time, when temperature conditions permitted H_2O to exist, the carbides were acted upon by it and hydrocarbons formed. By lightning, the hydrocarbon vapors and liquids were ignited and the atmosphere was enriched by CO_2 as a result. Evidence in favor of this theory is found in the existence of carbides and hydrocarbons in meteorites. It is possible that from CH_4 other organic compounds were produced. The oxides of Fe and Cu may have catalyzed the oxidation of CH_4 to CH_2O (I). (I), reacting with NH_3, formed by the catalytic union of its elements, might ultimately have led to the formation of asparaginic aldehyde. This, by polymerization and condensation, might have yielded a complex, which, on reduction with H_2 and H_2S, would give a substance approximating a protein in nature. (I) also might have polymerized to sugars, although the presence of acid vapors would have tended to make the end products simple sugars. Thus organic compounds, even to the extent of relatively complex proteins, could have come into existence without the catalyzing influence of chlorophyll and light.

LÖFQUIST, H. *See* abs. **193.**

LOHMAR, W. *See* abs. **1037.**

LOHNES, K. *See* abs. **1936.**

LÖHR, O. *See* abs. **3374.**

LOHRER, W. *See* abs. **1088, 1089.**

2133. LOHSE, H. W. Products From Carbon Oxides and Water Gas. Catalytic Chemistry, Chemical Publishing Co., New York, 1945, pp. 329–347.

LOKHVITZKAYA, A. P. *See* abs. **565.**

LONGUET, J. *See* abs. **1059.**

2134. LONGUET-ESCARD, J. [Reaction in the Solid State at Low Temperatures, in the Presence of Water.] Bull. soc. chim. France, 1949, D, pp. 153–156; Chem. Abs., vol. 43, 1949, p. 6531.

Formation of ferrites, chromites, sulfides, silicates, and aluminates was studied between room temperature and 100° in the presence of H_2O. The reaction products were identified by X-ray, thermomagnetic, and chemical methods. Several of the products formed were similar to those found in nature, notably franklinite, chalcopyrite, and antigorites. The hydroxides of Ni, Co, Zn, and Mg crystallized in the hexagonal system, type CdI_2.

2135. ———. [Structure of Several Hydroaluminates of Nickel.] Jour. chim. phys., vol. 47, 1950, pp. 238–243; Chem. Abs., vol. 44, 1950, p. 7612.

Addition of NaOH to a mixture of nitrates or chlorides of Ni and Al rich in Ni salts resulted, after washing and drying, in the formation of a hydroaluminate of Ni. An X-ray study was made of these types of compounds. The X-ray results were consistent with a structure composed of layers of hydroxyl ions and layers of metallic ions. The role of the Al might be to stabilize this type of structure by substitution for a small number of Ni ions. Such hydroaluminates of Ni have been used in the preparation of catalysts for the Fischer-Tropsch synthesis.

———. *See* abs. **1062.**

2136. LOPATIN, K. I. [Practical Technical Method for Removing Carbon Dioxide From Synthesis Gas.] Jour. Appl. Chem. (U. S. S. R.), vol. 20, 1947, pp. 23–35; Chem. Abs., vol. 41, 1947, p. 7061.

Elimination of CO_2 and CO from this gas is the first step in the preparation of a N_2–H_2 mixture for synthesis of NH_3. A method utilizing absorption by water is described and the effects of various factors indicated. Purification to about 0.5% CO_2 can be attained at the expense of about 100–120 $m.^3$ H_2O per 1,000 $m.^3$ gas.

2137. LÓPEZ-RUBIO, F. B., AND PACHECO, J. R. [Mechanism of the Catalytic Process for the Synthesis of Hydrocarbons by the Fischer-Tropsch Process.] Ion, vol. 8, 1948, pp. 86–89; Fuel Abs., 1949, No. 2916; Chem. Abs., vol. 42, 1948, p. 5643.

In the Fischer-Tropsch hydrocarbon synthesis the most active catalysts are Fe, Co, and Ni. Of these, Fe is probably the least active, but it has the advantage of being effective over a wide range of temperatures and is characterized by production of liquid hydrocarbons with CO_2 as byproduct. Co gives a product rich in olefins. Ni tends to produce CH_4, along with liquid and solid paraffins. Previous theories have attributed the catalytic action of these metals to either (1) formation of methylene groups, with carbides of the metals acting as intermediates, and polymerization of the methylene groups; or (2) formation of higher alcohols by the oxide content of the catalyst, with subsequent dehydration to olefins. According to a new theory, carbonyls of the metals are the primary active materials. The existence of a compound $[Fe(CO)_5]_4$ including long chains of CO groups is assumed. This is reduced to 2 mol. of C_8H_{18} and a Fe carbonyl of much lower CO content. After a number of reactions, with Fe_3C, C_3O_2, FeO, and Fe_2O_3 among the intermediate products, the lower carbonyl is reconverted to Fe. Over-all reactions are: $18CO+4Fe \rightarrow [Fe_2(CO)_9]_2$; $[Fe_2(CO)_9]_2+2CO \rightarrow [Fe(CO)_5]_4$; $[Fe(CO)_5]_4+34H_2 \rightarrow C_8H_{18}+15H_2O+CO_2+3CO+4Fe+H_2$. The volumes of CO and H_2 to produce 1 mol. of C_8H_{18} are $10CO+17H_2$ instead of the previously given $8CO+17H_2$, and the theoretical yield of octane is only 188.4 gm. per $m.^3$, instead of 203.5. The presence of Fe carbides and oxides in the catalyst is consistent with this theory, but these compounds only represent stages in the regeneration of the metallic Fe. Hydrocarbon formation is by substitution of H_2 for O_2 in $(CO)_n$ chains already formed. Polymerization of methylene groups is not inconsistent with this theory. The action of alkalies added to Fe catalysts may be either (1) removal of O from CO groups to give percarbonate, H then combining with C, and the percarbonate being subsequently reduced, or (2) polymerization of CO to chains, which combine with Fe to give carbonyls.

2138. LOPMANN, B. [Manufacture of Motor Fuels by the Fischer-Tropsch Process.] Oel u. Kohle, vol 40, 1944, pp. 183–190; Chem. Abs., vol. 38, 1944, p. 6514.

Rather detailed description of the operation of a plant for the manufacture of motor fuels by the Fischer-Tropsch process. The synthesis gas can be produced directly in the correct proportion of $CO:H_2$ (1:2) by passing coke-oven gas directly into the water-gas generator; the gas, together with steam, is passed through the hot coke bed used for making water gas. The generator cycle is automatically (hydraulic) controlled. The coke used should have a particle size of 40–60 mm. and 60–90 mm., and the melting point of the coke slag should be high, which is especially important when coke-oven gas is used directly in the generator because of the high temperature required for the conversion of CH_4. The operation of the generator must be carefully supervised, since otherwise much maintenance work is required. The gas flow through the generator during the different phases of the operation is shown in a diagram. The synthesis gas is passed through a conventional gas-purifying mass, which reduces the S content to 0.2–0.5 gm. H_2S and 10–20 gm. organic S compounds per 100 $m.^3$ of gas. Further purification is effected by passing the preheater (200°–300°) gas over a catalyst, which converts the organic S into H_2S. If coke-oven gas has been fed into the generator, the gas is passed over activated C before catalytic desulfurization, since a small amount of tarry matter containing S compounds is carried even past the generator. The temperature in the catalyst chambers is controlled by the circulation of water under pressure through a tube system (600 tubes per chamber) connected with a steam boiler. Because of the low heat conductivity of the catalyst, the cooling tubes are not in contact with the catalyst directly but with the metal plates on which the catalyst rests. The temperature is kept constant within a few tenths of a degree by regulating the steam pressure in the circulating system. The synthesis products are partly directly cooled by water injection and partly recovered by adsorption on activated C. The activated C is cooled after regeneration by contact with cooled gas. The residual gas is recycled 2 or more times, and the tail gas from the last stage is particularly well suited as fuel for coke ovens. The plant is largely automatically operated. The steam produced in the course of the process is used almost entirely for the generation of electricity, and the plant can be made independent from outside energy sources.

2139. LOPMANN, B., AND JAECKEL, B. [Compilation of Patents Now in Force in the Field of Methanol Synthesis.] Ber. Gesell. Kohlentech., vol. 4, 1931, pp. 1–20; Chem. Abs., vol. 26, 1932, p. 1896.

Review of German patent situation on catalysts, purification of gases, processes, equipment, and working up the product.

LORD, H. D. *See* abs. **330.**

2140. LORENZEN, G. [Gas Purification, Especially Desulfurization and Sulfur Recovery.] Chem. Fabrik, vol. 12, 1939, pp. 6–23; Chem. Abs., vol. 33, 1939, p. 2312.

Review of modern methods of removing dust, tar, NH_3, C_6H_6, NO, and S from gases intended for use in syntheses, with 48 cuts of apparatus and 55 refs.

2141. LORMAND, C. Industrial Production of Synthetic Methanol. Ind. Eng. Chem., vol. 17, 1925, pp. 430–432; Chem. Abs., vol. 19, 1925, p. 2027.

This paper, based on a lecture by Patart before the Société d'encouragement pour l'industrie national, reviews the development of the process for the synthesis of MeOH by catalysis under pressure. A small industrial plant is described, utilized primarily for studying the action of various catalysts. The process operates within a temperature range of 300°–600° C., at a pressure between 150–200 atm., and with a gaseous mixture of H_2: CO in the ratio of 2:1. The pressure may be increased to as much as 900 atm. without deleterious results. A catalyst of Cu and Zn appeared to be the most efficient, although the oxides of V, Cr, and Zn gave good results as did also metallic salts such as chromates, manganates, vanadates, molybdates, and tungstates. The cost of producing MeOH in a plant having a daily capacity of 7.5 ton is calculated at \$0.05–\$0.07 per l. or \$0.18–\$0.26 per gal.

2142. LOSANITSCH, S. M., AND JOVITSCHITSCH, M. Z. [Chemical Synthesis by Aid of the Dark Electric Discharge.] Ber. deut. chem. Gesell., vol. 30, 1897, pp. 135–139; Chem. Zentralb., 1897, I, p. 354; Jour. Chem. Soc., 1897, I, p. 179.

Using a current of 3–5 amp. and 70 v., a mixture of CO and H_2O yields HCOOH, while CO_2 and H_2O give HCOOH, and O_2; CO and H_2 yield CH_2O, which polymerizes; CO_2 and H_2 yield HCOOH. On subjecting mixtures of equal volumes of CH_4 and CO to the silent discharge, acetaldehyde and its condensation and polymerization products are obtained.

2143. LOTTERI, A. [Catalytic Incomplete Oxidation of Methane With Free Oxygen.] Kraftstoff, vol. 17, 1941, pp. 137–140; Brennstoff-Chem., vol. 22, 1941, p. 211; Chim. e ind. (Milan), vol. 23, 1941, pp. 126–129, 175; British Chem. Abs., 1942, B, I, p. 19; Chem. Abs., vol. 35, 1941, p. 5284.

Equilibrium constant at different temperature of the synthesis gas reactions $CH_4+\frac{1}{2}O_2=CO+2H_2+8.8$ cal. was calculated from the published equilibrium constants of the reactions (*a*) $CH_4=C+2H_2$, (*b*) $C+CO_2=2CO$, (*c*) $CH_4+H_2O=CO+3H_2$, and (*d*) $CH_4+2O_2=CO_2+2H_2O$. In mixtures of CH_4 and O_2 above 650°, incomplete combustion of CH_4 prevails over complete combustion (d) more and more with rising temperature. Calculation for a mixture comprising O_2, 33; CH_4, 66; and N_2, 1% shows that at 750°–850° the equilibrium has shifted almost entirely towards the formation of synthesis gas ($CO:H_2=1:2$). When a 2:1 mixture of 92.1% CH_4 and 97–98% O_2 was passed at different space velocities at 890°–960° through a quartz tube filled with a catalyst (ceramic carrier saturated with aqueous Ni nitrate containing activators, subsequently calcined and reduced with H_2), the experimental and calculated data were in good agreement. At 900°, only 1–2% of CH_4 remained at all space velocities employed, and at 920°–960° the residual CH_4 was <1%. Since small quantities of heavy hydrocarbons contained in the original gas mixture were completely converted at low temperature, they appear to be more readily oxidizable than CH_4. Tests made in alloy steel tubes yielded similar results; this fact together with the good performance of the catalyst, indicate that technical application of the process is possible but especially since the reaction velocity is > in the cases of conversion of CH_4 with CO_2 (*b*) or with H_2O (*c*).

2144. ———. [Synthesis of MeOH From a Mixture of CO_2+3H_2.] Chimica e industria (Milan), vol. 24, 1942, pp. 275–278; Chem. Zentralb, 1943, I, p. 209; Chem. Abs., vol. 38, 1944, p. 3411.

Calculations are given for the reaction rate over different catalysts, with CO_2 and H_2 from butyric acid fermentation.

2145. ———. [Incomplete Oxidation of Methane With Free Oxygen.] Rev. combust. liquides, vol. 1, 1947, pp. 19–29; British Abs., 1948, B, II, p. 581; Chem. Abs., vol. 42, 1948, p. 4442.

Incomplete oxidation of CH_4 with free O_2 is examined from both thermodynamical and experimental aspects. Mixtures of CO and H_2 in the ratio of 1:2 can be obtained, and can be used in the synthesis by high or low pressure processes of alcohols, hydrocarbons, and various other derivitives.

———. *See* abs. **2559.**

LOVE, K. S. *See* abs. **832.**

LOWDERMILK, F. R. *See* abs. **1429.**

2146. LOWRY, M. [Complete Synthesis of Fats. Synthetic Butter.] Mat. grasses, vol. 29, 1945, p. 66; Ind. chim., vol. 33, 1946, p. 46.

Fischer synthesis produces variable quantities, depending upon the pressures used, of high-molecular-weight paraffins. Oxidation of these by air transforms them into fatty acids, which can be esterified by means of synthetic glycerin made from propylene. The product has received the name "synthetic butter." It is not certain that the synthetic product has the same physiological properties as natural fats. Certain constituents are lacking, and they contain acids with both odd and even numbers of C atoms, whereas natural fats contain only the even-numbered atoms.

LUDE, A. *See* abs. **1647.**

2147. LUDECKE, —. [Synthetic Benzine.] Seifensieder-Ztg., vol. 55, 1928, pp. 6–8; Chem. Abs., vol. 22, 1928, p. 1458.

Summary of the status of coal hydrogenation and production of hydrocarbons from CO.

2148. LUEBKE, A. [Synthetic Production of Fat From Coal.] Süddeut. Molkerei Ztg., vol. 68, 1947, pp. 182–183; Chem. Abs., vol. 43, 1949, p. 6327.

Review of production of synthetic fats, with arguments for and against their use as food.

LUEDEKE, V. *See* abs. **2178.**

2149. LUGOL, G. [Utilization of Cracking Gas and Natural Gas in Chemical Synthesis.] Ann. mines et carburants, vol. 134, 1945, pp. 401–455; Chem. Abs., vol. 40, 1946, p. 1776.

The possibilities offered by large amounts of cracking gas available through the various processes of petroleum refining are studied. The discussion extends to the utilization of natural gas. 4 general types of applications are given in form of a review: (1) Polymerization and alkylation of the olefins by either thermal or catalytic procedures, whereby known American processes are discussed; (2) synthetic rubbers; (3) general reactions, such as the production of alcohols, formation of alkyl halides, oxidation of olefins with the production of ethers, and the formation of glycols; (4) the industrial reactions of CH_4 such as the production of CO–H_2 mixtures for hydrocarbon synthesis, manufacture of C black, manufacture of C_2H_2, and production of H_2.

LUK'YANOVA, L. I. *See* abs. **3369.**

2150. LURGI GESELLSCHAFT WÄRMETECHNIK M. B. H. Production of Synthetic Methanol. Board of Trade, German Div. Tech. Information and Documents Unit; F. D. 204/47, Nov. 18, 1946, 3 pp.; Fuel Abs., No. 2390, 1948.

Production of MeOH by catalytic reaction of CO and H_2 under high temperature and pressure and the preparation of crude gas from various raw materials are described. The Lurgi pressure gasification in combination with the Lurgi cracking plant for the cracking of CH_4 into CO and H_2 makes it possible to combine production of MeOH with that of town gas. The plant made by Lurgi and standardized for a capacity of

12–50 tons per day is claimed to have the special advantage that the heat exchanger and the vessel containing the catalyst are arranged in a single high pressure unit. Flow diagrams and operation data.

2151. LUYKEN, W., AND KRAEBER, L. [Magnetic Properties of Natural and Artificial Iron-Oxygen Compounds. I. Magnetic Measurements on Powdered Specimens.] Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf, vol. 16, 1934, pp. 169–178; Chem. Abs., vol. 29, 1935, p. 434.

Method was developed for measuring paramagnetic and ferromagnetic substances in the form of powder, and its application in the determination of magnetic properties of Fe-O compounds is described. Magnetization curves of different material.

2152. LUYTEN, L. [Kinetics of the Methane Synthesis on Nickel.] Natuurw. Tijdschr., vol. 23, 1941, pp. 25–26; Chem. Zentralb., 1942, I, p. 25; Chem. Abs., vol. 37, 1943, p. 3662.

Experiments on the poisoning effect of CO on the active Ni used as catalyst in the synthesis of CH_4 from CO and H_2, including those in which D was used, show that the reaction velocity, $S_{CH_4}=k[H_2]^{1/2}/[CO]^{1/2}$ and $S_{CD_4}=k'[D_2]^{1/2}/[CO]^{1/2}$, where $k'/k=1.15$ and 1.025 at 250° and 300°, respectively. The higher the CO content of the gas mixture and the smaller the activity of the catalyst, the greater the difference between the reaction velocities of the 2 isotopes becomes, since in both cases the number of active centers remaining for adsorption of H or D is smaller and the difference between the zero-point energies causes a relatively greater difference between the two isotopes. Apparent activation energies are: $E_{CH_4}=27{,}100$ cal.; $E_{CD_4}=24{,}900$ cal. $E_{apparent}=E_{actual}-3\lambda_{H_2}-\lambda_{CO}$, where λ is the heat of adsorption.

2153. LUYTEN, L., AND JUNGERS, J. C. [The Kinetics of the Catalytic Synthesis of Methane in Nickel.] Bull. soc. chim. Belg., vol. 54, 1945, pp. 303–318; Chem. Abs., vol. 41, 1947, p. 2310.

Reaction is characterized by a strong adsorption of CO on the catalyst and a comparatively weak adsorption of H_2 (or D). Expressions for the velocity of reaction, as derived from experimental measurements, are:

$$V_{CH_4}=k(p_{H_2})^{0.9}/(p_{CO})^{0.2},$$
$$V_{CD_4}=k'(p_{D_2})^{0.7}/(p_{CO})^{0.2}.$$

The reaction is not inhibited by the products of the reaction. The energies of activation are: $E_{CH_4}=27{,}000$ cal., $E_{CD_4}=25{,}000$ cal.

LYNCH, M. A. *See* abs. **355a.**

2154. LYON, W. H., AND CRAWFORD, R. M. Methane Cracking by Partial Combustion With Oxygen or Air in Germany. U. S. Naval Tech. Mission Tech. Rept. 556–45, 1945, 15 pp.; PB 23,076.

Coke-oven gas, hydrogenation tail gas, and Fischer-Tropsch tail gas were commercially cracked by partial combustion with O_2 or air to produce raw materials for various syntheses. Feed gas consisting of N_2 and H_2 was produced for NH_3 synthesis, and various CO–H_2 mixtures were made for use in the MeOH, isobutanol, and Fischer-Tropsch synthesis.

2155. ———. Synthesis-Gas Purification Processes in Germany. U. S. Naval Tech. Mission Rept. (unnumbered)–45, 1945, 16 pp.; PB 40,925; Bib. Sci. Ind. Rept., vol. 3, No. 3, 1946, p. 158.

Report covers those processes that are in commercial use for the purification of large volumes of gas, such as are employed in the production of NH_3, H_2, MeOH, and synthetic oils. The topics considered are: Dusts and tar removal; I. G. alkazid process for gas purification; I. G. Claus process for recovery of S from H_2S; H_2S removal with Fe oxide; removal of organic C, CO_2, and CO; and gas purification by activated C.

LYONS, L. E. *See* abs. **1580.**

LYSSAK, L. *See* abs. **2012.**

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2156. MACFARLANE, A. Synthetic Fuels. Rev. Petrol. Technol., 1936, pp. 252–258.

Developments in the Fischer-Tropsch process comprehensively discussed.

2157. MACFARLANE, W. A. Synthetic Oils From Coal. The Fischer-Tropsch Process. Chem. Age, vol. 40, 1939, p. 259.

Lecture to the Manchester Literary and Philosophical Society. Work of Fuel Research Station is reviewed.

2158. MADORIO, O. [Carburizing Equilibria and the Iron-Carbon Diagram.] Tetsu-to-Hagane, vol. 24, 1938, pp. 432–439.

2159. MAIER, C. G. Reduction of Cuprous Oxide by Carbon Monoxide. Bureau of Mines Rept. of Investigations 2926, 1929, 7 pp.; Chem. Abs., vol. 23, 1929, p. 3621.

Presence of less than 0.1 mm. CO pressure in an atmosphere of otherwise pure CO_2 will act reducingly toward Cu_2O below 1,064°. The equilibrium changes with temperature in such a way that below 900° decreasing quantities of CO suffice to reduce Cu_2O. At temperatures near and above the melting point of Cu, a partial pressure of 7.6 mm. CO in otherwise pure CO_2 should reduce the dissolved CuO to 0.008%.

2160. MAILHE, A. [Synthetic Hydrocarbons.] Jour. usines gaz, vol. 48, 1924, pp. 34–37; Chem. Abs., vol. 18, 1924, p. 1464.

Modern catalytic methods may often be used advantageously to replace the older methods besides offering an explanation of the production of certain industrial hydrocarbons. The article deals, among other things, with: The hydrogenation of CO and CO_2 with Ni at 250°; preparation of saturated aliphatic hydrocarbons from alcohols by the Grignard reaction; hydrogenation of C_nH_{2n} and C_nH_{2n-2} with Ni.

———. *See* abs. **3000.**

2161. MAILHE, A., AND DEGODON, F. [Catalytic Reduction by Means of Formic Acid, and the Products Obtained by Catalytic Condensation of Acetone.] Bull. soc. chim., vol. 21, 1917, pp. 61–64; Chem. Abs., vol .11, 1917, p. 3240.

HCO_2H, which, under the influence of such catalysts as Cu, Ni, and ZnO, decomposes into H_2 and CO_2, was used in the reduction of various ketones. The hydrogenation was carried out at about 300°, using Ni or Cu. The activating effect of Cu and Ni upon the dissociation was studied.

2162. MAKINO, S. [Synthesis of Higher Alcohols From Carbon Dioxide and Hydrogen at High Pressure.] Chem. Rev. (Japan), vol. 5, 1939, pp. 21–38; Chem. Abs., vol. 35, 1941, p. 7938.

Review with 35 refs.

———. *See* abs. **1882, 1883, 1884, 1885, 1888.**

MAKINO, S., KOIDE, H., AND MURATA, Y. Benzine Synthesis From Carbon Monoxide and Hydrogen. LIII. Influence of Aluminum Oxide, Silver and Other Addition Agents Upon the Iron Catalyst. *See* abs. **1889.**

MALAKOFF, H. L. *See* abs. **3592.**

2163. MALINOWSKI, S. [Syntheses From Carbon Monoxide.] Przemysl Chem., vol. 28, 1949, pp. 467–482.

Review of Fischer-Tropsch and related processes.

2164. MALISOFF, W. AND EGLOFF, G. Methane. Jour. Phys. Chem., vol. 22, 1918, pp. 529–575.

2165. MAMPEL, K. L. [Time Versus Amount of Reaction Formulas for Heterogeneous Reactions at the Phase Boundaries of Solids. I. Development of the Mathematical Methods and the Derivation of Surface Area Versus Amount of Reaction Formulas.] Ztschr. physik. Chem., vol. 187, A, 1940, pp. 43–57; Chem. Abs., vol. 35, 1941, p. 2058.

Mathematical and theoretical. The simplifying assumptions of other workers are eliminated. Mampel assumes only equal rates of nuclear formation for equal times and for equal areas of unaffected surface and a constant velocity of growth of the nuclei. The formulas apply to the induction period as well as to the principal period of the reaction. The equation of Fischbeck and Spingler for the induction period is derived.

2166. ———. [Time Versus Amount of Reaction Formulas for Heterogeneous Reactions at the Phase Boundaries of Solids. II. Time Versus Amount of Reaction Formulas for a Powder Consisting of Spherical Particles.] Ztschr. physik. Chem., vol. 187, A, 1940, pp. 235–249; Chem. Abs., vol. 35, 1941, p. 7809.

Mathematical and theoretical. Spherical particles of uniform size are assumed. For large radius the equation has the form $kt/r=1-\sqrt[3]{1-x}$, in which the symbols have their usual meaning. For small radius the equation is $x=1-c_1e^{-k_1r^2t}$. The intermediate case is approximated by either of these equations. This intermediate type is characterized by a reaction velocity greater than that of either of the other 2 cases. For all 3 cases there is an induction period during which the reaction follows a 4th-power time law; this period is short for the first 2 cases and long for the intermediate case. The experimental testing of the results is complicated by the tendency of particles to become smaller during the course of the reaction.

2167. MANCHOT, W., AND MANCHOT, W. J. [Preparation of Ruthenium Carbonyls and Nitrosyls.] Ztschr. anorg. Chem., vol. 226, 1936, pp. 385–415; Brennstoff-Chem., vol. 17, 1936, p. 232; Chem. Abs., vol. 30, 1936, p. 5139.

By reacting CO with Ru at 180° and 200 atm., an easily volatile Ru carbonyl is formed, which separates out at −80° in colorless crystals, melting at −22 to a colorless, optically sensitive liquid, which itself decomposes a little above its melting point with evolution of gas and formation of a yellowish color. After some time it crystallizes into beautiful orange flakes until finally the liquid phase completely disappears. The conversion occurs instantaneously at 50°. The formula of the volatile carbonyl is $Ru(CO)_5$, that of the orange crystals $Ru_2(CO)_9$. It is insoluble in H_2O and easily soluble in C_6H_6, alcohol, $CHCl_3$, CCl_4, and benzine; but the solutions on standing become yellow, indicating formation of $Ru_2(CO)_9$. In alkaline solution, it is a strong reducing agent. With I in C_6H_6, $RuI_2(CO)_2$ is probably formed. $Ru_2(CO)_9$ is easily produced by heating $Ru(CO)_5$ to 50°. It can be easily crystallized from C_6H_6. The crystals are quite stable to air and light, insoluble in H_2O, and soluble in organic solvents. Its solution in glacial AcH becomes lilac in direct sunlight. It is extremely stable and is believed to be due to a change in molecular size. Heated in air, $Ru_2(CO)_9$ begins to decompose at 150°. With I it forms $RuI_2(CO)_2$, orange-red. $Ru(CO)_5$ can also be prepared by heating 1 gm. RuI_3 with 5 gm. Ag in a Cu-coated autoclave with CO at 170° and 455 atm. for 24 hr. A green Ru carbonyl is formed as a byproduct in the conversion of $Ru(CO)_5$ into $Ru_2(CO)_9$. It is amorphous and insoluble in organic solvents but is soluble in pyridine and concentrated HCl. In general, it is similar to $Fe(CO)_4$ and may be the analogous Ru compound. If $Ru_2(CO)_9$ is heated in dry NO for 13 hr. at 120°, the temperature then gradually is raised to 150°, and the NO gradually is displaced by dry N_2, a red, crystalline product is obtained, $Ru(NO)_5$. It is very difficult to obtain this uncontaminated with $Ru(CO)_5$. It easily gives off NO, especially when moist. It is insoluble in H_2O, Et_2O, C_6H_6, slightly soluble in alcohol, somewhat better in acetone, and soluble in pyridine. It is reduced with H_2 at 220°; NH_3 is formed.

MANCHOT, W. J. *See* abs. **2167.**

2168. MANDO, A. [Synthetic Fuels From Lignites.] Florence, 1940, 225 pp.; Fuel Abs., March 1945, p. 236.

Direct hydrogenation of coal and the Fischer-Tropsch synthesis process are discussed. Processes for producing synthesis gas, for example, Viag, Winkler, etc., are diagrammatically described.

2168a. MANES, M. Distribution of Liquid and Solid Fischer-Tropsch Hydrocarbons by Carbon Number. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 3,148–3,151.

Equation has been derived for calculating the distribution by C number of Fischer-Tropsch hydrocarbons, based on the assumptions that chain growth in the synthesis proceeds by stepwise addition of single C atoms, and that the probability of growth, α, of a given hydrocarbon chain is independent of the C number $>C_5$, although it may vary with experimental conditions. The equation relates the distribution of the liquid and solid product to α. Its applicability to relatively crude fractionation data (gasoline, Diesel oil and wax) from a wide variety of sources indicates that the approximate constancy of α, previously observed for liquid hydrocarbons, extends to waxes, and that α is a convenient parameter for characterizing the product distribution. The eventual termination of chain growth is a necessary consequence of the equation so that selective cracking of waxes need not be postulated.

2168b. MANFREDI, G. [Synthesis-Gas Manufacture From Methane and Its Uses in the Chemical Industry.] Ingegnere, vol. 24, 1950, pp. 241–246; Chem. Abs., vol. 45, 1951, p. 2,157.

Review of the use of synthesis gas in the industries of NH_3, HNO_3, NH_4NO_3, urea, MeOH, HCHO, carbon black, HCN, and C_2H_4.

2169. MANKASH, E. K., BORISOVA, G. P., OROCHKO, D. I., AND FROST, A. V. [Kinetics of Catalytic Cracking of Paraffin Over Activated Aluminum Silicate.] Neftyanoe Khoz., vol. 24, No. 6–7, 1946, pp. 26–34; Chem. Abs., vol. 41, 1947, p. 2879.

Cracking of wax (a Fischer-Tropsch product melting 28°–42°, mol. wt. 320) in a reaction tube packed with activated Al silicate catalyst conforms closely to equations for a unimolescular, consecutive reaction. The velocity constant decreases slightly at low feed rates. The apparent energy of activation, calculated from these equations, is 13,550 for the overall decomposition of the feed, 16,400 for the decomposition of cracked gasoline, 11,900 for the formation of gasoline, and 15,000 cal. per mol. for the decomposition of the residue recycled to the 2d pass. The difference in the values for decomposition and formation of gasoline explains why maximum yield of gasoline is lower with increase in temperature. Formulas are derived for calculating the velocity constants of catalytic cracking as a function of temperature. Calculated data on the yield of products and the optimal volumetric velocity corresponding to maximum gasoline yield are tabulated along with experimental values. They agree fairly well.

MANN, C. A. *See* abs. **2122.**

2170. MANNES, L. [Byproducts of Paraffin Oxidation.] Die Chemie, vol. 57, 1944, pp. 6–11; Chem. Trade Jour., vol. 116, 1945, pp. 309, 311; Chem. Abs., vol. 38, 1944, p. 5200.

Comprehensive summary discussing raw materials, higher-molecular aliphatic acids, forerun fatty acids, aqueous and oily condensates, volatile products, hydroxy aliphatic acids, dicarboxylic acids, alcohols, aldehydes, ketones, and Na_2SO_4. 85 refs. A translation of this paper appears in BIOS Misc. Rept. 26, 1945, pp. 13–31, PB 93,709.

MANTICA, E. *See* abs. **2401b, 2706c.**

2171. MAQUENNE, L. [Action of the Oxides of Carbon on Water Vapor.] Ber. deut. chem. Gesell., vol. 16, 1883, p. 1358; Bull. soc. chim., vol. 39, Ser. 2, 1883, pp. 308–309; Jour. Chem. Soc., 1883, p. 860.

CO reacts with H_2O at 150° over Pt sponge so that after 30 hr. all the CO_2 is converted into CO and H_2. It is concluded that the system CO_2+H_2 is stable below the dissociation temperature of CO_2; and that CO is itself at low temperature a stronger reduction agent than H_2.

2172. MARCOTTE, E. [Liquid Fuels.] Rev. sci., vol. 62, 1924, pp. 517–522, 551–557; Chem. Abs., vol. 19, 1925, p. 2267.

Brief outline of the qualities required of liquid fuels and of the possibility of producing them by polymerization of CH_4, hydrogenation and transformation of gaseous into liquid hydrocarbons, polymerization of C_2H_2 into aromatic hydrocarbons, direct combination of CO and H_2, carbonization of coal, lignite, and peat, production of alcohol, and use of $EtOH–C_6H_6$ mixture.

MARDER, M. *See* abs. **3037.**

2173. MAREK, L. F., AND HAHN, D. A. Reactions Involved in the Synthesis of Hydrocarbons and Alcohols From Water Gas. Catalytic Oxidation of Organic Compounds in the Vapor Phase. Chemical Catalog Co., Inc., New York, 1932, chap. IV, pp. 100–135.

2174. MAREK, L. F., BOGROW, A., AND KING, G. W. Experimental Laboratory Study on Effect of Pressure on Carbon Deposition and Rate of Reduction of Iron Oxides in the Blast-Furnace Process. Am. Inst. Min. and Met. Eng., Metals Technol., vol. 14, No. 4, Tech. Pub. 2184, 1947, 24 pp.; Chem. Abs., vol. 41, 1947, p. 4745.

Commercial hematite was sized to 8–14 mesh and reduced with mixtures of commercial compressed CO, CO_2, and N_2, simulating gas compositions occurring in various zones of an actual blast furnace. The results showed that the reduction of Fe_2O_3 proceeds by 2 steps: To FeO and reduction of FeO to Fe. Pressures of approximately 5 atm. abs. increased C deposition under the conditions used. A maximum of C deposition occurred at about 489° at 5 atm. pressure and 1 hr. exposure. The maximum deposition at the peak was more than 3 times the deposition at temperatures 50° higher or lower. The rate of ore reduction is proportional to the linear velocity at constant pressure or to the pressure at constant linear velocity.

MARELLI, S. *See* abs. **8.**

MARK, H. *See* abs. **355.**

2175. MARKLEY, K. S. Synthetic Fatty Acids. I. G. Farbenindustrie A.-G., Ludwigshafen, FIAT Final Rept. 362, 1945, 4 pp.; PB 1,315.

Process used for the production of synthetic fatty acids at Oppau is the same as that used by the Deutsche Fettsäure Werke at Witten (abs. **2176** and abs. **3236**), except that the latter plant used only Fischer gatsch paraffins, whereas the Oppau plant used Riebeck paraffins obtained from brown-coal pitch and Tief-Temperatur Hydrierung paraffin obtained by hydrogenation of brown coal, as well as snythetic paraffins produced by the Fischer-Tropsch synthesis. A considerable amount of work had been carried out on the nutrition value and toxicity of synthetic fatty acids produced by oxidation of paraffins from all 3 sources, and various tests have indicated that synthetic fatty acid glycerides are superior to natural fats owing to the fact that they are composed very largely of saturated fatty acids. It is indicated from the results of physiological research that straight chain fatty acids, whether odd or even, are equally readily assimilated and utilized by the body at least in certain limited amounts. However, branched chain, hydroxy, keto, and dicarboxylic acids, all of which are present in the synthetic acids, are not readily assimilated, if at all, and lead to retarded growth and abnormal excretion products in the urine. However, it is possible to remove the oxygenated and dicarboxylic acids and the branched-chain acids by suitable treatment.

2176. MARKLEY, K. S., AND GOSS, W. H. Märkische Seifen Industrie. BIOS Final Rept. 86, 1945, pp. 25–32, PB 18,911; PB Rept. 225.

Besides the above-named plant (raw material capacity, 40,000 tons per yr.), 3 other plants have produced synthetic fatty acids: Oppau (capacity 20,000 tons); Heydebrech (20,000 tons); and Magdeburg (12,000 tons). The raw material is gatsch produced in the Fischer-Tropsch process. Material made in coal hydrogenation plants cannot be employed because it contains aromatic compounds. About 150–200 tons of fatty acids per month was the maximum used for the production of synthetic fats and margarine. Fatty acids $C_{10}–C_{18}$ (55–60% of the total fatty acids obtained) are used for edible purposes as compared with the $C_8–C_{22}$ acids (60–65% of the total fatty acids) used for soap making. A flow sheet of the process and plant for the manufacture of fatty acids is attached. The oxidation of the gatsch by air is carried out at 110° in Al vessels with stainless steel (V2A) tops and at atmospheric pressure in the presence of 0.2% $KMnO_4$ as catalyst. The reaction is continued until the mixture contains about 33–35% fatty acids, the remaining nonoxidized material being recycled. The overall yield of fatty acids is about 80%. Synthetic fats and margarine are made from the fatty acids by esterifying with glycerin at 120°–180° in the presence of a Zn catalyst. Whereas, the fatty acids themselves have a strong, unpleasant odor, the fats made from them are much better and have very good keeping qualities. It also is claimed that synthetic fats are utilized in the body as well as natural fats and are more suitable for diabetics, the explanation being that while diabetics burn the even number of C chains present in natural fats to give acetone, the odd number chains in synthetic fats, in addition to even number chains, are burned to propionic acid and finally give CO_2 and H_2O. The cost of synthetic acids in the different plants ranged RM 70–120 per 100 kg., whereas that from natural oils during the war was RM 140. The cost, however, depends upon the price of gatsch (during the war this was RM 30 per 100 kg.), and normally synthetic acids for soap making would cost 2 times as much as natural soapmaking oils in Germany and on the world market perhaps 3 times as much.

2177. ———. Oxo G. m. b. H., Ruhrchemie A.-G. BIOS Final Rept. 86, 1945, pp. 33–37; PB 18,911. PB Rept. 225.

Oxo G. m. b. H. is owned by the Ruhrchemie A.-G., I. G. Farbenindustrie A.-G., and Henkel & Cie. Fatty alcohols are made by treating the olefin products obtained from the Fischer-Tropsch process with CO and H_2 under 200 atm. pressure and 180° in presence of a Co–Mn–Th catalyst. The main part of the alcohols obtained are sulfated to obtain nonsoapy detergents. Fatty acids can be made from the alcohols by a further oxidation process, but the process is not economical. The chief alcohols made by the Oxo process have chain lengths ranging from $C_{11}–C_{18}$. The C_{13}, C_{17}, and C_{18} alcohols were very satisfactory as regards color, and the C_{17} and C_{18} alcohols were comparatively free from odor. The cost of the olefins was stated to be 35–40 pf. per kg., and they are sold to Oxo at 45 pf. The cost of the finished alcohols was 80–90 pf.

MARSCHNER, R. F. *See* abs. **3153, 3767, 3768.**

2178. MARSH, J. L., FREMON, G. H., GLENN, R. D., LUEDEKE, V. D., AND PORTER, D. J. Coming Search for Synthetic Motor Fuels. Chem. and Met. Eng., vol. 51, No. 6, 1944, pp. 107–111.

Survey, including the Fischer-Tropsch process.

2179. MARSHALL, A. L. Synthetic Formaldehyde From Carbon Monoxide and Hydrogen. Mechanism of the Sensitized Photochemical Reaction. Jour. Phys. Chem., vol. 30, 1926, pp. 1634–1640; Chem. Abs., vol. 21, 1927, p. 534.

Kinetic study is continued of the photochemical reaction between H_2 and CO when sensitized by Hg vapor to light of wavelength 2536.7 Å. U. from a H_2O-cooled Hg arc. The gases were saturated with Hg at 50°, and the reaction chamber was maintained at 80°. The apparatus and method were the same as those previously described. Measurements were made of the amount of energy absorbed while the reaction was proceeding. The data for the last of a series of 10 experiments were: Volume of apparatus, 890 cc.; initial gas mixture, 510 mm. CO, 279 mm. H_2; absorption rate, 1.35 $(10)^{19}$ quanta per min.; maximum rate of reaction 2.1 mm. per min. corresponding to 3.3 $(10)^{19}$ molecules of HCHO formed, or quantum yield of 2.44. The reaction product formed was largely HCHO or a polymer. In 1 experiment, 138 cc. of a theoretical 200 $cc.^3$ of HCHO were recovered. A study of the velocity constants calculated by various possible kinetic equations makes it apparent that the velocity depends in some way on the ½ power of the H_2 and the 1st power of the CO concentration. This would seem to mean that the velocity depends on the concentration of atomic H. The most satisfactory equation expressing the velocity is $d/dt(\mathrm{HCHO}) = k(\sqrt{P_{H_2}})(P_{CO})$. The reaction between CO_2 and H_2 was reinvestigated, and it was found that reaction proceeds at a relatively slow rate.

2180. MARSHALL, F. C. B. Scientific Utilization of Coal and Its Importance to the Paint Industry. Jour. Oil & Colour Chemists' Assoc., vol. 29, January 1946, pp. 3–13.

Emphasizes the importance of low-temperature tar in the paint industry and advocates the introduction of the Fischer-Tropsch process and processes based on C_2H_2, CaC_2 and water gas for providing chemicals for this and the plastics and rubber industries.

2181. MARTIN, F. [Benzine and Oil Synthesis From Water Gas.] Petrol. Ztschr., vol. 33, No. 33, 1937, pp. 1–6; Chem. Abs., vol. 32, 1938, p. 3577.

Flowsheet, representation by models, and photographs are used to explain the synthetic production of oils from water gas.

2182. ———. [Industrial Synthesis of Benzine and Oil From Water Gas.] Mitt. Forsch.-Anstalt. Gutehoffnungshütte Oberhausen A.-G., vol. 5, 1937, pp. 159–166; Oel u. Kohle Erdoel Teer, vol. 13, 1937, pp. 691–697; Ind. Chemist, vol. 13, 1937, pp. 320–326; Glückauf, vol. 73, 1937, p. 812; British Chem. Abs., 1937, B, p. 1005.

Author discusses problems arising from the large-scale application of the Fischer-Tropsch process and describes commercial plants and the properties of the synthetic products. Nature of the problems that had to be surmounted in the conversion of the Fischer-Tropsch process to the industrial scale is considered.

2183. ———. [Industrial Synthesis of Gasoline and Oil From Water Gas.] Cong. mondial pétrole, 2me Cong., Paris, Sec. 2, Phys. Chim. Raffinage, 1937, pp. 299–307; Chem. Abs., vol. 33, 1939, p. 359.

New and efficient processes have been worked out in the production of petroleum-like hydrocarbons from a mixture of CO and H_2; they solve the problems of (1) prolongation of the life of the contact mass, (2) inexpensive construction of the reaction chamber, (3) regeneration of rare metals and metal oxides from used contact masses and (4) transformation of primary synthetic product into marketable gasoline. Synthetic gas is obtained by the use of coke or lignite briquets. After passing the 1st contact mass, the primary product contains 92% liquid products, of which 22% is gas oil, 10% solid paraffins, and 60% liquids boiling up to 200°; the proportion of olefins in the lower-boiling liquids ranges from 30–55%; the gaseous products are rich in propylene and butlyene. The liquid products are converted into marketable gasoline to the extent of 80%, and the gas oil, which has a cetane no. above 100, can be recovered separately and used to improve low-grade diesel oils from other sources. High-grade lubricants also may be produced. With the contact masses now in use no material change in the boiling curve of the primary product is possible. By increasing the CO content of the entering gas, it is possible to increase the olefin content without materially changing the ratios of the various fractions, which makes it possible to obtain by polymerization a larger proportion of hydrocarbons of high molecular weight.

2184. ———. [Development of the Synthesis of Hydrocarbons From Water Gas.] Chem. Fabrik, vol. 12, 1939, pp. 233–240; British Chem. Abs., 1939, B, p. 905; Chem. Abs., vol. 33, 1939, p. 5630.

Methods of producing the gas from various fuels are reviewed and illustrated with cuts of apparatus. The effects of temperature, pressure, contact substance and the time of contact on the nature of the synthetic products are discussed. There is a suitable process available for the production of the gas from virtually every type of fuel, and with well-purified gas the synthesis of the primary hydrocarbons is independent of the source of the gas.

2185. ———. [Synthetic Paraffins for the Preparation of Fatty Acids.] Fette u. Seifen, vol. 48, 1941, pp. 395–396; Chem. Abs., vol. 37, 1943, p. 544.

Review.

2186. ———. [Fischer-Tropsch Hydrocarbon Synthesis.] Erdöl u. Kohle, vol. 1, 1948, pp. 26–29; British Abs., 1948, B, I, p. 684.

Reviews recent published work on the production of synthesis gas and its S purification, the properties of the different catalysts, and their reaction mechanisms and products.

2187. MARTIN, P. T. Synthesis Gas From Coal. Min. Cong. Jour., vol. 36, No. 2, 1950, pp. 55–58; Chem. Ind., vol. 66, No. 3, 1950, pp. 365–372.

Reviews all processes that have been or are being tried in producing synthesis gas for the production of synthetic liquid fuels. The process most favored appears to be that of utilizing continuous gasification of powdered coal in suspension with O_2 and steam. With present O_2 prices, it is the opinion that synthesis gas can be produced today at about $0.15/M cu. ft. from coal at $2.00/ton.

MARTIN, R. *See* abs. **2461.**

MARTIN, R. M. *See* abs. **750.**

MARTIN, W. *See* abs. **2933.**

2188. MARTINENGHI, G. B. [Experimental and Technical Preparation of the Higher Fatty Alcohols.] Olearia 1947, pp. 309–319; Chem. Abs., vol. 42, 1948, p. 4371.

Review on preparation and sulfonation of higher fatty alcohols. Points discussed are: Extraction from spermaceti, synthesis by hydrogenation of glycerides or fatty acids, synthesis by addition of CO to olefins from Fischer-Tropsch process and subsequent hydrogenation, and reduction of glycerides or other fatty acid esters with metallic Na. 29 refs.

MARUSHKIN, B. K. *See* abs. **2492.**

MARUSHKIN, M. N. *See* abs. **139.**

MASON, L. S. *See* abs. **49.**

2189. MATHEWS, J. A. Review and Bibliography of the Metallic Carbides. Smithsonian Miscellaneous Collections 1090 (1898).

2190. MATHIEU, K. [Measurements of Specific Magnetization and Their Use in Problems of the Metallurgy of Iron.] Arch. Eisenhüttenw., vol. 16, 1943, pp. 415–423; Chem. Abs., vol. 38, 1944, p. 708.

New magnetic pendulum balance is described by which the magnetization is determined by deflection. Several examples illustrate use of the instrument from −150° to +1,000°.

MATHIEU, K. *See* abs. **2059.**

MATHIEU, S. *See* abs. **551, 552, 553.**

2191. MATIGNON, C. [Physicochemical Study of Some Organic Syntheses.] Bull. soc. chim., vol. 37, 1925, pp. 825–836; Chem. Abs., vol. 20, 1926, p. 38.

It is readily possible to decide from the heats of reaction and van't Hoff's equation and the principles of equilibrium whether certain synthetic reactions, starting with simple gaseous substances, could be realized, granted a suitable catalyst, or would be entirely unattainable without the introduction of energy in some form. For example, $CO+2\ H_2=MeOH+27.2$ cal. $K=(p_1\times p_2^2)/x$, where p_1, p_2 and x are the pressures of the substances concerned in atmospheres. K can be calculated for any other temperature by the relation $\log K=-27{,}200/457\ T+3.5\log T+4.3$. Then for assumed, but possible, values for p_1, p_2, x can be calculated. If it is relatively large at the temperatures and pressures used, the reaction is possible, but if x is small, the reaction could not possibly be realized. In the above case, at 227° and $p_1=p_2=50$ atm., $x=1.8\times10^3$. At $p_1=p_2=1$, $x=1/70$. At 327°, the equilibrium is less favorable but still possible, while at 427° it would be virtually useless. Similar calculations are used to show that primary aliphatic alcohols, AcOH and $EtCO_2H$ could be made from CO and H_2 but that CH_2O could not be. From C_2H_4 and H_2 the saturated hydrocarbons could be formed, also Me_2CO and PrOH from C_2H_4, CO, and H_2. From CH_4 and H_2O, CO and H_2 might be made at a rather high temperature, but CH_4 and CO and H_2 could not give EtOH nor could CH_4 alone give C_2H_6, etc. Since in general any catalyst that assists a reaction toward equilibrium also assists the opposite reaction toward equilibrium, the search by catalysts for reactions shown by the above methods to be possible can be simplified by searching for decomposition catalysts for the final substances desired. For example, find catalysts for the decomposition of AcOH to CO and H_2, and the same catalysts will serve for the synthesis of AcOH from CO and H_2.

2192. ———. [Physicochemical Study of Some Organic Syntheses.] Chim. et ind., special No., September 1926, pp. 513–519; Chem. Abs., vol. 21, 1927, p. 731.

Discussion, a priori, of the synthesis of MeOH, of aldehydes and ketones, in general, and Me_2CO, in particular, of AcOH and of $EtCO_2H$ from CO and H_2, of EtOH, C_4H_{10}, C_6H_{14}, Me_2CO, and C_3H_7OH from C_2H_4, of the syntheses starting from CH_4 and of the synthesis of nitrogenous organic compounds by the use of NH_3.

2193. ———. [Future Position of Coals as Raw Materials of the Chemical Industry.] Chim. et ind. vol. 23, 1930, pp. 543–555; Chem. Abs., vol. 24, 1930, p. 4611.

Primary byproducts of coal carbonization and petroleum cracking (H_2, CO, CH_4, C_2H_4, etc.) are surveyed and their applications in NH_3 synthesis, hydrogenation, and the syntheses of MeOH and CH_2O are indicated. CH_4 in turn may become a starting point for C_2H_2, HCN, MeCl, etc.; C_2H_4 for EtOH; and ethylene glycol for butadiene and synthetic rubber.

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2194. MATIGNON, C., AND SEON, M. [Action of Water Vapor on Methane.] Compt. rend., vol. 195, 1932, pp. 1345–1348; Chem. Abs., vol. 27, 1933, p. 1565.

CH_4 pure or mixed with H_2, N_2, O_2, and CO yields H_2 and CO_2 when mixed with a large excess of H_2O vapor and passed slowly over the catalysts SiO_2, ZrO_2, asbestos sprinkled or impregnated with ZrO_2, ThO_2, Fe_2O_3, Fe_2O_3+10% K_2CO_3, or Al_2O_3 at 860°, 960°, 1,000°, or 1,050°. The best results for the mixture were obtained with ZrO_2. With pure CH_4 and ZrO_2 at 1,050° the reaction was complete.

2195. MATSUBARA, A. Chemical Equilibrium Between Iron, Carbon, and Oxygen. Trans. Am. Inst. Min. and Met. Eng., vol. 67, 1922, pp. 3–55; Chem. Abs., vol. 15, 1921, p. 1683.

Detailed report on an extended research on (1) the equilibrium composition of the gas phase in the system CO, CO_2, and Fe (containing 2–30% O) at the temperatures 873°, 1,070° and 1,175°; (2) the equilibrium composition of the gas phase in the systems (*a*) CO, CO_2, FeO (saturated with Fe), and Fe (saturated with FeO) and (*b*) CO, CO_2, Fe_3O_4 (saturated with FeO), and FeO (saturated with Fe_3O_4) at several temperatures above 700°; (3) the equilibrium composition of the gas phase of the systems (*a*) FeO, Fe_3C, CO, and CO_2 and (*b*) Fe, Fe_3C, CO, and CO_2 in the range 700°–1,100°. The specific reactions considered are (*A*) $3\ Fe_2O_3+CO\rightleftharpoons 2\ Fe_3O_4+CO_2$; (*B*) $Fe_3O_4+CO\rightleftharpoons 3\ FeO+CO_2$; (*C*) $FeO+CO\rightleftarrows Fe+CO_2$; (*D*) $2\ CO\rightleftarrows C+CO_2$; (*E*) $3\ FE+2CO\rightleftarrows Fe_3C+CO_2$; (*F*) $3\ FeO+5CO\rightleftharpoons Fe_3C+4CO_2$. Pure CO was admitted to a porcelain tube containing a sample of Fe_2O_3 heated to a definite temperature. After equilibrium was attained the gas phase was withdrawn and analyzed, and the boat containing the partly reduced Fe_2O_3 was weighed to check the amount of O remaining in the solid phase. This procedure was repeated until the O in the solid phase was reduced to about 2%. To make sure of the reversibility of the reactions concerned, an already reduced solid phase (Fe–FeO) was oxidized by successive charges of CO_2. These values agreed with those obtained by reduction with CO. The equilibrium pressures within the range 561°–1,175° for reactions (B) and (C) when each system contains amorphous C are calculated from the experimental values for the composition of the gas phase. The dissociation pressures for FeO and Fe_3O_4 are also calculated. When, by successive reductions with CO, the O in the solid phase of the systems considered above is decreased to a small quantity a new reaction begins, and the solid phase contains, besides O, some combined C. The reaction of carburization takes place according to (*E*) or (*F*). From determinations of the equilibrium constants for (*E*) and (*F*) it is concluded that the 1st period of carburizing reaction coincides with (*F*) and at a later period with (*E*); that there exist transient equilibria between the above 2, between the 1st and reaction (*C*) and between the 2d and (*D*); equilibria at lower temperature occur with a more oxidized form of the solid phase than at higher temperature even in the same carburizing reaction. The limits of temperature and pressure for carburization are determined from the experimental data. Above 1,300° the carburizing action of CO does not occur; carburized Fe is oxidized to FeO–Fe solid solution by pure CO at 1 atm. pressure. Under 1 atm. pressure, at 1,200° neither carburization nor decarburization occurs in pure CO; between 1,200° and 1,300°, C-bearing Fe is decarburized by pure CO, but O-bearing Fe may be carburized by the same gas, both reactions ending in the formation of O-bearing carboniferous Fe proper to that temperature; between 695°–1,200° a gas rich enough in CO will carburize Fe; below 695° no carburization in the ordinary sense can occur. The carburization theory is applied to the practice of casehardening, the making of malle-

able castings, and to the explanation of a blast-furnace diagram and the problem of quick smelting.

MATSUBARA, I. *See* abs. **1119, 1120.**

MATSUMOTO, E. *See* abs. **1906a.**

MATSUMURA, A. *See* abs. **1930.**

MATSUMURA, S. *See* abs. **2197, 2198, 2199, 2200, 2201, 2202, 2203, 2204, 2205.**

2196. MATSUMURA, S., TARAMA, K., AND KODAMA, S. Benzine Synthesis and Activated Adsorption of Hydrogen, Carbon Monoxide, Carbon Dioxide and Water on Cobalt and Iron. I. II. III. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 37, 1940, pp. 302–322 (in German); Jour. Soc. Chem. Ind. (Japan), vol. 43, suppl., 1940, pp. 175–184; Chem. Zentralb., 1940, II, p. 2842; Chem. Abs., vol. 34, 1940, pp. 6502–6503.

Physical adsorption of H_2 on Co or Fe occurs below 60°; above this temperature activated adsorption occurs until a maximum is reached at approximately 200° (Co) or 160° (Fe). Adsorption of CO by Co or Fe, although equilibrium is approached slowly, increases rapidly above 60°, the adsorption being reversible below 110° (Co), but decreases above 60° for Fe, adsorption increasing above 190°. Chemisorption of CO by Co or Fe probably results in carbide formation, Fe requiring a higher temperature for this process. Adsorption of CO_2 by Co is considerable; physical adsorption probably occurs below 100° and activated adsorption above 100°, with a maximum at 150°. Fe adsorbs considerable CO_2 at room temperature, but this adsorption decreases to a negligible amount at 300°. Co and Fe exhibit physical adsorption of N, adsorption virtually ceasing at 100° (Co) and 250° (Fe). Subtraction of the values on the adsorption curve for N on Co or Fe from those on the curve for wet N indicates roughly that activated adsorption of H_2O on Co starts about 60° and reaches a maximum at 100° and that for Fe activated adsorption begins at 200°. In the benzine synthesis, a carbide is first formed, which reacts with adsorbed atomic H to give CH_2 groups; these CH_2 groups undergo polymerization (various degrees depending on number of groups present), then reduction, and the hydrocarbons so formed volatilize from the catalyst surface. Temperatures above 160° for the synthesis of benzine with Co catalyst are necessary so that enough quantities of activated H_2 will be adsorbed on the catalyst. A higher reaction temperature is required with Fe on account of higher temperature of formation of Fe carbide. In the benzine synthesis, Co differs in its action from Fe in that H_2O instead of CO_2 is formed because of the greater desorption velocity of H_2O from the Co.

2197. KODAMA, S., MATSUMURA, S., AND TARAMA, K. Physicochemical Investigations on Coal Synthesis. IV. Velocity of Adsorbing Hydrogen by Cobalt. Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, pp. 823–825; Chem. Abs., vol. 42, 1948, p. 2080.

H_2 under atmospheric pressure is brought into contact with Co at 14.5°–275°, and the velocity of adsorption of H_2 by Co is measured. When t (in min.)$/x$ (cc. H_2 adsorbed per gm. of Co) is plotted against t for each temperature, a straight line is obtained in each case; this shows that there is a relation $t/x=t/A+1/A^2K$, which is the integrated form of $dx/dt=K(A-X)^2$, where A and K are constants characteristic of each temperature. This proves the fact that H is adsorbed in the dissociated state by two active centers of Co. Study of A and K determined for various temperatures shows that on the surface of Co there are active adsorbing centers of various degrees of activity, and at low temperature the centers of greater activity react. When the temperature is raised such centers soon become saturated with H, and then the centers of less activity begin to exhibit a measurable velocity of adsorption. Thus, the higher the temperature the greater the adsorption by active centers of smaller activity.

2198. KODAMA, S., MATSUMURA, S., AND ANDO, T. [Physicochemical Investigations on Gasoline Synthesis. V. Velocity of Adsorption of Hydrogen by a Catalyst of Cobalt and Infusorial Earth.] Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, pp. 920–924; Chem. Abs., vol. 42, 1948, p. 8439.

Mechanism of adsorption of H_2 under atmospheric pressure by Co precipitated on infusorial earth is the same as in the case of pure Co, but A, determined by the number of active adsorbing centers, is much greater for the supported catalyst. The values of K, measuring the velocity of adsorption, are small, perhaps because the activity of adsorbing centers increases and most of them are instantly saturated, so that only the adsorption of less active centers is within the scope of measurement. Variation in A with temperature shows the same tendency as in the previous case.

2199. ———. Physicochemical Investigations on Gasoline Synthesis. VI. Velocity of Adsorption of Hydrogen by Cobalt–Thoria–Infusorial Earth Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, pp. 920–924; Chem. Abs., vol. 42, 1948, p. 8440.

With a catalyst of Co, ThO_2, and infusorial earth in the ratio 100:18:150, there was no change in the mechanism of adsorption, but there was further increase in A, with adsorption taking place more rapidly and with the final amount of H_2 adsorbed being greater than in previous cases. Addition of Th not only increased the number of active adsorbing centers, but also produced centers of greater activity at lower temperature, so that it greatly decreased the temperature of activated adsorption of H_2.

2200. KODAMA, S., MATSUMURA, S., TARAMA, K., ANDO, T., AND YOSHIMORI, K. Physicochemical Research on Gasoline Synthesis. VII. Velocity of Adsorption of Hydrogen by Iron. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 254–258; Chem. Abs., vol. 43, 1949, p. 2412.

Similar experiment to that previously described (abs. **2197**), in which Fe was used instead of Co, was carried out at 0°–306°. When t/x is plotted against t for each temperature one straight line for 0° and 30° was obtained, and one broken line (broken at 1 point) for temperatures above 60°, except 99.6°, for which no line or lines were obtained, leading to 1 or 2 sets of values of A and K. It is concluded that H_2 is adsorbed by Fe in the dissociated form as by Co, that the surface of Fe is not homogeneous, and adsorption at the centers of the weaker activity is observed at higher temperatures. No reason for the irregularity at 99.6° was found. Values of A above 150° were much higher than below, which shows that above 150° the number of active centers of adsorption suddenly increases.

2201. ———. Physicochemical Research on Gasoline Synthesis. VIII. Velocity of Adsorption of Hydrogen by Iron on Infusorial Earth. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 254–258; Chem. Abs., vol. 43, 1949, p. 2413.

Similar experiment was performed by using Fe hydroxide precipitated on infusorial earth and dried. The result was similar to the previous experiment except that there was a shift in temperature at which irregularity and broken lines appeared. In general, it was also noticed that infusorial earth had an effect of increasing the number of active centers and increasing the activity of those centers.

2202. ———. Physicochemical Research on Gasoline Synthesis. IX. Velocity of Adsorption of Hydrogen by a Composite Iron Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 254–258; Chem. Abs., vol. 43, 1949, p. 2413.

Similar experiment was carried out with a catalyst containing Fe, Cu, Mn, and infusorial earth in the ratio 100 : 25 : 2 : 125, respectively, which was reported by Tsuneoka and others (abs. **1885**) to be a good catalyst in gasoline synthesis. Results similar to the case of pure Fe were obtained, except that the t/x–t curve was irregular at 25° and 60°, and above 100° it was a broken line, showing that the adsorption of H_2 above 100° conformed to the second order reaction velocity equation. In comparison with the Fe-infusorial earth catalyst, there was no marked change in the amount of H_2 adsorbed and its change with temperature at higher temperature, but below 100° the amount of H_2 adsorbed increased. This increase is considered to be caused by Cu.

2203. ———. Physicochemical Research on Gasoline Synthesis. X. Adsorption of Carbon Monoxide on Cobalt, Cobalt–Kieselguhr, and Cobalt–Kieselguhr–Thoria Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 47, 1944, pp. 1–5; Chem. Abs., vol. 43, 1949, p. 2413.

Adsorption of CO was measured at 0°–250°. In all cases, adsorption accompanied by decomposition of CO and formation of metallic carbide took place above 110° and ordinary activated adsorption took place below 110° The addition of kieselguhr and ThO_2 greatly increased the number of centers of activity and promoted the formation of carbide.

2204. ———. Physicochemical Research on Gasoline Synthesis. XII. Adsorption of Carbon Monoxide on Iron, Iron–Kieselguhr, Iron–Kieselguhr–Copper–Manganese Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 47, 1944, pp. 1–5; Chem. Abs., vol. 43, 1949, p. 2413.

Adsorption of CO at 0°–300° was measured. In all cases, adsorption accompanied by the formation of carbide took place above 150°, and the addition of kieselguhr and Cu+Mn greatly increased the velocity of carbide formation. The effectiveness of kieselguhr as carrier and promoter in gasoline synthesis is considered to be due to the increase in the number of active centers for H_2 and CO, the increase in the amount of activated adsorption of H_2 and the velocity of carbide formation, while the effectiveness of Cu+Mn as promoter lies in the increase in the number of active centers for carbide formation. The reaction temperatures of the catalysts of the Fe series are higher than those of the Co series because the Fe catalysts form carbides at higher temperatures.

2205. KODAMA, S., MATSUMURA, S., YOSHIMORI, K., NISHIBAYASHI, Y., KADOTA, N., AND IWAMURA, E. Physicochemical Studies on Gasoline Synthesis. XIII. XV. Influence of Potassium Carbonate and Boric Acid on the Activated Adsorption of Hydrogen and Carbon Monoxide on Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), Sec. vol. 51, 1948, pp 80–100; Chem. Abs., vol. 44, 1950, p. 9136.

By adding K_2CO_3 to the catalyst containing 100 Fe+25 Cu+2 Mn+125 kieselguhr, activated adsorption of CO above 200° is increased, while that of H_2 is not, especially when 6% K_2CO_3 is added. By adding H_3BO_3 to the same catalyst, adsorption of CO is decreased and adsorption of H_2 increased at 200°. When 20% H_3BO_3 and 2% K_2CO_3 are added, adsorption of both CO and H_2 at 200° is increased. The above tendency conforms with results of gasoline synthesis with the same catalyst: Increase in the length of synthesized molecules and of the I values of the oil by adding K_2CO_3 or a decrease with H_3BO_3, and an increase in yield by the addition of both.

2206. MATTHEWS, M. A. Oxo Synthesis. BIOS Final Rept. 747, 1945, pp. 2–4, PB 52, 880.

Brief description of plant and operation at Ruhrchemie, Holten.

2207. ———. Acetylene by the Arc; Also the Oxosynthesis at Ruhrchemie, Holten. BIOS Final Rept. 747, Sept. 1946, 4 pp.; PB 52,880.

Besides the production of C_2H_2 from CH_4 by high-temperature cracking, some details are given regarding a plant that was under construction for the production of alcohols from the C_{11}–C_{18} olefins obtained from Fischer-Tropsch Kogasin by the Oxosynthesis, that is, addition of CO and H_2 under pressure to give the aldehyde and subsequent reduction by H_2 under pressure to the alcohol. The catalyst is the normal Fischer-Tropsch catalyst of Co–ThO_2–kieselguhr. The yield of alcohols is approximately 100% by weight of the olefins present in the reaction mixture. The mixed alcohols are to be used for manufacture of detergents.

2208. MATTHEWS, M. A., AND WOOD, W. L. Oxidation of Hydrocarbons to Ethylene and of Methane to Acetylene With Conversions of Acetylene to Acetone. BIOS Final Rept. 877, 1945, 7 pp.; PB 52,854.

Investigation was made by oxidizing C_2H_6, C_3H_8, C_4H_{10}, and Kogasin from the Fischer-Tropsch synthesis into C_2H_4, as well as oxiding CH_4 to C_2H_2 and manufacturing acetone from C_2H_2.

2209. ———. Production of Alcohols and Ketones From Olefins at the Treibstoffwerk, Rheinpreussen. BIOS Final Rept. 131, 1946, 12 pp., PB 18,926; Fuel Abs., vol. 3, No. 5, 1946, Abs. 2315.

Waste gases from the Fischer-Tropsch plant were used as raw material, but, owing to the great need for synthetic gasoline, expansion of this work did not receive official sanction as it appears that synthetic gasoline was more urgently needed than synthetic alcohol. The same situation arose when a proposal was made by the Treibstoffwerk to crack part of their product to gaseous olefins or to run the Fischer-Tropsch reaction with a reduced H_2 partial pressure.

MATTHIAS, B. T. *See* abs. **1136.**

MATUI, A. *See* abs. **2502, 2503, 2504.**

2210. MATUI, A., AND YASUDA, M. Oxidation of Methane Under Pressure. I. Jour. Soc. Chem. Ind. (Japan), vol. 43, suppl., 1940, pp. 453–454; Chem. Abs., vol. 35, 1941, p. 3796.

Partial oxidation of a natural gas containing 94.95% CH_4 in the presence of 30% air, was studied at 350°, the variable being gas pressure and velocity of gas flow. At 100 atm. pressure (kg. per $cm.^2$) over Fe_2O_3 as catalyst 400 mg. CH_3OH per 100 l. gas was formed; CuO and AgO gave 360 mg. and 285 mg. CH_3OH, respectively, under the same conditions. With increase of pressure the Fe_2O_3 and CuO curves increased in slope while the AgO curve decreased. The same gas mixture yielded 30 mg. HCHO over AgO and over CuO catalysts, and 23 mg. over Fe_2O_3 under 100 atm. pressure at 350° and a gas flow of 10 l. per min. The yield of CH_3OH over AgO tended to increase, over Fe_2O_3 and CuO to decrease, with increase of velocity of gas flow, while the yield of HCHO was less-affected over these catalysts.

2211. MATUSHITA, T., AND NAGASAWA, K. Mechanism of the Tempering of Steels. Jour. Iron Steel Inst. (London), vol. 10, 1927, 12 pp.; Chem. Abs., vol. 21, 1927, p. 3876.

The change in electric resistance and intensity of magnetization are determined for a quenched C steel containing 1.02% C, 0.33% Si, 0.30% Mn, 0.015% P, and 0.022% S, and it is found that during the decomposition of martensite, the electric resistance decreases and the intensity of magnetization increases, both in 2 steps below 300°. It is concluded that there are 2 kinds of martensite, α and β, of which during the heating at a normal rate, the first decomposes at 100°–170° and the second at 170°–300°. In decomposing, martensite yields free C rather than cementite, and this combines with Fe in the interval 300°–400° to

form cementite. This formation of cementite is believed to explain the second contraction in the thermal expansion curve as well as the sharp increase in magnetic hardness between 300° and 400°. This also is illustrated with a W steel containing the double carbide $4Fe_3C.WC$. The authors propose the following classification of the tempered structures of quenched C steels: martensite+troostite—100°–300°; troostite—300°; troostite+sorbite—300°–400°; sorbite (osmondite)—400°; sorbite+granular pearlite—400°–550°; granular pearlite—550° to Ac_1 point. This is only valid for a normal rate of heating.

2212. MAXTED, E. B. Employment of High Pressures in Chemical Industry. Jour. Soc. Chem. Ind., vol. 45, 1926, pp. 366–370T; Chem. Abs., vol. 20, 1926, p. 2712.

High pressures are used (1) to increase reaction velocity, (2) to change equilibrium conditions, (3) to influence the course of a reaction, and (4) to facilitate heat transfer. Joints should be tongue and groove with metallic or vulcanized-fiber gaskets. Pipe joints should be flanged, with the end of the pipe projecting slightly to form the actual joint. Sliding parts can only be packed by some form of leather bucket. Internal heaters may have their leads carried through vessel walls by bolts in fiber sleeves with fiber gaskets protected by steel washers under the nuts. Thermocouple leads are passed through fiber tubes in the wall and the gland, with a disk of fiber under the gland as packing; or they may have a metal disk soldered to the wire and packed in the stuffing box by fiber washers above and below the disk. Brief mention is made of the significance of high pressures in the synthesis of NH_3, CH_3OH, "synthol," H_2 from H_2O and Fe, isopropyl alcohol, and hydrogenation of naphthalene.

2213. ———. Application of Catalysis in Industry. Chem. and Ind., vol. 57, 1938, pp. 759–766.

Growth of the catalytic industry is demonstrated, and the general aspects of catalysis are discussed. In heterogeneous catalysts, the surface: mass ratio is important; promoters that are not normally catalysts increase the activity of catalysts by providing a dispersion medium that avoids the formation of large crystal growths and thus increases the effective surface. Other promoters are themselves catalysts; there is direct evidence that complex associations are formed. The promoting action of alkali is discussed, although the explanation is not yet understood. Hydrogenation catalysis is discussed at some length. Hydrogenation of CO with Co–Th catalyst is employed for the production of paraffins and of unsaturated hydrocarbons, which can be polymerized to a satisfactory lubricating oil. The reaction gas mixture of H_2 and CO is cleaned of H_2S by an Fe oxide purifier, and of organic S by an alkalized Fe contact mass at 200°–300°. Thermal stability—the temperature range must be kept within 1°—is maintained by thermal stabilizing tubes containing high-pressure H_2O at 185°–215° or oil. Coal hydrogenation using 2-stage catalysts of Sn and Mo is touched upon.

2213a. ———. Poisoning of Metallic Catalysts. Advances in Catalysis, Academic Press, Inc., New York, vol. 3, 1951, pp. 129–177.

Review covers catalysts susceptible to poisoning, principal types of catalyst poisons, form of catalyst-poisoning curves, factors, influencing toxicity and beneficial poisoning. 50 refs. listed.

2213b. MAXTED, E. B., AND HASSID, N. Studies in Gaseous Adsorption. III. The Thermal Activation Effect in the Adsorption of Hydrogen on Platinum and Nickel. Jour. Chem. Soc., 1932, pp. 1532–1539; Chem. Abs., vol. 26, 1932, p. 3978.

Pt and Ni were allowed to adsorb H_2 at a low temperature. They were then heated to a higher temperature in H_2. The amount of adsorption at higher temperatures was normal. After cooling to a lower temperature an abnormal adsorption is obtained. The sum of the additional values obtained stepwise is substantially the same as if the heating is all one unit. The effect per degree is greater the lower the original temperature on the scale. If the heating and cooling are in a vacuum instead of in H_2 the adsorption at the lower temperature is normal. An explanation without assumption of distinctly different adsorption types is presented.

2214. MAXWELL, H. L., AND HAYES, A. Free Energy and Heat of Formation of Iron Carbide for the Temperature Interval 650°–700°. Jour. Am. Chem. Soc., vol. 48, 1926, pp. 584–593; Chem. Abs., vol. 20, 1926, p. 1349.

Equilibrium constants for the reaction $3Fe(\alpha)+2CO=CO_2+Fe_3C$ were measured at 1 atm.; a flow method was used and resultant gases were analyzed. The volume % CO_2 at equilibrium was 35.7±0.1 at 650°, 25.25±0.05 at 700°. From data of Rhead and Wheeler for equilibrium constants of reaction $2CO=C$ (graphite) $+CO_2$, ΔF for reaction $3Fe(\alpha)+C=Fe_3C$ is 3,138 cal. at 650° and 2,281 cal. at 700°. These data give ΔH at 675°=19,162 cal.

2215. MAXWELL, L. R., AND BRUNAUER, S. Thermomagnetic Investigations of Promoted Iron Oxide and Iron Catalysts. Phys. Rev., vol. 76, 1949, p. 175, abstract L7.

Curie point and specific magnetization of singly and doubly promoted catalysts were determined. Singly: $Fe_3O_4+Li_2O$, Na_2O, K_2O, Cs_2O, CaO, BaO, B_2O_3, Al_2O_3, SiO_2. Curie point virtually unchanged, but specific magnetization reduced nearly 50% upon adding 1.7% by weight of BaO. Doubly: Fe_3O_4 and $Al_2O_3+Li_2O$, Na_2O, K_2O, MgO, CaO, BaO, SiO_2. Curie point varied only slightly and was >Curie point of Fe_3O_4. Large reductions of specific magnetization were observed. Some of these, reduced in H_2 behaved like pure Fe.

2216. MAXWELL, L. R., SMART, J. S., AND BRUNAUER, S. Thermomagnetic Investigations of Promoted and Unpromoted Iron Oxide and Iron Catalysts. Jour. Chem. Phys., vol. 19, 1951, pp. 303–309.

The Curie temperature (Θ) and intensity of magnetization of certain unreduced and reduced Fe oxide catalysts have been determined. For the singly promoted unreduced systems of Fe_3O_4, containing small amounts of one of the following, Na_2O, K_2O, Cs_2O, BaO, B_2O_3, Al_2O_3, or SiO_2, Θ was found to be virtually the same as for Fe_3O_4, but large reductions in the saturation intensity of magnetization were observed. The doubly promoted unreduced systems studied contained additions to Fe_3O_4 of Al_2O_3 and one of the following in small amounts: Na_2O, K_2O, BaO, or SiO_2. Θ for these materials varied only slightly and was either equal to or less than that for Fe_3O_4. Large reductions in magnetization were found. Magnetic measurements on the reduced materials gave values of Θ the same as for pure Fe. The extent to which the promoters go into solid solution, both for the unreduced and reduced materials, is determined. Additional unreduced unpromoted Fe oxides were investigated that had variable ratios (γ) of Fe^{++}/Fe^{+++}. Starting at $\gamma=0.352$, magnetization was found to increase with increasing γ to a maximum at $\gamma=0.50$, agreeing with the known value for magnetite, and then to decrease to a small value for large γ. The value found for magnetization at $\gamma=0.352$ is in agreement with Néel's theory of ferrimagnetism as applied to cubic Fe_2O_3 and Fe_3O_4. Θ was found to be constant at about 583° C for γ from 0.352 to 1.276.

MAYER, K. *See* abs. **3071.**

2217. MAYER, M., AND ALTMAYER, V. [Equilibrium of Methane.] Ber. deut. chem. Gesell., vol. 40, 1907, pp. 2134–2144; Jour. Chem. Soc., vol. 92, 1907, I, p. 457.

From equilibrium data calculated on the basis of investigations of the reaction $C+2\ H_2 \rightleftharpoons CH_4$ in the pres-

ence of Ni or Co at temperatures 470°–620°, doubts are expressed that Bone and Jerdan (abs. **296**) could have effected the synthesis of CH_4 at 1,200°. Probably the C employed contained impurities that yielded CH_4.

2218. ———. [Synthesis of Methane With Calcium Hydride.] Ber. deut. chem. Gesell., vol. 41, 1908, pp. 3074–3080; Chem. Abs., vol. 3, 1909, p. 64.

CaH_2 forms CH_4 with CO, the maximum yield (65.6%) being at 500°. The yield decreases as the temperature rises. Other products of the reaction are C and CaC_2. With CO_2 and CaH_2, the maximum yield of CH_4 is 60.24% at 500°. Less CaC_2 is produced and traces of Ca formate and oxalate and considerable quantities of $CaCO_3$ also are formed. Soot and CaH_2 at 270° give H_2 and N_2; above 270° CH_4 also is obtained. The maximum yield is 40.68% at 500° or in a stream of H_2 19%. Some Ca_3N_2 also is produced.

2219. MAYER, M., HENSELING, F., ALTMAYER, V., AND JACOBY, J. [Gas Reactions.] Jour. Gasbeleucht., vol. 52, 1909, pp. 166–171, 194–201, 238–245, 282–286, 305–313, 326–328; Chem. Zentralb., 1909, I, p. 1853; Chem. Abs., vol. 4, 1910, p. 2724.

This work proceeds from the methods of Sabatier and Senderens for the preparation of CH_4 from H_2 and CO and from mixtures of CO_2 and H_2 with the aid of CO and Ni as catalyzers, thus: $CO+3H_2=CH_4+H_2O$; $CO_2+4H_2=CH_4+2H_2O$; $2CO=C+CO_2$. These reactions were studied in detail, the most noteworthy result of which was the synthesis of CH_4 from its elements, $C+2H_2=CH_4$; Ni, Co, and Fe were the catalyzers used. While Co brings about the union of C and H_2 almost as readily as Ni, yet with Fe only small amounts of CH_4 were obtained, which fact is explained by the oxidation of Fe by the oxides of C. As for the form of C to be used, the finely divided grade obtained by decomposition of CO afforded the most rapid reaction. From graphite, lampblack, and electrolytic C only small quantities of CH_4 were obtained. Using the same catalyzers, further investigations were made with steam in place of H_2, to which the following water-gas reactions are applicable: $CO+H_2O=CO_2+H_2$, $C+2H_2O=CO_2+2H_2$ and secondarily $CO_2+4H_2=CH_4+2H_2O$. The information so obtained was then considered in connection with illuminating gas, and possible technical applications with reference to the water gas process discussed. Since gas reactions, in general, are limited by equilibrium, and their determination is possible from equilibrium constants, the thermal relations, and the specific heats of the substances according to thermodynamic formulas, the conditions of the synthesis of CH_4 were more closely studied. Finally, it was demonstrated how, theoretically, by combining the conditions of equilibrium of CO_2 and CH_4 the quantitative relations of the equation $CO_2+CH_4 \rightleftharpoons 2CO+2H_2$ are developed. If this last equation is combined with the expression of equilibrium $CO_2+H_2 \rightleftharpoons CO+H_2O$, the equations for the synthesis of CH_4 result: $CO+3H_2 \rightleftharpoons CH_4+H_2O$ and $CO_2+4H \rightleftharpoons CH_4+2H_2O$.

2220. MAYLAND, B. J., AND HAYS, G. E. Thermodynamic Study of Synthesis-Gas Production From Methane. Chem. Eng. Progress, vol. 45, 1949, pp. 452–458; Chem. Abs., vol. 43, 1949, p. 7200.

General thermodynamic equations for synthesis-gas production from natural gas are presented. From these a chart was prepared for determining an equilibrium mixture, outside the C deposition boundary, at pressures 1–21.4 atm., temperatures 1,200°–2,500° F. and H_2: CO ratios 1.75–2.25. This chart is particularly applicable to calculations related to the steam-CO_2 reforming process wherein, maximum yield, based on the natural gas, is obtained at maximum conversion, and consumption of steam and CO_2 depends on the excess required to prevent C deposition at equilibrium. This assumes that only CO and H_2 are formed with no C, C_2H_2, or C_2H_4. The maximum yield and the minimum consumption of CO_2 and steam are favored by high temperatures and pressures. The equilibrium calculations for the adiabatic reaction of CH_4 and O_2 and of CH_4 and air to give synthesis gas are presented also. In order to obtain final equilibrium temperatures in the range of 2,350° F., which are necessary to attain equilibrium without the use of a catalyst, a considerable excess of O_2 is required. Maximum yield of synthesis gas, based on natural gas or O_2 consumption, are obtained at some temperatures below 2,200° F. depending upon the pressure used. Therefore, a catalyst is necessary for maximum yields in the partial oxidation process.

2221. MAYOR, Y. [Manufacture of Formaldehyde.] Rev. chim. ind. (Paris), vol. 46, 1937, pp. 34–40, 70–77, 110, 111–116, 136–140; Chem. Abs., vol. 31, 1937, p. 6191.

General description and discussion of the various methods of manufacture of CH_2O (dehydrogenation or oxidation of MeOH, partial oxidation of hydrocarbons, hydrogenation processes), with a description of the various forms in which CH_2O is marketed and their preparation. 147 refs.

2222. ———. [Manufacture of Methanol and Formaldehyde by Oxidation of Methene.] Ind. chim. belge, vol. 26, 1939, pp. 291–292; Chem. Abs., vol. 34, 1940, p. 4053.

Review with 13 refs.

2223. ———. [Synthetic Fats.] Rev. sci., vol. 78, 1940, p. 149; Chem. Zentralb., 1940, II, p. 569.

Short description of preparation of higher fatty acids from paraffin.

2224. ———. [Synthetic Gas. Its Application in the Chemical and Fuel Industries.] Chaleur et ind., vol. 26, 1945, pp. 63–70; Ind. chim., vol. 32, 1945, p. 252.

Review of actual and possible uses of synthetic gas and the modern methods of production. Special mention is made of the water gas process by means of external heating developed by G. Szigeth and adopted in the German Didier process and the French Cie. générale de construction de fours and known as the Syngaz process. It produces a gas suitable for the Fischer synthesis with a ratio of $CO:H_2::1:2$. A French company is actually constructing a plant of this type in the south of France using the Fuveau lignites as raw material. The gas will be used for producing MeOH and for producing fuel by the hydrogenation of raw materials of that region, such as heavy petroleum oils, shale and lignite oils, etc.

2225. MAZZA, F. P. [Synthetic Petroleum and Benzine.] Saggiatiore, vol. 3, 1942, pp. 9–12; Chem. Zentralb., 1942, II, p. 2964.

Brief review of the petroleum industry, cracking and pressure hydrogenation of hydrocarbons, tars, coal liquefaction, CO hydrogenation, and the processes involving the products, such as oxidation to fatty acids, lubricants from the polymerization of olefins, isobutyl alcohol, and synthetic rubber from cracking gases.

MCATEER, J. H. *See* abs. **2325a.**

2226. MCCANCE, A. Balanced Reactions in Steel Manufacture. Trans. Faraday Soc., vol. 21, 1925, pp. 176–201; Jour. Soc. Chem. Ind., 1926, B, p. 364.

Equilibrium constants of several reactions in steel manufacture have been derived theoretically, and the equations for Fe and Fe oxides have been evaluated.

MCCARTNEY, J. T. *See* abs. **54.**

2227. MCCARTNEY, J. T., AND ANDERSON, R. B. Crystalline Aggregation of Cobalt Powder. Jour. Appl. Phys., vol. 18, 1947, pp. 902–903; Chem. Abs., vol. 42, 1948, p. 805.

In electron-microscopic studies of Fischer-Tropsch catalysts, an interesting phenomenon was observed in Co metal powder reduced from cobaltous oxide. The oxide particles sintered into larger smooth droplets of Co that were aggregated into thin, hexagonal platelets. X-ray diffraction analysis showed the presence of the hexagonal crystal phase of Co. A possible explanation is that the aggregates are formed by forces similar to those operating in normal crystal formation, but of reduced magnitude insufficient to destroy the identity of the component particles. It is not evident why this phenomenon has been observed only in Co.

2227a. ———. Electron Microscopic Replica Studies of Porosity in Fused-Iron Catalyst. Jour. Appl. Phys., vol. 22, 1951, pp. 1441–1443; Chem. Abs., vol. 46, 1952, p. 4339.

Preparation of various replicas of a fused-Fe (Fe_3O_4–MgO–K_2O) synthetic NH_3 catalyst is described. Micrographs of these replicas show comparable fine structures that are attributed to the pores developed in the catalyst upon reduction. Dimensions of these fine structures compare reasonably well with pore diameters calculated from pore volume-surface area determination.

2228. McCartney, J. T., Seligman, B., Hall, W. K., and Anderson, R. B. Electron Microscopic Study of Metal Oxides and Metal Oxide Catalysts. Jour. Phys. and Colloid Chem., vol. 54, 1950, pp. 505–519; Chem. Abs., vol. 44, 1950, p. 5691.

Changes in structure of Fe_2O_3 gel, hydrous NiO, CuO powder, Ag_2O powder, CoO powder, Co basic carbonate, Co–ThO_2–MgO (100 : 6 : 12) catalyst, Co–kieselguhr (100 : 200) catalyst, Co–ThO_2–MgO–kieselguhr (100 : 6 : 12 : 200) catalyst, and Fe_2O_3 catalyst (Fe : Cu : K_2CO_3, 100 : 10 : 0.5) on reduction were studied by determination of weight losses and comparisons of electron micrographs and surface areas by N_2 adsorption. Surface areas determined from particle sizes from micrographs and by adsorption permit estimating porosity. The individual differences in structure and changes on reduction are described. Precipitated oxides and catalysts always showed decrease in surface area on reduction, and a sizable portion of this decrease occurred in reduction rather than by sintering. Decrease in sintering on reduction of Co basic carbonate is effected by the addition of promoters and kieselguhr, the order of increasing effectiveness being kieselguhr$<ThO_2$, MgO$<ThO_2+$MgO. Electron micrographs are useful but difficult to interpret unless combined with the surface-area determinations by gas adsorption.

McDonald, H. J. *See* abs. **3158.**

McGee, J. P. *See* abs. **768, 3100.**

McKeever, C. H. *See* abs. **3670.**

2229. McKinney, A. R. Decomposition of Ethylene and Carbon Monoxide on Metallic Catalysts. Jour. Phys. Chem., vol. 47, 1943, pp. 152–163; Chem. Abs., vol. 37, 1943, p. 3659.

Metals Fe, Co, and Ni rapidly decompose CO above 250°, whereas Os, Pt, Cu, and Pd are comparatively inactive. The active group of metals all form carbonyls. The order of decreasing activity for C_2H_4 decomposition by Ni, Co, Fe, and Cu is compared to their respective atomic radii, 1.24, 1.25, 1.27, and 1.28 Å. Ni and Co decompose C_2H_4 increasingly to CH_4 as the temperature is raised; the C_2H_6 formation goes through a maximum at about 280°. Cu produces no CH_4 up to 460°, the reaction products being H_2 and C_2H_6. With Fe large amounts of both H_2 and CH_4 are formed. From an equimolecular C_2H_4–CO mixture the decomposition of C_2H_4 reaches 90% at 10°–60° lower temperature than without CO. The relative yields of H_2, C_2H_6, and CH_4 are considerably influenced by the CO. Evidence as to the source of catalytic activity is reviewed.

2230. McMillan, W. G., and Teller, E. Assumptions of the Brunauer, Emmett, and Teller Theory. Jour. Phys. and Colloid Chem., vol. 55, 1951, pp. 17–21. Chem. Abs., vol. 45, 1951, p. 3220.

An adsorption-isotherm equation valid in the region of multilayer adsorption is obtained, which takes into account both the effect of surface tension of the adsorbate and the effect of the extension of the adsorbent attractive forces beyond the 1st adsorbed layer. The differences between this derived equation and one of identical functional form obtained earlier are usually negligible numerically.

2231. Medsforth, S. Promotion of Catalytic Reactions. I. Action of H_2 on CO and CO_2. Jour. Chem. Soc., vol. 123, 1923, pp. 1452–1469; Chem. Abs., vol. 17, 1923, p. 3271.

CO was 99.8% pure. The H_2 was electrolytic and 99.9% pure. CO_2 was used directly from cylinders. The catalyst, Ni, was deposited from purified salts on purified pumice in the proportions 0.1 gm. of reduced Ni to 1 gm. of pumice. The reactions involved were $CO+3H_2=CH_4+H_2O$ and $CO_2+4H_2=CH_4+2H_2O$. To provide an excess of H_2, the proportions used were H_2 : CO : : 5 : 1 and H_2 : CO_2 : : 6 : 1, by volume. The maximum catalytic effect was measured by the maximum speed at which the mixed gas could be passed over the catalyst and promoter with almost complete removal of the CO or CO_2. The reaction chamber was a straight tube fused to a preheating coil that surrounded it. The several promoters associated with 0.1 gm. of Ni on 1 gm. of pumice in the order of decreasing efficiency in accelerating the speed of the gaseous reactions are as follows: Ce, Th, Be, Cr, Al, Si, Zr, Mo, and V oxides (Sn and Mg oxides and Cu and Ag produce no acceleration). The formation of CH_4 from H_2 and CO or CO_2 probably consists in the formation of intermediate addition products of the MeOH type followed by the splitting off of H_2O. The CH_2 resulting is immediately hydrogenated to CH_4. Or a complex intermediate product, H_4NiCOH_2, forms and decomposes into Ni, CH_4, and H_2O. In either case, Ni must caatlyze by acting as both a hydrogenating agent and as a dehydrating agent. It is not a good agent for the latter process. The substances that promote its catalytic action are good dehydrating agents. When CH_3OH+3H_2 is passed over Ni the decomposition into CO and H_2 is much more rapid that the formation of CH_4 and H_2O. If thoria is added, the rate of formation of CH_4 is increased 14-fold. When Fe catalyzes the interaction of CO and H_2O to form CO_2 and H_2 the most effective promoters are O carriers and hydrating agents. This indicates that H_3 is produced through the formation of formic acid as well as by alternate oxidation and reduction. The oxidation of a gas in a gas mantle may be considered to consist of the addition of O_2 to form an intermediate compound and its subsequent dehydration. The catalyst should be a powerful O carrier and a strong dehydrating agent. The promoter acts (1) by decomposing intermediate compounds formed by the catalyst, or (2) by causing substances to combine, or (3) by adsorption to increase concentration. Promoters may act selectively.

2232. Medvedev, S. S. [Catalytic Oxidation of Methane to Formaldehyde. I.] Trans. Karpov Chem. Inst., No. 3, 1924, pp. 54–65; Chem. Abs., vol. 21, 1927, p. 2457.

Medvedev experimented with Au, Pt, Mn_2O_3, NiO, Al_2O_3, CuO, Ag_2O, PbO, and CeO_2 catalysts on an asbestos base. At low rates of flow (1 l. in 20 min.) and at low temperatures (250°–350°) only CO_2 is obtained. Mn_2O_3 proved to be the most, CuO the least active catalyst. At temperatures above 500° and a rate of 1 l. per min., traces of HCHO and a little CO appear besides CO_2 with CuO as a catalyst, but not with the others. This Medvedev interprets as evidence of the

acceleration of all reactions by the catalysts or their nonspecificity. Glass at 600° gives a large yield of HCHO, which is attributed to the lesser chemical activity of such a surface in not being able to form peroxides as in the case of metals and their oxides. With CH_4 (containing 3–7% H_2) Pb catalysts (borates, phosphates, and their mixtures) gave the highest yields of HCHO at 500°–700°. The activity of these catalysts, however, was referred to the presence of volatile impurities, as lead chloride, since a long series of experiments showed that small concentrations of HCl (0.13%) in the gases was very beneficial in raising the relative yield of HCHO. Medvedev's best results are exceptionally high. Thus at 600° from a mixture containing 13.8% CH_4 and 17.98% O_2 with a velocity of 0.23 l. per min., the yield of HCHO was 5.02% of the CH_4 taken, 8.65% CH_4 being decomposed, that is, 58.04% of the decomposed CH_4 decomposed to HCHO.

MEHL, R. F. *See* abs. **3648, 3649.**

2233. MEISENHEIMER, K. [Experiments With the Fischer Synthesis at Normal Pressure.] FIAT Reel R–20, frames 7,546–7,551, Oct. 21, 1938; PB 73,564.

Experiments at the Ammonia Laboratory, Oppau, deal with the influence of certain processes on the manufacture of Co catalysts and the effect of other additional catalyst metals. It was found that washing out of the Co carbonate precipitated on the carrier must be thoroughly done. Addition of Mn oxide to the Co catalyst leads to a more constant yield of paraffin after a longer reaction time. Of the rare metals La oxide and Th oxide proved to be the best additions tested. As substitutes for diatomaceous earth, kaolin and some brands of Al oxides are of importance. Diatomaceous earth is not considered to be very suitable. Finally Cu-containing Co catalysts were considered. They can be used without a preliminary reduction.

2234. MELAN, G., AND WEISS, B. Proof and Constitution of Branched Acids From Fischer-Gatsch Fatty Acids for Soap. I. G. Farbenindustrie A.-G., Ammonia Laboratory. FIAT Reel R–19, Frames 7160–7173, Feb. 14, 1942; PB 73,594; TOM Reel 25, Item 15, 1942, Frames 1460–1472; Standard Oil Development Co. Transl. Ella 2697, 1947, 10 pp.

Detailed method is described for determining the constitution of paraffin carboxylic acids, particularly those with branched chains. By treating with Br and MeOH, α–bromomethyl ester is produced from the carboxylic acid, and from this the α–hydroxyacid is purified. In the oxidative cleavage with lead tetraacetate and simultaneous flowing with air, CO_2 and an aldehyde are obtained from the hydroxyacid. The aldehyde is oxidized to a new carboxylic acid with one C atom less than in the starting material. In case of a branching in the α–position to the COOH group, a ketone is obtained instead of an aldehyde, which is not further oxidized. According to this method Fischer-Gatsch fatty acids for soap with C_{10} and C_{11} were examined and the fatty acids identified. The results are given in detail.

MELHORN, G. *See* abs. **1993.**

2235. MELLER, A. Catalytic Hydrogenation of CO–CH_4 Synthesis From Water Gas. Australian Chem. Inst. Jour. and Proc., vol. 10, 1943, pp. 100–114, 123–129; Chem. Abs., vol. 38, 1944, p. 238.

Laboratory and pilot plant experiments on the enrichment of CO–H_2 mixtures (ratios 3:5—1:2) are described. A catalyst containing 90% Ni and 10% Al_2O_3 gave high yields with 3:5 gas mixtures at 280° and a space velocity of 800–1,000 cm^3 of gas per gm. of reduced catalyst per hr. Under these conditions the catalyst has a long life provided organic S compounds are absent. Higher temperatures and higher space velocities favor a side reaction associated with C deposition and decline of catalyst activity. Higher CO : H_2 ratios favor C deposition; lower ratios permit higher space velocities. S compounds decrease the active catalyst surface and cause C deposition. Lower CO : H_2 ratios enable the catalyst to resist higher concentrations of S. A 95–98% yield was obtained at a space velocity of 800–1,000 during a continuous run of 1,500 hr., when the organic S content was not greater than 0.5 grain per 100 cu. ft.

2236. MELVILLE, H. W. Utilization of Coal for Oil Production. Catalytic Hydrogenation the Ideal Process. Petrol. Times, vol. 50, 1946, pp. 18, 43.

Digest of the Romanes lecture at the University of Aberdeen. Outstanding achievements in the treatment of coal to produce liquid fuels are high-pressure hydrogenation and Fischer-Tropsch synthesis. The first is undoubtedly the right way to obtain oil from coal; the degree of hydrogenation is easily controlled and final products can be worked up in the same way as petroleum. Economically, the disadvantage is the necessity for expensive equipment, and the problem is to find a simpler method of adding H_2. The Fischer-Tropsch synthesis needs the use of an excess of H_2, the expense of which weighs heavily against it and presents a fundamental difficulty that cannot be overcome. Costs of producing gasoline by various methods are as follows: High pressure hydrogenation 13 d. per imperial gal., Fischer-Tropsch from coal 11 d., Fischer-Tropsch from natural gas 5 d., high-pressure hydrogenation of petroleum 3.5 d., crude oil refined 3.5 d.

2237. MENGEL, —. Continuous Chlorination of Kogasin and Recovery of Chlorine-Free Hydrochloric Acid. PB 758, 1942, 4 pp.

Continuous semicommercial production of chlorkogasin, (Lederoel Ho 1/90) is described in detail. Kogasin, a hydrocarbon mixture containing 6–8% unsaturates and an average molecular weight of 190–200 is chlorinated, HCl is removed, and the chlorinated product is stabilized by filtering through NaOH. The product has a consistency of machine oil and an average molecular weight of 320–330. It is a suitable substitute for train oil for the leather industry. Diagram of apparatus.

2238. MERCK, F., AND WEDEKIND, E. [Magnetic Analytic Investigation of Cobalt Oxide as Catalyzer of Carbon Monoxide Combustion at Room Temperature.] Ztschr. anorg. Chem., vol. 186, 1930, pp. 49–74; Chem. Abs., vol. 24, 1930, p. 2036.

It is concluded that the cobaltic oxide catalyzer consists essentially of 2 crystalline phases, CoOOH and Co_3O_4, Co_2O_3 being chiefly converted into the latter. Of these 3, the components CoOOH and Co_3O_4 are catalytically ineffective. The cobaltic oxide in the Co_3O_4 lattice is superfically reduced by the diluted CO. Magnetic measurements were made by Wedekind's microchemical method (*see* abs. **3619**) and show that magnetism increases in going from hydrate to oxide. For Co_3O_4, χ is about 32×10^{-6} and varies relatively little as the titratable O content varies. In the transformation from hydrate to oxide, an active intermediate state is present, characterized by a dependence of susceptibility upon field strength. This vanishes on sintering and also on aging with partial reconversion into hydrate. At room temperature the hydrate is more stable than oxide+H_2O.

2239. MERKEL, H. [Study of Fischer-Tropsch Iron Catalysts. I. Magnetic Investigation of Unused Iron Catalysts. II. Model Test With Copper Ferrite.] Brennstoff-Chem., vol. 31, 1950, pp. 208–212; Chem. Abs., vol. 44, 1950, p. 8564.

Fe catalysts with and without the addition of Cu were investigated thermomagnetically after precipitation and in different stages of drying at 105°. Directly after the precipitation, the precipitate appeared strongly ferromagnetic, yet its magnetization curve

was still very irregular. After several hours of drying, Fe catalysts containing Cu gave uniform magnetization curves with a Curie point at 470°–475°. The intensity of magnetization was just as great as after the formation. If drying was continued for 29 hr. the Curie point, in spite of progressive oxidation of the constituents, remained virtually unchanged. The compound taken as a basis for the Curie point 470°–475° was no longer stable in the temperature range of the synthesis.

Heating to 220° for 3½ hr. resulted in complete decomposition whereby Fe_3O_4 in magnetically equivalent amounts appeared as the conversion product. Heating to 800° resulted in a sharp decline in the magnetization. By means of a model test it was seen that the compound taken as a basis for the Curie point 470°–475° had to do with a strongly ferromagnetic Cu ferrite whose magnetization curve still appeared after mild reduction conditions. In contrast to the behavior of Cu-containing Fe catalysts, a prepared Cu ferrite showed a sharp increase in magnetization after a heat treatment at 800°. This different behavior is due to the presence of oxidic iron in the catalyst after the ferrite formation, which does not appear magnetically. A Fe preparation without the addition of Cu showed after 8 hr. of drying, strong Fe_3O_4 formation. With progressive oxidation an increase in the Curie point was established. After a 30-hr. drying the Fe had been oxidized quantitatively into the trivalent form with formation of ferromagnetic Fe_2O_3. The Curie point of this oxide could not be accurately determined since the magnetization curve falls off almost linearly in the ferromagnetic conversion range. It lies in the temperature range of 600°–610°. Heating to 800° causes the loss of the magnetism of the Fe_2O_3, so that only the magnetism of the stable Fe_3O_4 remains. Beside the known effect of Cu on the forming and synthesis processes it is shown that this metal also influences the oxidation of Fe during the drying. By using Fe chloride for the initial solution, Cu-free materials easily form forremagnetic γ-Fe_2O_3 in quantitative amounts. In this condition the catalyst is difficult to reduce and cannot be used for the synthesis at normal pressure. On the other hand, ferritic combined α-FE_2O_3 is formed with extensive addition of Cu. Oxidation is thereby incomplete, 20–25% of the Fe remains in the bivalent form.

———. *See* abs. **2683, 2684, 2685.**

2239a. MERKEL, H., AND WEINROTTER, F. [Thermomagnetic Studies of Iron Catalysts for Hydrocarbon Synthesis.] Brennstoff-Chem., vol. 32, 1951, pp. 289–297; Chem. Abs., vol. 46, 1952, p. 662.

When precipitated Fe catalysts are reduced with technical H_2, the low partial pressure of CO, CO_2 and CH_4 is sufficient to cause appreciable carbide formation. Catalysts treated in this way are fully active for synthesis in a few minutes, in contrast with those reduced with electrolytic H_2. In addition to Fe_2C with a Curie point of 265°, Fe_3O_4 and Fe were also found. the Fe content may be the cause of the CH_4 peak noted early in the synthesis. Since precipitated Fe catalysts can be converted into Fe_3C at temperatures >400° by means of technical H_2, without the formation of free C, there is a possibility of preparing pure cementite by reduction of Fe preparations containing no additives. This product was inactive as a catalyst. Metallic Fe is generally formed in the pretreatment of fused Fe catalysts with technical H_2. Carbides are only formed when additives favoring carbide formation (alkalies) are present; Fe_3C is formed due to the higher temperatures used.

2240. MERZ, V., AND TIBIRICA, J. [Synthesis of Formic Acid.] Ber. deut. chem. Gesell., vol. 10, 1877, p. 2117; vol. 13, 1880, pp. 23–33.

By passing CO over soda lime at 220°, formate is obtained in good yield. Above 220° the formate is decomposed with formation of carbonate and free H_2.

2240a. MESSNER, G., AND FRANKENBURGER, W. [Intermediate Compounds in the Catalytic Synthesis of Ammonia. Detection of the Formation of a Surface Nitride Between Nitrogen and Tungsten.] Ztschr. physik. Chem., Bodenstein-Festband, 1931, pp. 593–607; Chem. Abs., vol. 25, 1931, p. 5,515.

NH_3 and H_2 are adsorbed on W in the normal manner. N_2 apparently forms a surface compound with the W, since it is taken up irreversibly and in amounts that increase with the temperature. H is held similarly by chemical forces on a W surface already covered with N; the amount retained by the N-covered surface increases with temperature.

METLIN, S. *See* abs. **3655a, 3655b.**

2241. MEUNIER, J. [Oxidation Reactions of Methane.] Chim. et ind., vol. 60, No. 6, 1948, pp. 550–558; Chem. Age, vol. 60, 1949, pp. 293–296; Chem. Abs., vol. 43, 1949, p. 2923.

Oxidation reactions or the conversion of CH_4 into synthesis gas are assuming increasing industrial importance. These reactions, in which CH_4 is acted upon by O_2, steam, or CO_2 either alone or in binary or even ternary mixtures, are capable of being graphically represented by making use of the Gibbs triangle. When the reactions are effected in the presence of a catalyst, as is frequently the case, chemical equilibrium is quite easily attained. The author represents graphically the static conditions that may arise by thermal dissociation of CH_4 in the homogeneous phase as well as in the presence of C. Some typical cases are studied, and the effect of different factors, such as temperature, pressure, relative proportions of CH_4, and other reactants, is examined.

MEUSEL, A. *See* abs. **1030, 1031.**

2242. MEYER, A. J. P., AND TAGLANG, P. [Magnetic Moments and Curie Points of Hexagonal and Cubic Cobalt.] Compt. rend., vol. 231, No. 13, 1950, pp. 612–614.

By methods and extrapolation, using isoelectronic cubic alloys of electron d. 27, Θ of hexagonal and M (magnetic moment in Bohr magnetons) of cubic Co, at obsolute zero, were determined. For hexagonal Co Θ=1,070° K. M=1.70 μ_B. For cubic Co Θ=1,404° K. packed, have 12 nearest neighbors, and have almost M=1.745 μ_B. Since both Co. structures are close-identical shortest Co–Co distances (2.513 Å. for β–Co and 2.514 Å. for α–Co, the differences in Θ and M must be sought in interaction of not-closest neighboring atoms.

2243. MEYER, G., AND SCHEFFER, F. E. C. [Carbide of Nickel.] Rec. trav. chim., vol. 46, 1927, pp. 1–7; Chem. Abs., vol. 21, 1927, p. 1236.

When CO is passed over Ni at approximately 250° for several hours, CO_2 and a carbide of Ni are formed. The existence of the latter is shown by its interaction with concentrated HCl to form hydrocarbons, which can be analyzed by ordinary methods. Combustion with CuO or by exploding a mixture of the hydrocarbons and O_2 gave identical results for CO_2, but the latter method gave lower values for H_2. This difference is ascribed to the presence of some unsaturated hydrocarbons. Experiments at 700° accord with the data on the dissociation of CH_4; no carbide is formed by the interaction of CO and Ni, and the carbide formed at lower temperatures is decomposed into Ni and C on heating at that temperature.

2244. ———. [Dissociation of Carbon Monoxide.] Rec. trav. chim., vol. 46, 1927, pp. 754–762; Chem. Abs., vol. 22, 1928, p. 714.

Equilibria were measured at 500°–750° by passing CO over a Ni catalyst. Equilibrium constants for $C+CO_2 \rightleftarrows 2CO$ are expressed by $\log K_c = (8{,}829/T) - 7.067$ and $\log K_p = (9{,}217/T) - 9.369$. True equilibria

were not obtained with a Ni catalyst until it was heated well above 420° to break up Ni carbide.

2245. ———. [Formation of Carbides in the Systems Metal–Carbon–Hydrogen and Metal–Carbon–Oxygen.] Rec. trav. chim., vol. 46, 1927, pp. 359–368; Chem. Abs., vol. 21, 1927, p. 3011.

Conditions for the existence of carbides in the systems M–C–O and M–C–H, in the presence of CO and CO_2, are discussed from the standpoint of the phase rule. Diagrams are given. Carbides rich in C and stable at low temperatures are probably formed during the reactions of water gas with metallic catalysts. A Ni carbide of the above type has been isolated.

2246. ———. [Formation of Carbides in the System Metal–Carbon–Oxygen.] Rec. trav. chim., vol. 47, 1928, pp. 401–405 (in French); Chem. Abs., vol. 22, 1928, p. 1919.

Theoretical considerations are augmented. The knowledge of the values of the heats of formation of the different equilibria helps to determine to which one of the 4 types of P–T diagrams a certain system belongs. The system Ni–C–O is taken as an example to prove the conclusions.

2247. ———. [Water-Gas Equilibrium.] Rec. trav. chim., vol. 57, 1938, pp. 604–608; Chem. Abs., vol. 32, 1938, p. 8246.

Direct determinations of the constant of the water-gas equilibrium at different temperatures led to the formula $\log K = -(1860/T) + 1.662$. By means of an indirect method, a slightly different result was obtained: $\log K = -(1881/T) + 1.705$. The average of the 2 gives: $\text{Log } K = -(1870/T) + 1.683$.

2248. MEYER, H. H. [Speed of Reduction of Iron Ores in Flowing Gases.] Mitt. Kaiser Wilhelm Inst. Eisenforsch. Düsseldorf, vol. 10, 1928, pp. 107–116. Chem. Abs., vol. 23, 1929, p. 1371.

At 650° the ores reduced in H_2 begin to sinter, and H diffuses less readily to the center of the kernels. As a result, the speed of reduction falls rather sharply. At 900°, the speed is again accelerated, since H diffuses more rapidly into the γ-Fe. In CO, sintering is effectively prevented by the separation of C. The speed of reduction, however, is slower than with H_2 so long as there is no sintering. For technical purposes a mixture of CO and H_2 is very effective, because of the reactivity of the H_2 and the prevention of sintering by the CO. Magnesite reduces chiefly on the surface, and the higher the temperature the greater must the degree of reduction be before C is set free. The presence of H_2 promotes C formation. With minette (Fe silicate) the phenomena are the same, but because of its greater porosity the reduction is more rapid. Likewise the separation of C in the interior of the kernel tends to break it up. Above 1,000° silicates are formed that close up the pores and retard the reaction. Where no sintering occurs the speed of reduction is about 4 times greater with H_2, and in both cases the speed is proportional to the surface of the ore and the concentration of the gas, the reaction velocity constant being d/D, where d is the diffusion coefficient and D is the thickness of the adsorbed gas layer. The temperature coefficient of the speed of reaction is consequently quite small. In H_2–CO mixtures, the CO does not appear to reduce directly, but converts the H_2O formed into H_2 and CO_2.

MEYER, K. *See* abs. **988, 989, 990, 991, 992, 993, 1048, 2622, 3070, 3071, 3072.**

2249. MEYER, K., AND HORN, O. [Reaction of Carbon Monoxide and Hydrogen in Coke-Oven Gas With Molybdenum Catalysts.] Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 389–394; Chem. Zentralb., 1934, II, p. 875; Chem. Abs., vol. 29, 1935, p. 6732.

No reduction of CO occurs at 1 atm. At 100 atm. reduction to CH_4 occurs, but a higher temperature (400°) is needed with a Mo than with a Ni catalyst. Mo is activated by Mn, Cr, Th, and Cu but not by W. Alkali destroys the activity. Mo and Mo–Th catalysts for the hydrogenation of C_2H_4 are not poisoned by H_2S.

2250. MEYER, R. E. Petroleum Products vs. Petroleum Chemicals. Chem. Eng. News, vol. 28, 1950, pp. 1906–1910.

Discussion is made of the production of petroleum chemicals such as light hydrocarbons (liquid petroleum gases), nylon and acrylonitrile plastics, acetylene products, hydrocarbon oxidation products, such as acrolein, phthalic anhydride, phenol from benzol, ethylene oxide and ethylene glycol, and products of the Fischer-Tropsch synthesis and the Oxo process. The utilization of the large quantities of byproducts from these 2 processes and their separation and purification are definitely unsolved problems and it cannot yet be foreseen what the effect will be on the chemical markets and the price structure.

2251. MEYER, W. [Technical Progress in the Production of Fatty Acids and Alcohols From Hydrocarbons.] Pharm. Ztg., vol. 82, 1937, pp. 1189–1194; Chem. Zentralb., 1938, I, p. 1659; Chem. Abs., vol. 32, 1938, p. 1652.

Review with 112 refs.

2252. ———. [Review of the Development of the Oxidation of Hydrocarbons to Fat Acids, Fat Alcohols, and Wax Esters.] Seifensieder-Ztg., vol. 65, 1938, pp. 215–217, 238–239, 256–258, 277–278, 297–299, 317–319, 338–340. Süddeut. Apoth. Ztg., vol. 78, 1938, pp. 47–49; Chem. Abs., vol. 32, 1938, p. 9532.

Oxidation methods using atmospheric O_2 various oxidizing compounds, for example, oxides of N_2, O_3, etc., are considered in this review citing 283 refs.

2253. ———. [Soap From Coal.] Süddeut. Apoth.-Ztg., vol. 78, 1938, pp. 47–49; Chem. Abs., vol. 32, 1938, p. 2770.

Brief outline of various methods and suggestions looking to the technical production of fatty acids and alcohols from hydrocarbons through oxidation of unsaturated hydrocarbons with atomic and molecular O and O_3, combination of olefin formation and oxidation, and finally oxidation of saturated hydrocarbons by combined O and molecular O_2.

2254. MEYER, W. F. [Investigations of Cobalt and the System Cobalt–Carbon.] Ztschr. Krist., vol. 97, 1937, pp. 145–169; Chem. Abs., vol. 31, 1937, p. 8339.

X-ray photographs at temperatures up to 1,100° show no 2d transformation of Co. On heating with illuminating gas up to 230°–270° a mixed crystal of variable composition is formed, which is unstable at room temperature. At 500°–800° stable Co_3C is formed, analogous to Fe_3C. Its unit cell dimensions are $a=4.52$, $b=5.08$, $c=6.73$ Å. Heating with benine and CO also produces Co_3C.

2255. ———. [Cobalt–Carbon System.] Metallwirtschaft vol. 17, 1938, pp. 413–416; Chem. Abs. vol. 32, 1938, p. 4866.

When illuminating gas is heated with Co in the temperature range 230°–470° the CO dissociates under the catalyzing effect of Co and a mixed crystal forms. The crystal is attainable only between 230° and 270°, when a diffusion equilibrium exists; above this range the outward diffusion of C is too rapid. Between 500° and 1,200°, Co also catalyzes CO dissociation and a mixed crystal forms. Between 500° and 800°, benzene as well as illuminating gas acts on Co to form a stable Co carbide, whose lattice structure corresponds to that of Fe_3C; the lattice dimensions, to an accuracy of ±0.5% are: $a=4.52$ Å., $b=5.08$ Å., $c=6.73$ Å. 11 refs.

———. *See* abs. **1935.**

2256. MEYER-DOERING, H. H. [Is the Use of Synthetic Fatty Acids for Food Dangerous?] Klin. Wochschr., vol. 27, 1949, pp. 113–116; Chim. et ind., vol. 63, 1950, p. 159; Chem. Abs., vol. 44, 1950, p. 4161.

Paraffinic products obtained by the Fischer-Tropsch process can be partly converted into fatty acids by oxidation in presence of appropriate catalysts such as Mn and Co. A mixture of fatty acids is obtained containing 55% of products having more than 10 C atoms, 20–25% with less than 10 C atoms, of which 50% are HCOOH, CH_3COOH, and CH_3CH_2COOH, besides esters, anhydrides, lactones, ketones, etc. The mixture is saponified by soda, and the C_{10}–C_{23} acids are precipitated and separated from the unsaponifiable constituents by distillation and esterified to fatty acids with glycerin. It would seem that such acids would not be free from danger. In fact they may contain isoacids, which have a marked toxic action. The presence of dicarboxylic acids may likewise cause trouble, as well as the synthetic or fermentation glycerin used for the esterification. It appears then that the use of artificial fats must be considered dangerous. The following considerations are against the use of synthetic fats for food: (1) There is no published procedure for the determination of isofatty acids, certain of which are definitely toxic; (2) there is no specific method for determining dibasic acids in fats; (3) the many animal experiments that have been cited do not prove the harmlessness of the fats, unsuitable experimental animals were used, the experiments were too short, and improper methods were used for studying liver or kidney damage; (4) there is an increase in excretion of dibasic acids, a strong acidity of the urine, and the possibility of kidney damage in human subjects; (5) in human experiments with synthetic fats, their harmlessness was not shown since the experiments were too short, not enough chemical methods were used, and common clinical methods were often neglected; (6) the metabolism of the odd-numbered fatty acids is still not clear.

MEYERSON, S. *See* abs. **2754a, 3618.**

2257. MICHAEL, —. [Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen.] TOM Reel 148, frames 99–102, Aug. 14, 1942, 5 pp.

Emulsion method consists in carrying out the reaction in a sludge characterized by very small particles of gas and catalyst. As sludge the high-boiling reaction products are used. Gas distribution was produced by foam stones with pores of 0.10–0.15 mm. diam. The catalyst can also be fixed in place by using finely divided metal 1–5 μ particle size in a heavy sludge. In order to counteract a sinking of the catalyst particles and to conduct away the heat of reaction, the heavy sludge is slowly agitated between the reactor and the cooler so that the heavy emulsion has an opportunity to be degassed at the highest point in the circulation system. Temperatures of 240°–280° can be used, usually 250°. Exact conditions and materials to be used are given.

2258. ———. [Status of Experiments on Synthetic Oils.] TOM Reel 148, frames 244–249, June 1, 1942, 5 pp.

Experiments have been continued on the foam process with ovens of various capacities. Intensive stirring was tried in place of the foam plates, but difficulty arose at the stuffing boxes of the stirring well so the tests were discontinued. Details of the oven construction are given. Describes catalyst, its suspension in oil, and its regeneration. The conditions for operation of the ovens are: 20 atm. pressure, $CO:H_2=55:45$, temperatures 250°–280°. Foam plates containing sulfate must not be used. Quartz and glass powder plates of 0.1 and 0.2 mm. pore diam. were used, but were found to be too sensitive to thermal expansion on a large scale. Chamotte plates are preferred.

2259. ———. [Status to Date of Hydrocarbon Synthesis According to the Emulsion Method.] TOM Reel 148, frames 235–241, May 18, 1942, 5 pp.

Emulsion method using a 1.5 $m.^3$ oven has not shown any technical difficulties. There is no doubt that also in an industrial plant, using ovens of 40–50 $m.^3$ capacity, the same results would be obtained. The essential parts of the plant are shown. Chamotte-stones are used as porous foam stones. In using an oven 8 m. high, the correct pore diameter is 0.15 mm. It has not been found whether the 8-m. oven is the right one to use, and tests are being extended. A relation exists between the fineness of the foam and the yield and also between the fineness of the foam and the height of the oven.

2260. MICHAEL, J. M., AND HAGER, K. F. Corrosion-Inhibited Fuels. Ind. Eng. Chem., vol. 41, 1949, pp. 2616–2622.

Methods for preventing corrosion in pipelines, storage containers, tanks, and other equipment in contact with fuels even under severe conditions are surveyed. Of the possibilities investigated, only the admixture to the fuels of corrosion inhibitors to produce surface passivity offers extended technical application and enough endurance in practical use. The data presented show that fuels inhibited by hydrocarbon-sulfamido-carboxylic acids offer the greatest advantage. Extensive investigations on emulsifying agents led to the surprising result that, without regard to the construction materials used, even a small addition of the Na salt of Mepasin-sulfamido-acetic acid to the fuel prevents any corrosion. Mepasin is a high-boiling fraction of the hydrocarbons obtained by the Fischer-Tropsch synthesis having a chain length of about 12–18 C atoms. A mixture of about equal parts of Mepasin-sulfamido-sodium acetate and unchanged Mepasin is a very efficient emulsifier known in Germany under the trade name Bohrmittel Hoechst.

2261. MICHAEL, W. Experience With the Synthesis Reactor Stall 506. June 28, 1941. Bureau of Mines Transl. T–434, January 1948, 5 pp., incl. 3 figs.

Paper from Dr. Pier's files, discussing gas circulation versus the foaming process in reactor operation.

2262. MICHAEL, W. Present Status of the Synthetic Oil Experiments, Jan. 6, 1942. Bureau of Mines Transl. T–439, Jan. 1948, 6 pp.

Foam synthesis method has been adapted to industrial production by placing in operation a 1.5 $m.^3$ capacity reactor provided with a foam plate, made of chamotte or quartz with sintered powdered glass with pores 0.1–0.2 mm. diameter, for the distribution of the synthesis gas. Stirring methods had to be discontinued because of difficulties in the stuffing boxes of the mixer shaft. The reactor apparatus consists of a vessel near the bottom with a perforated foam plate and a degasifier at the head of the reactor in which the rising foam gives up its gas, the liquid being returned by an outside line to the bottom of the reactor and recirculated under such a pressure (about 20 atm.) as to counteract the tendency of the powdered catalyst to settle. The rate of circulation is further determined by the need of removing the heat of reaction in the liquid phase by a cooler located in the reactor jacket. For example, with a temperature rise of the liquid of 10°, the liquid would need to circulate at a synthesis temperature of 250° at the rate of once every 3 min. Oil is used as the intermediate cooling agent surrounding the reactor and is pumped in a circuit through the cooler. The catalyst consists of Fe from Fe oxide obtained by burning Fe carbonyl, pasted with a solution of potassium borate, dried, reduced in H_2 at 450°, and ground in heavy oil to a particle size 1–5 μ. The amount of catalyst is 300–400 kg. per $m.^3$ of the liquid, the dispersion medium being the high-boiling fraction obtained in

the synthesis. The synthesis is performed under pressure, at 250°–300°, with a synthesis gas $CO:H_2::55:45$. The space-time yield of products range from 0.2–0.3 kg. per l. catalyst space per day at 250° to 0.7–0.8 kg. at 300° with a conversion of 80 to even 95% of the gas by purifying the recycle gas from CO_2. The compositions of the products in % at 250° and 300°, respectively, are as follows: Gasol, 4–6 and 8; gasoline boiling at 200°, 30–40 and 50–55; middle oil boiling at 350°, 32–37 and 30–35; paraffin above 350°, 20–30 and 5–10; alcohols, 6 and 3; octane number of gasoline, 50 and 78; olefins in middle oil, 60 and —; gasification, 5 and 5.

2263. ———. Principal Data on the Foaming Process for the Hydrocarbon Synthesis. High-Pressure Experiments, Ludwigshafen 558, Feb. 27, 1943. Bureau of Mines Transl. T–431, January 1948, 2 pp.

Paper from Dr. Pier's files outlining the operation and giving some results and yields of experiments carried out over a 7-mo. period.

2264. MICHAEL, W., AND EHRMANN, —. Difficulties Encountered in the Foaming Method of Synthesis of Hydrocarbons and Their Solution. High-Pressure Experiments, Ludwigshafen 558, Feb. 18, 1943. Bureau of Mines Transl. T–432, Jan. 1948, 7 pp.

Paper from Dr. Pier's files. No fundamental difficulties have been encountered in large-scale experimental work on the foaming process, and no important unsolved problems remain. Any troubles encountered were caused by stuffing boxes, chiefly of rapidly rotating shafts, and by the sticking of the catalyst to the walls in the sump and gas spaces and could be overcome by relatively simple measures.

2265. ———. Deposition of Finely Divided Catalysts on the Reactor Walls in the Foam Process, Jan. 5, 1944. Bureau of Mines Transl. T–438, January 1948, 12 pp.

Paper from Dr. Pier's files on high-pressure experiments, Leuna. A peculiar phenomenon is observed in the foam process of hydrocarbon synthesis in the disappearance of the catalyst in the liquid phase and its deposition on the reactor walls, increasing from bottom to top. It is undesirable in that it prevents the full performance of the catalyst and reduces the available reaction space. It is thought to be due (and an analysis gives credence to the idea) to an increasing concentration of CO_2 and steam in the upper part of the reactor and the formation of $FeCO_3$.

2266. MICHAELIS, P. [Development of Coal Processing. I. Coal as a Source of Solid Products.] Oel u. Kohle, vol. 37, 1941, pp. 701–705; Chem. Zentralb., 1942, I, p. 137; Chem. Abs., vol. 37, 1943, p. 5845.

Review of the processing of coal; the use of coke for the manufacture of carbides and C_2H_2, and the chemical products derived from it; low-temperature carbonization of coal; the preparation of briquets and cleaned coal and the uses of the latter; and the classification, properties, and uses of coal according to age and seam.

2267. ———. [Development of the Conversion of Coal. II. Coal as a Source of Liquid Products.] Oel u. Kohle, vol. 37, 1941, pp. 851–858; Chem. Abs., vol. 36, 1942, p. 3025.

Different known processes—for example, coking, tar, distillation, phenol, and benzene production—are discussed, and tables of the properties of the obtained products are given.

2268. ———. [Development of the Conversion of Coal. III. Coal as a Raw Material for Gaseous Products.] Oel u. Kohle, vol. 37, 1941, pp. 949–955; Chem. Abs., vol. 37, 1943, p. 3584.

Review of 79 German papers on coal-gas production, processing, and uses, published from 1926–41, outlines briefly the production of city gas; such gas purification methods as the Alkazid, Thylox, Polythionate, and Katasulf processes; recovery of H_2, S, and NH_3 from coal gas; production of water gas; and production of hydrocarbons and O-containing organic compounds by the Fischer-Tropsch process.

2269. MICHEL, A. Magnetic Properties of Some Solid Solutions.] Ann. chim., vol. 8, 1937, pp. 317–423; Chem. Abs., vol. 32, 1938, p. 1989.

First part of this monograph gives the results obtained by thermomagnetic studies on α–Fe_2O_3, $Fe_2O_3 \cdot BaO$, $Fe_2O_3 \cdot SrO$, $Fe_2O_3 \cdot PbO$, the cubic sesquioxide of Fe, and the ferrites of Ni, Mg, and Cu. The effects of method of crystallization and grain size are discussed. In Part II the results are given for solid solutions of α–Fe_2O_3 in F_3O_4, Fe_3O_4 in α–Fe_2O_3, mixtures of rhombic sesquioxide with cubic sesquioxide, solid solutions of magnetite and the ferrites of Ba, Sr, and Ca, the unstable ferrites of Be, and the ferrites of Ag, Hg, and Li. Part III gives the results of a similar study of pyrrhotite, and solid solutions of FeS with S, Si, As, Te, Ti, W, Co, Ni, Cu, Zn, Sb, Mn, Ag, Fe, Cd, Pb, and Bi. The general significance of the results and the interpretation of the anomalies in the temperature-magnetization curves are discussed. Extensive bibliography appended to each part.

2270. ———. [Substitutions in Magnetite and Preparation of New Cubic Sesquioxides of Iron.] Bull. Soc. chim. France, 1949, D128–D131; Chem. Abs., vol. 44, 1950, p. 17.

Preparation of magnetite is described in which a bivalent Fe ion is replaced by K, Na, Mn, or Mg, and a trivalent Fe ion is replaced by Al or Cr. Variation of parameters and of the Curie point is given for these substituted magnetites and for the cubic sesquioxides obtained by heating. Temperatures of transformation for cubic $(Fe_{1-x}Al_x)_2O_3$ are: for $x=0$ ~450°; for $x=0.03$ 610°–615°; for $x=0.09$ ~650°. Thermomagnetic analysis revealed significant differences between the heating and cooling period. These differences increase, but Curie point for both periods decrease, at higher Al_2O_3 contents. Al_2O_3 stabilizes the cubic form of the sesquioxides. The cubic structure of $(Fe,Al)_2O_3$ is obtained also by calcination of the nitrates and to some extent by calcination of the sulfates.

2270a. ———. [Application of Thermomagnetic Analyses to the Study of Catalysts.] Ind. chim. belge, vol. 17, 1952, pp. 643–651; Chem. Abs., vol. 47, 1953, p. 31.

Relation betwen the thermomagnetic and catalytic properties of Fe, Ni and Co catalysts for Fischer hydrocarbon synthesis ($CO+2\ H_2$) was studied (a) for a variety of conditions of catalyst preparations and (b) with several catalyst promoters. In general, good catalysts exhibited a distinct type of thermomagnetic curve. However, this relation should not be unduly emphasized until more is known about other properties that are responsible for catalysis.

———. *See* abs. **209, 742a, 743, 1279, 2076.**

2271. MICHEL, A., AND BERNIER, R. [Thermomagnetic Study of Cementite Stability.] Rev. mét., vol. 46, 1949, pp. 821–824; Chem. Abs., vol. 44, 1950, p. 1868.

Cementite was prepared by passing a mixture of CO and 2 H_2 over spectroscopically pure Fe oxide held at 560°–1,000°. Thermomagnetic analysis of this Fe_3C showed its Curie point at 210° and its comparative stability under conditions of thermal testing. About ⅓ of cementite is graphitized when heated for 15 hr. in vacuum at 825°, and heating at 900° destroys ⅔ of it. Heating both in H_2 and in N_2 rapidly decomposes this cementite.

2272. MICHEL, A., AND CHAUDRON, G. [Stabilized Cubic Ferric Oxide.] Compt. rend., vol. 201, 1935, pp. 1191–1193; Chem. Abs., vol. 30, 1936, p. 692.

Solid solutions of varying amounts of $NaFeO_2$ in Fe_2O_3 were prepared by adding various amounts of

aqueous NaOH to precipitated $Fe(OH)_3$, the product being reduced to Fe_3O_4, oxidized at 300° and then heated to 650°. The Curie point decreased regularly with increasing content of Na_2O, while the side of the unit cube (a) increased with equal regularity, the figures for an oxide containing about 5% Na_2O being about 400° and 8.52 Å., and (by extrapolation) 675° and 8.32 Å. for pure Fe_2O_3. The dissociability of Fe_2O_3 (into Fe_3O_4 and O_2) decreases rapidly with increase in Na_2O, and with 5% thereof it is virtually undissociable at 300°. Though the content of Na_2O is reduced by hydrolysis in hot H_2O or by AcOH, no change in Curie point or a occurs until after reheating to 650°. Solid solutions of other ferrites behave similarly, the limit solutions of those of Be, Ag, and K having Curie points at 220°, 270°, and 250°, respectively.

2273. MICHEL, A., AND GALLISSOT, M. [Thermomagnetic Anomaly at Ordinary Temperatures in Microcrystalline Ferromagnetic Substances.] Compt. rend., vol. 207, 1938, pp. 140–142; Chem. Abs., vol. 32, 1938, p. 6919.

Cause of the anomaly in the magnetization: temperature curves of various ferromagnetic substances, Fe_2O_3 and various ferrites, according to the state of crystallization, are discussed, and the explanation is suggested that the Curie points of the minute crystallites in the microcrystalline varieties vary, being lower the smaller the crystallite, but always above 20°, below which the normal law is followed. Thus a hyperbolic form of curve may be due to physical as well as chemical heterogeneity.

2274. MICHEL, A., AND POUILLARD, E. [New Family of Cubic Iron Sesquioxides.] Compt. rend., vol. 228, 1949, pp. 680–681; Bull. soc. chim. France, 1949, p. 152; Chem. Abs., vol. 43, 1949, p. 8934.

Mixed crystals of cubic $(Fe_{1-x}Al_x)_2O_3$ were obtained by oxidation of magnetite, $x(Al_2O_3)$ $(1—x)Fe_2O_3.FeO$, in which Fe^{+++} ions are partly substituted by Al^{+++} ions. The limit of solution is near to 10% Al_2O_3 at room temperature. The parameter of the lattice decreases from 8.324 Å. for cubic Fe_2O_3 to the value 8.20 Å. continuously. The solubility of Al_2O_3 increases at higher temperature. The content of Al_2O_3 stabilizes the cubic form. The temperature of quick transformation from the cubic form into the rhombohedral form is 200° for pure Fe_2O_3, 610° for the substitution $x=0.03$, and 650° for the substitution $x=0.07$. A stabilized cubic mixture with 32% Al_2O_3 was obtained by quenching from 600°; its Curie point was 410°. No modification in the stability of cubic Fe_2O_3 was obtained by Cr_2O_3, since it is insoluble in Fe_2O_3.

2275. MICHEL, A., BENARD, J., AND CHAUDRON, G. [Mechanism of the Superficial Oxidation of Iron.] Bull. soc. chim., vol. 11, 1944, pp. 175–179; Chem. Abs., vol. 40, 1946, p. 2370.

Specimens of electrolytic Fe were heated at temperatures from 250°–900° in air. The structure of the separated oxide scale was determined by use of the Debye-Scherrer method of X-ray diffraction and the thermomagnetic method of analysis. At 250°, the oxide consists largely of γ Fe_2O_3 and a small quantity of Fe_3O_4. The reaction mechanism is given by the equation $Fe \rightarrow Fe_3O_4 \rightarrow \gamma\text{–}Fe_2O_3$. In the interval of 400°–600° variable mixtures of γ Fe_2O_3 and Fe_3O_4 are formed. The mechanism is given by the equation $Fe \rightarrow Fe_3O_4 \rightarrow \gamma\text{–}Fe_2O_3 \rightarrow \alpha\text{–}Fe_2O_3$. Above 600° FeO is the major component. At 900° after 3 hr. of oxidation and a rapid cooling the oxide consists largely of FeO. A small quantity of Fe_3O_4 is found in the superficial layer and a film of α–Fe_2O_3 on the surface. The mechanism of oxidation is $Fe \rightarrow FeO \rightarrow Fe_3O_4 \rightarrow \alpha\text{–}Fe_2O_3$. The FeO is assumed to decompose on cooling by the reaction $4FeO \rightarrow Fe_3O_4 + Fe$. It is concluded that both Fe and O_2 diffuse in the oxidation reaction. The distribution of reaction products is determined by the magnitude of each process.

2276. MICHEL, A., BERNIER, R., AND LECLERC, G. [Thermomagnetic Study of Fischer Catalyst Containing Nickel.] Jour. chim. phys., vol. 47, 1950, pp. 269–273; Chem. Abs., vol. 44, 1950, p. 7638.

Results of a thermomagnetic and structural study of Ni catalysts. An intimate relation existed between the catalytic activity of Ni and the crystal size. The most active catalysts possessed a certain type of magnetization-temperature curve that was correlated by means of X-rays with the crystal size. Under certain conditions of catalysis, the Ni catalyst was transformed into a paramagnetic hexagonal carbide of Ni. In the initial stages of catalysis the C formed a solid solution with the Ni and expanded the face-centered cubic structure. The lowering of the Curie point of active Ni catalysts after use for 100 hr. suggested that small amounts of C were present in these catalysts.

2277. MICHOT-DUPONT, F. [Treatment of Imperfect Fuels by Methylation to Obtain Aromatic Fuels.] Cong. mondial pétrole, 2me Cong., vol. 2, 1937, pp. 197–212.

Michot-Dupont methylation-distillation method for producing aromatic fuels is reviewed with regard to the features of the process, the constitution and utilization of the products, yields, starting materials, industrial application, reaction mechanism,, temperature study, initial costs, comparison with other low-temperature processes, sulfur recovery, and use of salts other than acetates.

MICKELSON, H. G. *See* abs. **1488.**

2278. MIGNOLET, J. [Investigations on Adsorption at Present in Progress.] Rev. univ. mines, vol. 19, 1943, pp. 111–113; Chem. Zentralb., 1943, II, pp. 1781–1782; Chem. Abs., vol. 38, 1944, p. 5719.

Adsorption of H_2 on catalysts of MoO_2 base is being investigated. Contrary to the results of other authors this oxide has not been found to be stable in the presence of H_2. In the temperature range in which Mignolet worked, a slow reduction of the MoO_2 was observed, and it is now the aim to find the reduced form stable under conditions suitable for the technical use of MoO_2. The apparatus used in the experiments is described.

2279. MILLER, A. E. Motor Fuel From Coal—Description of the Recent Work of Bergius, Fischer, and Patart. Bull. Am. Petrol. Inst., vol 8, No. 6, 1927, pp. 152–159; Petroleum (London), vol. 24, 1928, pp. 103–105, 139–141; Chem. Abs., vol. 21, 1927, p. 1532.

Processes of Bergius, of Badische Anilin-u. Soda-Fabrik, of Fischer-Tropsch, and of Patart are described. Bibliography of 130 refs.

2280. MILLER, B. [Active Carbon Recovery of Gasoline in the Fischer-Tropsch Process.]. Apparatebau, vol. 50, 1938, pp. 97–98.

Steps in the operation and costs.

2281. ———. Chemical Utilization of Natural Gas. Petrol. Refiner, vol. 24, No. 5, 1945, pp. 121–124; Petroleum Eng., vol. 16, No. 8, 1945, pp. 216, 218, 220, 222, 224, 226, 228; Nat. Petrol. News, vol. 37, No. 23, 1945, pp. R–430, 432–434, 436; Oil Weekly, vol. 117, Apr. 30, 1945, pp. 50–54.

After a discussion of the uses of natural gas in the production of He, C black, synthetic NH_3, natural gasoline, synthetic rubber, plastics, and MeOH, attention is directed to the Fischer-Tropsch process as offering a means of converting natural gas into liquid hydrocarbons suitable for motor fuel, supplying a market that could absorb the entire natural-gas production. It is pointed out that if improvements now thought profitable in this field should be realized, natural gas

would become a more economical source of motor fuel than petroleum.

2282. ———. Synthetic Liquid Fuels and the Manufactured-Gas Industry. Gas Age, vol. 97, No. 4, 1946, pp. 19–21, 68.

Discussion of means whereby the synthesis gas industry and the manufactured gas industry can be made complementary with the view of creating another source of city-gas production. It is not thought that the production of synthetic liquid fuels from natural gas can be considered a permanent solution of the problem of supply if and when our petroleum is exhausted; only coal is available in enough quantity to offer a solution of the problem. If the Fischer process is to be operated on coal economically, a process must be developed for production of synthesis gas from low-grade coals. It is suggested that the gas industry supply the process and the equipment to carbonize low-grade coal for gas and char production and sell the char to the synthetic liquid-fuel industry for the manufacture of water gas and synthetic gasoline, turning back to the manufactured gas industry the residual liquid products from the refining of the synthetic gasoline to be used as carburetting material for city gas. Continued research in the field of synthetic liquid fuels is almost certain to bring forth improvements that can be applied in the gas industry, and the latter can look with optimism upon such developments.

MILLER, G. H. *See* abs. **2993.**

2283. MILLETT, H. C. Lurgi Process for Complete Gasification of Coal With Oxygen Under Pressure. Jour. Inst. Fuel, vol. 10, 1936, pp. 15–21; Chem. Abs., vol. 31, 1937, p. 3238.

Large-scale experimental plant is described. The generator consists of a cylindrical shaft with an effective cross-sectional area of 10.4 sq. ft. operating with a fuel bed 10 ft. deep. With lignite, a daily output of 700,000 cu. ft. of gas was obtained. With a mixture of steam and O_2 under 20–30 atm. pressure, a gas comparable, after simple purification, with normal town's gas was obtained. It is possible to obtain by this process a high output of gas from a small plant. The successful operation of the high-pressure gasification process is shown to depend on the obtaining of the correct balance between the rate of production of CH_4 and the rate of gasification of coke in steam.

———. *See* abs. **691, 692, 693, 694.**

MILLIGAN, W. O. *See* abs. **3635, 3636.**

2284. MILLIGAN, W. O., AND HOLMES, J. X-Ray Diffraction Studies in the System CuO–Fe_2O_3. Jour. Am. Chem. Soc., vol. 63, 1941, pp. 149–150; Chem. Abs., vol. 35, 1941, p. 1336.

Report of the results of a systematic X-ray study of mixtures of varying composition of cupric and ferric oxides, which were precipitated at 25°, aged under water at 100°, and heated to 1,000°. The radiograms show no indication of the formation of cupric ferrite on precipitation at 25° or on aging the precipitate at 100°. In the samples heated to 1,000°, $CuFe_2O_4$ is formed; it is the only compound formed in the system CuO–Fe_2O_3.

2285. MILLS, G. A., BOEDEKER, E. R., AND OBLAD, A. G. Chemical Characterization of Catalysts. I. Poisoning of Cracking Catalysts by Nitrogen Compounds and Potassium Ion. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 1554–1560; Chem. Abs., vol. 44, 1950, p. 6611.

Basic organic N compounds, such as quinoline, are held on SiO_2–Al_2O_3 (–MgO, –ZrO_2) catalyst surfaces by physical and chemical forces. These forces are widely different so that at 250°–500° the physically held quinoline can be distinguished from that chemically held. At a given temperature, the amount of physically held N compound is increased with an increase in its partial pressure. The amount chemisorbed is decreased with an increase in temperature. The cracking activity of the catalysts studied was proportional to their capacity to chemisorb quinoline at cracking temperatures. Catalysts that have basic N compounds chemisorbed or that have K added by base exchange are poisoned for cracking. From a study of partial poisoning an exponential relationship was found between the amount of certain N compounds chemisorbed and the yield of C_6H_6 from the dealkylation of cumene. A relatively small fraction of the total surface of SiO_2-metal oxide cracking catalysts is responsible for catalytic activity. The chemical properties exhibited by this part of the surface identify the active principal as an acid.

MINACHEV, K. M. *See* abs. **3179.**

2286. MINCHIN, L. T. Liquid Purification—Some British and Continental Developments. Coke and Gas, vol. 13, 1951, pp. 27–29.

Some of the more recent processes and plant for removal of H_2S from town gas or coke-oven gas by liquid reagents are described: The Dutch State Mines-Otto process, which uses a washing liquid containing initially ferrous sulfate and potassium ferrocyanide; the Collin process installed at Duisburg in the Ruhr district of Germany using NH_3 liquor of about 6 oz. strength in the form of a spray; the Szombathy process, which uses an aqueous solution of sodium thiosulfate and a water-soluble catalyst (not given), which functions as an O carrier and oxidizes the H_2S to H_2O and S. The H. Koppers Co. owns the patents. Test results are not yet available. A full-scale plant to deal with 7 million cu. ft./day is under construction.

2287. MINING AND METALLURGY. Liquid-Fuel Production by Hydrogenation Today. Vol. 17, 1936, pp. 439–440; Chem. Abs., vol. 30, 1936, p. 8570.

Sketch of development of pressure hydrogenation and economic possibilities of satisfying the world's gasoline requirements.

MIROSHNICHENKO, G. K. *See* abs. **846.**

MISHIMA, A. *See* abs. **1916, 1917.**

2288. MITCHELL, J. A. Organic Catalytic Reactions. Jour. Chem. Education, vol. 9, 1932, pp. 59–71; Chem. Abs., vol. 26, 1932, p. 1235.

Complete survey of the development of the MeOH process and synthesis of higher alcohols from CO and H_2, a discussion of oxidation of cyclic compounds to produce maleic anhydride, phthalic anhydride and anthraquinone. Gives extensive bibliography of articles in English.

2289. MITCHELL, R. Petroleum Reprieve. Wisconsin Eng., vol. 52, No. 2, 1947, pp. 10, 32; Chem. Abs., vol. 42, 1948, p. 5201.

Production of cheap O_2 has made the Fischer-Tropsch process for producing synthetic hydrocarbons practical in America. The development of the fluid-bed catalyst reactor has improved quality. By controlling the rate of heat removal from the reacting constituents, different properties can be given to the product.

2290. MITCHELL, R. F. Oxygen-Steam Producer Blast. Canadian Chem. Process Ind., vol. 30, No. 8, 1946, pp. 34–42.

Deals with the O_2-steam gasification of coke at atmospheric pressure in Wellman-Galusha clean gas generators for the production of gas for NH_3 synthesis at Trail, British Columbia, Canada. Reports brief survey of early investigations on the use of an O_2 steam blast, and briefly describes 4 processes: Lurgi, Winkler, Thyssen-Galoczy, and Abstich (slagging) producers.

———. *See* abs. **3744.**

2291. MITSUI, K. Summary of Research on the Conversion of Coal to Oil at the First Naval Fuel Depot,

Ofuna. U. S. Naval Tech. Mission to Japan, X–38 (N)–7, Encl. (A), 1945, pp. 31–36; PB 58,701.

Summary of studies leading up to operation of the Bergius and Fischer-Tropsch processes for the synthesis of liquid fuel from coal in Japan.

2292. MITTASCH, A. [Contact Catalysis.] Ber. deut. chem. Gesell., vol. 59, **B**, 1926, pp. 13–36; Chem. Abs., vol. 20, 1926, p. 1164.

As an example of directive catalysis the reaction between CO and H_2 is presented, whereby a wide range of products can be obtained, depending upon the nature of the catalyst and the operating conditions.

2293. ———. [Iron Carbonyl and Carbonyl Iron.] Ztschr. angew. Chem., vol. 41, 1928, pp. 827–833; Chem. Abs., vol. 22, 1928, p. 4731.

Fe pentacarbonyl is produced on a large scale by circulating CO under pressure over sponge Fe at 150°–200° and cooling the gases evolved. It has d_4^{20} 1.453, a surface tension of 22 dynes per cm. and a viscosity of 0.0075 c. g. s. unit at 20°. Its heat of formation (liquid) is 54.2 kcal., latent heat of fusion 3.25 kcal. per mol., and heat of combustion 384.5 kcal. per mol. In alkaline solution it behaves as a powerful reducing and dechlorinating agent for organic compounds. In pentane solution it combines with Br, forming a yellow unstable compound, which rapidly decomposes with evolution of CO and formation of the reddish-brown compound, $Fe(CO)_4Br_2$. Iron pentacarbonyl decomposes at 250° in a hollow vessel heated by radiation, yielding a finely divided Fe containing about 1% C. If this is melted in a vacuum high-frequency furnace together with the requisite quantity of pure FeO, obtained by combustion of the carbonyl, an exceedingly pure Fe of high permeability, low hysteresis, and small wattage loss is obtained.

2294. ———. [Complex Catalysts.] Ztschr. Elektrochem., vol. 36, 1930, pp. 569–580; Chem. Abs., vol. 25, 1931, p. 21.

Historical review of the development of complex or mixed catalysts. Discusses reaction of CO with H_2 to give MeOH.

2294a. ———. Early Studies of Multicomponent Catalysts. Advances in Catalysis, Academic Press, Inc., New York, 1950, vol. 2, pp. 81–104.

Historical development of multicomponent catalysts is given. Their activity in NH_3 synthesis, catalytic production of H_2, hydrogenation of CO to CH_4, hydrogenation of unsaturated organic compounds, production of organic compounds by catalytic reduction of CO with H_2 under pressure, and catalytic oxidations is discussed. 52 refs. listed.

2295. MITTASCH, A., AND KEUNECKE, E. [Aluminum Oxide Activation of Iron Catalysts for Synthesis of Ammonia.] Ztschr. Elektrochem., vol. 38, 1932, pp. 666–669; Chem. Abs., vol. 26, 1932, p. 5707.

Fe catalysts containing about 10% Al_2O_3 have been prepared by different methods and their relative activities for NH_3 synthesis have been determined. Preparation of the Fe oxide–Al oxide by fusion, by coprecipitation followed by ignition in air to either 1,000° or 500°, by mixing the precipitated Fe_2O_3 with either α–or γ–Al_2O_3 and igniting to 1,100°, and by mixing γ–Al_2O_3 with precipitated Fe_2O_3 and igniting in air to 500°, all gave catalysts on reduction with H_2 that were capable of producing between 8.5 and 11.6% NH_3 at 500°, 200 atm. and space velocity of 20 l. per hr. Mixing precipitated Fe_2O_3 with α–Al_2O_3 and igniting to 500° gave a very poor catalyst. Fe prepared by the reduction of pure Fe_2O_3 gave a catalyst whose initial activity is as high as the final activity of the samples promoted with Al_2O_3; the principal function of the promoter appears, therefore, to be the prevention of crystal growth in the reduced Fe catalysts.

2296. MITTASCH, A., AND KUSS, E. [Ammonia Synthesis With Catalysts Derived From Complex Cyanides of Iron.] Ztschr. Elektrochem., vol. 34, 1928, pp. 159–170; Chem. Abs., vol. 22, 1928, p. 2441.

Complex cyanides of Fe or carbides derived from these cyanides are not themselves effective catalysts for the synthesis of NH_3. The active agent is elementary Fe resulting from the decomposition and reduction of the complex cyanide. The activity of the Fe may be enhanced by the presence of other materials that arise during the decomposition of the complex cyanides. The effective catalyst is then only a promoted Fe catalyst. This conclusion is supported by extensive chemical, X-ray, and magnetic studies of the complex cyanides and their decomposition products. The bearing of this research on the NH_3 catalyst patent situation in Germany is indicated.

2297. MITTASCH, A., KUSS, E., AND EMERT, O. [Thermal Decomposition of Complex Iron Cyanides in Connection With the Ammonia Synthesis.] Ztschr. anorg. Chem., vol. 170, 1928, pp. 193–212; Chem. Abs., vol. 22, 1928, p. 2441.

Complex Fe cyanides as such are not NH_3 catalysts, but the products of their decomposition and reduction are. $(NH_4)_4Fe(CN)_6$ and $KAlFe(CN)_6$ are decomposed at high temperature in a N_2–H_2 mixture with intermediate formation of a substance corresponding in composition to $Fe(CN)_2$. The purely thermal decomposition of $Fe(CN)_2$ gives Fe, C, Fe_3C, Fe nitride and N_2, probably with the intermediate formation of FeC_2. In N_2+H_2, $Fe(CN)_2$ reacts as follows: At 230°, the C and the N in the CN groups are reduced at the same rate, and the completed reaction yields Fe. At 400° the rates of reduction differ and there is obtained, probably through the intermediate formation of FeC_2, a mixture of Fe, Fe_3C, C, and probably the 2 latter in varieties easily reduced by the N_2–H_2 mixture. These varieties are changed by prolonged heating above 400°, although the Fe_3C can still be reduced. Fe must always be formed first; Fe_3C could not be prepared under any conditions without the formation of Fe, while it is possible to control the conditions so as to obtain only Fe. The NH_3 contact catalysts prepared from complex Fe cyanides must always contain Fe and are composed chiefly or exclusively of products of reduction. These are activated by the N_2–H_2 mixture and constitute then a catalyst. Fe_3C in finely divided form is readily reduced by H_2 to a compact form, at least superficially, so that the catalytic action of Fe_3C as such has never been observed.

2298. MIYAHARA, S. [Theory of the Transformation of Magnetite at Low Temperatures. I.] Proc. Phys. Math. Soc. Japan, vol. 24, 1942, pp. 49–54; Chem. Abs., vol. 41, 1947, p. 6093.

Magnetic character of magnetite is discussed on the basis of the Wilson model of semiconductors and the Bloch theory of ferromagnetism. It is concluded that the transformation of magnetite at low temperatures is not caused by the change of axis of easiest magnetization but is primarily connected with the special electronic structure of this crystal.

2299. OKAMURA, T., AND OGAWA, S. [Magnetic Behavior of Magnetite at Low Temperature. II.] Proc. Phys. Math. Soc. Japan, vol. 25, 1943, pp. 43–46; Chem. Abs., vol. 41, 1947, p. 6093.

Magnetization intensities of magnetite in 3 directions (110), (111), and (100), were measured at —195°. They are much smaller than those at 10° and different according to the directions when the magnetizing field is smaller than about 6,000 oersteds. They coincide with each other at 7,500 oersteds. Above this field strength, the low-temperature magnetization curve is a little higher than the room-temperature curve.

2300. MIYAKE, S. Orientations of Metallic Crystals, Formed by the Evaporation Method. I. Iron Crystals Formed on the Cleavage Plane of Zinc Blende. Proc. Phys. Soc. (Japan), vol 1, 1946, pp. 6–11; Chem. Abs., vol. 44, 1950, p. 9207.

Electron-diffraction experiment of a film of Fe crystals, formed by the evaporation method on the cleavage plane of Zn blende, was made. The orientation of the Fe crystals in the film depends upon the temperature of the Zn-blende crystal at the time of the film formation, because the temperature affects the quantity of gas molecules absorbed in the Zn-blende crystal. Heating after the formation of the Fe crystals has no effect on their orientations. The film formed at high temperatures or heated after their formation gives irrational spots or mesh pattern in the electron diffraction. This is attributed to finely repeated twins of the Fe crystals.

2301. MOEHRLE, E. [Production of Diesel and Fuel Oils From Coal Tar.] Tech. Mitt. Krupp, vol. 5, No. 2, 1937, pp. 38–39; Brennstoff-Chem., vol. 18, 1937, p. 305; Chem. Abs., vol. 31, 1937, p. 8875.

Process is described for separating pitch and oil from coal tar by fractional solution in gas oil at boiling temperature. A virtually asphalt-free mixture of gas oil and tar oil is obtained. Some improvement in the method has been found by substituting synthetic Kogasin for the gas oil.

MOGILEVSKAYA, A. M. *See* abs. **360.**

MOHAMMAD, A. *See* abs. **2770.**

MOHR, W. *See* abs. **1044.**

2302. MOIGNARD, L. A. AND DENT, F. J. Catalytic Synthesis of Methane for Town-Gas Manufacture. Joint Research Comm., 49th Rept. Gas Research Board Pub. 20; Gas Times, vol. 47, 1946, No. 601, pp. 41–43; No. 603, pp. 40–42; No. 605, pp. 40–41.

Report of investigation of methods is given for the control of the reaction involved in the catalytic synthesis of CH_4 from H_2 and CO so that the reaction can be carried out at relatively low temperatures and at the high space velocity necessary for gas manufacture. The problems of C deposition and sintering were studied experimentally. By increasing the rate of dissipation of heat and the proportions of alumina, the deposition of C is decreased and less sintering occurs.

MOIGNARD, L. S. *See* abs. **694.**

MOISE, J. E. *See* abs. **2459.**

2303. MOLSTAD, M. C., AND DODGE, B. F. Zinc Oxide-Chromium Oxide Catalysts for Methanol Synthesis. Ind. Eng. Chem. vol. 27, 1935, pp. 134–140; Chem. Abs., vol. 29, 1935, p. 2313.

Mixtures of ZnO and Cr oxide, made by NH_3 precipitation from a solution of the mixed nitrates, are active, rugged MeOH catalysts. The most active mixture in a short test is $Zn_{75}Cr_{25}$, in agreement with other investigators that excess Zn is necessary. Catalysts containing more Cr increase in activity during tests, and the improvement is accelerated by temperatures up to 100° above maximum-activity temperature so that the best catalyst for long service is $Zn_{50}Cr_{50}$, which produces almost pure MeOH and is unaltered by long use at temperatures considerably above the normal operating temperature.

MOMEN, S. A. *See* abs. **2446.**

2303a. MONCEAUX, P. [Controlled Oxidation of the Gas of Saint-Marcet in Air at Atmospheric Pressure.] Mém. services chim. état. (Paris), vol. 32, 1945, pp. 253–298; Chem. Abs., vol. 42, 1948, p. 4327.

Oxidation of CH_4, C_2H_6, and natural gas was studied under various conditions of temperature, ratio of air to CH_4, and rate of flow. The natural gas was 92% CH_4 with <1% C_2H_6 and 5–6% N_2. The noncatalytic oxidation of CH_4 was studied over a temperature range of 500°–900° by using gas mixtures containing 10–50 parts of CH_4 in air with flow rates from 50–300 l. per hr. In all experiments the conversion of CH_4 to HCHO did not exceed 1%. With increasing time of contact the yield passed through a maximum. The yield increased with increase of temperature, the maximum shifting to shorter contact times. <700° the most favorable composition of the gas was 20% CH_4 and 80% air, while at higher temperature it was 10% CH_4. There was, however, a rapid decrease in the quantity of O_2 present which was shown to be due to the direct oxidation of CH_4 to CO and H_2. A study of the decomposition and oxidation of HCHO was made which showed that >600° the decomposition in N_2 was extremely rapid at first and then approached complete decomposition more slowly. <600° the decomposition was much slower but still appreciable. In the presence of air the HCHO was oxidized as well as decomposed. The order of the reaction for the formation of HCHO in respect to O_2 was found to lie at 1–2. The oxidation of CH_2 yielded only slightly more HCHO than did CH_4 and slightly < the natural gas. An increase in the surface of the reaction tube, with quartz, caused a decrease in the yield of HCHO and also an increased rate of decomposition of HCHO. A surface of C increased the yield of HCHO. At temperatures < 750° the % of O_2 entering into the reaction was markedly reduced by a C surface. The catalytic action of oxides of N was caused by NO_2 and not by NO.

2304. MOND, L., HIRTZ, H., AND COWAP, M. D. Note on a Volatile Compound of Cobalt With Carbon Monoxide. Chem. News, vol. 98, 1908, p. 165; Chem. Abs., vol. 2, 1908, p. 3315.

Finely divided Co and CO at 150° and under 50 atm. yielded small quantities of Co carbonyl; at 200° under 100 atm. the yield was higher. The Co was prepared by converting CoC_2O_4, free from Ni and Fe, to oxide, and reducing the latter to metal with H_2 in the retort used for the production of the carbonyl. The carbonyl was obtained in large orange crystals, agreeing in composition with the formula $Co(CO)_4$. It decomposes in air to a violet substance, as yet uninvestigated, and is best preserved by sealing up in H_2 or CO. It is but slowly attacked by nonoxidizing acids but very readily by oxidizing agents, for example, $Co(CO)_4+Br_2 \rightarrow CoBr_2+4CO$. It is insoluble in N_2O but more or less soluble in CS_2, ether, naphtha, alcohol, and Ni carbonyl. If these solutions stand for some time or are warmed, decomposition sets in, D_{18} 1.827; vapor tension at 15°, 11 mm. Both of these values, however, are affected by the ease with which the carbonyl decomposes and are not to be regarded as final. In an atmosphere of CO_2, the decomposition begins at 40°–45° and is complete at 130°–135°, leaving metallic Co. The melting point is 42°–46°.

2305. ———. [Some New Metallic Carbonyls.] Ztschr. anorg. Chem., vol. 68, 1910, pp. 207–219; Jour. Chem. Soc., vol. 97, 1910, pp. 798–809; Chem. Abs., vol. 4, 1910, p. 2118.

Formation and properties of $Co(CO)_3$, $Fe(CO)_5$, $Mo(CO)_6$, and Ru carbonyl (composition unknown) are discussed. Gives table of the known carbonyls and their properties.

2306. MOND, L., LANGER, C., AND QUINKE, F. Action of Carbon Monoxide on Nickel. Proc. Chem. Soc., vol. 86, 1890, pp. 112–113; Chem. News, vol. 62, 1890, p. 97; Jour. Soc. Chem. Ind., vol. 9, 1890, p. 808.

CO in contact with Ni at temperatures 350°–450° was found to decompose, a compound of C and Ni being formed. It was identified as Ni carbonyl $Ni(CO)_4$. Similar experiments with other metals, such as Co, Fe, Cu, and Pt, gave negative results.

2307. MOND, R. L. [Metal Carbonyls.] Chim. et ind., vol. 21, 1929, pp. 681–700, 937–940; Jour. Soc. Chem. Ind., vol. 49, 1930, pp. 271–278T; Chem. Abs., vol. 23, 1929, p. 4417.

Address reviewing the preparation, properties, and applications of metallic carbonyls, with a bibliography of 91 literature refs. and 69 patents.

2308. MOND, R. L., AND WALLIS, A. E. Researches on the Metallic Carbonyls. Jour. Chem. Soc., vol. 121, 1922, pp. 29–32; Chem. Abs., vol. 16, 1922, p. 2457.

Composition of Mo carbonyl, redetermined by 2 methods, corresponds to $Mo_2(CO)_{26}$. It is insoluble in the common solvents. 2 yr. were required to prepare 170 mg. Ru gives 2 carbonyls, one volatile is crystalline and soluble in C_6H_6, and the other is nonvolatile, amorphous, and insoluble in C_6H_6, but soluble in C_2H_5OH and in H_2O. The formula of the latter appears to be $Ru(CO)_2$. Optimum conditions are described for the preparation of $Fe(CO)_5$. $Ni(CO)_4$, air, and moist CO heated at 200° react to give a yellow deposit, which is shown to be a colloidal basic Ni carbonate of varying composition.

MONROE, G. S. *See* abs. **1579, 1579a.**

MONTGOMERY, C. W. *See* abs. **117, 3599.**

2309. MONTGOMERY, C. W., AND WEINBERGER, E. B. Product Distribution in the Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. Jour. Chem. Phys., vol. 16, 1948, pp. 424–425; Chem. Abs., vol. 42, 1948, p. 4437.

It is pointed out that thermodynamic equilibrium among the n-paraffins yields a distribution that is qualitatively similar to that observed experimentally. Comprises general viewpoint set forth by Craxford, that product distribution is a result of some polymerization-depolymerization equilibrium in the last stages of the process and probably involves paraffin hydrocarbons.

2310. MONTGOMERY, C. W., WEINBERGER, E. B., AND HOFFMAN, D. S. Thermodynamics and Stoichiometry of Synthesis Gas Production by the Partial Oxidation of Methane. Ind. Eng. Chem., vol. 40, 1938, pp. 601–607; Chem. Abs., vol. 42, 1948, p. 4329.

In considering the economics of Fischer-Tropsch synthesis gas production by the partial oxidation of CH_4, situations may arise where either the cost of O_2 or the cost of CH_4 may be of controlling importance. This paper presents a treatment of the thermodynamics of the CH_4–H_2O–H_2–CO–CO_2–C system, which has been extended to cover solutions of 2 maximum problems not ordinarily dealt with; namely, determination of the conditions of temperature, pressure, and O_2: CH_4 ratio for maximum yield of synthesis gas per mol. of O_2 and per mol. of CH_4. The numerical calculations have been made with the assumption of isothermal equilibration so that the results are of more value as standards for comparison with actual synthesis-gas units rather than as a basis for the design of such units. The calculations show that the maximum yield of synthesis gas per mol. of CH_4 or O_2 is favored at high temperatures and low pressures. In addition, the conditions of temperature, pressure, and O_2: CH_4 ratio necessary to prevent the formation of unburned C is given. It also is shown that the numerical calculations are much simplified if the H_2: CO ratio is taken as the independent variable rather than the O_2: CH_4 ratio. The calculations serve to illustrate the general desirability of effecting equilibration of the combustion gases at high temperatures and low pressures. Relatively long residence time of the gases in contact with catalytic materials at lower temperatures, such as might be encountered in a reactor having a long dropping temperature gradient might be expected to cause deviations from the theoretical compositions. The magnitude of these deviations from the calculated values may be taken as a measure of the extent of re-equilibration occurring. The calculations also show that the point of maximum yield per mol. of CH_4 always requires a higher O_2: CH_4 ratio than the point of maximum yield per mol. of O_2. In the preferred high-temperature–low-pressure range, however, these maxima approach each other. The problem of calculating maximum yield per unit cost of reactants is, thus, very much simplified.

MOORE, G. E. *See* abs. **1729.**

2311. MOORE, H. Liquid Fuels and Organic Chemicals From Coal and Home-Refined Petroleum. Gas Jour., vol. 243, 1944, pp. 149–150, 155, 180, 183, 213–214; Gas World, vol. 120, 1944, pp. 166–172, 191–199; Jour. Inst. Fuel, vol. 17, 1944, pp. 65–74, 102–104; Petrol. Times, 1944, pp. 67–68, 70, 79–81, 83–84, 86; Chem. Abs., vol. 38, 1944, pp. 1861, 2469, 6066.

Reviews methods for producing liquid fuels and organic chemicals in use during 1938 and suggests outline of policy to be followed for their production in Great Britain after the war. By increasing the demand for gas, the materials for production of more liquid fuels and chemicals will become available.

2312. MOORE, W. J. Parabolic Oxidation Rates of Metals. Jour. Chem. Phys., vol. 18, 1950, p. 231; Chem. Abs., vol. 44, 1950, p. 5686.

Constants, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta F^{\ddagger}$, of the transition-state theory (abs. **1283**) for the oxidation of Al, Fe, Zr, Ti, Ni, Cu, Co, Zn, and Be are compared. Except for Be, there is little variation in the $\Delta F^{\ddagger}$ values; hence reactions with high $\Delta H^{\ddagger}$ also have high $\Delta S^{\ddagger}$. A schematic diagram of the potential-energy barriers for vacancy formation and diffusion shows that, for equal diffusion barriers, the higher the heat of adsorption, the lower the effective $\Delta H^{\ddagger}$. Since a high heat of adsorption implies an immobile adsorbed film, it may also be associated with a large negative ΔS of adsorption; this may help explain the approximate constancy of $\Delta F^{\ddagger}$.

MORCOM, A. R. *See* abs. **1629.**

MOREAU, J. *See* abs. **190.**

2313. MORGAN, G. T. Organic Syntheses Facilitated by Pressure. Chem. and Ind., vol. 50, 1931, pp. 104–109; Chem. Abs., vol. 25, 1931, p. 1809.

Review with many references to the patent literature of important syntheses facilitated by pressure. Among the reactions discussed are the formation of hydrocarbons, alcohols, aldehydes, ketones, etc., by pressure reactions in the gas phase from CO and H_2 with various catalysts.

2314. ———. [Synthesis of Aliphatic Compounds Under Pressure.] Bull. soc. chim. Belg., vol. 45, 1936, pp. 287–312; British Chem. Abs., 1936, A, p. 1090.

Review. At 400° per 200 atm. using $CoSO_4$ with some CuO and MnO as catalyst, CO_2 and H_2 gave a mixture containing MeOH (17%), EtOH (22%), higher alcohols, chiefly normal (11%), and CH_4 (47%). Other reactions are reviewed.

2315. MORGAN, G. T., AND BONE, W. A. Discussion on Catalytic Reactions at High Pressures. Proc. Roy. Soc., London, vol. 127, A, 1930, pp. 240–267; British Chem. Abs., 1930, A, p. 867.

Work on the NH_3 synthesis and on the synthesis of MeOH from CO and H_2 is briefly and historically reviewed. The aldolization hypothesis, which accounts for the formation of higher aldehydes and alcohols in the latter synthesis, is discussed. Work in the high pressure gas research laboratories at the Imperial College during the last 3 yr. is reviewed with special reference to the formation of formaldehyde, MeOH, and CH_4 from CO and H_2. By selecting a suitable catalyst and temperature, any one of these 3 substances may be produced to the practical exclusion of the other 2. The absence of satisfactory equilibrium data

in regard to the MeOH synthesis previous to the present series of investigations is pointed out, and the extreme importance of determining the equilibrium constant by approaching the equilibrium from both sides is emphasized. Discusses errors due to the fact that at the high pressures used the equilibrium mixtures do not obey the simple gas laws.

2316. MORGAN, G. T., AND TAYLOR, R. Ethyl Alcohol, a Product of High-Pressure Synthesis. Nature, vol. 125, 1930, p. 889; Proc. Roy. Soc. (London), vol. 131, A, 1931, pp. 533–540; British Chem. Abs., 1931, B, p. 833; Chem. Abs., vol. 24, 1930, p. 3985.

This alcohol has been obtained by Morgan and Taylor with various catalysts from CO and H_2.

2317. ———. Ethyl Alcohol, a Product of High-Pressure Synthesis. Proc. Roy. Soc., London, vol. 131, 1931, A, pp. 533–540; Chem. Abs., vol. 25, 1931, p. 4521.

Seven different catalysts, the composition of which is given, were found to give appreciable quantities of EtOH. 1 of these catalysts, prepared from Co nitrate and Zn permanganate with an addition of clay, contained after use: ZnO, 7.9; MnO, 26.34; Co, 29.9; K_2O, $+Na_2O$, 7.4; SiO_2, 8.8; Al_2O_3, 2.5; CaO, 0.4; Fe, 0.3; and C, 8.9%. The gas mixture contained $H_2:CO::2:1$. The pressure was 200 atm. and temp. was 380°–410° C. In these circumstances, EtOH was found to account for 9.8% of the total CO converted. Other products were: Other alcohols, 25.5; acids, 7.4; acetaldehydes, 5.3; and CH_4, 50.0%.

2318. MORGAN, G. T., HARDY, D. V. N., AND PROCTOR, R. A. Methanol Condensation as Modified by Alkalized Catalysts. Jour. Soc. Chem. Ind. (London), vol. 51, T, 1932, pp. 1–7; British Chem. Abs., 1932, B, p. 250; Chem. Abs., vol. 26, 1932, p. 4792.

Cr and Mn oxide catalysts in molecular proportions gave higher yields of higher alcohols and lower yields of MeOH in the MeOH synthesis from CO and H_2 when precipitated by alkali hydroxides than when formed by ignition of the nitrates. The catalyst impregnated with 9.8% Rb gave the highest yield of higher alcohols. Theories to account for this effect are discussed. A careful analysis was made of the product obtained by using a Cr–Mn catalyst containing 15% Rb.

2319. MORGAN, G. T., TAYLOR, R., AND HEDLEY, T. J. Synthesis Under High Pressure. Interaction of Carbon Monoxide and Hydrogen. Jour. Soc. Chem. Ind., vol. 47, 1928, pp. 117–122T; Chem. Abs., vol. 22, 1928, p. 2919.

Chemical Research Laboratory at Teddington, devoted to general investigations of high-pressure synthesis, is described in detail. Numerous illustrations and drawings of high-pressure equipment are reproduced. A Tantiron apparatus for generating CO from HCO_2H and H_2SO_4 is described. MeOH has been synthesized at 400 atm. in relatively large quantities by circulation of $CO–H_2$ mixtures over any one of several catalysts made by mixing ZnO with other metallic oxides. Other ZnO catalysts containing alkaline substances were used to synthesize mixtures of MeOH and higher alcohols. These mixtures invariably contained small quantities of aldehydes, acids, and esters. It was observed that primary alcohols only were identified; the aldehydes formed corresponded to the alcohols; addition of Co to the basic Zn chromate catalyst favored the production of higher alcohols; rise in temperature of the catalyst favored MeOH formation. The reactions are assumed to involve primary HCHO synthesis. The results so far obtained on the MeOH equilibrium are in agreement with Audibert and Reineau's equation: $\log K_p = P_{MeOH}/P_{CO} \cdot (P_{H_2})^2 = 27{,}000/(4.517T) - 3.5 \log T - 3.6$.

2320. MORGAN, G. T., AND OTHERS. Application of High Pressure in the Synthesis of Organic Compounds. Trans. World Power Conf., 3d Conf., London, June 1936, Chem. Eng. Cong., 22 pp.

Work at Chemical Research Laboratory, Teddington, since 1926 is summarized.

MORI, I. *See* abs. **3173.**

MORIKAWA, K. *See* abs. **3606, 3607, 3608, 3609, 3610, 3611.**

2321. MORIKAWA, K., BENEDICT, W. S., AND TAYLOR, H. S. Activity of Specific Bonds in Complex Molecules at Catalytic Surfaces. I. The Carbon-Hydrogen Bond in Methane and Methane-d_4. Jour. Am. Chem. Soc., vol. 58, 1936, pp. 1445–1449; Chem. Abs., vol. 30, 1936, p. 6632.

CH_4 undergoes exchange with D_2, CD_4, and D_2O on active Ni catalysts at 138° and above. At 184° the rate of reaction decreases in the order CD_4, D_2, and D_2O. The activation energy of reaction for CD_4 is approximately 19 kg.-cal., and for D_2 approximately 28 kg.-cal. The reaction is explained by an activated, dissociative absorption of CH_4 on surface areas not occupied by H–D or D_2O.

2322. ———. Activation of Specific Bonds in Complex Molecules at Catalytic Surfaces. II. Carbon–Hydrogen and Carbon–Carbon Bonds in Ethane and Ethane-d. Jour. Am. Chem. Soc., vol. 58, 1936, pp. 1795–1800; Chem. Abs., vol. 30, 1936, p. 7435.

C_2H_6 and D_2, heated in contact with a Ni catalyst, undergo an exchange reaction at 100°–130°, and yield mixed methanes at 160°–300°. The CH_4 reaction was followed by measuring the infrared absorption and by volume changes in the gas mixture. H_2 is preferentially adsorbed on the catalyst and tends to inhibit CH_4 formation. At low H_2 concentrations, the side reactions $2C_2H_6 \rightarrow C + 3CH_4$ and $C + 2H_2 \rightarrow CH_4$ become predominant. The activation energy of formation of CH_4 from C_2H_2 and H_2 is approximately 43 kg.-cal., and that of CD_4 is approximately 5 kg.-cal. higher. These reactions are explained in terms of a dissociative adsorption theory. More energy is required to activate the C–C bond than the C–H bond. C_2D_6 was prepared by 2 treatments of C_2H_6 with pure D_2 at 138° for 2–3 hr.

MORITA, K. *See* abs. **1681, 1682.**

MORLET, E. *See* abs. **2094a.**

2323. MORLEY, R. J. Winkler Generators for Manufacture of Water Gas. BIOS Final Rept. 333, 1945, 37 pp., PB 25,587; TOM Reel 227.

All the available information concerning Winkler generators, contained in CIOS reports and in documents brought back from Germany in 1945 is collected and combined with literature references to give a comprehensive account of the history and present status of the process. The process is technically sound, and it is possible to operate Winkler generators on bituminous coals, low-temperature coke from bituminous coal or even anthracite; operation, however, is not satisfactory, and, in general, it appears that the process is not economic for such fuels, where cheap fuel and coke-oven water-gas generators are available. The Winkler process is not suited to making town's gas, as the calorific value is low, and its field of application appears to be limited to the large scale production of water gas, to be used for manufacture of H_2, MeOH, or Fischer-Tropsch synthesis gas, of producer gas to be used as a fuel or power gas, and of NH_3 synthesis gas, but, in all cases, based on a cheap fuel. The 2 great disadvantages of the Winkler process are its relatively poor thermal efficiency (66 and 60%, respectively, for water-gas and power-gas production at Leuna; the thermal efficiency is raised somewhat if all the C in the escaping dust is recovered for boiler fuel) and the cost of O_2. A further disadvantage of O_2-gasification is that any O_2 added must eventually appear as CO_2 in the synthesis gas, hence greater compression and water scrubbing costs

are incurred to remove it with corresponding capital costs. The capital cost of a Wrinkler plant, including O_2 plant, waste heat boilers, etc., is somewhat greater than that of a corresponding coke water-gas plant, including coke ovens. The O_2 plant probably costs more than the Winkler plant it supplies. A rough figure for labor costs of water gas may be taken as 0.4 man-hr. per 1,000 m.^{3} of synthesis gas. Maintenance costs at Leuna averaged in 1935 RM 1.75 per 1,000 m.^{3} for an output of 20,000 m.^{3} per hr. of synthesis gas; for power gas RM 0.46 per 1,000 m.^{3} for an output of 50,000 m.^{3} per hr. Extensive data are given for plant operation and performance for production of both water and power gas from grude-coke and brown coal.

2324. ———. Wintershall-Schmalfeldt Process for the Manufacture of Synthesis Gas at Lutzkendorf. BIOS Final Rept. 1142, 1947, 33 pp., PB 78,242.

Detailed description of the process with figures and flow sheets. The process consists essentially of gasification of dry brown-coal dust in the entrained state. The heat of reaction is supplied by burning producer gas in 1 of 2 regenerators, used alternately, the heat being stored in checker brick and then given up to a mixture of recycled synthesis gas and steam. Heat also had been supplied by burning O_2 in the recycled gases. The producer gas is made by gasifying dried brown-coal dust entrained in the recycled gas and steam, heated to over 1,000°, while passing up and down 2 large generators in series. The sensible heat in the final gases was used to dry and disintegrate the raw brown coal. The process is now technically established, but dust losses are high, and synthesis gas contains organic S-ring compounds and gum-forming compounds deleterious to the Fischer-Tropsch catalyst, although not to the hydrogenation of oil and tar. It is reported that active C had been used in the purification train to remove these undesirable impurities and with considerable success. The plant is very large for the output, and capital costs are high, probably three times that of the Winkler plant. In its present state of development, the process appears to be less economic than the Winkler process, operating under similar circumstances. The operating cost per 1,000 m.^{3} of synthesis gas is calculated at RM 27.4 and RM 22.9, respectively. Additional costs, which should be debited to the Schmalfeldt process, have to cover the cost of disposal of the large amounts of muddy effluent, that of the higher inert content of water gas (6% as against 3% in Winkler gas), and the extra purification if the gas is used for the Fischer-Tropsch synthesis.

———. I. G. Farbenindustrie A.-G. Works at Leuna. III. Methanol and Higher Alcohol Synthesis. *See* abs. **1476.**

2325. Morozov, N. M. Kinetics of Sorption Processes of Hydrogen on Iron. Trans. Faraday Soc., vol. 31, 1935, pp. 659–668; Chem. Abs., vol. 29, 1935, p. 4233.

In the temperature range —190°–400°, the sorption of H_2 on pure Fe (reduced from precipitated Fe_2O_3) occurs as 3 types: Van der Waals adsorption, activated adsorption, and activated diffusion. In certain temperature ranges, it is possible to separate these processes and investigate the kinetics of each. Heats of activation are approximately 20,000 kg.-cal. for activated adsorption and 8,000 kg.-cal. for activated diffusion. Between 300° and 400°, the activated adsorption is instantaneous and entirely reversible; this permits the calculation of heats of adsorption, which, for 1.0, 1.25, and 1.50 cc. of H_2 adsorbed on 24 gm. of Fe, are, respectively: 9,220, 6,820, and 6,140 cal. per mol. Activated adsorption diminishes van der Waals adsorption, although under certain experimental conditions the absence of such relation was found.

———. *See* abs. **1653.**

2325a. Morrell, C. E., Carlson, C. S., McAteer, J. H., Robey, R. F., and Smith, P. V. Products From Hydrocarbon Synthesis. Am. Chem. Soc., 121st Meeting Abs., March–April 1952, p. 19–I.

Reaction of CO and H_2 over promoted Fe catalysts produces a valuable mixture of hydrocarbons and oxygenated organic chemicals. On a molal basis, CH_4 is obtained in greatest yield with progressively lower yields of hydrocarbons of increasing molecular weights. Yields of 2–C oxygenated compounds, including acetaldehyde. Ethanol and acetic acid are greater than those of both higher and low number of C atoms. Yields of higher molecular weight compounds decrease progressively with increasing molecular weight. Approximately 10 wt. % oxygenated organic compounds is obtained in the H_2O phase, including alcohols containing 1–5, aldehydes 2–5, ketones 3–6, esters 3–6, and acids 1–4 C atoms. The alcohols are predominately normal, primary alcohols, but up to 20 wt. % of the alcohols are secondary, tertiary, and branched chain primary alcohols. For the separation and purification of these H_2O-soluble chemicals, fractional distillation alone is not enough, but H_2O extractive distillation or extractive distillation with polar and nonpolar type organic solvents can be used. Caustic extraction and hydrogenation may be used to simplify the recovery problem. Approximately 20 wt. % oxygenated organic compounds are obtained in the oil phase, including alcohols containing 1–14, aldehydes and ketones 2–14, acids 2–14 and esters 3–20 or more C atoms. The molal yields of alcohols, carbonyls and acids are a maximum at 3, 2 and 5 C atom compounds, respectively. Alcohols have been isolated from narrow boiling fractions of synthesis oils by formation of nonvolatile esters with boric acid or phthalic anhydride. Extraction with hot H_2O removes acids and alcohols from the oil. Room temperature extraction with aqueous MeOH is effective in removing oxygenated compounds of all types from synthesis oils.

Morrell, J. C. *See* abs. **204, 776.**

2326. Morrell, J. C., and Egloff, G. Many Future Sources of Motor Fuel. Oil Gas Jour., vol. 26, No. 18, 1927, pp. 202, 400, 402, 404; Chem. Abs., vol. 22, 1928, p. 152.

Summary of the present status of motor fuel manufacture with a discussion of probable future developments. Starting with crude petroleum, the other sources are taken up with a brief explanation of the manufacturing necessary to convert raw material into fuels. The Fischer-Tropsch and the Bergius processes are described briefly and their commercial possibilities pointed out.

2327. Morris, H., and Selwood, P. W. Magnetic Moments on Some Catalytically Active Substances. Jour. Am. Chem. Soc., vol. 65, 1943, pp. 2245–2252; Chem. Abs., vol. 38, 1944, p. 294.

Directions for making magnetic-susceptibility measurements; significance of such measurements is pointed out in the determination of the ferromagnetism of a catalyst and its effect upon the activity.

Morris, H. E. *See* abs. **301, 302.**

2328. Morris, V. N., and Reyerson, L. H. Qualitative Study of the Catalytic Hydrogenation of the Oxides of Carbon. Proc. Indiana Acad. Sci., vol. 36, 1927, pp. 203–206; Chem. Abs., vol. 22, 1928, p. 345.

Attempts were made to synthesize HCHO and MeOH at atmospheric pressure. The most favorable results for HCHO were obtained when using a platinized gel as catalyst with mixtures of H_2 and CO_2. With H_2, CO, and a Cu catalyst the result appeared to be a mixture of the products. Pressures varying 8–27 atm. gave no better results than 1 atm. for these syntheses.

MORRISON, J. L. *See* abs. **2409.**

MOULIN, J. *See* abs. **2721.**

2329. MOUREV, H., CHOVIN, P., AND GARCIN, M. [Utilization of Methane.] Ann. mines et carburants, No. 4, 1944; Génie civil, vol. 122, June 15, 1945, p. 95; Fuel Abs., vol. 2, No. 5010, November 1945.

Discusses modern industrial processes using CH_4 as raw material including pyrolysis to give C-black, H_2, C_2H_2, C_2H_4, etc., conversion to HCHO and MeOH, and synthesis gas for the Fischer-Tropsch process.

2330. MOVIUS, H. G., AND SCOTT, H. Similarity of the Magnetic Change in Cementite and Ferrite. Chem. Met. Eng., vol. 22, 1920, pp. 1069–1070; Chem. Abs., vol. 14, 1920, p. 2327.

Thermal curves were taken by the inverse rate method. The materials studied were a pure Fe, a eutectoid C steel, and a 1.94 C Fe–C alloy containing 0.1% Si and 0.005% S.

2331. MOYNOT, H. [Adaptation of Fuels to Modern Diesel Engines.] Sci. et ind., Tech. ind. pétrole, 1939, No. 284, pp. 88–94; Chem. Abs., vol. 33, 1939, p. 7520.

Discusses combustion of fuels in diesel engines. Gives suggested specifications for diesel fuels. Fischer-Tropsch gas oils have higher calorific values than normal gas oils, the values of which are very similar and seldom determine.

MUCHLINSKI, A. *See* abs. **3578.**

MUELLER, A. C. *See* abs. **2441, 2442.**

MÜHLBERT, H. *See* abs. **1650.**

2332. MUHLERT, F. [Franz Fischer's Synthesis of Benzines.] Apparatebau, vol. 38, 1926, pp. 143–144; Chem. Abs., vol. 20, 1926, p. 2743.

2333. ———. [Fuels and Combustible Liquids. Recent Developments in Germany.] Chaleur et ind., vol. 15, 1934, pp. 229–234; Chem. Abs., vol. 29, 1935, p. 907.

General literature review of recent progress in Germany on the treatment of coal for the production of gaseous and liquid products.

2334. ———. [Production of Synthesis Fuels and Oils in England.] Chaleur et ind., vol. 17, 1936, pp. 119–123; Chem. Abs., vol. 30, 1936, p. 5389.

Describes Bergius and Fischer-Tropsch processes, and points out their economic value.

2335. ———. [Growth of Synthetic Liquid Hydrocarbon Industries in Germany.] Chaleur et ind., vol. 20, 1939, pp. 355–360; Chem. Abs., vol. 33, 1939, p. 6019.

Review of development of processes for synthesis of liquid hydrocarbons from bituminous and brown coals. Illustrated description of Fischer-Tropsch Ruhrchemie plant.

2335a. MULFORD, R. N. R., AND RUSSELL, W. W. Catalytic Hydrogenation of the Oxides of Carbon to Higher Hydrocarbons. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 1,969–1,974.

The effects of carbonate, chloride, sulfate, thiosulfate, and sulfide, added singly as K or Na salts prior to catalyst precipitation, upon Ce-promoted, Cu-containing Co catalysts in the synthesis of hydrocarbons from the oxides of C at atmospheric pressure have been studied. All of these Co catalysts produced oil when the initial CO_2–H_2 mixture was first passed over a supported Fe, water gas catalyst, but with no water gas catalyst present only the Co catalysts containing K_2CO_3 or K_2SO_4 produced oil. In general the effects of certain of these catalyst additives were to alter the distribution between liquid and gaseous synthesis products, to increase oil yields, and to shift the temperature range of maximum oil yields. The effects of the additives are attributed to selective activation and/or beneficial poisoning of the Co catalysts.

MÜLLER, A. *See* abs. **3674.**

2336. MÜLLER, E. R., AND KALLENBERG, S. [Production of Petroleum Hydrocarbons From Carbon Monoxide and Hydrogen at Ordinary Pressure.] Ing. Vetenskaps Akad. Handl., No. 106, 1930, 39 pp.; Brennstoff-Chem., vol. 12, 1931, p. 215; Chem. Abs., vol. 26, 1932, p. 2302.

Description of the application of the Fischer-Tropsch process. Pine charcoal was gasified with steam giving 1 $m.^3$ water gas from 300–400 gm. charcoal. This was treated in an electrically heated converter consisting of an upright Cu cylinder with 7 catalyst tubes 20 x 300 mm. Efficient catalysts were Co–Fe–Zn (2.5 : 1 : 2) and Co–Fe–Zn–Cu (2.5 : 1 : 1 : 1) precipitated from the nitrates with soda, washed with water, dried and reduced at 350° with H_2. In this apparatus, with 3,000 cc. of catalyst and a temperature 270°–290°, 800 l. of water gas produced in 21 hr. 55 gm. of liquid and solid hydrocarbons (70 gm. per $m.^3$ water gas). The benzine boiled 90% below 180°, the oil 70% below 250°.

2337. MÜLLER, F. [Low-Temperature Carbonization of Coal in Conjunction With the Fischer-Tropsch Hydrocarbon-Synthesis Process.] Tech. Mitt. Krupp, Tech. Ber., vol. 6, 1938, pp. 47–49; Brennstoff-Chem., vol. 20, 1939, pp. 141–144; Chem. Abs., vol. 33, 1939, pp. 6025, 9590.

It was previously pointed out that, by using low-temperature coke for water-gas production for the Fischer-Tropsch process instead of high-temperature coke, a maximum oil yield would be attained. When using low-temperature tar as fuel oil, the importance of mixing it with other oils is not as great as was formerly assumed. Moreover, low-temperature tar can be used directly as fuel oil. The low-temperature carbonization of coal in combination with the Fischer-Tropsch process is particularly suitable where coke ovens are not available and gas production is not of interest. In this way, the yield of clean oil amounts to 20–30% more than with high-temperature carbonization. Moreover, because of the specifically better usefulness of low-temperature coke for the water-gas process, a saving of coal is obvious. It is immaterial whether gas coal or flame coal is used, since both of them will yield an appropriate coke in indirectly heated ovens. Moreover, the water gas made from low-temperature coke more nearly meets the specified composition for synthesis gas—a $CO : H_2$ ratio of 1 : 2—the water gas from high-temperature coke showing a ratio of 1 : 1.25 and that from low-temperature coke 1 : 1.15–1.6.

2338. ———. [Hard-Coal Processing Development.] Glückauf, vol. 75, No. 33, 1939, pp. 706–711; Coke Smokeless-Fuel Age, vol. 2, 1940, p. 70.

Paper presented before the Verein bergbaulichen Interessen discusses the technology and operation of the German byproduct coking industry combined with the production of metallurgical coke, the low-temperature carbonization of hard coal and the production of semicoke, the preparation of coal for coking and chemical treatment, the liquefaction of coal, and the advantages of the Fischer-Tropsch process for producing a wide range of synthetic products from coal, coke, semicoke, or coke-oven gas. It is emphasized that best results are secured by combining the process with low-temperature rather than high-temperature carbonization of hard coal.

MÜLLER, H. Generation of Water Gas From Brown Coal in the Pintsch-Hillebrand Generator of the Hamburg Gas Works. II. *See* abs. **3277.**

MÜLLER, J. *See* abs. **3052, 3053.**

2339. MÜLLER, W. J., AND GRAF, E. [Theory of the Generator and Water-Gas Processes.] Brennstoff-Chem., vol. 20, 1939, pp. 241–246; Chem. Abs., vol. 34, 1940, p. 3904.

Attempt to follow the processes quantitatively on a kinetic basis.

2340. MÜLLIN, C. E. Higher Fatty Alcohols. Soap Sanit. Chemicals, vol. 14, No. 12, 1938, pp. 27–29, 69; Chem. Abs., vol. 33, 1939, p. 1263.

Several methods for the production of higher aliphatic alcohols are discussed briefly among which is the direct catalytic synthesis from H_2 and CO.

MULTER, H. J. *See* abs. **202.**

MUNDERLOH, H. *See* abs. **1124.**

2341. MUNGEN, R., AND KRATZER, M. B. Partial Combustion of Methane With Oxygen. Ind. Eng. Chem., vol. 43, 1951, pp. 2782–2787.

Partial combustion of CH_4 with O_2 at 300 p. s. i. g. has been studied on a pilot-plant scale. The independent variables given primary attention were the O_2: C feed ratio, the preheat temperatures of the feed streams, and the space velocity. The reaction is assumed to proceed in 2 steps—a primary reaction when CO_2 and H_2O are the main products of the reaction of CH_4 and O_2 followed by reforming of CH_4 with CO_2 and H_2O to CO and H_2. The reforming reaction appears to be the rate-controlling step in the process. Equilibrium was not attained under the conditions employed. The calculated final reaction temperatures ranged from 2,000°–2,500° F. The partial combustion of CH_4 with O_2 under assumed commercial conditions was shown to be a practical method of supplying feed gas to the hydrocarbon synthesis process.

MURAKAMI, T. *See* abs. **1483.**

2342. MURAOUR, —. [Manufacture of Liquid Fuels From Coal.] Recherches et inventions, vol. 6, 1925, pp. 390–392; Chem. Abs., vol. 19, 1925, p. 1487.

Brief outline of the results obtained in Germany by application of the following processes: Low-temperature carbonization; manufacture of Synthol; manufacture of MeOH from water gas; direct hydrogenation of coal.

MURATA, K. *See* abs. **2500a.**

2343. MURATA, Y. Synthesis of Solid Paraffins From Carbon Monoxide and Hydrogen. Chem. Rev. (Japan), vol. 7, 1941, pp. 352–370; Chem. Abs., vol. 35, 1941, p. 8251.

Review with over 70 refs.

———. Gasoline Synthesis From Carbon Monoxide and Hydrogen. LXXII. Composition of Gases and Flow Velocity. *See* abs. **1906.**

———. *See* abs. **1859, 1860, 1861, 1862, 1863, 1864, 1865, 1868, 1872, 1875, 1876, 1877, 1882, 1883, 1889, 1905, 3468.**

MURATA, Y., AND HARA, I. Gasoline Synthesis From Carbon Monoxide and Hydrogen. LXXIV. Influence of Water Vapor on Iron Catalysts. *See* abs. **1906b.**

MURATA, Y., AND MAKINO, S. Benzine Synthesis From Carbon Monoxide and Hydrogen. LII. Influence of the Initial Materials, Carriers, and Filling Agents Upon the Iron Catalyst. *See* abs. **1888.**

MURATA, Y., AND TSUNEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXX. Influence of Catalyst Concentration. *See* abs. **1866.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXIII. Relation of Free Space in the Reaction Tube and the Reaction Rate of the Initial Gas, and Also the Influence of Materials Mixed With the Catalyst. *See* abs. **1869.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXVIII. Relation Between Conditions of Synthesis and the Unsaturation of the Benzine Produced. *See* abs. **1874.**

MURATA, Y., AND YAMADA, T. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. LIV. Influence of Carbon Dioxide in the Initial Gas Upon the Iron Catalyst. *See* abs. **1890.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. LV. Influence of Nitrogen, Methane, Oxygen, and Ammonia in the Initial Gas Upon the Iron Catalyst. *See* abs. **1891.**

MURATA, Y., AND YASUDA, M. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LIX. Activation of Iron-Copper Catalysts by Boron. *See* abs. **1895.**

MURATA, Y., ISHIKAWA, S., AND TSUNEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXI. Influence of Current Velocity. *See* abs. **1867.**

MURATA, Y., MAKINO, S., AND TSUNEOKA, S. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLVIII. Influence of Addition of Copper and Alkali on New Iron Catalysts. *See* abs. **1884.**

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLIX. Influence of Various Metals, Metal Oxides and Precipitants on Iron-Copper-Kieselguhr Catalysts. *See* abs. **1885.**

MURATA, Y., MATSUMOTO, E., AND HOSHINO, S. Gasoline Synthesis From Carbon Monoxide and Hydrogen. LXXIII. Action of Carbon Monoxide on Iron Catalysts. *See* abs. **1906a.**

MURATA, Y., SAWADA, Y., AND TAKEZAKI, Y. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LVIII. Mutual Influence of Boric Acid and Alkali in Promoting Activities of Iron-Copper Catalysts. *See* abs. **1894.**

MURATA, Y., YASHIRO, R., AND TASHIRO, E. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LX. Effect of Copper on Iron Catalysts. *See* abs. **1896.**

MURATA, Y., NAKAGAWA, M., TASHIRO, E., AND UMEMURA, T. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXIV. Methods of Preparing Iron Catalysts. *See* abs. **1900.**

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXV. Reduction by Hydrogen and Heat Treatment of Iron Catalysts. *See* abs. **1901.**

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXVI. Reduction of Iron Catalysts. *See* abs. **1902.**

MURATA, Y., TATSUKI, Y., YAMADA, H., AND SAWADA, Y. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LVII. Effect of Some Added Substances on Iron-Copper Catalysts. *See* abs. **1893.**

MURATA, Y., YOSHIOKA, Y., OJI, G., AND SAITO, S. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXI. Reaction Temperature and Durability of Iron Catalysts. *See* abs. **1897.**

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXII. Durability of Iron Catalyst and the Composition of Gas Used in the Synthesis. *See* abs. **1898.**

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXIII. Iron Cat-

alysts and the Composition of Gas Used in the Synthesis. *See* abs. **1899.**

2344. MURPHREE, E. V. Research and Development in the Oil Industry. Petrol. Refiner, vol. 25, No. 10, 1946, pp. 161–162.

The use of natural gas and coal as raw materials for gasoline in competition with crude oil is discussed and emphasis is put upon the application of the fluidized catalyst to the Fischer-Tropsch process. The importance of using the fluidized catalyst is made evident by the great reduction possible in the number of reactors required for an equivalent production of liquid fuel. For a plant to produce 10,000 bbl./day of synthetic hydrocarbons, using the German plant design, 128 reactors would be required having a cooling surface of 5,800,000 sq. ft. By using a fluidized catalyst, it is possible to reduce the number of reactors to 4 and the total cooling surface to 250,000 sq. ft. This means a great reduction in investment costs as well as a considerable decrease in maintenance and operating costs. This use of catalyst in fluidized form in the Fischer-Tropsch synthesis is one of the outstanding advances in the oil industry. Improvements also have been made in methods of producing synthesis gas. One process being considered commercially for both natural gas and coal involves partial combustion with O_2 to produce the $CO–H_2$ gas mixture required. In the case of coal, steam is used along with the O_2. From an economic standpoint, production of liquid products from natural gas using a modified Fischer-Tropsch operation appears reasonably attractive. The cost of producing gasoline may be slightly lower than the cost of production of gasoline from crude oil. There is, however, a substantially higher investment involved in the production from natural gas. A plant to produce about 9,000 bbl./day of gasoline along with 1,800 bbl. of gasol from coal, using the fluidized technique, is estimated to cost $42,000,000. In addition to the gasol and gasoline produced, about 40,000,000 cut. ft. of gas/day of 1,000 B. t. u. would be produced. Crediting this at $0.25/1,000 cu. ft. and the gasol and certain chemicals at a suitable figure, then the cost of gasoline based on coal at $2.50/ton comes roughly to $0.0725/gal., a cost not greatly exceeding that of a similar grade gasoline from crude oil at present crude prices.

2345. ———. Natural Gas, Coal, Oil Shale as Sources of Liquid Fuels. Oil Gas Jour., vol. 46, No. 49, 1948, pp. 66, 68–70, 95–96.

Statement to the Committee on Interstate and Foreign Commerce on the House of Representatives Bill 5475 dated March 5, 1948. Resources of crude oil and raw materials for synthetic liquid fuels production in the United States are outlined, and brief descriptions are given of processing methods. Preliminary figures are given on possible costs and material requirements for production of synthetic fuels from natural gas, coal, and oil shale in comparison with petroleum.

Approximate investments and steel requirements for maximum gasoline production

Plant location	Gulf coast		Western Pa.	Colo.-Calif.[1]
Product market area	Eastern seaboard			Calif.
Raw material	Crude oil	Natural gas	Coal	Oil shale
Gasoline, % total liquid products.	87	90	89	87
Investment, $ per bbl. per day, gasoline.	6,500	8,200	8,500	8,400
Steel requirement ton per bbl. per day, gasoline	7.8	7.9	5.2	7.4

[1] Shale mined and retorted in Colorado. Raw shale oil transported by pipeline to California for refining.

Approximate cost of gasoline for maximum gasoline production

	Crude oil	Natural gas	Coal	Oil shale
Raw-material charge, assumed or estimated.	$2.78 per bbl.[1]	$0.10 per M cu. ft.[2]	$3.20 per ton.	$1.00 per ton.
Gasoline cost, cents per gal.:				
Raw material	8.8[1]	2.9[2]	3.9	4.2.
Manufacturing less credits	4.3	8.9	12.7	11.8.
Production, transportation.	1.0	1.0		
Total including 15% capital charges.	14.1	12.8	16.6	16.0.
Effect of increase in raw-material charge.	$1.00 per bbl. adds $0.032 per gal.	$0.10 per M cu. ft. adds $0.029 per gal.	$1.00 per ton adds $0.012 per gal.	$1.00 per ton adds $0.042 per gal.
Effect of 10% capital charge on investment in:				
Manufacturing	$0.016 per gal.	$0.037 per gal.		
Manufacturing and mining.			$0.056 per gal.	$0.055 per gal.

[1] Price delivered to refinery.
[2] Price in field after gathering.

Approximate investments and steel requirements for maximum middle-distillate production

Plant location	Gulf coast		Western Pa.	Colo.-Calif.
Product market area	Eastern seaboard			Calif.
Raw material	Crude oil	Natural gas	Coal	Oil shale
Investment $ per bbl. per day, total oil products	4,300	7,400	7,600	6,100
Steel requirements, ton per bbl. per day	5.7	7.1	4.6	5.7

2346. ———. Synthetic Fuels Picture. World Oil, vol. 128, February 1949, pp. 46–50. Petrol. Refiner, vol. 28, No. 3, 1949, pp. 95–96.

Some brief statistics are presented on the deposits and reserves of raw fuels in the United States, and approximate estimates of the investments required per unit of capacity for producing gasoline from crude oil, natural gas, coal (based on Fischer-Tropsch process), and oil shale are made. From a straight economic standpoint, it is believed that the production of liquid fuels from natural gas is competitive today with production of similar products from crude oil. With further improvements in manufacturing technique and possibly in mining or with further increases in the cost of finding and producing crude oil, production of liquid fuels from coal and oil shale may well become quite attractive from a cost standpoint. Substantial progress is bound to result from the large amount of research and development now being carried out.

2347. MURPHREE, E. V., GOHR, E. J., AND KAULAKIS, A. F. Applications of the Fluid Solids Technique to Producing Synthetic Liquid Fuels. Jour. Inst. Petrol., vol. 33, 1947, pp. 608–620. Petrol. Processing, vol. 3, 1948, pp. 355–361; Chem. Abs., vol. 42, 1948, p. 3162.

This paper, which was read before the 11th International Congress of Pure and Applied Chemistry, explains the basic elements of the fluid solids technique and describes 3 special applications of this development in the petroleum field, namely, the catalytic processing of gas oils, the extraction of liquid fuels from shale, and the synthesis of the higher hydrocarbon homologs from natural gas. Simplified diagrams showing the basic features of the above processes are shown. Other

applications are under active development, among which are the coking of residual fuel oils and the carbonization and gasification of coal.

2348. MUSZKAT, K. [Synthesis of Liquid Hydrocarbons From Water Gas.] Przemysl Chem., vol. 18, 1934, pp. 483–489; Chem. Abs., vol. 29, 1935, p. 6022.

Most active catalyst, consisting of 4:1 Ni–SiO_2, loses 80% of its activity after 50 hr., while 9:1 Ni–BaO, Ni–ThO_2, and Ni–Al_2O_3 are virtually as active as at the beginning. Coating of the catalyst surfaces with the hydrocarbons produced does not affect its activity. All catalysts examined are instantly inactivated by O_2 in the reaction mixture.

2349. MYDDLETON, W. W. [Synthetic Internal-Combustion Motor Fuels.] Chim. et ind., vol. 37, 1937, pp. 863–864; Chem. Abs., vol. 31, 1937, p. 5975.

Brief discussion bringing out the superiority of the motor fuel, from the standpoint of its performance in the motor, produced by the British process (using water gas directly) over that produced by the Fischer process (using a gas mixture adjusted to a ratio of $2H_2:1$ CO). The latter process could be improved by using Ni in place of Co, water gas in place of gases rich in H_2, and by operating in several steps.

2350. ———. Production of Hydrocarbon Oils From Industrial Gases. Colliery Guard., vol. 157, 1938, pp. 286–290; Jour. Inst. Fuel, vol. 11, 1938, pp. 477–492; Oel u. Kohle, vol. 14, 1938, pp. 723–726, 761–763; Chem. Age, vol. 38, 1938, pp. 404–407; Chem. Abs., vol. 32, 1938, p. 8105.

Process described is owned by Synthetic Oils Limited and is similar to the Fischer-Tropsch process. It is just entering upon a semiscale operation, a plant being under construction that will treat about 200,000 cu. ft. of gas per day, with an estimated yield of 180 gal. of oil. The process differs somewhat from the Fischer-Tropsch process. In the first place, by limiting the hydrogenation of the primary oil of synthesis, olefins rather than saturated hydrocarbons are produced, thus increasing the antiknock value of the motor fuel and producing more oils that can be converted into lubricants. This is partly accomplished by reducing the initial partial pressure of the H_2 in the reaction mixture, and partly by using a Co catalyst of less activity than that usually employed in the Fischer-Tropsch process. A gasoline has been produced with an octane no. of 68 and containing 70% olefins. It has also been found unnecessary to maintain in the synthesis gas the ratio $CO:H_2=1:2$; the conversion works satisfactorily at ratios between 1:1 and 1:1.5 making possible the direct use of blue water gas or Pintsch gas with a resultant reduction in cost. Furthermore, it is claimed that the catalyst used is stable to S, and that such slight poisoning as may occur has a beneficial effect in reducing the activity of the catalyst and promoting olefin formation. Even with 25 grains of S per 100 cu. ft., the catalyst has functioned satisfactorily.

2351. ———. Application of Free-Energy Equations to the Study of the Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. Jour. Inst. Petrol., vol. 30, 1944, pp. 211–224, 248.

Equations have been derived relating free energy of reaction to temperature in the synthesis of a series of gaseous hydrocarbons from CO and H_2. In building up these equations, molecular heat-temperature curves were drawn for each reactant and product and molecular heat-temperature equations were fitted over the range 25°–250° C., existing equations being generally unsatisfactory for the temperature range covering synthesis. Some use has been made of molecular heat and entropy values calculated from statistical and spectroscopic data. The suppression of reactions in which CO_2 is formed, in spite of free-energy changes favorable to them, is attributed to special conditions prevailing at the catalyst surface. The appearance of traces of ethylene among the products of synthesis instead of appreciable quantities predicted by the free-energy relationships is accounted for by the incorporation of ethylene actually formed into the building up of hydrocarbon chains. The possibility of increasing the yields of isobutane and isobutene is considered worthy of attention. The formation of aromatic hydrocarbons requires a special orientation of reactants on the surface of the catalyst, and the probability of the necessary conditions occurring is slight.

———. *See* abs. **9.**

MYDDLETON, W. W., AND WALKER, J. Production of Hydrocarbon Oils From Industrial Gases. II. *See* abs. **10.**

N

2352. NAESER, G. [Heat of Formation of the Iron Carbide Fe_3C.] Mitt. Kaiser-Wilhelm-Inst. Eisenforsch. Düsseldorf, vol. 16, No. 1, 1934, pp. 1–7; Chem. Abs., vol. 28, 1934, p. 2985.

Review of measurements of heat of formation of Fe_3C shows very variable values between positive and negative maximum. It was determined again from amorphous C and α–Fe at room temperature by converting the carbide (under separation of C) and the pure Fe into the iodide and chloride, respectively. From both methods, the heat of formation was found to be $+8\pm0.25$ kcal. per mol., which corresponds to 44.6 ± 1.4 cal. per gm. cementite, 47.8 ± 1.5 cal. per gm. Fe, 668 ± 20 cal. per gm. C. The heat of combustion of finely distributed amorphous C on disintegration of carbide was found to be 107.9 kcal. per mol. The heat of reaction in the formation of FeS from α–Fe and rhombic S was 23.89 ± 1.16 kcal. per mol. The final result is that the heat of formation of Fe_3C lies in the range of +8 to −4 kcal. per mol. according to the state of C and decreases with increasing graphitization. 46 refs.

2353. ———. [Specific Heat of the Iron Carbide Fe_3C.] Mitt. Kaiser-Wilhelm-Inst. Eisenforsch. Düsseldorf, vol. 16, 1934, pp. 207–210; Chem. Abs., vol. 29, 1935, p. 2434.

Heat contents of pure crystalline Fe_3C were measured between −190° and +770°, and average and true specific heats were calculated; the values are tabulated. The rule of additivity of atomic heats does not hold good for cementite. Heat of reaction of the magnetic transformation is about 1.5 cal. per gm. 18 rfs.

2354. ———. [Thermal Disintegration of Iron Carbide Fe_3C.] Mitt. Kaiser-Wilhelm-Inst. Eisenforsch. Düsseldorf, vol. 16, 1934, pp. 211–212; Chem. Abs., vol. 29, 1935, p. 2434.

Thermal disintegration of Fe_3C was determined by observing the behavior of cementite in a magnetic field as a function of temperature. Distintegration begins at 1,050°–1,060°.

———. *See* abs. **3675.**

NAGAI, H. *See* abs. **2504, 2508.**

NAGASAWA, K. *See* abs. **2211.**

NAGEL, R. H. *See* abs. **1469.**

NÄGELI, A. *See* abs. **1937.**

NAICKER, K. *See* abs. **3141.**

NAIDITCH, I. M. *See* abs. **1275.**

NAKAGAWA, M. *See* abs. **1900, 1901, 1902.**

2355. NAKAI, A. Studies on the Fischer-Tropsch Synthesis. I. Activation of Cobalt Catalyst by Hydrogenation. U. S. Naval Tech. Mission to Japan, X–38(N)–7, Encl. (B) 19, 1946, pp. 171–178; PB 58,701.

Experiments were made to determine the best conditions for activation of the standard Fischer-Tropsch Co catalyst (Co : MgO : ThO_2 : kieselguhr=100 : 8 : 3 : 200). The apparatus, the procedure, and the catalyst preparation by precipitation are described, and the experimental results are tabulated. The results disclose that activation by H_2 gas is highly satisfactory for this catalyst under conditions of 375°–380°, at an optimum space velocity of 2,500–3,750 and a reduction time of 1½–2 hr. A special apparatus and a method are described for determining the optimum degree of reduction. It is shown from the above conditions that for the strongest catalytic activity the reduced Co catalyst contains not only about 50% of metallic Co but also lower oxides of Co. It is also found that when the above catalyst is used for the synthesis of oil at normal pressure and 175°–390°, a gas contraction of 85% and a yield of more than 160 cc. of oil (specific gravity about 0.75) for each $m.^3$ of water gas (H_2 : CO= 2 : 1) are obtained.

2356. ———. Studies on the Fischer-Tropsch Synthesis. II. Studies on Iron Catalyst. U. S. Naval Tech. Mission to Japan, X–38 (N)–7, Encl. (B) 19, 1946, pp. 179–181; PB 58,701.

Experiments were made to investigate the effectiveness of iron catalysts for synthesis of oil from water gas at normal pressure. Reference is made to previous work of Tsuneoka on iron catalysts. The influence of metals or their oxides on the catalytic activity of the catalysts Fe : Cu : kieselguhr : Na_2CO_3=100 : 20 : 200 : 4 and Fe : Cu : ThO_2 : kieselguhr : Na_2CO_3=100 : 20 : 4 : 200 : 4 was investigated, and various compounds were tested as promoters. MgO was found to be most effective. The most satisfactory catalyst at lower reaction temperatures of 235°–240° was Fe : Cu : ThO_2 : MgO : kieselguhr : Na_2CO_3=100 : 20 : 4 : 20 : 175–200 : 4. To activate the catalyst, it was best to circulate water gas rapidly at the reaction temperature. The yield of synthetic oil with this iron catalyst was 61.6 gm. per $m.^3$ of water gas (H_2 : CO=6 : 4) at 235°, atmospheric pressure, and gas space velocity of 41 per hr.

2357. ———. Studies on the Fischer-Tropsch Synthesis. III. Studies on Liquid-Phase Synthesis With Iron Catalyst. U. S. Naval Tech. Mission to Japan X–38(*n*)–7, Encl. (B) 19, 1946, pp. 183–186; PB 58,701.

Investigation of a method for removing reaction heat from the synthesis apparatus by circulating the synthetic oil through the reaction system. Experiments were made to determine the activity of Fe catalysts in the liquid-phase synthesis. Various Fe catalysts were prepared by precipitation from nitrate mixtures with an excess of NaOH. Fe–Cu catalysts, containing small amounts of alkali, had a strong synthesis activity at temperatures under 250°. A similar catalyst, but containing no alkali, showed a weaker activity for oil synthesis but strong hydrogenating power at 250°–270°. The best catalyst for the liquid phase reaction appeared to be Fe : Cu : CaO=100 : 25 : 100–150. The catalysts Fe : CaO=100 : 100–150 and Fe : Cu : CaO=100 : 25 : 100–150 could be made into very hard tablets suitable for liquid-phase synthesis at 260°–270° and 10 kg. per $cm.^2$ pressure. The catalysts Fe : CaO=100 : 10 and Fe : Cu : CaO=100 : 25 : 10 had better activity than the above, but binders were required to make satisfactory tablets.

NAKBAYASHI, T. *See* abs. **1911, 1912.**

2358. NAMYSLOWSKI, S. [Problem of Synthetic Fatty Acids.] Przemysl Rolny i Spozywczy., vol. 4, 1950, pp. 173–177; Chem. Abs., vol. 45, 1951, p. 4062.

Review of the methods of oxidation of paraffins. It is estimated that 1,500,000 tons of the paraffin fraction from Fischer-Tropsch synthesis will be needed for covering the Polish demand for technical fats.

2359. NAPHTHALI, M. [Methanol, Coal Liquefaction, Combined Hydrogenating and Cracking Processes.] Gas- u. Wasserfach, vol. 72, 1929, pp. 1178–1184; Chem. Abs., vol. 24, 1930, p. 942.

Review of patents and literature on the Bergius and I. G. Farbenindustrie processes of coal liquefaction, MeOH synthesis, and hydrogenation of hydrocarbons. The construction and heating of high-pressure reaction vessels are reviewed.

2360. ———. Fischer-Tropsch Process for Production of Synthetic Gasoline. Refiner and Nat. Gasoline Mfr., vol. 17, 1938, pp. 47–51; Chem. Abs., vol. 32, 1938, p. 4319.

Description of process, effect of varying operating conditions, and properties of products.

NARRACOTT, E. S. *See* abs. **259.**

2361. NARTOWSKI, B. [Synthetic Fuels in Poland.] Nafta, vol. 2, 1946, pp. 344–345; Chem. Abs., vol. 43, 1949, p. 3591.

Discusses prospects for a synthetic motor-fuel industry in Poland based on the Fischer-Tropsch process.

2362. NASH, A. W. Recent Developments in the Formation of Synthetic Fuel From Carbon Monoxide and Hydrogen. Chem. and Ind., vol. 45, 1926, pp. 876–878; Chem. Abs., vol. 21, 1927, p. 638.

Review and brief discussion of theory and practical application of Fischer-Tropsch process.

2363. ———. Reports on the Progress of Naphthology During 1926. Synthetic Fuels. Jour. Inst. Petrol. Technol., vol. 13, 1927, pp. 597–601; Chem. Abs., vol. 21, 1927, p. 3734.

Brief review of developments.

2364. ———. Possible Auxiliary Sources of Liquid Fuels. Jour. Inst. Petrol. Technol., vol. 13, 1929, pp. 681–712; Chem. Trade Jour., vol. 81, 1927, pp. 205–207; Chem. Age., vol. 18, 1927, pp. 338–339; Chem. Abs., vol. 22, 1928, p. 152.

Discusses power alcohol, low-temperature carbonization of coal, the Bergius process, and the conversion of water gas into liquid fuels.

2365. ———. Synthetic Fuels and Lubricating Oils. Trans. World Power Conf., 1st Conf., Tokyo, 1929, pp. 466–481, 573–574; Chem. Abs., vol. 26, 1932, p. 2298.

Present known methods for production of synthetic fuels are described, and the oils are critically compared with their competitive petroleum products.

2366. ———. Reports on the Progress of Naphthology. Synthetic Fuels. Jour. Inst. Petrol. Technol., vol. 16, 1930, pp. 313–324; British Chem. Abs., 1930, B, p. 699.

Progress of research during the last 2 yr. concerning the Bergius process and the production of liquid hydrocarbons from gases.

2367. ———. Synthetic Fuels and Lubricating Oils. Jour. Inst. Fuel, vol. 3, 1930, pp. 347–353; British Chem. Abs., 1930, B, p. 849.

Paper was presented at the World Power Conference, Tokyo, in 1929. The sources and methods available for the production of synthetic fuels and lubricating oils are discussed. It is pointed out that the reduction of CO by H_2 at atmospheric and high pressures with or without catalyst is a possible source of fuel.

———. *See* abs. **817, 818, 843, 3258, 3259, 3260.**

2368. NASH, A. W., AND BOWEN, A. R. Reports on the Progress of Naphthology During 1927. Synthetic Fuels. Jour. Inst. Petrol. Technol., vol. 14, 1928, pp. 643–650; Chem. Abs., vol. 23, 1929, p. 266.

Synthetic fuels from coal (berginization), CO and CH_4, or natural gas are reviewed briefly, indicating the hydrogenation of coal as most promising.

2369. NASH, A. W., AND STANLEY, H. M. Possible Chemical Utilization of Methane, With Special Reference to Natural Gas. Fuel, vol. 7, 1928, pp. 397–401; Chem. Abs., vol. 22, 1928, p. 4772.

In considering the various possibilities of its chemical utilization, a survey of the present knowledge of the properties of CH_4 is made. Its chlorination, oxidation, thermal decomposition, reaction with steam, and conversion into higher hydrocarbons are discussed. It is believed that the solution of this problem lies within the range of high-pressure and high-temperature reactions, which are now imperfectly understood.

2370. NATANSON, G. L. [Genesis of Iron Catalysts for the Synthesis of Ammonia.] Jour. Chem. Ind. (U. S. S. R.), vol. 13, 1936, pp. 401–405; Chem. Abs., vol. 30, 1936, p. 4630.

Most important point in the preparation of NH_3 catalysts is the formation of a solid solution of the promoter in the catalyst, since in this case smaller crystals are formed and a more-porous product is obtained.

2371. NATHAN, F. L. Fuel for Internal-Combustion Engines. Jour. Soc. Chem. Ind., vol. 46, 1927, pp. 211–220T; Chem. Abs., vol. 21, 1927, p. 2974.

Present and possible future sources, production, manufacture, utilization, and comparative costs of petroleum, gasoline, benzene, tetralin, EtOH, Natalite, liquid fuels from coals, MeOH, synthol, coal gas, and producer gas for use as motor fuels are reviewed and discussed from both national and world production and consumption standpoints. Apparently gasoline will continue for a long time to be the principal liquid fuel, especially in view of the enormous quantities of known oil shales existent. Only limited quantities of benzene and naphthalene, for tetralin, are ever likely to be available. Alcohol from whatever sources cannot compete as a fuel with gasoline at anything like present prices. Low-temperature carbonization and hydrogenation of coal and the production of synthetic fuels from CO and H_2 may soon become important means of liquid-fuel supply. Suction gas producers, using anthracite, coke, or charcoal, should be developed, especially for use with motor lorries.

2372. NATIONAL PETROLEUM NEWS. Diesel Fuel From Fischer Process. Vol. 31, 1939, No. 28, R, p. 296.

Synthetic fuel for high-speed diesel engines is now being produced in Germany on a commercial scale, according to a recent report to the U. S. Department of Commerce from the American Consulate General, Frankfort-am-Main. The process uses as raw material a mixture of tar oils produced in the coking of bituminous coal and so-called "Kogasin II," a material produced from gasified coke or CO and H_2. The Rheinpreussen Coal Mining Co. established the 1st large-scale plant for producing this fuel. The new fuel is handicapped by high cost. For giving market protection to the new synthetic product, the German Government again raised the import duty upon foreign diesel oil by 20% to a total of 12 from RM 9.6 per 100 kg., involving an increase in market price of 10–12%. Imports provide about 90% of Germany's requirements for diesel oil. These have increased considerably in recent years, being nearly 4 times as great in 1938 as in 1932. Imports in 1938 were close to 10,800,000 bbl.

2373. ———. Diesel Fuels From the Synthine Process. Tech. Sec., vol. 36, No. 36, Sept. 6, 1944, p. R585; Fuel Abs., May 1945, no. 2436.

Synthine (Fischer-Tropsch) process is a source of diesel fuels, which surpass any made from crude petroleum. Fischer-Tropsch oils are highly paraffinic, and those boiling at 200°–300° have a cetane number of 100, and, when diluted with tar oils or heavy petroleum oils, give a satisfactory Diesel fuel. A diesel-fuel fraction of about 85 cetane no. can be prepared by cracking Fischer-Tropsch wax. Straight Synthine diesel fuels have a drawback in their high solidification point, about 2° C. The cost of Synthine diesel fuels is higher than that for petroleum-derived diesel fuels, but extensive research has been conducted for some years by several companies, and lower costs should result. It is reported that the Texas Oil Co. is to construct a pilot plant for the Synthine process at its Los Angeles refinery. The process offers a new way of obtaining high-ignition-quality fuels without upsetting the balance of refinery-gasoline operation.

2374. ———. Plan to Build Synthetic-Oil Plant at Hugoton. Sept. 20, 1944.

Plans to build a Fischer-Tropsch plant to synthesize gasoline from natural gas in the Hugoton field, Oklahoma-Kansas, have been announced by Fred C. Koch, consulting engineer and partner in Winkler-Koch Engineering Co.

2375. ———. Petroleum Substitutes. Vol. 37, No. 36, 1945, p. R744; Business Week, July 21, 1945, p. 74.

Hydrocarbon Research, Inc., announces that it will construct a commercial Synthine (Fischer-Tropsch) plant in East Texas. The plant will have a capacity of 7,000 bbl. per day of finished products, 80–85% of which will be high-octane motor gasoline. Production will be at the rate of 1 bbl. of oil per 1,000 cu. ft. of gas. The process, developed in the past 20 mo., has been sponsored by 3 oil producers—the Magnolia Petroleum Co., the LaGloria Corp., and the J. S. Abercrombie Co. The process is based on German laboratory research applied to American oil-industry techniques concerning plant design and construction and the use of cheaper catalysts. The plant, it is said, will be constructed at a fraction of the cost of similar German plants and will produce a higher quality gasoline.

2376. ———. Bureau of Mines Takes Too Much Credit for Development of Synthetic Fuels. Vol. 38, No. 26, 1946, pp. 10–11.

Editorial polemic.

2377. ———. Domestic Use of Oxo Process Revealed. Vol. 38, 1946, p. R567.

Brief description of the Oxo process, and a statement of its possible adaptation by Standard Oil of Indiana for making higher-boiling alcohols from the olefins obtained by cracking petroleum-derived paraffin wax.

2378. ———. Fischer-Tropsch Process Patents Available for Licensing. Vol. 38, No. 8, 1946, p. 44.

Office of Alien Property Custodian has made available for licensing a group of patents relating to synthetic gasoline production by the Fischer-Tropsch process. The licenses are available on a royalty-free, nonexclusive basis for a $15.00 administrative fee. Full information and list of patents may be obtained from Patent Use and Development Section, Office of Alien Property Custodian, Washington 25, D. C.

2379. ———. Synthetic-Gas-Plant Construction Loan Authorized. Vol. 38, No. 19, 1946, p. 51.

Reconstruction Finance Corporation has authorized a loan of $9,000,000 to Carthage Hydrocol, Inc., to complete a plant at Brownsville, Tex., for synthesizing gasoline from natural gas. Total cost of the plant is about $20,000,000. Construction of the plant will be directed by Hydrocarbon Research, Inc., which controls patents under the Hydrocol process. The process is a modification of the Fischer-Tropsch process and has been improved through the development of low-cost O_2 to produce a low-cost, high-octane gasoline that will be competitive with that produced from petroleum. Operating under royalty-free patents, it is estimated that a 78–80 octane gasoline will be produced at slightly more than $0.04 per gal.

2380. ———. Synthetic Gasoline Plant Plans Studied by Stanolind Oil Co. Vol. 38, No. 28, 1946, p. 48.

Tentative plans are being studied by Stanolind Oil & Gas Co. to erect a synthetic gasoline plant, based on the Fischer-Tropsch synthesis of liquid hydrocarbons from CH_4 on the Kansas side of the Hugoton field. Plant will be designed to produce aproximately 6,000 bbl. gasoline per day and 1,200–1,500 bbl. diesel fuel from about 60,000,000 cu. ft. of natural gas. Actual construction date is uncertain. Stanolind has been conducting research and pilot-plant investigation for several years at its Tulsa laboratory. The process is not yet fully developed, and engineering designs are incomplete.

2381. ———. Synthine Developments Continue at Rapid Pace. Vol. 38, 1946, pp. R567–568.

Review of recent developments as reported in the current news.

2382. ———. Stanolind to Build 2 Plants to Make Chemicals From Gas. Vol. 39, No. 34, 1947, p. 16; Chem. Eng. News, vol. 25, 1947, p. 2436.

Stanolind Oil & Gas Co. will build chemical recovery and separation plants adjacent to each of the synthetic gasoline plants now under construction—Carthage Hydrocol near Brownsville, Tex., and the Stanolind plant, Hugoton, Kans.—to refine byproduct chemicals from them. A contract has already been made with United States Industrial Chemicals, Inc., for the sale of water-soluble oxygenated hydrocarbon chemicals to be produced. Furthermore, the latter will build its own plants at the 2 locations to manufacture an additional line of chemicals. Each of the synthetic gasoline plants will produce around 100,000,000 lb. per yr. of water-soluble oxygenated hydrocarbons. These chemicals consist mainly of straight-chain alcohols, aldehydes, acids, and ketones containing 2–4 C atoms per mol. Stanolind has not yet completed its plans for refining and marketing the higher molecular weight alcohols, acids, aldehydes, and ketones containing 5–12 or more C atoms. The chemical recovery and separation plants are expected to be completed in about 2 yr. The cost of the plant is not given. It is estimated that the chemicals from the 2 synthetic gasoline plants may exceed a total of 300,000,000 lb. per yr. Commodities to be produced are listed.

2383. ———. Synthetics Subsidy? Vol. 39, No. 31, 1947, p. 5.

Editorial.—The possibility is being discussed in government research circles that, once technology of synthetic liquid-fuels research is developed to the point where commercial production can be planned, the Federal Government may consider granting subsidies for construction and operation of privately-owned plants. This would be following the pattern of other countries—England, Sweden, France, Australia—which made Government grants to private plants for production of liquid fuels from coal and oil shale. Subsidies, it is said, will be needed because oil from coal and shale probably will not be competitive with conventional liquid fuels for some time. However, there is a possibility that the Government itself may build several commercial-type plants—each with production capacity of 5,000–10,000 bbl. per day—to test various coal hydrogenation, Fischer-Tropsch, and oil-shale processes.

2384. ———. Texaco Offers to License Hydrocol Process. Vol. 40, No. 6, 1948, p. 49.

Texas Co., through its affiliate Texas Development Corp., will license the Hydrocol process for manufacture of synthetic liquid hydrocarbons to any interested company. The opinion is expressed that 50 plants for gasoline synthesis from natural gas, with combined output of 350,000 bbl. per day might be built within 10 yr., barring non-economic acceleration of program to meet national defense requirements. The limiting factor is the number of gas pools large enough to support an economical plant. Without infringing on gas supplies earmarked for other uses, 50 plants of 7,000 bbl. per day capacity can be built. Liquid fuel from natural gas probably will meet about 5% of the total demand for all oils by 1960. A 5,000-gal. per day Hydrocol pilot plant has been completed at Montebello, Calif., and work is being done on gasification of coal and heavy oil, but not on oil from shale. The company spent approximately $1,000,000 in 1947 on synthetics research and will do the same in 1948.

2385. NATTA, G. [Relation of the Activity of Proposed Catalysts for the Synthesis of Methyl Alcohol and Their Chemical and Crystalline Structure.] Giorn. chim. ind. applicata, vol. 12, 1930, pp. 13–23; British Chem. Abs., 1930, A, p. 552; Chem. Abs., vol. 24, 1930, p. 2717.

Catalysts available are: (1) Cu salts, which are easily poisoned by S compounds; and (2) Zn salts, which, alone, soon lose their activity. However, certain oxides, notably Al_2O_3, and especially Cr_2O_3, by acting as protecting colloids, prevent the crystallization of the ZnO with its consequent loss of activity. Above 500°, these oxides begin to form spinels, and therefore lose some of their protective action. Some oxides form solid solutions with ZnO by entering its space lattice. The oxides of bivalent metals whose ionic diameter is 0.6–0.9 Å. U. Mg, Ni^{II}, Cu^{II}, Co^{II}, Fe^{II}, and Mn^{II} are included. Cu and Ni are reduced to metal, the former helping, the latter hindering the catalysis. Of the oxides entering the space lattice, those causing most deformation, that is, whose diameters are further from that of ZnO, are most effective; FeO is most effective. The alkali and alkaline earth oxides, because of their basicity, promote not only the formation of MeOH, but of other organic products as well, especially higher alcohols.

2386. NATTA, G., AND CASAZZA, E. [Activity of Catalysts Proposed for the Synthesis of Methanol and Their Chemical and Crystalline Structure. II.] Giorn. chim. ind. applicata., vol. 13, 1931, pp. 205–212; Chem. Abs., vol. 26, 1932, p. 80.

Coefficients of absorption of CO_2, CO, and H_2 by substances, which have been used as catalysts in the production of MeOH have been studied. Pure ZnO (1), ZnO derived from smithsonites from various sources (2), reduced $ZnCrO_4$ (3), Cr_2O_3 (4), 50 ZnO–1Co (5), 5ZnO–1Cu (6), 4 ZnO–1Al_2O_3 (7), and 5ZnO·1MgO (8) were all studied. Those catalysts that absorb high amounts of H_2 (4, 5, 6) are not efficient as they catalyze side reactions involving hydrogenation, while those showing high CO_2 and CO absorption with low H_2 absorption, that is, (2, 7), are most effective. The absorption increases with increasing pressure up to 35–40 atm. Above this the absorption curve becomes virtually horizontal, increasing pressure having practically no effect.

2387. NATTA, G. [Synthesis of Methanol and Higher Alcohols From Water Gas.] Österr. Chem.-Ztg., vol. 1937, pp. 162–170; British Chem. Abs., 1937, B, p. 756; Chem. Abs., vol. 31, 1937, p. 5978.

Curves showing the equilibrium constant and velocity constant for the synthesis and the decomposition of MeOH are given. The synthesis is a trimolecular reaction. The best catalyst is ZnO obtained by heating natural smithsonite at 350°. The calcined catalyst has a porosity of 47%, high mechanical strength, and will absorb 10,000 vol. of CO_2 at low pressures. With calcined smithsonite impregnated with K acetate as a catalyst and a gas containing an excess of H_2, CH_3OH, and higher alcohols are obtained. If the gas contains an excess of CO, the alcohols contain a high % of ketones, aldehydes, and acids. Reactions are given and experimentally verified in which the alkali in the contact mass acts directly in the formation of the higher alcohols. The higher alcohols contain high % of isobutanol and *n*-PrOH and low % of EtOH iso-PrOH and

n-BuOH. MeOH with ⅓ of its volume of higher alcohols is miscible in all proportions with benzine. MeOH requires 6.33 kg. air per kg., while benzine required 14.8 kg. air per kg. 10% of MeOH instead of 26% EtOH or 60% benzene is required to raise the octane value of a benzine from 66 to 80.

2388. ———. [New Large-Scale Organic Syntheses.] Chimica e industria, vol. 20, 1938, pp. 186–198; British Chem. Abs., 1938, B, p. 762.

Lecture in which industrial processes involving the syntheses of organic substances from C and from H_2 and O_2 (either in the elementary state or combined as H_2O) are summarized, for example, synthesis of water gas, MeOH, hydrocarbons, higher alcohols, CH_2O, explosives, and rubber.

2389. ———. [Preparation of Mono- and Polyhydroxy Alcohols.] Chimica e industria, vol. 24, 1942, pp. 389–393; Chem. Zentralb., 1943, I, p. 2242; Chem. Abs., vol. 38, 1944, p. 4252.

Some new methods of large-scale technical synthesis of mono- and poly-OH alcohols from water gas (MeOH synthesis) and from CO_2 and H_2 are described. In the latter case, the CO_2 is a byproduct in the production of $Ca(NO_3)_2$ from $CaCO_3$; the H_2 is produced by electrolysis. The yield of MeOH synthesized by this process reaches 92%, as compared with 86–89% by the usual water-gas process.

2390. NATTA, G., AND BOCCAREDDA, M. [Motor Fuel of High Octane Number. Synthesis of Isooctane From Water Gas.] Riv. ital. petrolio, vol. 6, No. 65, 1938, pp. 14–19; World Petrol., vol. 10, 1939, p. 69; British Chem. Abs., 1939, B, p. 571.

Isobutylene, obtained by dehydrogenation of BuOH produced in the synthesis of MeOH from water gas, mixed with a small amount of gaseous HCl, is heated to 100°–250° and passed over solid Al_2O_3 previously activated by heating to 400°–450°. The isooctene produced is then hydrogenated to isooctane.

2391. NATTA, G., AND PASTONESI, G. [Kinetics of the Synthesis of Methanol.] Chimica e industria, vol. 19, 1937, pp. 313–318; Chem. Zentralb., 1937, II, p. 3297; Chem. Abs., vol. 31, 1937, p. 8337.

Equilibrium data for the synthesis of MeOH are best expressed assuming that the change occurs in 2 stages $CO+H_2=CH_2O$ and $CH_2O+H_2=MeOH$. The first equation is slow, while the second is almost instantaneous, so that analysis shows only a minimum of CH_2O present at any time. The equation of the reaction curve is expressed as

$$d(K',t)/dx=1/\{2(a-x)^2-[Kx/2(a-x)]\},$$

where a=partial pressure of CO, x=amount of CO converted in time t, and thus equals the amount of CH_2O formed. The heat of reaction is calculated as 21,000 cal.

2392. ———. [Kinetic Method for Determining the Equilibrium Constants in the Methanol Synthesis.] Chimica e industria, vol. 20, 1938, p. 587–591; Chem. Abs., vol. 33, 1939, p. 2023.

With the equation of Newton and Dodge (abs. **2457**) for calculating the equilibrium constant of a reaction as a basis, a method was devised for calculating the constant for the synthesis of MeOH using experimental data for the partial pressures involved. Calculation is made assuming the synthesis to be a trimolecular reaction $MeOH=CO+2H_2$; and also assuming bimolecular reactions in 2 stages with the intermediate formation of CH_2O. The latter assumption gives data that approximate experimental determination of the equilibrium constant more closely.

2393. NATTA, G., AND PINO, P. [Some New Applications of the Oxo Synthesis.] Chimica e industria, vol. 31, 1949, pp. 109–111; British Abs., 1949, B, II, p. 943.

Oxo synthesis is a method of wide applicability for producing aldehydes from CO, H_2, and compounds containing an olefinic double bond in presence of metallic Co or CoI_2. Cyclic mono-olefins can be used as starting materials, and terpenes interact even more readily than do olefins. Esters may also be obtained. With metallic Co as catalyst, a long induction period occurs varying with the method of preparation and surface changes.

2394. NATTA, G., AND PIONTELLI, R. [Utilization of Methane in the Production of Hydrogen.] Chimica e industria, vol. 19, 1937, pp. 177–182; British Chem. Abs., 1937, B, p. 777; Chem. Abs., vol. 31, 1937, p. 8128.

Incomplete combustion of CH_4 in the presence of CO_2 and H_2O has been investigated in the temperature range 800°–1,400°. Complete equilibrium diagrams of the 2 systems CH_4–H_2O–O_2 and CH_4–CO_2–O_2, and the best conditions for producing H_2 and CO in the ratio of 2:1, are determined.

2395. NATTA, G., AND RIGAMONTI, R. [Synthesis of Aliphatic Alcohols by the Catalytic Reduction of Carbon Monoxide.] Giorn. chim. ind. applicata, vol. 14, 1932, pp. 217–225; Chem. Zentralb., 1932, II, p. 2264; Chem. Abs., vol. 26, 1932, p. 5062.

CO obtained from water gas was reduced with H_2 at 350–400 atm. in the presence of calcined ZnO, smithsonite, and KOAc as catalyst. The crude product contained only 0.9–1.1% aldehydes, 0.02–0.5% hydrocarbons, 1.4–2.4% free acids, and 2.5–2.6% ethers. Increasing the amount of K_2O in the catalyst increased the proportion of higher alcohols. The following alcohols were identified: Iso-Bu, 51.3–46.6; Pr, 13.1–11.6; β-methylbutyl, 4.9–4.8; Et, 3.3–4.2; iso-Pr, 2.6–3.7; β-methylpentanol, 2.5; Bu, 1,8–2.0; Am, 0.4; β-methylhexanol, 1.6%. Traces of the following also were identified: γ-methylpentanol, isoamyl alcohol, 2,3-dimethylbutanol, ethylisopropylcarbinol, diisopropylcarbinol, propylisopropylcarbinol, and tertiary Bu and Am alcohols. Of the total alcohols, 94.7–98.4% are primary, and those with an odd number of C atoms predominate in the straight-chain group, while the β–Me predominate in the side-chain group.

2396. ———. [Manufacture of Hydrogen by Conversion of Carbon Monoxide Under Pressure.] Chimica e industria, vol. 18, 1936, pp. 623–630; Chem. Abs., vol. 31, 1937, p. 2365.

Catalytic action of MgO and ZnO on the reaction $CO+H_2O\rightarrow CO_2+H_2$ has been determined. ZnO is much more effective than Mg as a catalyst. Addition of K_2CO_3 increases the % conversion at 363° from a value of 58.8% with ZnO to 93% with K_2CO_3, while 5% Na_2CO_3 raises the % conversion only to 78%.

2397. ———. [Gasification of Italian Fuels by Means of Oxygen.] Atti X° cong. intern. chim., vol. 4, 1939, pp. 312–319; Chem. Abs., vol. 34, 1940, p 2568.

Results of continuous retorting on a semi-industrial scale of coal, lignite, etc., containing volatile matter by means of mixtures of O_2 and steam, according to a process first applied to coal in volatile substances, are summarized. The process in 1 case led to the production of a very pure water gas most suitable for chemical syntheses (MeOH, higher alcohols, Fischer gasoline, etc.), for conversion and for the production of H_2, and synthetic NH_3.

2398. NATTA, G., AND STRADA, M. [Synthesis of Alcohols Higher Than Methanol From Water Gas.] Giorn. chim. ind. applicata, vol. 12, 1930, pp. 169–174; Chem. Zentralb., 1930, II, p. 659; Chem. Abs, vol. 24, 1930, p 4505.

In the presence of ZnO, active form made by calcining certain smithsonites at low temperature, together with alkali (K, Rb, Ce) carbonate, hydroxide, acetate or propionate, water gas, when heated to about 400° under

high pressures, gives a mixture of higher alcohols free of CH_4 and other hydrocarbons. Metals of groups 4–8, as well as their oxides, should be excluded so as to avoid formation of undesirable byproducts, particularly hydrocarbons. The formation of higher alcohols occurs in stages, MeOH being first formed, then MeOK, or Rb, Ce, then addition of CO_2 to form the higher homolog. These intermediate products were identified during the course of the reaction, and these can be added as additional catalysts, which retain their activity over long periods of time.

2399. ———. [Synthesis of Aliphatic Alcohols From Mixtures of Carbon Monoxide and Hydrogen.] Giorn. chim. ind. applicata, vol. 13, 1931, pp. 317–325; Chem. Zentralb., 1931, II, p. 1958; Chem. Abs., vol. 26, 1932, p. 693.

Experiments carried out on a semi-industrial scale show that in the presence of catalysts consisting of compounds of Zn and the alkali metals CO and H_2 will react under pressure to form aliphatic alcohols. By excluding any metals of groups 4–8, many harmful secondary reactions, as formation of CH_4 are reduced greatly. The hypothesis that MeOH is first formed and reacts with CO to form higher homologs is strengthened by the observation that in the presence of HCO_2K a higher yield of MeOH is obtained, while CH_3CO_2K and $EtCO_2K$ increase the yields of EtOH and PrOH, respectively.

2400. ———. [Low-Temperature Production of Coal Gas by Using Oxygen.] Giorn. chim. ind. applicata, vol. 14, 1932, pp. 76–86; British Chem. Abs., 1932, B. p. 407; Chem. Abs., vol. 26, 1932, p. 3359.

Coals with low volatile contents may be heated at 700°–800° by using O_2; the gases produced are rich in H_2 and CO and very low in hydrocarbons and inert gases. Gases suitable for the synthesis of MeOH, that is, having a ratio $H_2 : CO$ of 1.5 : 4, may be obtained by burning 0.28 kg. C in 0.18 $m.^3$ of O_2 at about 750°.

2401. NATTA, G., PINO, P., AND BEATI, E. [Considerations on the Oxo Synthesis.] Chimica e industria, vol. 31, 1949, pp. 111–113; British Abs., 1949, B, II, p. 998.

Probable mechanism of the reaction is discussed, based on kinetic measurements and thermodynamic considerations. The equilibrium constant is calculated for the synthesis of propionaldehyde from C_2H_4. Comparison is made with the Fischer-Tropsch reaction.

2401a. NATTA, G., PINO, P., AND ERCOLI, R. Hydrogen Transfer Reactions Accompanying the Cobalt-Catalyzed Addition of Carbon Monoxide to Olefinic Compounds. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 4,496–4,498.

Co-catalyzed reaction of CO and olefins with alcohols and with amines normally yields esters and amides. In some instances, however, products containing added H_2 are formed. The H_2 is furnished by the reactants, possibly by way of the formation and decomposition of Co hydrocarbonyl.

2401b. NATTA, G., PINO, P., AND MANTICA, E. [Synthesis of Esters by Reaction of Olefins, Carbon Monoxide, and Alcohols.] Gazz. chim. ital., vol. 80, 1950, pp. 680–701; Chem. Abs., vol. 46, 1952, p. 904.

Possible mechanisms of the carboxylation of olefins in the presence of CO are discussed. It is suggested provisionally that the catalytically active compound is Co hydrocarbonyl. It adds to the unsaturated bonds of the olefins with formation of intermediate compounds, which, in their turn, react with compounds containing mobile H atoms.

2402. NATTA, J. [Synthesis From Carbon Monoxide. I., II. Synthesis of Methanol, of Higher Alcohols and of Fuel, and the Oxo Process.] Industria y quim., vol. 11, 1949, p. 115; vol. 12, 1950, pp. 2–3; Chem. Zentralb., 1951, I, p. 3287.

MeOH synthesis as practiced in the plant at Rio Tercero, Argentina, is described. Fischer-Tropsch synthesis in the United States with fluidized catalysts also is reported.

2403. NAUDAIN, E. [Synthetic Liquid-Fuel Industry.] Ind. chim., vol. 23, 1936, pp. 82–85, 162–169, 247–249; Chem. Abs., vol. 30, 1936, p. 4647.

Review.

2404. ———. [Industries Based on Syntheses From Coke-Oven Gas.] Tech. ind. chim., No. 277, 1938, pp. 20–26; Chem. Abs., vol. 33, 1939, p. 3113.

Syntheses of NH_3 MeOH, gasoline, and C_2H_4 derivatives are discussed.

2405. NAUMANN, F. K. [Steels for Plants Producing Motor Fuels.] Chem. Fabrik, vol. 11, 1938, pp. 365–376; Chem. Abs., vol. 32, 1938, p. 7387.

Fischer benzine synthesis at low pressures and temperatures requires no special steel equipment, but cracking processes up to 70 atm. and 600° require steels with special resistance to attack by H_2S and to high temperatures. Hydrogenation up to 700 atm. places still higher requirements on steels, the extent to which alloyed steels meet these demands was investigated, and some effects on chemical composition and physical properties are shown by 18 graphs, 22 photomicrographs and numerous cuts. A plan of equipment for test steels in H_2 up to 1,000 atm. is given. 12 refs.

2406. ———. [Steels Used in Plant for Production of Motor Fuel.] Tech. Mitt. Krupp, vol. 6, 1938, pp. 77–87; British Chem. Abs., 1938, B, p. 1307.

Compositions and properties of steels used in apparatus for the cracking of petroleum, the high-pressure hydrogenation of coal, and the production of hydrocarbons by the Fischer-Tropsch process are reviewed.

NAUMOVA, A. I. *See* abs. **893.**

2407. NAUSS, O. [Enhancing the Value of Coal.] Gas- u. Wasserfach, vol. 70, 1927, pp. 832–834.; Chem. Abs., vol. 21, 1927, p. 3728.

Review of the use of coal as a raw material for the production of low-temperature coke, tar, oils, and gas of high calorific value, as well as the hydrogenation of coal (Bergius process) and the Fischer synthesis of hydrocarbons.

2408. NAVARRE, R. [Lubricant Substitutes.] Chim. et ind., vol. 48, 1942, pp. 295–301, 355–360; Chem. Zentralb., 1943, I, p. 2165; Chem. Abs., vol. 38, 1944, p. 4417.

After a detailed survey of the lubricant needs of France, it is agreed that of the various possibilities for their procurement, the order is: The petroleum industry, oil from coal, shale oil and rosin, and polymerization of olefins or unsaturated hydrocarbons obtained from Fischer-Tropsch synthesis.

2409. NAY, M. A., AND MORRISON, J. L. Molecular Adsorption Areas of Hydrocarbon Gases on Charcoal. Canadian Jour. Research, vol. 27, B, No. 4, 1949, pp. 205–214.

Low-temperature adsorptions of CH_4, C_2H_6, C_3H_8, n–C_4H_{10}, iso–C_4H_{10}, C_2H_2, C_2H_4, and N_2 on a series of coconut charcoals of different degrees of activation were determined. Langmuir isotherms were obtained in every case. The measurements indicate horizontal orientation of the hydrocarbon molecules on the charcoal surface. By comparing the maximum number of millimoles adsorbed for each gas on each charcoal with the respective maximum number of millimoles of N_2 adsorbed, and by assuming a molecular adsorption area of 16.2 square Ångstroms for N_2, the following average molecular adsorption areas were obtained: CH_4, 19.4; C_2H_6, 25.9; C_3H_8, 36.0; n–C_4H_{10}, 42.1; iso–C_4H_{10}, 47.4; C_2H_2, 19.8; and C_2H_4, 23.1 square Å.

2410. NEDELMANN, H. Hydrogenation and Fischer-Tropsch Synthesis. Chem. Ind., vol. 1, No. 2, 1949, pp. 62–64.

Status of synthetic fuel production in Germany and the effect of dismantling the plants on the German economy are discussed.

2411. NEGISHI, R. Qualitative Consideration on the Mechanism of Synthesis of Higher Alcohols From Carbon Monoxide and Hydrogen and From Lower Alcohols. I. Mechanism for Primary Alcohols. Rev. Phys. Chem. Japan, vol. 18, 1944, pp. 47–57; Chem. Abs., vol. 41, 1947, p. 4770.

From the already established results that BuOH is obtained from 2 mol. EtOH, PrOH from EtOH and MeOH, and $MePrCH_2OH$ from EtOH and iso-PrOH, the mechanism of synthesis of higher alcohols from lower alcohols in the presence of CaC_2 can best be explained by Graves' extension of Guerbet's direct dehydration theory except for the modification that a H atom of $-CH_3$ reacts readily, provided the $-CH_3$ is in the α position (adjacent to the carbinol radical).

2412. ———. Qualitative Consideration on the Mechanism of Synthesis of Higher Alcohols From Carbon Monoxide and Hydrogen and From Lower Alcohols. II. Mechanism for Secondary Alcohols and the Comparison of Different Mechanisms. Rev. Phys. Chem. Japan, vol. 18, 1944, pp. 58–70; Chem. Abs., vol. 41, 1947, p. 4770.

After discussing Fischer-Tropsch's intermediate acid theory, Morgan and coworkers' aldol condensation theory, and Frolich's and Graves' modifications of Guerbet's direct dehydration theory, the author supports the last as the most probable mechanism of synthesis of higher alcohols from lower alcohols or from CO and H_2, with the concession that the aldol condensation may take place if aldehydes and ketones are formed during the synthesis as secondary reactions.

———. *See* abs. **2420.**

NEGISHI, R., AND KAMIIKE, O. Hydrocarbons From Carbide. IV. Noncatalytic Polymerization Under Ordinary Pressure. Acetylene-Carbide System and General Remarks. *See* abs. **2417.**

———. Hydrocarbons From Carbide. V. Noncatalytic Polymerization Under Ordinary Pressure—Acetylene Carbide Systems. *See* abs. **2423.**

———. Hydrocarbons From Carbide. III. Noncatalytic Polymerization Under Ordinary Pressure—Carbon Dioxide-Carbide Systems. *See* abs. **2421.**

———. Hydrocarbons From Carbide. V. Noncatalytic Polymerization Under Elevated Pressure. Comparison Between Ordinary and Elevated Pressure Reactions. *See* abs. **2418.**

———. Hydrocarbons From Carbide. VI. Noncatalytic Polymerization Under Ordinary Pressure—Considerations and Comparisons Between Nascent and Ordinary Acetylene Polymerizations. *See* abs. **2424.**

———. Hydrocarbons From Carbide. II. Noncatalytic Polymerization Under Ordinary Pressure. Hydrogen Systems and General Experimental Details. *See* abs. **2415.**

———. Hydrocarbons From Carbide. III. Noncatalytic Polymerization Under Ordinary Pressure. Systems of Calcium Carbide With Carbon Dioxide, Carbon Monoxide, and Hydrogen Chloride. *See* abs. **2416.**

2413. NEGISHI, R., AND SAKON, K. Heat of Reaction in the Synthesis of Hydrocarbons From Carbide. Jour. Chem. Soc. Japan, vol. 64, 1943, pp. 1515–1522; Chem. Abs., vol. 41, 1947, p. 3359.

Utilization of the heat of reaction of carbide with H_2, CO_2, and H_2O for the cracking of fluid paraffin was studied. In the synthesis of isobutanol from the mixture of CO and H_2 at 320° in the presence of carbide, the heat of reaction is found to be 179 kcal. per mol. of carbide. Absorption of the heat of reaction takes place by cracking of fluid paraffin; the temperature of the reaction mixture remains uniform.

NEGISHI, R., KAMIIKE, O., AND KATAOKA, S. Hydrocarbons From Carbide. IV. Noncatalytic Polymerization Under Ordinary Pressure—Carbon Monoxide–Carbide System and Hydrogen Chloride–Carbide Systems. *See* abs. **2422.**

2414. NEGISHI, R., KIMURA, O., AND KAMIIKE, O. Hydrocarbons From Carbide. Rev. Phys. Chem. Japan, vol. 15, 1941, pp. 31–41; Chem. Abs., vol. 35, 1941, p. 6501.

Many hydrocarbons can be synthesized directly from CaC_2, without first preparing C_2H_2 to be polymerized later. The free energy of formation is calculated for a number of chain hydrocarbons and cyclic hydrocarbons, both from CaC_2 and H_2O to produce hydrocarbon and CaO and also from CaC_2, CO, and H_2 to form hydrocarbon and $CaCO_3$. The free-energy changes are very large, especially for the hydrocarbons with the greater number of C atoms. The ΔF at 300° is 83.5 kg.-cal. greater for the preparation of benzene from CaC_2 and H_2O, than from C_2H_2, and the increase in ΔF is even larger for similar syntheses of 1,3-butadiene or *n*-octane. The affinity of CaC_2 for H_2O, and of CaO formed during the reaction for CO_2, may increase the reaction rate by effectively removing these reaction products. The temperature coefficients of the reactions in which $CaCO_3$ is formed are greater than those in which CaO is formed. The addition of CaC_2 and the greater reactivity of nascent C_2H_2 molecules result experimentally in a faster rate and greater yield of polymerized C_2H_2 than is obtained by catalytic polymerization with a Co–Ni–Cr_2O_3 clay catalyst or a Fe–Ni–kieselguhr catalyst.

2415. NEGISHI, R., AND KAMIIKE, O. Hydrocarbons From Carbide. II. Noncatalytic Polymerization Under Ordinary Pressure. Hydrogen Systems and General Experimental Details. Bull. Chem. Soc. Japan, vol. 17, 1942, pp. 118–125; Chem. Abs., vol. 41, 1947, p. 4434.

Study of the synthesis of hydrocarbons directly from carbide at 250°–450° has been carried out. Reaction at 340° proved to be most suitable for the synthesis of liquid hydrocarbons. The effects of temperature on the formations of the products are discussed. These effects are intimately associated with the heat of reaction involving the carbide.

2416. ———. Hydrocarbons From Carbide. III. Noncatalytic polymerization Under Ordinary Pressure. Systems of Calcium Carbide With Carbon Dioxide, Carbon Monoxide, and Hydrogen Chloride. Bull. Chem. Soc. Japan, vol. 17, 1942, pp. 244–251; Chem. Abs., vol. 41, 1947, pp. 4434–4435.

Effects of CO, CO_2, and HCl on the synthesis of hydrocarbon liquids directly from Ca carbide in the temperature range of 340°–420° have been studied. The results are in agreement in general with those in the H_2 system. The main reaction of the nascent C_2H_2 molecules is only slightly affected by the carrier gases In the CO_2 system, the yield of liquid products has been found as high as 43% of the total reacted C_2H_2. CO_2 takes part only in the formation of CaC_2. The presence of H_2 seems to have no effect on the character of the liquid products. Whereas CO_2 has favorable effects, CO has unfavorable effects, and HCl has no effect at all on the yield of liquid hydrocarbons.

2417. ———. Hydrocarbons From Carbide. IV. Noncatalytic Polymerization Under Ordinary Pressure. Acetylene Carbide System and General Remarks.

Bull. Chem. Soc. Japan, vol. 17, 1942, pp. 345–354; Chem. Abs., vol. 41, 1947, p. 4435.

Results of the series of investigations, on the systems H_2, CO_2, CO, HCl, and C_2H_2 with CaC_2 are given: CO has a harmful effect, although CO_2 has a beneficial effect; HCl gives somewhat harmful effects only when its concentration is high; and C_2H_2 increases the total yield because it polymerizes. When C_2H_2 is diluted with an inert gas, such as H_2 or CO_2, its effect on the total liquid yield disappears; the presence of a small amount of C_2H_2 has a striking effect on the suppression of the formation of free C_2H_2. [The nascent C_2H_2 molecules, which related to polymerization, are suggested to have the structure $n(C_2H_2)=(C_2H_2)_n$.] There are indications that the efficacy of the synthesis of hydrocarbon liquids from CaC_2 is higher than even the catalytic polymerization.

2418. ———. Hydrocarbons From Carbide. V. Noncatalytic Polymerization Under Elevated Pressure. Comparison Between Ordinary and Elevated Pressure Reactions. Bull. Chem. Soc. Japan, vol. 17, 1942, pp. 355–364; Chem. Abs., vol. 41, 1947, p. 4435.

Effects of species of gases, pressure, and temperature on the character and yield of liquid products in the synthesis of hydrocarbons from Ca carbide under high pressures have been studied. The yield of liquid products increases with increase of total pressure of the system up to about 100 atm. and then decreases with further increase in the pressure. In the low-pressure runs, CO has noticeably harmful effects, whereas CO_2 has beneficial effects on the yield of liquid products. There are slight differences in the yields and the properties of the products under elevated and ordinary pressures, and these differences are explained as owing rather to the effects of the time of contact and temperature than to any change in the mechanism of the polymerization reaction.

NEGISHI, R., NIBAYASHI M., AND KAMIIKE, O. Hydrocarbons From Carbide; Noncatalytic Polymerization Under Elevated Pressure. II. Hydrogen–Carbide and Water Gas–Carbide System. *See* abs. **2426.**

2419. NEGISHI, R., KATAOKA, S., KAMIIKE, O., AND NIBAYASHI, M. Hydrocarbons From Carbide. I. Noncatalytic Polymerization Under Ordinary Pressure—Hydrogen–Carbide Systems. Jour. Soc. Chem. Ind. (Japan), vol. 44, suppl. binding, 1941, pp. 450–451 (in English); Chem. Abs., vol. 44, 1950, p. 8853.

Liquid hydrocarbons have been obtained directly from carbide with H_2 as a carrier gas for water vapor. Satisfactory yields were obtained at 340°–420° and a saturation temperature of 80°. There is an optimum grain size of the carbide; smaller grains retard the reaction while larger ones tend to form more gaseous products.

2420. KAMIIKE, O., KATAOKA, S., NIBAYASHI, M., AND NEGISHI, R. Hydrocarbons From Carbide. II. Noncatalytic Polymerization Under Ordinary Pressure—Analysis and Liquid Products. Jour. Soc. Chem. Ind. (Japan), vol. 44, suppl. binding, 1941, p. 451 (in English); Chem. Abs., vol. 44, 1950, p. 8853.

Gaseous products were analyzed by the modified Schuftan method for CO_2, C_2H_2, C_2H_4, $C_2H_{2n}(?)$, CO, O_2, H_2, N_2, and saturated gases. The liquids were analyzed chemically and were distilled into fractions, the molecular weight of such fractions being determined by the lowering of the freezing point of C_6H_6. A pilot plant yielded products very similar to those from the laboratory experiments. The liquid products were mainly aromatic and condensed aromatic hydrocarbons.

2421. NEGISHI, R., AND KAMIIKE, O. Hydrocarbons From Carbide. III. Noncatalytic Polymerization Under Ordinary Pressure—Carbon Dioxide-Carbide Systems. Jour. Soc. Chem. Ind. (Japan), vol. 44, suppl. binding, 1941, p. 451 (in English); Chem. Abs., vol. 44, 1950, p. 8853.

Yield of liquid hydrocarbons is as high as 43.3% based on the C_2H_2, which reacts. The liquid products contain some oxygenated compounds and some evidence exists indicating that they are alcohols. The CO_2 reacts almost quantitatively with the CaO formed from the carbide and water vapor but not with that contained in the original carbide as an impurity.

2422. NEGISHI, R., KAMIIKE, O., AND KATAOKA, S. Hydrocabons From Carbide. IV. Noncatalytic Polymerization Under Ordinary Pressure—Carbon Monoxide–Carbide System and Hydrogen Chloride–Carbide Systems. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, p. 46; Chem. Abs., vol. 44, 1950, p. 10299.

These systems were investigated to determine if a typical Fischer-Tropsch reaction is effected with the carbide and its reaction products, but in the absence of the usual catalyst, to increase the total yield of liquid products and to learn the catalytic effect of HCl. The reaction between CO and H_2 occurred only to a slight extent in the range 150°–450°, resulting in no liquid products. The effect of HCl vapor was that, as the concentration of acid increased, the yield of liquid hydrocarbons decreased.

2423. NEGISHI, R., AND KAMIIKE, O. Hydrocarbons From Carbide. V. Noncatalytic Polymerization Under Ordinary Pressure—Acetylene–Carbide Systems. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, p. 46 (in English); Chem. Abs., vol. 44, 1950, p. 10299.

Effects of C_2H_2 used as a carrier of water vapor on the liquid yield were studied in the hope that the total liquid yield might be increased by the polymerization of the introduced C_2H_2 and, further, that by its introduction, the formation of free C_2H_2 from the carbide might be suppressed, thus permitting the nascent C_2H_2 to become more readily available for the liquid synthesis. When the concentration of C_2H_2 was high, the total liquid yield also was high, showing that a part of the introduced C_2H_2 was polymerized. When its concentration was reduced, for example, by diluting it with H_2, or CO_2, the yield fell. In the presence of C_2H_2 mol., the formation of free C_2H_2 from the carbide is suppressed.

2424. ———. Hydrocarbons From Carbide. VI. Noncatalytic Polymerization Under Ordinary Pressure—Considerations and Comparisons Between Nascent and Ordinary Acetylene Polymerizations. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, p. 47 (in English); Chem. Abs., vol. 44, 1950, pp. 10299–10300.

Main reaction of nascent C_2H_2 is probably $nC_2H_2=C_{2n}H_{2n}$ to form principally aromatic and condensed aromatic compounds. The efficiency of the polymerization of nascent C_2H_2 from carbide is higher than that of ordinary C_2H_2 in the presence of an active catalyst. Because of the high reactivity of nascent C_2H_2, carbide may be used to accelerate certain sluggish reactions. Note should be made of the fact that the polymerization of nascent C_2H_2 is difficult to stop at a specfic point and that the heat of reaction involving carbide is very high.

2425. NEGISHI, R., NIBAYASHI, M., SAKON, K., AND KAMIIKE, O. Hydrocarbons From Carbide—Noncatalytic Polymerization Under Elevated Pressure. I. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, p. 141; Chem. Abs., vol. 44, 1950, p. 8853.

Catalytic effect of the autoclave material in the synthesis of liquid hydrocarbons from carbide under elevated pressure is discussed. The autoclave reaction of CO and H_2 is reported to give (1) CH_4 and H_2O,

(2) C_2H_6 and H_2O, and (3) CO_2 and H_2. Reaction (3) is catalyzed by $Al(OH)_3$. No liquid hydrocarbon was formed when carbide was absent.

2426. NEGISHI, R., NIBAYASHI, M., AND KAMIIKE, O. Hydrocarbons From Carbide; Noncatalytic Polymerization Under Elevated Pressure. II. Hydrogen–Carbide and Water Gas–Carbide Systems. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, suppl. binding, pp. 215–216 (in English); Chem. Abs., vol. 45, 1951, p. 535.

Yield of liquid product in the CaC_2–H_2–$Al(OH)_3$ system increases with increasing total pressure up to 100 kg./sq. cm. and then decreases. The amount of saturated gases increases with the total pressure. Decreasing the temperature increases the ratio of unsaturated to saturated compounds. Water gas in place of H_2 gives about the same yields of liquid products, and pressure has the same effect. The yield of saturated gases depends on the partial pressure of H_2. CO_2 in place of H_2 increases the yield of liquid product. The mechanism is discussed.

2427. NEIDIG, C. P. Formaldehyde Presents a Changing Economic Picture. Chem. Inds., vol. 61, 1947, pp. 214–217.

Formaldehyde production has tripled since 1939. In addition to an increase in the facilities for its manufacture by MeOH oxidation, production by direct oxidation of petroleum hydrocarbons continues to gain on a relative basis. From only 3 producers in 1937, the number has increased to 12 producers with 17 plants and 6 under construction. Eight plants use an Ag catalyst, at least 2 use an Fe–Mo oxide catalyst for the oxidation of MeOH. 2 plants use petroleum gases as the raw material and 1 will use a natural-gas cut. Little CH_2O is expected from the modified Fischer-Tropsch plants now being constructed. They will produce small quantities of MeOH, but, in the main, the oxygenated products will be C_2 and higher.

2428. NEIL, D. J. Sheet Specimen Scanner for X-Ray Diffraction. Canadian Jour. Tech., vol. 29, No. 2, 1951, pp. 84–86.

An improved and simple design is described and illustrated. Simultaneous back reflection and transmission photographs at distances of 3 and 5 cm., respectively, and at any glancing angle from 0° to 90° are possible. The area scanned is approximately 2 $cm.^2$ at rates of either 2 $cm.^3$/hr. or 4 $cm.^2$/hr. Useful exposures can be obtained with exposure times as low as 10 min.

2429. NEKRASOV, P. [Substitutes for Petroleum in U. S. S. R.] Planovoe Khoz., 1939, No. 11, pp. 28–44; Khim. Referat. Zhur., 1940, No. 6, p. 106; Chem. Abs., vol. 36, 1942, p. 4994.

Motor fuel can be produced in U. S. S. R. by destructive hydrogenation of fuel, by semicoking of coals and shales, and by synthesis from gases. Benzene, alcohol, and gases can be used as motor fuel. Fuel suspensions and mixtures of coal with sulfurous fuel oil can be used in the metallurgical and the transportation industries.

NELSON, E. F. *See* abs. **776.**

2430. NELSON, W. L. Fischer-Tropsch Process for Natural Gas. Oil Gas Jour., vol. 43, 1944, No. 12, p. 189.

An exact statement on the possibilities of the Fischer-Tropsch process is difficult at the present time because of the lack of knowledge of recent German developments. However, it is believed that much of the motor fuel being used by the Germans is made by synthesis from CO and H_2. Coal is the raw material rather than natural gas.

2431. NEMCHINSKIĬ, A. L. AND DELLE, V. A. [Carbide Formation During Carburization.] Metallurg., vol. 13, December 1938, pp. 55–60; Met. Abs. (in Metals and Alloys), vol. 10, No. 5, 1939, p. 278; Chem. Abs., vol. 33, 1939, p. 5783.

During carburizing of C steel with wood charcoal or with a mixture of wood charcoal (60%) and $BaCO_3$ (40%), the saturation of the steel with C is not limited by the *Acm* line of the Fe–C diagram but continues to the formation of carbides. The limit of saturation is less with C than with a mixture of C and $BaCO_3$. At higher temperatures of cementation the carbide formation is sometimes slower than at lower temperatures. This may be due to formation of a carbide network at high temperatures, which hinders the diffusion of the C into the austenite grains. Cr steel has a greater speed of carbide formation than plain C steel. The limit of saturation is higher for Cr–Ni than for C steel.

2432. NETTER, J. [Methods for Study of Catalysts for Synthesis and Transformation of Hydrocarbons.] Mem. services chim. état (Paris), vol. 32, 1945, pp. 299–318; Fuel Abs., November 1948, abs. 3986.

Mechanism of contact catalysis, especially for the catalytic synthesis and transformation of hydrocarbons. Numerous diagrams and detailed description of equipment used.

NEUMANN, B. *See* abs. **3098.**

2433. NEUMANN, B., AND BILJCEVIC, P. [Catalytic Preparation of Formaldehyde.] Ztschr. angew. Chem., vol. 40, 1927, pp. 1469–1474; Chem. Abs., vol. 22, 1928, p. 760.

Theoretical considerations show that in CO_2–H_2 mixtures at equilibrium only traces of HCHO can be present. Only traces were produced in porcelain and SiO_2 tubes at varying temperatures without catalyst or with the following: Silica–gel, Ce_2O_3, V_2O_5, NaOH–CaO, $CuCl_2$, activated C and Cl_2, $CuCl_2$, on silica–gel, Pd sponge, hopcalite, Fe–Pd, Ni–Fe–Pd, Fe–Co, Mn–Co, and others.

2434. NEUMANN, B., AND JACOB, K. [Equilibrium in Formation of Methane From Carbon Monoxide and Hydrogen, or From Carbon Dioxide and Hydrogen.] Ztschr. Elektrochem., vol. 30, 1924, pp. 557–576; Brennstoff Chem., vol. 6, 1925, p. 197; Chem. Abs., vol. 19, 1925, p. 1083.

Correlated survey of equilibrium conditions for the formation of CH_4 by the reactions (1) $CO+3H_2 \rightleftharpoons CH_4+H_2O$ and (2) $CO_2+4H_2 \rightleftharpoons CH_4+2H_2O$ over the temperature range 300°–1,050°. The experimental determinations of the equilibrium were made by the dynamic method, highly purified gas mixtures being passed over a Ni catalyst. The catalyst was made by igniting $Ni(NO_3)_2$ that had been deposited on MgO granules. The supported NiO thus formed was reduced at about 280° by H_2. All experiments were at atmospheric pressure. The velocity of gas flow was in all cases 5 $cm.^3$ per min. In experiments on reaction (1) the catalyst was 6.6 gm. Ni deposited on 45 gm. MgO. Reduction of CO to CH_4 began at 170°, was complete at 288°, and remained so up to 303°. Above 303° the CH_4 yield decreased regularly, until at 1,052° it had become zero. At temperatures above 389° the methanation reaction (1) is complicated by the secondary reactions $2CO \rightleftharpoons CO_2+C$, $CO+H_2O \rightleftharpoons CO_2+H_2$ and $CO_2+4H_2 \rightleftharpoons CH_4+2H_2O$. In the temperature region 450°–780° all 4 reactions go on together. Above 780° the secondary reactions subside. In experiments on reaction (2) the same amount of catalyst was used. Reduction of CO_2 to CH_4 began slightly over 180° and reached a maximum at 328°, corresponding to a CH_4 yield of 95.3%. The CH_4 yield decreased above 328° and reached zero at 1,020°. Above 540° the reaction (2) is complicated by many secondary reactions. Among them are $C+CO_2 \rightleftharpoons 2CO$, $CO_2+H_2 \rightleftharpoons CO+H_2O$, $CO_2+Ni \rightleftharpoons NiO+CO$. In experiments on reaction (3) $CH_4+H_2O \rightleftharpoons CO+3H_2$ the catalyst was 1.6 gm. Ni deposited on 45 gm. MgO.

The gas mixture was 43% CH_4 and 57% steam. No reaction was observed below 330°. From 330°–1,034° the amount of CH_4 undergoing reaction increased regularly. In the region 300°–860° the reaction is complicated by secondary reactions, as in the reverse reaction (1). Above 860° the reaction proceeds exclusively in accordance with the equilibrium reaction (3). Experiments on reaction (4) $CH_4+2H_2O \rightleftharpoons CO_2+4H_2$ from 320°–1,040° show plainly that, in spite of the presence of excess steam, the principal reaction is that corresponding to reaction (3). The observed values for the equilibruim constants $P\ CO \times P^3H_2/P\ CH_4 \times P\ H_2O$ in the temperature region 860°–1,052°, agreed fairly well with those calculated by combination of the equilibruim constants for the 3 reactions $C+CO_2 \rightleftharpoons 2CO$, $C+2H_2 \rightleftharpoons CH_4$ and $CO_2+H_2 \rightleftharpoons CO+H_2O$. The experimental results show somewhat better agreement with those calculated by means of "chemical constants" (Nernst). Agreement between the observed values for the equilibrium constants of reaction (2), $P\ CO_2 \times P^4\ H_2/P\ CH_4 \times P^2\ H_2O$, and those calculated by combining the equilibrium constants of the 3 reactions $C+CO_2 \rightleftharpoons 2CO$, $C+2H_2 \rightleftharpoons CH_4$ and $2(CO_2+H_2 \rightleftharpoons CO+H_2O)$ was very poor.

2435. NEUMANN, B., AND KÖHLER, G. [Equilibrium Relations in the Water-Gas Reaction in the Temperature Range 300°–1,000°]. Ztschr. Elektrochem., vol. 34, 1928, pp. 218–237; Chem. Abs., vol. 22, 1928, p. 2868.

Equilibrium values for the reaction, $CO+H_2O \rightleftharpoons CO_2+H_2$, were accurately determined at temperatures 300°–1,000° by a dynamic method. The catalyst used was Co oxide; this was replaced at the lower temperatures by Fe oxide in order to avoid the formation of CH_4. Small amounts of Al_2O_3 and KOH were present in the catalyst to increase its hardness and to act as a promoter. The values obtained for the equilibrium constant, $K=(CO)(H_2O)/(CO_2)(H_2)$, were reproducible and were virtually the same at each temperature regardless of the direction in which the equilibrium was approached. From the value $K_{936°}=1.61$, a value slightly higher than that obtained by Hahn, the integration constant of the reaction isochore was found to be 0.84 and $\Delta H_0=9{,}500$ cal. The curve obtained from the isochore with these values agrees with the experimental data. The value of the integration constant also agrees with that obtained from vapor pressure data according to the Nernst heat theorem. The constants calculated by combination of the equilibria Fe–O–H and Fe–O–C, from the results of Eastman (abs. **762**) and of Hofmann (abs. **1451**) agree only partly with the observed values.

2436. NEUMANN, B., KRÖGER, C. AND FINGAS, E. [Water-Gas Generation From Coal and Coke.] Gas- u. Wasserfach, vol. 75, 1932, pp. 972–973, 973–974; Ztschr. Elektrochem., vol. 38, 1932, pp. 936–938; Chem. Abs., vol. 27, 1933, p. 827.

Polemical (abs. **713**). The degree of attainment of the water-gas equilibrium depends more on the ash content of the given coke than on its reactivity. Dolch's conclusions also apply only to a limited temperature range. Dolch has not proved that CO_2 is not formed directly by the reaction of H_2O on C. Experiments with graphite showed that additions of Fe_2O_3, CuO, and K_2O all increased its reactivity but that only the 1st oxide permitted attainment of the water-gas equilibrium.

2437. NEUMANN, R. AND SCHROEDER, W. C. Fischer-Tropsch Plant of Hoesch Benzin A.-G. at Dortmund, Germany. FIAT Rept. 239, 1945, 5 pp.; PB 1279, TOM Rept. 22, TAC Rept. SnMC–8, TOM Reel 199.

This plant employed the medium-pressure process using the normal Co–ThO_2–MgO–kieselguhr catalyst at about 10 atm. pressure and 180°–205° with synthesis gas of CO : H_2 ratio of 1 : 2 made from blue water gas. The catalyst chamber house contained 68 converters of the usual concentric double-tube design. They were operated in 3 stages: 1st 40 chambers, 2d 16–20, and 3d 4–8. Each stage was followed by indirect coolers and, following the final stage, gas pressure was reduced, and the C_3 and C_4 hydrocarbons were removed in the usual active C absorbers. There were no facilities for recycling the gas through any stage. The rate of feed of synthesis gas to the first stage was 1,000 $m.^3$ per hr. per chamber. The gas contraction was 50–60% for the 1st stage, 35–40% for the 2d and 30% for the 3d. The average yield of primary product was 150 gm. per $m.^3$ of synthesis gas or a total production of 50,000 ton per yr. The procedure of adding fresh catalyst in any stage instead of in the 3d stage only differs from the usual practice as recommended by Ruhrchemie. The regeneration of the catalyst with H_2 was claimed unsatisfactory and extraction with middle oil from the process was practiced instead. The catalyst gave only 1,500–2,000 hr. service when it was removed and shipped back to Ruhrchemie as spent catalyst. The products obtained from the primary product were approximately: Benzine 20–25% with 40–45 octane no., Diesel oil 30% with 100 cetane no., heavy oil 25%, paraffin 20–25% with melting point of 60°–70° and an initial boiling point of approximately 350°. Little research had ever been carried out at this plant.

2438. NEUWIRTH, F. [Production of Benzine From Coal.] Sparwirtschaft, vol. 15, 1937, pp. 129–134; Chem. Abs., vol. 31, 1937, p. 5538.

Review dealing mainly with hydrogenation of coal and the Fischer-Tropsch process.

2439. ———. [Benzine From Coal.] Österr. Chem.–Ztg., vol. 41, 1938, pp. 75–82; Chem. Abs., vol. 32, 1938, p. 3127.

Processes for the production of gasoline by low-temperature carbonization of brown coals, the hydrogenation of tar or coal, and synthesis of water gas are outlined.

2440. ———. [New Coal-Utilization Methods.] Österr. Ing. Architekt. Ver., vol. 90, 1938, pp. 196–201; Chem. Abs., vol. 33, 1939, p. 835.

Summary of new developments in coking, burning, gasification, hydrogenation and pressure-extraction of coal. Fischer-Tropsch and other processes are described.

NEVILLE, H. A. *See* abs. **3340.**

NEWALL, H. E. *See* abs. **450.**

2441. NEWEY, H. A., SHOKAL, E. C., MUELLER, A. C., BRADLEY, T. F., AND FETTERLY, L. C. Drying Oils and Resins—Segregation of Fatty Acids and Their Derivatives by Extractive Crystallization With Urea. Ind. Eng. Chem., vol. 42, 1950, pp. 2538–2541; Chem. Abs., vol. 45, 1951, p. 2230.

When a mixture of fat acids or their derivatives (Me esters, alcohols, nitriles) is allowed to react with urea, with or without solvent, the more saturated components form insoluble adducts. A stereochemical explanation is given. Thus 250 gm. linseed-oil fat acids (I No. 180) in 250 gm. MeCOCHMeEt is mixed with 2 l. of saturated aqueous urea, the resulting precipitate filtered off and decomposed with H_2O, yielding 16% of a fraction of I No. 54. Glyceride oils did not form precipitates. Numerical data on the segregation of various fat acids and derivatives are given. 25 refs.

2442. ———. Separation of Fatty Acids and Their Derivatives by Extractive Crystallization With Urea. Am. Paint Jour., vol. 34, May 1, 1950, pp. 76–78; Chem. Zentralb., 1951, I, p. 1662.

When fatty acids are mixed with saturated, aqueous, or alcoholic solutions of urea, the more-saturated components form complex insoluble compounds which can

be separated by filtration. There remains behind a raffinate of high I number. The method is cheap, operable at room temperature, and useful for separating the alcohols and nitriles of fatty acids.

2443. NEWITT, D. M. Design of High-Pressure Plant and the Properties of Fluids at High Pressures. Oxford University Press, London, 1940, 491 pp.

———. *See* abs. **3028.**

2444. NEWITT, D. M. AND GARDNER, J. B. Initial Formation of Alcohols During the Slow Combustion of Methane and Ethane at Atmospheric Pressure. Proc. Roy. Soc., vol. 154, A, 1936, pp. 329–335; Chem. Abs., vol. 30, 1936, p. 4461.

By removing and analyzing the products formed by the surface reactions during the induction periods of the slow combustion of CH_4 and C_2H_6, it was found that MeOH and EtOH were formed in quantities comparable with those of the corresponding aldehydes, the alcohol: aldehyde ratio diminishing, however, as the induction approached completion. It was also proved that the formation of the alcohols preceded that of the aldehydes.

2445. NEWITT, D. M., AND HAFFNER, A. E. Formation of Methanol and Formaldehyde in the Slow Combustion of Methane at High Pressures. Proc. Roy. Soc. (London), vol. 134, A, 1932, pp. 591–604; Chem. Abs., vol 26, 1932, p. 2697.

In the slow combustion of CH_4 at high pressures, considerable quantities of the primary product, MeOH, survive and can be isolated. As combustion proceeds in an 8:1 CH_4+O_2 mixture, the rate of formation of MeOH increases with the CH_4: O_2 ratio until a point is reached when the concentration of steam and CO in the products begin to exert a retarding effect. At any particular pressure there is a definite temperature at which optimum amounts of MeOH and HCHO survive. The effect of increasing pressure is not only to increase the amounts of both products surviving, but also to increase the ratio MeOH: HCHO. The oxidation of CH_4, under the experimental conditions described is mainly a surface effect and is characterized by a marked induction period.

2446. NEWITT, D. M., AND MOMEN, S. A. Synthesis of Aliphatic Acids by Interaction of Olefins With Carbon Monoxide and Steam and Related Reactions. Jour. Chem. Soc., 1949, pp. 2945–2948.

It is shown that C_2H_4 and CO, in the presence of a suitable catalyst and at temperatures of 250° and upward, can unite with neutral or basic molecules, such as H_2O, EtOH, benzyl alcohol, NH_3, and aniline, to give acids, esters and amines. The synthesis of propionic acid by this reaction has been studied at 150–400 atm. and 250°–330°. The yield of acid in the products depends on the relative rates of its formation and thermal decomposition and also on the extent to which CO undergoes decomposition to CO_2.

2447. NEWITT, D. M., AND SZEGO, P. Slow Oxidations at High Pressures. I. Methane and Ethane. II. Methanol, Ethyl Alcohol, Acetaldehyde, and Acetic Acid. Proc. Roy. Soc. (London), vol. 147, A, 1934, pp. 555–571; Chem. Abs., vol. 29, 1935, p. 1770.

Large amounts of MeOH (EtOH) are formed in the early stage of the slow oxidation of CH_4 (C_2H_6) at 50 atm. Under similar conditions, the products obtained from EtOH, MeOH, AcH, and AcOH are such as to indicate a hydroxylation mechanism of combustion. The oxidation of AcOH at reduced pressures (in silica) is predominantly homogeneous. At 426°–486° at 200 mm. there is no marked induction period. The products are CO, CO_2, CH_4, and H_2O, with traces of AcOMe and acetone.

2448. NEWITT, D. M., BYRNE, B. J., AND STRONG, H. W. Equilibrium in the System: Methanol–Hydrogen–Carbonic Oxide. Proc. Roy. Soc. (London), vol. 123, A, 1929, pp. 236–252; British Chem. Abs., 1929, A, p. 508; Chem. Abs., vol. 23, 1929, p. 3148.

Equilibrium in the system CH_3OH–H_2–CO was approached from both sides by static and dynamic methods. Total pressures of the order of 100 atm. were measured by movement of a disk observed by optical methods. The composition at equilibrium was determined by gas analysis. Partial pressures were calculated assuming no deviation from Boyle's law. The results from 260°–380° are not in agreement with prediction for the equilibrium position made by Kelley or by Audibert and Raineau. The free-energy equation derived from the measurements is $\Delta F=70.5T-30{,}500$.

2249. NEWMAN, L. L. Thyssen-Galocsy Slagging Gas Producer. CIOS Rept. XXIX–51, 1945, TOM Reel 198, Solid Fuels Rept. 46, PB 955.

Report of the operation of a Thyssen-Galocsy slagging gas producer of 40 ton per day gasifying capacity at the Wanne-Eickel plant of the Krupp Treibstoffwerk. The purpose was to demonstrate the feasibility of gasifying any grade of fuel in any size or combination of sizes 5–80 mm., coking or noncoking, regardless of the ash-fusing temperature. The generator was shaped like a blast furnace, 35 ft. high and 10 ft. in diameter, 3 levels of tuyères with 5 tuyères at each level, those of the lowest level being water-cooled and burning gas from the producer itself, or any other source in a mixture of O_2 and steam and admitted into the fuel bed at a temperature high enough to cause the steam and CO_2 to react with the C. The tuyères at the upper levels admit additional O_2 to supply heat to balance the amount required for the reduction of the steam and CO_2 and to melt the ash. Only 1 of the 2 upper levels is used at a time. The slag is removed through a tap hole 650 mm. above the bottom of the shaft, which is lined to a height of 1 m. with slag resistant refractory. A temperature of 1,600° in the fuel bed was found necessary for trouble-free operation. O_2 for the operation was supplied by the Hibernia Stickstoffwerk, but it was thought that cheap O_2 (1–2 pf. per $m.^3$) could be produced by using coal screenings to generate steam at high pressure for driving the turbo-blowers and compressors in the Linde-Fränkl plant and by using the exhaust steam in the gasification process. The results of 1 day of a typical 3-day test are presented: O_2, 90% pure, consumed 25,000 $m.^3$, steam 18.9 tons, auxiliary gas, produced in the process, 17,250 $m.^3$, coke, 40–60 min. diam., ash 8.5%, 6,865 kcal. per kg., 41.3 tons: yields of gas, less auxiliary gas, 89,270 $m.^3$, analysis CO_2 2.1, O_2 0.1, CO 71.0, H_2 23.3, CH_4 0.2 and N_2 3.3%, 2,760 cal. per $m.^3$, steam decomposition 90.1%, gasification 86.7%, requirements for each cubic meter of oxygas, 0.29 $m.^3$ O_2, 0.21 kg. steam and 0.46 kg. coke. It is not considered that these tests have reached the peak of capacity of the unit, but that higher results will be attained when unlimited supplies of O_2 are available.

2450. NEWMAN, L. L. Oxygen Gasification Processes in Germany. Coal Technology, vol. 1, 1946; Am. Inst. Min. and Met. Eng., Tech. Pub. 2116, 1946, 16 pp.; Chem. Abs., vol. 41, 1947, p. 1079.

Review and digest of recent CIOS reports on gasification processes under 4 headings: Processes (1) in which fine fuel is gasified in a fluidized bed (example, the Winkler process); (2) in which fine fuel is gasified in suspension (example, Koppers and Schmalfeldt processes); (3) in which fine fuel is gasified in a fixed bed (example, the Lurgi process); (4) in which lump fuel is gasified in a fixed bed (example, the Thyssen-Galocsy slagging generator and the Leuna slagging generator). Typical operating data are given for each process, and diagrams of the plants are shown. The economics of O_2 production by the Linde-Fränkl process is presented. It is stated that power requirements in

Germany for producing O_2 of 98% purity were about 12 kw.-hr. per 1,000 cu. ft. and that in plants of 75,000 cu. ft. per hr., capacity the cost of power was 50% of the total cost, amortization and interest 40%, and labor and materials 10%. If the same relations between power costs and other costs should prevail in America, O_2 of 98% purity should be obtainable for $0.12 per 1,000 cu. ft. with power at $0.005 per kw-hr.

2451. ———. Oxygen Production, Utilization in Gas-making Processes. Proc. Am. Gas Assoc., vol. 28, 1946, pp. 444–467.

Review of the methods of O_2 manufacture and coal gasification.

2452. ———. Oxygen Production, Utilization in Gas-making Processes. Gas, vol. 22, No. 12, 1946, pp. 43–44.

Digest of a paper presented at the American Gas Association convention, October 1946. The use of O_2 in place of air in a gas producer makes the problem of complete gasification relatively simple. A survey of manufacturers of large-scale O_2 plants has put the cost of O_2 at about $0.14–$0.18 per 1,000 cu. ft. Several processes have been developed for the utilization of O_2 in gas making: Those with the fixed-fluidized beds such as the Winkler, the O_2 requirements of which are high; the powdered-fuel types with fuel in suspension which promise economy in fuel and O_2 consumption and adaptability to any suitably grindable coal; the fixed-fuel-bed types with mechanical grates and high pressures; the pressure types which have a high capital cost and a high fuel and steam consumption and require a noncaking coal. In general local conditions of fuel, labor and power costs will determine which process is most likely to succeed. The high investment cost of O_2 plant will make the production of gas by the use of O_2 economical only as a base-load proposition.

2453. ———. Synthetic Oil. Federal Sci. Progress, vol. 1, 1947, pp. 11–13.

Nontechnical exposition of American progress in the development and utilization of the Fischer-Tropsch process for producing liquid fuels from coal and natural gas. Simplified flowsheet is included.

2454. ———. Use of Oxygen in the Production of Hydrogen or Synthesis Gas. Ind. Eng. Chem., vol. 40, 1948, pp. 559–582; Chem. Abs., vol. 42, 1948, p. 4329.

Processes for the large-scale production of H_2 and synthesis gas are basically identical, and the cost of these gases represents a major item of expense in the production of liquid fuels by the Bergius and Fischer-Tropsch methods. To produce only 25,000 bbl. of primary liquid fuels by the Fiscrer-Tropsch process 700,000,000–800,000,000 cu. ft. of synthesis gas would be required. To produce these huge volumes of synthesis gas, high-capacity processes must be employed, and the low-priced generator fuels are required in order to make the process economical. These can best be gasified in continuous, internally heated processes using O_2. The principal processes for this include 4 types: Winkler, gasifying fines in a fixed fluidized bed; Koppers, gasifying pulverized coal in suspension; Lurgi, gasifying fines in a fixed bed under pressure; Thyssen-Galocsy and Leuna, gasifying lump fuel and disposing of the ash as a molten slag. Each of these processes, their operating characteristics and economic status are discussed thoroughly. Other less-important processes are briefly described: Fuel Research Board vortex chamber, gasifying pulverized coal in a rotating, porous fuel bed; Wintershall-Schmalfeldt, gasifying coarse brown coal with circulating gas and steam; and Metallgesellschaft dust-gasification process, gasifying coal dust with recirculation of hot gases. It is concluded that American requirements may be best satisfied by gasification processes using pulverized fuel in suspension. These will permit the use of higher rank caking or noncaking coals, as well as the lower-rank subbituminous coals or lignite.

———. *See* abs. **1468, 3743.**

2455. NEWMAN, L. L., SCHMIDT, L. D., AND BATCHELDER, H. R. Manufacture of Fuel and Synthesis Gas in the United States. Trans. World Power Conf., 4th Conf., London, Sec. D–1, Paper 5, 1950, 12 pp.; Chem. Abs., vol. 44, 1950, p. 7039.

Use of gas in the United States is increasing steadily, but most of it is natural gas, owing to the increasing cost of materials for gas manufacture. Production of chemicals consumes large amounts of gas and the production of synthetic liquid fuels is on the verge of realization. Increasing quantities of gas will have to come from coal. New technical developments in commercial gas manufacture include conversion of water-gas generators to oil-gas operation, and reforming processes for liquefied petroleum gases and other hydrocarbons. O_2 is being applied commercially for synthesis-gas production from coke, and investigations are under way relative to the use of O_2 for the pressure gasification of lump coal and for the gasification of granular or pulverized coal.

2456. NEWTON, R. H., AND DODGE, B. F. Equilibrium Among Carbon Monoxide, Hydrogen, Formaldehyde, and Methanol. I. The Reactions $CO+H_2 \rightleftharpoons HCHO$ and $H_2+HCHO \rightleftharpoons CH_3OH$. Jour. Am. Chem. Soc., vol. 55, 1933, pp. 4747–4759; Chem. Abs., vol. 28, 1934, p. 955.

Trace of CH_2O is synthesized from CO and H_2 over a Cu–Zn catalyst at 225°–250° and 3 atm.; the equilibrium approached from both sides gives $\log K_p=(374/T)-5.431$ approximately. CH_2O is readily hydrogenated at 120°–200° and 1 atm. over various Cu-alloy and other catalysts, but Os, Pt and pure Zn are inactive: $\log K_p=(4{,}600/T)-6.470$ approximately. A change in the composition or structure of the catalyst has a marked effect on the nature and amount of side reaction, Ni catalysts promoting decomposition of CH_2O, while some Cu catalysts yield 53–72% HCO_2Me. Conclusion: Direct thermal synthesis of CH_2O is not feasible; its production from MeOH requires a temperature of 400°.

2457. ———. Equilibrium Among Carbon Monoxide, Hydrogen, Formaldehyde, and Methanol. II. The Reaction $CO+2H_2 \rightleftharpoons CH_3OH$. Jour. Am. Chem. Soc., vol. 56, 1934, pp. 1287–1291; Chem. Abs., vol. 28, 1934, p. 4651.

Uncertainty in the heat data for CO and MeOH permits several possible theoretical equations for the synthesis of MeOH from CO and H_2. The equation $\log Kp_o=(3724/T)-9.1293 \log T+0.00308\ T+13.412$ fits results obtained at 225°, 250°, and 275° and 3 atm. for 4–55 hr. over a Cu–Zn catalyst.

2458. ———. Activity Coefficients of Gases. Application to Calculation of Effect of Pressure on Homogeneous Chemical Equilibria and to Calculation of Integral Joule-Thomson Effects. Ind. Eng. Chem., vol. 27, 1935, pp. 577–581; Chem. Abs., vol. 29, 1935, p. 3900.

Use of Newton's curves of activity coefficients in calculating chemical equilibrium constants is illustrated by application to the synthesis of NH_3 and of MeOH. A simple approximate method of calculating the temperature drop on isenthalpic expansion of a gas is given; specific-heat data and the activity coefficients are used. The results of both types of calculation are compared with experimental data.

NEWTON, W. L. *See* abs. **855.**

NIBAYASHI, M. *See* abs. **2419, 2420, 2425, 2426.**

2459. NICHOLSON, E. W., MOISE, J. E., AND HARDY R. L. Fluidized-Solids Pilot Plants. Ind. Eng. Chem., vol.

40, 1948, pp. 2033–2039; Chem. Abs., vol. 43, 1949, p. 1613.

Main commercial application to date of the fluidized-solids technique has been in the field of catalytic cracking of petroleum oils. Due to its extreme flexibility and versatility it will undoubtedly be applied to an increasing number of processes. The technique is particularly adaptable to mixed-phase (solid-gas) processes requiring the addition or removal of large amounts of heat, especially where isothermal conditions are desirable. The fluidized solids may be catalysts, reactants, inert heat-transfer mediums, or adsorbents. One of the most interesting new developments is in the field of hydrocarbon synthesis and commercial plants employing this fluid technique are being planned. The steps necessary for the practical design of a pilot plant utilizing the fluidized solids technique are presented. An apparatus which has been used for fluidization studies essential to unit design is illustrated. The translation of data obtained in such equipment to the design of reaction vessels, circulating equipment, gas and solids inlet distributors, solids recovery, etc., is outlined. Methods of measurement and control of temperature, pressure, solids flow rate and space velocity are discussed.

2460. NICOLAI, J., D'HONT, M., AND JUNGERS, J. C. [Synthesis of Methane From Carbon Dioxide and Hydrogen Over Nickel.] Bull. soc. chim. belg., vol. 55, 1946, pp. 160–176; Chem. Abs., vol. 41, 1947, p. 4699.

Kinetics are compared for the hydrogenation of CO and CO_2 over Ni in the pressure range 0.1–1 atm. and temperature range 180°–300°. Kinetics of the CO–H_2 reaction indicate that H_2 is feebly adsorbed, CO strongly adsorbed by Ni. The velocity is not significantly affected by the presence of the products. Reaction is more rapid when D_2 is used in place of H_2. Kinetics of the CO_2–H_2 reaction indicate that both reactants are weakly adsorbed, the products retard the reaction and D_2 behaves exactly like H_2. Hydrogenation of CO is slower and has a higher activation energy than that of CO_2. When a mixture of CO and CO_2 is hydrogenated, the CO, very strongly adsorbed, reacts completely first, the CO_2 then reacts more rapidly.

2461. NICOLAÏ, J., MARTIN, R., AND JUNGERS, J. C. [Kinetics of the Hydrogenation of Benzene.] Bull. soc. chim. belg., vol. 57, 1948, pp. 555–574; Chem. Abs., vol. 44, 1950, p. 419.

The reaction cyclohexane+CO=benzene+CH_4+H_2O is thermodynamically favorable but does not go well over Ni. Since CO is readily hydrogenated, it was desired to observe the dehydrogenation of cyclohexane (I), but this is limited by equilibrium at some of the temperatures of interest, so the reverse reaction of hydrogenation of benzene (II) was studied at 60°–330°. The catalyst was prepared by reduction of $NiCO_3$ deposited on kieselguhr. Data obtained in a static system are presented in curves. At 70°–150° the hydrogenation produces (I) and has an activation energy of (II) kcal. At 150°–250° it is complex. Above 250° the product is CH_4 (III) and the activation energy is 45 kcal. Thus at low temperatures there is an additive adsorption of (II), whereas at high temperatures there is a dissociative adsorption to products that are hydrogenated to (III). The orders of reaction in H_2 and (II) are fractional, about 0.5 in the low-temperature region. In the region of formation of (III) the order is first in (II) and negative in H_2. When (I) is treated in H_2 at 260° there is first dehydrogenation to (II) and then production of (III). The hydrogenation of (II) in the presence of various gases was observed; (I) did not inhibit at low temperatures, and (III) did not inhibit at high temperatures. The adsorption of CO was stronger than that of (II), and CO was hydrogenated first. Adsorption of CO_2 was about the same as that of (II). MeOH was not strongly adsorbed and below 160° had no effect, whereas at high temperatures it was decomposed and then converted to (III). The hydrogenation of mixtures of CO and (I) at 250°–280° showed first hydrogenation of CO, then dehydrogenation of (I) to (II), then conversion of (II) to (III). Thus CO does not aid in the dehydrogenation, for it is adsorbed more strongly and is hydrogenated first. The effect of CO_2 is similar though less marked. In mixtures containing CO, (I), and MeOH at 250° the first reaction was decomposition of the MeOH. Failure of the desired transfer of H_2 from (I) to CO is caused by 2 effects. First at temperatures above 180° where CO can be converted to (III), (II) formed is destructively adsorbed and the catalyst activity is lowered by carbonization unless much H_2 is present. Second, CO is preferentialliy adsorbed and keeps (I) from the catalyst.

2462. NIELSEN, H. Oil From Coal. Gas. Jour., vol. 174, 1926, pp. 591–592, 650–653, 732–734; Chem. Abs., vol. 21, 1927, p. 2371.

Processes of low-temperature carbonization, the Bergius process, and Fischer's Synthol process are compared from the point of view of the economic conversion of coal into oil. Emphasis is laid on the importance of producing a primary oil by low-temperature carbonization. The Fischer-Tropsch Synthol process (abs. **1015**) is discussed, and it is concluded that the most efficient method at present available for conversion of coal into oils consists in (*a*) low-temperature carbonization in the Laing and Nielsen retort, and (*b*) use of the coke as a source of water-gas and conversion of the latter into Synthol.

2463. NIENBURG, —. [Transformation of a Synthetic Olefin Into Oxo-Alcohols.] FIAT Reel R–20, frames 7571–7580, Dec. 30, 1941; PB 73.564.

Report from the I. G. Farbenindustrie Ammonia Laboratory, Oppau, deals with tests on conversion of synthetic olefins into Oxo-alcohols and on separation of these from unsaponifiable matter by the boric acid ester method. Separation and fractionation proved to be difficult and incomplete. The essential result is that 30% of the olefins and the alcohols derived from them show a branched structure. Numerous tables are presented.

2464. ———. [Cracking of High Molecular Paraffin and Oxidation Gatsch.] FIAT Reel R–20, frames 7600–7614, Mar. 9, 1942; PB 73,564.

Differences between corresponding fractions of oxidation products obtained either from high-molecular paraffin or from medium-pressure paraffins are discussed and shown in tables. The fraction derived from the high-molecular paraffin is considerably inferior. It is thought that structural change, such as cyclization, occurs which is inherent in the material itself or which takes place during the cracking process.

2465. NIENBURG, H. J. [Work on the Oxo Reaction 1940–1944.] BIOS Misc. Rept. (in German) 113, 1947, Appendix II, 16 pp; BIOS Final Rept. 1646, 1946, pp. 30–47, PB 91,685.

Changes in constitution brought about by the Oxo reaction were examined with pure olefins such as cetene and dodecylene. Independent of the purity of the initial olefin, a large number of isomeric Oxo alcohols or acids were obtained. Special Oxo reactions were carried out with olefins from first-running ketones, Fischer-Tropsch synthesis olefins, di- and tri-isobutylene, cracking olefins and with unsaturated, O-containing olefins. The latter did not yield uniform Oxo products. By treating olefins with NH_3 and CO acid amides were obtained. With isobutylene and generally, with all olefins having the double bond between tertiary and quaternary C atoms, it was found that the formyl grouping goes solely to the tertiary C atom. Work was done on building up high knock-rating hydrocar-

bons, using the Oxo reaction and starting with isobutylene, trimethylethylene, 2,4-dimethylpentene-2, diisobutylene and tetramethylethylene. It was found that these compounds avoid an increase in branching by a double-bond shift which precedes addition. In contrast to the Oxo reaction, 1,3-dioxanes give with tetramethylethylene, trimethylethylene and 2,4-dimethylpentene-2, the desired highly branched primary alcohols after hydrogenation. The oxation of propylene was intensively studied in a trickle (Riesel) apparatus, and a sump-phase apparatus was developed to handle 5 l. liquid propylene/hr. Propylene yielded equal quantities of normal- and isobutyl-aldehyde and the corresponding alcohols on hydrogenation.

NIERHAUS, H. *See* abs. **2043.**

2466. NIIRANEN, W. [Gasification of Wood and Peat With Special Reference to the Preparation of Synthesis Gas.] Suomen Kemistilehti, vol. 10, 1937, A, pp. 37–40; British Chem. Abs., 1937, B, p. 515.

Destructive distillation of dried wood shavings at 540° gives a large amount of tarry matter. This can be eliminated and more volatile hydrocarbons obtained by passing O_2 into the retort, the oxidation being adjusted to give the maximum CO : H_2 ratio for conversion into Kogasin.

2467. ———. [Synthesis of Liquid Fuels and Lubricating Oils.] Suomen Kemistilehti, vol. 10, A, 1937, pp. 7–9; Chem. Abs., vol. 31, 1937, p. 2773.

Brief survey.

2468. NIKITIN, N. I. [Absorption of Hydrogen and Carbon Dioxide by Pyrophoric Iron, Nickel, and Cobalt.] Jour. Russian Phys.-Chem. Soc., vol. 58, 1926, pp. 1081–1094; Chem. Abs., vol. 22, 1928, p. 8.

Finely divided Fe, obtained by the action of H_2 on the carbonate at 515°–525°, adsorbed H_2 at —185° according to the equation $a=\beta p^{1/n}$. No adsorption was observed at —80° and +16°, while at 330° the gas diffuses through Fe. The adsorption isotherm of Ni at 19° is parallel to the axis of pressures showing compound formation. No combination occurs at —185°, since the corresponding isotherm begins at the origin. The 336° curve crosses that for 19°; its lower portion represents the dissociation of the Ni and H_2 compound. The above equation holds for Fe and CO_2 at 18° ($1/n$=0.207). Readsorption, after evacuating the system at 500°, was much smaller although similarly represented by a straight line; a slow reaction occurs at 500°. Ni adsorbs little CO_2 at 14° and 335°; the gas is only partly recovered by evacuation. Erratic results were obtained with Co prepared at 340°. A sample reduced at 525°–550° exhibited a continuous adsorption isotherm for CO_2 at 14°. Co lies between Ni and Fe as an adsorbent of CO_2.

2469. ———. [Hydrogen and Carbon Dioxide Absorption by Pyrophoric Iron, Nickel, and Cobalt.] Ztschr. anorg. Chem., vol. 154, 1926, pp. 130–143; Chem. Abs., vol. 20, 1926, p. 3255.

Experiments were carried out to determine the adsorption and solution of H_2 and CO_2 by pyrophoric Fe, Ni, and Co at different temperatures and pressures. A specially constructed apparatus for this is illustrated and described. Finely divided metals were obtained on slow reduction, in about 30 hr., of the respective carbonates with H_2, the reduction temperature being kept at 525° for Fe and at 350° for Ni and Co. The following results were obtained: For 5 gm. Fe the maximum H_2 adsorption at —185° and 667 mm. pressure was 8.3 cc. At —80° and 16° there was virtually no adsorption, while at 380° and 500° there was again a larger adsorption. The results obtained at different pressures exhibited in isotherms show an adsorption curve at —185°, following Freundlich's equation: $a=\beta p^{1/n}$, where β and $1/n$ are determined constants. A proof for the application of this equation is the straight line obtained on plotting log a against log p, the tangent to the angle between this end and X–axis being $1/n$. That surface adsorption and not solution occurred at —185° was proved by the easy removal of the H_2 on evaluation, while the H_2 taken up at 400° could be removed only by heating strongly. The results obtained with Ni and H_2 at —185°, 19° and 336° showed a maximum adsorption at 336°, which was 3.8 cm.^{3} for 5 gm. Ni at 714.9 mm. pressure. The isotherm for 19° exhibits a straight line parallel to the X–axis and points to the formation of a superficial layer of Ni–H. A similar formation is not present at —185° inasmuch as the isotherm starts at the O–point of the coordinate axis. The isotherm for 336° starts below that of 19°, because the loose Ni–H compound dissociates at higher temperature and lower pressure. Fe had a strong tendency to adsorb CO_2, 1 vol. Fe taking up 35 vol. CO_2 at ordinary temperature and pressure and 2 times as much at —80°. Ni adsorbed virtually no CO_2 at 335°. The application of Freundlich's equation for the CO_2 adsorption by Ni at lower temperatures was not safe because of the small values obtained. The results with Co and H_2 were all uncertain. Adsorption values for CO_2 and Co were found between those for Fe and Ni. 5 gm. Co adsorbed 13 cm.^{3} CO_2 at 14° and 760 mm. pressure.

2470. NIKITIN, N. I., AND SHARKOV, V. I. [Adsorption of Gases by Finely Disintegrated Metals.] Jour. Russian Phys.-Chem. Soc., vol. 58, 1926, pp. 1095–1100; Chem. Abs., vol. 22, 1928, p. 1074.

Adsorption of H_2, CO_2 and NH_3 gases was investigated. The following powders were used: Cu, Pb, Fe, Co, Ni, Ni–Al_2O_3 mixture and Ag. Pb and Cu powders were obtained by reducing the basic compounds. Ag was obtained from the silver gel, which was dried in vacuum. Virtually no adsorption could be noticed with Pb or Cu powders; this is probably due to recrystillation of metals during the process of reduction. Ag adsorbed only a small amount of H_2, considerably more of CO_2. 5.512 gm. adsorbed 13.9 cc. of CO_2 (converted to 760 mm. and 0°) at —81°. Pyrophoric Fe adsorbed 11.5 cc. NH_3 at 97° and 158.6 mm. and 53.7 cc. at —18.2° and 556 mm. No adsorption occurred at higher temperature. Co adsorbs 10 times less than Fe. Ni powder did not adsorb any gases except when mixed with Al_2O_3. A mixture of 82.4% Ni and 17.6% Al_2O_3 was able to adsorb gases. 4.454 gm. adsorbed at 15°, 760 mm., 190 cc. NH_3; at —18.2°, 760 mm., 281 cc. After heating and applying vacuum, this mixture was freed from NH_3, gas and used again for the adsorption of CO_2. At 15° and 760 mm. 15.9 cc. CO_2 gas was adsorbed. Al_2O_3 without Ni, 4.6338 gm., adsorbed at 15° and 760 mm., 168 cc. gas. H_2 was not adsorbed by Al_2O_3.

2471. NIKITIN, V. M. [Effect of the Conditions of Synthesis on the Quality of Methanol.] Jour. Chem. Ind. (U. S. S. R.), vol. 12, 1935, pp. 1233–1236; British Chem. Abs., 1936, B, p. 404; Chem. Abs., vol. 30, 1936, p. 2170.

Catalysts containing more Cr than $8ZnO \cdot 1.2Cr_2O_3$ give larger amounts of byproducts in synthetic MeOH. The quantity of H_2O and higher molecular compounds formed is increased as the temperature is raised. When the rate of passing the gases over the catalyst is increased, the formation of aldehydes, ketones, and esters decreases more rapidly than that of acids. If the ratio of H_2 : CO is not 2, more byproducts are formed. Inert gases act as diluents and lower the quality of the MeOH.

2472. ———. [Byproducts of Methanol Synthesis.] Org. Chem. Ind. (U. S. S. R.), vol. 2, 1936, pp. 382–387; Chem. Abs., vol. 31, 1937, p. 1759.

Study of the properties of all combinations of binary systems of iso-BuOH, iso-BuOAc and H_2O includes

mutual solubilities at various temperatures, equilibrium of liquid and vapor phases, azeotropic mixtures, density and *n*. The experimental results are tabulated, graphed and discussed. With increasing temperature the solubility of iso-BuOH in H_2O decreases and that of H_2O in iso-BuOH increases. The azeotropic mixture is composed of 68 mol. % of H_2O and 32 mol. % of iso-BuOH.

2473. ———. [Byproducts of Methanol Synthesis. II.] Org. Chem. Ind. (U. S. S. R.), vol. 3, 1937, p. 364; Chem. Abs., vol. 31, 1937, p. 7040.

Boiling points of mixtures of PrOH with H_2O are tabulated and graphed.

2474. ———. [Treatment of the Byproducts From the Methanol Synthesis. III.] Jour. Chem. Ind. (U. S. S. R.), vol. 14, 1937, pp. 993–996; Chem. Abs., vol. 32, 1938, p. 1647.

Isobutyl acetate prepared from the iso-BuOH in synthetic MeOH can be dried by neutralizing with Na_2CO_3 and distilling into a continuous separator, or dried over $CaSO_4$. The higher-boiling oil from the MeOH is best-dried by salting out the NaCl and drying over CaO or $CaSO_4$.

2475. ———. [Paper of D. A. Pospekhov on the Role of Copper in Methanol Catalysts.] Jour. Chem. Ind. (U. S. S. R.), vol. 14, 1937, pp. 1229–1230; Chem. Abs., vol. 32, 1938, p. 911.

Criticism of Pospekhov's paper (abs. **2724**).

2476. ———. [Purification of Crude Synthetic Methanol by Oxidizers.] Jour. Chem. Ind. (U. S. S. R.), vol. 14, 1937, pp. 1067–1072; Chem. Abs., vol. 32, 1938, p. 484.

Addition of $KMnO_4$ to crude MeOH and rectification to 75° gives a pure distillate. $CaOCl_2$ and $K_2Cr_2O_7$ are not quite as satisfactory oxidizers. Fe and Cu in the crude alcohol increase the rate of oxidation of impurities.

———. *See* abs. **892.**

NILLSON, K. T. *See* abs. **186.**

NISHIBAYASHI, Y. *See* abs. **2205.**

NISHIO, A. *See* abs. **1873, 3468.**

NISHIYAMA, Z. *See* abs. **1484.**

2477. NISSAN, A. H. Thermal Catalysis of Carbon Monoxide and Hydrogen to Produce Hydrocarbons and Oxygenated Organic Compounds. Oil Gas Jour., vol. 37, No. 10, 1938, pp. 49–50, 55; No. 11, 1938, pp. 89–90, 93, 96; Chem. Ind., vol. 43, 1939, pp. 281, 283, 284; Chem. Abs., vol. 33, 1939, p. 7525.

Discusses economic value and technical applications of the hydrocarbons and oxygenated compounds formed. Reviews various reactions by which CH_4, MeOH and higher alcohols can be obtained. Fundamental thermodynamic and catalytic conditions for the production of hydrocarbons are dealt with in some detail and the conditions necessary for their successful technical synthesis are reviewed. Examples of the properties of the products are given, and the erection of commercial-scale plants is discussed from the economic viewpoint.

NISSEN, B. H. *See* abs. **5.**

2477a. NISTLER, F. [New Methods for Producer-Gas Generation From Bituminous Coal.] Glückauf, vol. 88, 1952, pp. 346–349; Chem. Abs., vol. 46, 1952, p. 7,736.

Special slagging-gas producer for manufacturing a cheap gas from coal dust is described. The gas is similar to blast-furnace gas with a gross heating value of about 1,051 kcal. per $m.^3$. This producer should be well adapted for use with a steam–O_2 mixture for generation of synthesis gas.

2478. NITZSCHMANN, R. [Oxidation of Carbon Monoxide by Steam.] Metallbörse, vol. 20, 1930, pp. 5–6, 118–120; Chem. Abs., vol. 24, 1930, p. 2365.

Equations and table of constants involved in calculations based on the reaction $CO+H_2O=H_2+CO_2+$ 10,400 cal.

———. *See* abs. **260, 261.**

2479. NITZSCHMANN, R., AND LIPKA, H. [Volumetric and Equilibrium Relations of the Reaction $CH_4+H_2O \rightleftharpoons CO+3H_2$.] Metallbörse, vol. 19, 1929, p. 1014–1015; Chem. Abs., vol. 23, 1929, p. 3611.

Equations, tables, and illustrative problems.

NOBORI, H. *See* abs. **1683, 1684, 1685, 1687, 1688, 1689, 1690, 1691, 1692, 1694.**

NOBORI, H., AND KAWAI, S. Manufacture of Fatty Acids by the Oxidation of Paraffin. XXIII. Oxidation of High-Melting Paraffins. *See* abs. **1696.**

NOGUCHI, M. *See* abs. **1684, 1685, 1688.**

2480. NOTON, C. H. Synthetic Fuel From Peat. Ind. Chemist, vol. 17, 1941, pp. 304–306; British Chem. Abs., 1942, B, p. 70.

Peat is completely gasified in a Pintsch-Hillebrand plant to yield a synthesis gas with the proper ratio of $CO:H_2=1:2$ at a gas-making efficiency of over 69%. The necessary heat for operating the regenerator (95 B. t. u.) is supplied 45 B. t. u. by the waste gas from the Fischer-Tropsch plant and 50 B. t. u. by burning peat. The cost, with peat at RM7/ton, is RM 0.34 per 1,000 cu. ft. of synthesis gas.

2481. NOVAK, H. [Synthetic Production of Oils and Methyl Alcohol.] Chem. Obzor., vol. 1, 1926, pp. 48–51; Chem. Zentralb., 1927, II, p. 1319.

Processes of F. Fischer, G. Patart, and E. Audibert are described. It is pointed out that, at present prices, the use of MeOH in motors is not practical.

2482. NOVIKOV, I. [Apparatus for High-Temperature Processes Under High Pressures.] Novosti Tekhniki, 1939, No. 30, pp. 36–37; Khim. Referat. Zhur., 1940, No. 6, p. 138; Chem. Abs., vol. 36, 1942, p. 4739.

Experimental plant of the Academy of Science of U. S. S. R. constructed an autoclave for syntheses (NH_3, MeOH, etc.), cracking, hydrogenation, etc. The autoclave consists of a reaction chamber within an electric oven. The pressures on both sides of the walls of the reactor are regulated by passing out the excess gases through valves in the reactor and the oven. With a 500-atm. outside pressure for the reactor, inner working pressures of 800, 1,000, and 1,200 atm., with corresponding working temperatures of 800° 700°, and 600°, respectively, are possible.

2483. NOWOTNY, H., AND JUZA, R. [Cobalt Reduced in Hydrogen.] Ztschr. anorg. Chem., vol. 253, 1945, pp. 109–112; Chem. Abs., vol. 43, 1949, p. 2883.

Possibility that in different preparations of Co by reduction, the Co may have the hexagonal structure or the hexagonal- or cubic-close packing has been confirmed on the basis of energy relationships.

2484. NOYES, A. A., AND SMITH, L. B. Dissociation Pressures of Iron Nitrides. Jour. Am. Chem. Soc., vol. 43, 1921, pp. 475–481; Chem. Abs., vol. 15, 1921, p. 1245.

Equilibrium conditions of the reaction between Fe, NH_3, solid Fe nitrides, and H_2 at 460° are determined. The equilibrium constant given by the expression $(p_{NH_3})^2/((p_{H_2})^3$ was found to vary with the proportion of N present in the solid phase. Thus with increasing N content this expression remained constant at the value 1.0 until the atomic ratio N : Fe became 1 : 9; later increased rapidly, namely, to 5.2 for N : Fe=1 : 7.7 and to 30 for N : Fe=1 : 4.9; and finally assumed the much smaller value 2.1 for N : Fe=1 : 2.6. These results in-

dicate the formation: 1st, of a nitride of small N content, perhaps Fe_8N; then either of a metastable nitride, such as Fe_4N in solid solution with the 1st one, or of 2 separate metastable nitrides, such as Fe_8N and Fe_4N as separate solid phases; and, finally, of a stable nitride, probably the well known Fe_2N. By combining this equilibrium constant with the constant $(pHN_3)^2/pN_2(pH_2)^3$ for the formation of ammonia, the dissociation pressures pN_2 of the nitrides in the various solid phases were computed to be 20,000, 102,000, 590,000, and 41,000 atm., respectively.

2485. NURY, G. Influence of the Disappearance of Antiferromagnetism of Nickel Oxide on the Chemical Activity of This Oxide. Compt. rend., vol. 234, 1952, pp. 946–948; Chem. Abs., vol. 46, 1952, p. 10723.

Amount of reduction of NiO in 2 hr. in H_2 at temperatures 200°–425° shows maximum at 265° and 350° and is essentially zero in the ranges 300°–340° and 355°–400°. The metallic Ni formed is estimated by a magnetic method. The 265° maximum may be related to the dilation anomaly in NiO. The general low rate in the 300°–400° range appears related to the loss of antiferromagnetism of NiO in this range. The sharp maximum at 350° appears related to the Curie point of Ni.

———. *See* abs. **1060, 1061.**

NUSSBAUM, R., Jr., AND FROLICH, P. K. Catalysts for Formation of Alcohol From Carbon Monoxide and Hydrogen. VII. Studies of Reduction of Methanol Catalyst. *See* abs. **1103a.**

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2486. OBERDISSE, K. [Utilization of Synthetic Fats in the Human and Animal Organism.] Ztschr. ges. exptl. Med., vol. 114, 1944, pp. 60–74; Chem. Abs., vol. 44, 1950, p. 2615.

Fatty acids, obtained in the Fischer-Tropsch synthesis, were nearly saturated and contained even and odd numbers of C atoms between C_{10} and C_{20}. In man an average of 6.5%, in dogs 7.9%, of a simple dose of fat was found in the feces; ⅔ of it was in the form of free fatty acids and soaps. The blood-fat level rose to a maximum in men and dogs 3 hr. after feeding. The blood ketone bodies increased 95 and 100% in men and dogs, respectively, the maximum being reached some time after the maximum fat value. The alkali reserve was not affected. The synthetic fats were as well tolerated as the natural ones.

2487. OBERFELL, G. G. Utilization of Natural Gas in the United States. Oil Gas Jour., vol. 44, No. 32, 1945, pp. 76–78; Gas Age, vol. 96, No. 13, 1946, pp. 12–15, 50; vol. 97, No. 1, 1946, pp. 25–29, 58–60; Am. Gas Assoc. Monthly, vol. 28, No. 1, 1946, pp. 7–13, 48; Nat. Petrol. News, Tech. Sec., vol. 38, No. 1, 1946, R, pp. 46–51; Petrol. Refiner, vol. 25, No. 1, 1946, pp. 94–104; Petrol. Eng., vol. 17, No. 4, 1946, pp. 158, 160, 164, 166, 168, 170, 174, 176, 178; Min. and Met., vol. 27, 1946, pp. 165–172.

Paper read before the Chicago section of American Institute of Mining and Metallurgical Engineers. The competitive position of natural gas with respect to coal as a raw material for Fischer-Tropsch type processes in the United States will depend upon the relative economics, efficiencies of utilization, and over-all reserves of coal and natural gas available. It is generally agreed that gasoline from dry natural gas as a starting material is cheaper to produce than the same product from coal as the raw material. For example, with natural gas at $0.05 per 1,000 cu. ft., the cost per bbl. of gasoline produced (10,450 cu. ft. per bbl.) is approximately $0.52. To compare favorably with this, the price of coal per ton would need to be about $0.77 on the basis of 1,360 lb. of coal per bbl. of gasoline. On the other hand, the synthesis process using natural gas will not be able to compete with present refinery methods utilizing crude petroleum until the price of crude reaches about $1.75–$2.00 per bbl. The successful commercial development of the Fischer-Tropsch process should lead to its integration with the natural gasoline industry, with which it is complementary in that it affords an outlet for residual gas and for dry gas without a pipeline market and with the natural gas fuel industry with which it promises to compete. Furthermore, the process is of considerable economic importance to the chemical industry in its application to the synthesis of many chemical products.

2488. ———. Reserves of Natural Gas. Oil Gas Jour., vol. 47, No. 46, 1949, pp. 118, 122, 125, 126, 129, 133, 137.

As of January 1, 1949, the total proved reserves of natural gas in the United States amount to 174 trillion cu. ft. or about a 37-yr. supply based on consumption in 1948. It is expected that further exploration will add materially to this figure and that such additions, plus an everchanging competitive fuel picture, will result in adequate natural-gas supplies for many years to come. The uses and probable development along chemical lines are discussed, and the conversion to liquid fuels by the Fischer-Tropsch synthesis process is reviewed. It is not believed that the peak synthetic-gasoline production from natural gas will ever amount to more than a minor proportion of the total gasoline supply of the Nation, because of the many other profitable markets for natural gas.

2489. OBERFELL, G. G., AND THOMAS, R. W. Picture for Liquefied Petroleum Gases. Oil Gas Jour., vol. 45, No. 5, 1946, pp. 60–61.

Condensed paper presented at the annual meeting of the Liquefied Petroleum Gas Association. A recent development that enters the liquefied-petroleum-gas picture is the so-called Fischer-Tropsch process, which uses natural gas as raw material for the production of heavier hydrocarbons. The production of gasoline and other products by this method may yield sizable quantities of C_4H_{10} and C_3H_8. Therefore, installations of this process for the production of petroleum products are not expected to diminish the overall supply of liquefied petroleum gases.

2490. OBERHOLTZER, J. E. Natural-Gas Industry of Alberta, Canada. Coke and Gas, vol. 11, 1949, pp. 55–58.

Alberta has large reserves of natural gas. The gas is approximately 90% CH_4 and has a heat value of about 1,000 B. t. u. per cu. ft. Available reserves are increasing faster than consumption. The production of synthetic gasoline by the Fischer-Tropsch process is worthy of serious consideration as related to the reserves of both coal and natural gas. The production of a wide range of chemicals and plastics is also a future possibility.

OBLAD, A. G. *See* abs. **2285.**

2491. OBOLENTSEV, R. D. [Research on Isomerization of Liquid Normal Aliphatic Hydrocarbons.] Jour. Gen. Chem. (U. S. S. R.), vol. 16, 1946, pp. 77–93; U. O. P. Co. Survey Foreign Petroleum Literature Transl., 634, 1946.

As one of the starting materials, synthin, which consisted of a mixture of paraffins (63.5 wt. %), olefins (20.6%), and aromatics (15.9%), was used. The catalyst was a fused mixture of $AlCl_3$ with other salts. The synthin was first hydrogenated over Ni to a Br no. of 0–1 and the product freed from aromatics with fuming H_2SO_4 to a negative formolite test. The resulting mixture was fractionated and refractionated in laboratory distillation columns, yielding finally about

10 l. of concentrates containing normal hexane, heptane, and octane. Their content of branched chain hydrocarbons was within 8–12%. Many fractionations of these concentrates gave the normal paraffins desired in 94–97% concentration.

2492. OBRYADCHIKOV, S. N., AND MARUSHKIN, B. K. [Investigation of the Fluid Catalyst Process.] Neftyanoe Khoz., vol. 24, No. 11, 1946, pp. 36–45; Chem. Abs., vol. 41, 1947, p. 3946.

Laws relating to the behavior of finely divided solid particles in conditions simulating the fluid catalyst process were studied on models made of glass, by using fine sand suspended in a stream of water. Data obtained on the particle concentration (in gm./cc.) and the height of the fluidized layer of sand of different sizes, at various water-feed rates, are given in graphs. It is shown that the pressure losses are directly proportional to the weight of the particules in the fluidized layer. In a system with continuous circulation of the catalyst from the bottom towards the top, the concentration of the catalyst at various levels of the reactor can be determined by measuring the pressure gradient at the different levels or, conversely, with uniform concentration of the flowing catalyst in the cylindrical portion of the reactor, the pressure loss is proportional to the height of the layer.

2493. O'CONNOR, B. Silica-Gel Percolation. Ind. Eng. Chem., vol. 40, 1948, pp. 2102–2103; Chem. Abs., vol. 43, 1949, p. 1169.

Discusses use of silica-gel percolation in studying the types of compounds present in the products of the Fischer-Tropsch synthesis. The compounds of similar boiling point are separated according to their adsorption affinity with silica gel, which increases in the order of paraffins, olefins, aromatics, and oxygenated compounds. The differentiation of the 2 latter compounds is improved by using an azo dye.

ODE, W. H. *See* abs. **3159.**

2494. ODELL, W. W. Commercial Possibilities in the Use of Synthetic Hydrocarbon Processes in the Gas Industry. Bureau of Mines Rept. of Investigations 2903, 1928, 15 pp.; Fuel, vol. 8, 1929, pp. 178–187; Chem. Abs., vol. 23, 1929, p. 1245.

Peak requirements demand available gas-generating apparatus, which is idle a large part of the year. To care for irregular demand, as well as to insure independence of petroleum products for enriching, it has been suggested that water-gas and synthetic hydrocarbon production be carried out together to give an enriched gas. During off-peak demand, liquid hydrocarbons could be prepared for motor fuels and for enriching requirements of future peak gas production. Enough data are not available to determine the applicability of this process; purification requirements are uncertain, and the commercial development of the proper type of catalyst has not been studied.

2495. ———. Possibilities in Synthetic Hydrocarbon Processes. Gas Age-Record, vol. 63, 1928, pp. 37–41, 48–50; Chem. Zentralb., 1930, I, p. 1409; Chem. Abs., vol. 23, 1929, p. 4553.

Discusses commercial and economic possibilities of making hydrocarbons synthetically from water gas in some detail. Gives tables of yields and costs.

2496. ———. Re-Forming Natural Gas in Water-Gas Generators, With Substantially Complete Elimination of Entrained Carbon. Bureau of Mines Rept. of Investigations 2973, 1929, 10 pp.; Chem. Abs., vol. 24, 1930, p. 710.

When steam and a hydrocarbon gas are admitted to the incandescent fuel bed of a standard water-gas generator, a re-formed gas is produced, which is comprised chiefly of H_2, CO, and CH_4. When the amount of steam is too low, C resulting from the cracking of the hydrocarbons is entrained in the gas. A higher temperature is required to crack CH_4 than the higher hydrocarbons. The composition of the re-formed gas can be controlled, and the specific gravity and heating value can be adjusted as necessary. Increased air blasting (increased temperatures) decreases CH_4 content and increases H_2. The low limit is about 10% CH_4 and 60% H_2, giving a gas of 350 B. t. u. heating value. Relative amounts of steam and hydrocarbon influence the H_2 : CO ratio. The low limit is substantially the same as that for water gas, 1.2 : 1; the upper limit without entrained C is about 3 : 1. Less heat is required for the generation of a unit vol. of reformed gas than straight water gas; hence less generator fuel is used. Gasmaking capacity is increased materially by a blow run. Gives operating data.

2497. ———. Re-Forming Natural Gas. Bureau of Mines Tech. Paper 483, 1930, 54 pp.; Chem. Abs., vol. 25, 1931, p. 1058.

When the ignited fuel bed of a water-gas generator is blasted alternately with air and both steam and natural gas in controlled proportions, re-formed gas is produced substantially without entrained C, the gas consisting of CO, H_2, and lesser CH_4. The thermal efficiency and gasmaking capacity are higher in generating re-formed gas in this manner than in making water gas, and the fuel used per 1,000 cu. ft. of reformed gas is lower. Gives operating data and factors influencing results.

2498. ———. Gasification of Solid Fuels in Germany by the Lurgi, Winkler, and Leuna Slagging-Type Gas-Producer Processes. Bureau of Mines Inf. Circ. 7415, 1947, 46 pp.; PB 97,778.

Each of the 3 processes uses O_2 and steam, and the Winkler fluidized and the Lurgi pressure processes use finely divided, highly reactive fuel, whereas the slagging-type process uses sized furnace coke. It is believed that the Winkler process as now developed and the Lurgi process with some improvement or in a modified form may be used effectively under certain conditions and with particular fuels in the United States. This is especially true with low-cost fuel and O_2. Operating data relative to the 3 processes are presented in tabulated and summarized form. Some analysis of O_2 cost is given, and some data on the manufacture of city gas in conjunction with the production of synthetic liquid hydrocarbons are appended.

OELSEN, W. *See* abs. **1965.**

2499. OEL UND KOHLE. French Efforts at Self-Sufficiency in the Provision of Motor Fuels. Vol. 14, 1938, pp. 587–588.

Production of liquid fuel by coal hydrogenation and the Fischer-Tropsch processes and the use of gas producers using charcoal on vehicles.

2500. OFFENBERG, W. [Gasification of Solid Fuels With Oxygen Under Pressure.] Stahl u. Eisen, vol. 63, 1943, pp. 936–939; British Abs., 1946, B, I, p. 123.

Solid, noncaking fuel (brown coal, lean bituminous coal, gas coke) in a 2–25 mm. size is gasified in a refractory-lined, water-jacketed reaction vessel by a mixture of superheated steam and O_2 at 20–30 atm. The gas after cooling is washed with oil and then with H_2O, which removes most of the CO_2 and H_2S. Residual H_2S is removed by Fe_2O_3, and the purified gas is delivered at 20–25 atm. to high-pressure mains. The gas has a gross calorific value of 4,000–4,500 kcal. per $m.^3$, depending on the reactivity of the solid fuel. That from a brown coal contained CO_2, 3.0; C_nH_m, 0.5; O_2, 0.1; CO, 22.8; H_2, 48.7; CH_4, 22.6; N_2, etc., 2.3%; the total S was 0.1 gm. per 100 $m.^3$, and NO was 0.052 cc. per $m.^3$ The consumption of O_2 is approximately 0.18 $m.^3$ and that of steam 1.25 kg. per $m.^3$ of purified gas. Production cost is competitive with that of other gasification processes.

OGARKOV, N. P. *See* abs. **2754.**

2500a. OGAWA, E., AND MURATA, K. Catalytic Action of Nickel-Iron-Cobalt Wire Under Tension on the Reaction Between Ethylene and Hydrogen. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, pp. 386–387 (in English); Chem. Abs., vol. 44, 1950, p. 7,636.

Activation energy of the $H_2+C_2H_4$ reaction is raised from 16,400 to 17,800 cal. by placing under tension Ni–Fe–Co alloy wire used as a catalyst. The difference is caused by the orientation of the magnetic axis of each magnetic domain from its random distribution.

2501. OGAWA, E., TADA, M., AND OKUNA, T. Studies of Catalytic Action by Conversion Between Para-Hydrogen and Ortho-Hydrogen. I. (a) Conversion by Magnetized Nickel Wire. (b) Conversion by Catalyst for Ammonia Synthesis. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, pp. 387–389; Chem. Abs., vol. 44, 1950, p. 7637.

At 73°, the activation energy of the *o–p*-H_2 conversion over Ni was 3,000 cal. for unmagnetized catalyst and 6,000 for magnetized catalyst. At 112° the effect of magnetization disappeared, indicating that the conversion changes from a magnetic to activated adsorption mechanism. The same change of mechanism exists in NH_3 synthesis.

OGAWA, S. *See* abs. **2299.**

OGAWA, T. *See* abs. **1754a, 3176.**

OGAWA, T., KIMUMAKI, J., AND FUJISAKI, T. Iron Catalyst for Synthetic Petroleum. II. Some Characteristic Properties of Iron Catalyst for Synthetic Petroleum. *See* abs. **3177.**

2502. OGAWA, T., MATUI, A., AND SENOO, H. Oxidation of Methane. I. Reaction Between Methane and Ferric Oxide. Jour. Soc. Chem. Ind. (Japan), vol. 41 1938, suppl. pp. 399–400; Chem. Abs., vol. 33, 1939, p. 3327.

Gases produced by the reaction at 900°, 1,000°, and 1,100° of 200 gm. powdered Fe_2O_3 in a porcelain tube, 2.6 cm. in diameter, heated by an electric furnace and CH_4 introduced at the rate of 2 l. per hr. were analyzed at intervals for CH_4, CO, CO_2, and H_2, and the results were plotted. At first the reaction yielded CO_2 and H_2O, then chiefly CO and H_2 at a constant ratio of approximately 1:2 for several hr., and finally the concentration of H_2 increased owing to the reaction $CH_4=C+2H_2$. At 1,100° after 2.5 hr., the product consisted of about 21% CO and 40% H_2. The catalyst was regenerated with a limited amount of atmospheric O_2 in a separate vessel. Conclusion: The catalyst is suitable for the synthesis of $(CO+2H_2)$.

2503. ———. Oxidation of Methane. II. Reaction Between Methane and Bog Iron Ore. Jour. Soc. Chem. Ind., (Japan), vol. 41, 1938, suppl., p. 400; Chem. Abs., vol. 33, 1939, p. 3327.

Bog iron ore (I) (61.5% Fe_2O_3, 21.1% SiO_2, and 2.9% MnO_2) and regenerated (I) were substituted for the Fe_2O_3 in the tests made at 1,100°. At the end of 2.5 hr., about 20% CO and 45% H_2 were present in the products when (I) was used. When a 200-gm. portion of (I) was completely reduced to metallic Fe (+impurities) and regenerated with a limited amount of O_2 (4.2–4.5 liters), less than 5% each of CH_4 and CO_2 was produced from the start, and the production of CO and H_2 was fairly constant at 22–24% CO and 58–60% H_2.

2504. OGAWA, T., MATUI, A., NAGAI, H., AND HIDETAKA, S. Oxidation of Methane. III. Experiment on the Apparatus Heated by Internal Combustion. Jour. Soc. Chem. Ind. (Japan), vol. 43, 1940. suppl., pp. 116–117; Chem. Abs., vol. 34, 1940, p. 5627.

Mixtures containing CO and H_2 in ratio of approximately 1:2 were prepared by alternately passing, at a rate of 3 $m.^3$ per hr., CH_4–air mixtures, which burn to produce a temperature of 1,380°, and CH_4, which absorbs heat on cracking and lowers the temperature to 1,220°, through a Ni–Cr alloy tube containing a Ni catalyst (exact composition not given) and ignited Fe balls made of equal amounts of Fe_2O_3 and MgO. The exit gas from a typical run had the following composition: CO_2, 3.5; O_2, 0.9; CO, 21.8; H_2, 56.5; CH_4, 16.3; and N_2, 1.0%. The mount of conversion was increased by putting Ni–kaolin balls above the Fe balls in the tube. In a typical run with this latter arrangement, the exit gas contained CO_2, 8.7; O_2, 0.9; CO, 27.4; H_2, 56.7; CH_4, 3.6; and N_2, 2.7%. Gives diagram of the apparatus and tabulates results. It is stated that the process could be used industrially.

OGDEN, G. *See* abs. **3341.**

2504a. OGURA, T. Decomposition of Methane by Oxidation. Bull. Chem. Soc. Japan, vol. 16, 1941, pp. 303–324, 356–367; Chem. Abs., vol. 41, 1947, p. 4,435.

Reaction between CH_4 and steam was carried out in the presence of a Ni catalyst under various conditions. The influence of amount of steam, temperature, and pressure of the reaction mixture on the decomposition rate of CH_4 were studied. The decomposition of CH_4 containing O_2, CO_2, or CO was carried out in the presence of oxides of metals, Ni, Co, Cu, Fe, and Cr. The influences of amount of mixing gases, reaction temperature, and pressure on the decomposition rate of CH_4 were studied.

2505. ———. [Oxidative Decomposition of Methane.] Bull. Chem. Soc. Japan, vol. 16, 1941, pp. 262–273 (in German); Chem. Abs., vol. 36, 1942, p. 3777.

55 references are listed for the oxidation or partial oxidation of CH_4 to (1) H_2O, CO_2, or CO; (2) H_2, CO_2, or CO; and (3) MeOH, CH_2O, HCO_2H, AcOH, acetone, and other substances. Equilibrium data were calculated for the reaction of CH_4 with (1) steam, (2) O_2, and (3) CO_2.

———. *See* abs. **1651.**

2506. OGURA, T., AND HUZIMURA, T. Reaction Between Methane and Steam. Jour. Chem. Soc. Japan, vol. 60, 1939, pp. 139–148; Chem. Abs., vol. 34, 1940, p. 2569.

Reaction $CH_4+2H_2O=CO_2+4H_2-38.5$ cal. was studied with natural gas containing CH_4, 95.2; C_2H_6, 1.9; CO_2, 1.6; C_nH_m, 0.3; air, 1.0%. For this reaction a catalyst is necessary. With an effective catalyst the reaction is completed at 550°–600°. $H_2O:CH_4=7:10$ is the best ratio. Ni is the best catalyst: However, if it is used alone its catalytic activity decreases at higher temperature, 700°, owing to its melting. Addition of a promotor prevents this inactivation. With Al_2O_3 as promotor, $Ni:Al_2O_3=1:0.025$ in mols. gives the greatest activity. Addition of a minute amount of alkali does not affect the catalytic activity but decreases the durability of the catalyst. Concentration of the catalyst 10%, particle size 3–4 mm., contact period of 25–30 sec. are recommended. Temperatures below 700° for the roasting and below 300° for the reduction give the best catalyst. A Ni–Al_2O_3–kaolin catalyst prepared according to these observations gave good results in an experiment lasting 150 hr.

2507. OGURA, T., AND ICHIMARU, T. Reaction of Methane and Oxygen. Jour. Soc. Chem. Ind. (Japan), vol. 47, 1944, pp. 540–543; Chem. Abs., vol. 42, 1948, p. 6082.

For the purpose of obtaining a mixture of CO and H_2, CH_4 was oxidized under various conditions. When no catalyst was used, CH_4 and O_2 did not react below 600°. As catalyst, Co was the most effective and Ni was the next. With Co as catalyst, the reaction takes place even below 300° when more than 2 times the volume of O_2 is added to CH_4, producing CO_2 and H_2O. When an equivalent amount of CH_4 and O_2 is taken, CO_2 and H_2O are produced, and a part of the CH_4

remains below 800°, while above 800°, all CH_4 is changed to CO and H_2. Admixture of N_2 retards the reaction, and admixture of H_2O promotes it. When mixtures of CH_4 and O_2 were exploded, the product was variously CO_2, CO, H_2O, and H_2, according to the ratio at which CH_4 and O_2 were taken. A semi-industrial experiment showed that preparation of a mixture of CO and H_2 by suitably oxidizing natural gas is successful.

2508. OGURA, T., AND NAGAI, H. Reaction Between Methane and Carbon Dioxide. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 170–173; Chem. Abs., vol. 43, 1949, p. 1944.

Reaction of CH_4 and CO_2 in various proportions at 500°–1,200° under ordinary pressure in the presence of Co or Ni catalysts was studied on experimental and semi-industrial scales for the purpose of finding the best conditions for obtaining good yields of CO and H_2 with natural gas and some industrial waste gases as raw materials. The reaction was accelerated by using good catalysts and by raising the temperature. When there was not enough CO_2, deposition of C was noticed. This was prevented by adding steam to the mixed gas.

2509. ÖHMAN, E. Crystal Structure of Martensite. Nature, vol. 127, 1931, pp. 270–272; Chem. Abs., vol. 25, 1931, p. 2400.

Present knowledge of tetragonal martensite is summarized, and results of earlier investigators are reviewed with reference to C content and lattice dimensions. The author employed Cr–K–radiation and obtained photograms of quenched steel specimens in which the line (101) of the tetragonal phase is separated from the γ–Fe line (111). Thus, it was possible to determine the lattice dimensions of the tetragonal structure. Results agree with those of Kurdumoff and Kaminsky that the tetragonal martensite is a supersaturated solution of C in α–Fe. Ferrite and tetragonal martensite are thus one and the same phase, but, as they are often present in one and the same specimen as separate constitutents, it seems convenient to denote the tetragonal phase as α′. Westgren and Phragmen suggested that the C atoms dissolved in γ–Fe do not occupy any points of the face-centered lattice but are statistically distributed in the interstices between the Fe atoms. Seljakow, Kurdumoff, and Goodtzow suggested that the same might be the case in the α′–phase but the author thinks this improbable as the space available for the C atoms would be extremely small. Another probable explanation is that there is a complex substitution in such a way that a group of 2 C atoms is substituted for 1 Fe atom in the lattice. These compounds have a tetragonal structure in which the C_2 group is oriented parallel to the tetragonal axis, an explanation that holds equally well for tetragonal martensite. By density measurements, it is shown that the assumption of a complex substitution of C atoms is in good agreement with X-ray intensities. The only suggested structure of tetragonal martensite that explains the observed density, the increase of volume with the C content, and the elongation of 1 of the crystallographic axes may be described as follows: In the body-centered lattice groups of 2 C atoms statically distributed replace some of the Fe atoms. The C atoms are most probably oriented in such a way that the axes of the C_2 groups parallel the tetragonal axis of the lattice.

2510. ———. X-Ray Investigation on the Crystal Structure of Hardened Steel. Jour. Iron Steel Inst. (London), vol. 123, 1931, p. 445; Chem. Abs., vol. 25, 1931, p. 4502.

X-ray study of quenched steels confirmed the existence of the tetragonal phase, the axial ratio of which increased with increasing C content. From a consideration of these data it is concluded that martensite consists of a solid solution of C in body-centered Fe. On effective quenching, the tetragonal phase has the same composition as the parent austenite, as proved by the direct relationship between C content and space-lattice dimensions. It appears probable that the C atoms disolved in α-Fe form a complex substitutional group in which 2 C atoms replace 1 Fe atom. On tempering, the tetragonal phase decomposes continuously with a progressive decrease in axial ratio. The causes of the hardness of martensite are discussed. 47 refs.

2511. ———. [Carbides in the Iron–Manganese–Carbon System.] Jernkontorets Ann., vol. 128, 1944, pp. 13–16; Chem. Abs., vol. 39, 1945, p. 3198.

X-ray study made in 1926 of the carbides *present* in the above system revealed a hitherto unknown double carbide of Mn and Fe, which has a monoclinic crystal structure. By solution of C in molten Mn, carbides are produced, which, according to X-ray powder photographs, are isomorphous with the Cr carbides $Cr_{23}C_6$ and Cr_7C_3. As the powder photographs are in exact agreement with those obtained for the above Cr carbides, the Mn carbides probably have the formula $Mn_{23}C_6$ and Mn_7C_3. The latter has been observed only in alloys with more than 80% Mn, whereas $Mn_{23}C_6$ is found with up to 50% Fe and less than 6% C present. With more than 50% Fe cementite is the only carbide formed. Both cementite and $Mn_{23}C_6$ are present even when the Mn content is up to 70%. Mn can replace Fe in cementite to a considerable extent.

2512. OHME, W. [Neutralization of Fatty Acids Formed in Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Oel u. Kohle Erdoel Teer, vol. 38, 1942, pp. 465–467; Chem. Abs., vol. 37, 1943, p. 5569.

Acids cannot be completely neutralized by aqueous $NaHCO_3$ unless they are in contact with the latter for very long periods. The aqueous Na_2CO_3 used in practice for neutralization is converted, to a large extent, into $NaHCO_3$ at the prevailing temperature and pressure owing to the high CO_2 content of the synthesis end gases. When the CO_2 content of the latter is high, special neutralization processes are necessary.

2513. ———. Conversion of Fat Acids From the Fischer-Tropsch Synthesis to Ketones. Oel u. Kohle Erdoel Teer, vol. 40, 1944, pp. 87–89; Ind. Chemist, vol. 21, 1945, pp. 270–274; Chem. Abs., vol. 39, 1945, p. 277.

Fat acids formed as byproducts in the Fischer-Tropsch synthesis were obtained by extracting certain hydrocarbon fractions with caustic and acidifying the solution. Part of the fat acids was distilled at 0.5 mm. Hg and another part was directly converted into the Ca salts by reaction with an excess of lime. The Ca salts were subjected to dry distillation at 350°–650°, and the ketones formed were distilled at atmospheric pressure and redistilled under vacuum. The bulk of the ketones boiled 240°–300°, and the melting point varied from −10° to +30°; it is assumed that mixed ketones with 12–17 C atoms have been formed. The fractions obtained by distillation of the original fat acids represent C_5, C_6, C_{10}, C_{11}, C_{12}, C_{15}, and C_{18} fat acids. Each fraction was individually converted into the corresponding ketones at temperatures ranging 280°–600°, and the average yield amounted to 70–80%. The ketones were not uniform, as indicated by their rather wide boiling range (50°–70°). The melting point of the ketones increases with the number of C atoms from −50° to −62° for C_5 ketones, over −10° to +20° for the C_{11} ketones, and to 32°–44° for the C_{15} ketones. The ketones are partly liquids of agreeable odor and partly waxlike substances; they might find use as plasticizers and in the perfume industry.

2514. OHTSUKA, H., AND TOMITA, N. Analysis of Synthetic Gasoline Obtained by Fischer Process. Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, pp. 746–747; Chem. Abs., vol. 42, 1948, p. 2080.

If the material is found by hydrogenation to contain no aromatic hydrocarbons, the following short procedure of the analysis gives a result accurate enough. Fractionate the sample into 4 portions: (A) boiling up to 65°, (B) 65°–105°, (C) 105°–140°, (D) 140° to dry point. Wash each fraction with 2 vol. 87% H_2SO_4, and in fractions (A) and (B) consider the loss as unsaturated hydrocarbons and the remainder as saturated. In fractions (C) and (D), wash the remaining portion with 3 vol. 99% H_2SO_4, and consider the final remainder as saturated hydrocarbons, and the balance as unsaturated.

2515. OIL AND GAS JOURNAL. Chicago Corporation to Build Carthage Field Plant. Vol. 43, No. 39, February 3, 1945, p. 79.

Chicago Corp., Corpus Christi, will construct a cycling plant in the Carthage gas field, East Texas, capable of processing 150,000,000 cu. ft./day. Preliminary plans have been discussed with PAW officials for installing a Fischer-Tropsch plant, which would mark the 1st commercial installation of this type for synthetic production of liquid petroleum products from natural gas.

2516. ———. Fischer-Tropsch Hydrocarbon Synthesis. Vol. 43, No. 47, 1945, p. 214.

This process involves the catalytic conversion of water gas or natural gas into hydrocarbons. Synthesis gas is obtained thus:

$$(1)\ C+H_2O=CO+H_2,$$

$$(2)\ CH_4+H_2O=CO+3H_2.$$

If the latter mixture is reacted in this proportion, the tendency is to form CH_4 and lower molecular weight hydrocarbons. Lower % of H_2 and higher temperatures form mainly CH_4, especially with Ni as catalyst. Fe catalysts show the best results in synthesizing high-octane number products; it produces more isoparaffinic and olefinic products than do either Co or Ni; a sintered Fe catalyst is reported as the most efficient so far developed in this country. The mixture of charge gases for reaction with Fe catalysts should be richer in CO, probably more nearly a 1:1 ratio. Ni catalyst tends to form highly saturated, low molecular-weight hydrocarbons; Co also produces saturated hydrocarbons but generally of higher molecular weight!; Ru produces paraffins of extremely high molecular weight up to 23,000. Lubricating oils are made by polymerizing olefins formed in the synthesis with Fe or other olefin-forming catalyst, as with $AlCl_3$. Flow sheet.

2517. ———. High-Octane Motor Fuel From Natural Gas. Vol. 43, No. 36, 1945, pp. 48–49.

Development is announced of the Fischer-Tropsch process, which makes possible the production of gasoline from natural gas with a yield of 80% and an octane No. of 75 motor (83 research) for about $0.05 per gal., based on natural gas at $0.05 per 1,000 $ft.^3$ and a plant depreciation of 10%. The new method is said to overcome successfully the problem of heat dissipation and accurate temperature control. Prewar European yields by the then existing methods were 30–40% of approximately 25 octane No. gasoline. The Kellogg Co. is prepared to build hydrocarbon synthesis plants using the process. Recently sintered Fe catalysts have been introduced, resulting in a product of a mixture of varying molecular weight hydrocarbons in which isoparaffins and even naphthenic and aromatic mixtures are the main constituents instead of the predominant normal paraffins formed with the Co and Ni catalysts.

2518. ———. Alberta Company Plans Gas-Synthesis Plant. Vol. 45, No. 5, 1946, p. 62.

Calgary Oil Co. is reported to be erecting a $100,000 pilot plant for making gasoline from natural gas, using a process said to be entirely original with the developing company. The plant will have a capacity of 2,000,000 cu. ft. gas per day, producing about 5 gal. of gasoline per 1,000 cu. ft. It is expected to be in operation by fall according to the United States Bureau of Foreign and Domestic Commerce.

2519. ———. Natural-Gas Investigation by the Federal Power Commission, Washington. Vol. 45, No. 8, 1946, pp. 60–61.

Abstract of testimony by P. C. Keith, president of Hydrocarbon Research, Inc., on the development of processes for making gasoline from natural gas and for gasifying and liquefying coal. (*See* abs. **1718.**) Fuel reserves as of January 1, 1946, if converted into crude oil, would make a total of 6,326 billion bbl., divided; 21 billion bbl. from crude, 25 billion bbl. from natural gas, and 6,280 billion bbl. from coal synthesis. It is predicted that commercial production of gasoline from natural gas and from coal will take place within 5 yr. Experiments had been made in the production of city gas from coal, and a gas had been obtained of 600–900 B. t. u. at a cost of $0.17 per 1,000 cu. ft. It is estimated that gas could be produced at West Virginia coal mines and transported to New York for $0.242 per 1,000 cu. ft. By this process, 10,000 tons of coal would produce about 200,000,000 cu. ft. of gas. It is also stated that gasoline can be made from coal for $0.06 per gal., assuming the cost of coal at $2.00 per ton. The time will probably come in the not-too-distant future when this price will be competitive with petroleum and natural gas.

2520. ———. Stanolind Synthol Plant Now in Engineering Stage. Vol. 45, No. 37, 1947, p. 97; Petrol. Eng., vol. 18, No. 4, 1947, p. 24; Chem. and Eng. News, vol. 25, 1947, p. 240; Petrol Refiner, vol. 26, No. 2, 1947, pp. 168–169.

Stanolind Oil & Gas Co. reports that engineering work is now under way on the proposed commercial-scale Synthol plant to be built in the Hugoton gas field in Southwestern Kansas. It is expected to obtain a yield of 2.52 gal. of high-quality gasoline and 0.42 gal. of distillate fuels from each 1,000 cu. ft. of natural gas processed. The plant is being designed to process about 100,000,000 cu. ft. per day of low-heating-value gas currently unsuitable for sale as fuel. In the proposed process, feed gas is burned under a pressure of 300 p. s. i. with relatively pure O_2 to yield synthesis gas of closely controlled composition. A yield is estimated of 1 bbl. of crude synthetic oil and substantial amounts of oxygenated compounds from each 15,000 cu. ft. of gas charged to the plant. The synthesis is carried out under pressure in large fluid type reactors utilizing a special powdered–Fe catalyst.

2521. ———. Stanolind's Synthol Plant to be in Operation in 1949. Vol. 46, No. 2, 1947, p. 54.

According to J. H. Forrester, manager of manufacturing for Stanolind, the proposed synthol plant of Stanolind Oil & Gas Co., Kans., will be producing gasoline from natural gas on a commercial scale in 1949. The new plant will produce 5,300 bbl. of gasoline, 800 of fuel oil, and 1,060 of light hydrocarbons, and about 500,000 lb. of chemicals per day. J. E. Latta of the Tulsa laboratories said that the oxygenated compounds formed as byproducts will be useful in various fields as solvents, antifreeze preparations, and raw materials for the manufacture of fine chemicals. Included are alcohols, ketones, organic acids, and aldehydes.

2522. ———. Survey of Sites for Synthetic Fuels Plants. Vol. 47, No. 9, 1948, pp. 42–43.

Nation-wide survey of possible sites for erecting synthetic liquid-fuels plants was begun recently with award by the Army's Engineer Corps of a contract to the firm of Ford, Bacon & Davis, Inc., to make sample studies in western Kentucky, northwestern Colorado, and southeastern Texas. These areas were selected because they have large known supplies of coal, oil shale, and natural gas. The study will be completed in 4–6 mo., and may be continued in other areas of the country where the basic raw materials are known to exist. The survey is not intended to designate specific sites for plants or determine the total coal, natural-gas, and oil-shale reserves of the United States, but merely to determine general areas where the requirements for 1 or more plants can be met.

2523. ———. Future of German Synthetics Industry. Vol. 47, No. 51, 1949, p. 122.

United States, British, and French military governors have agreed on the security limitations to be imposed upon West German industry. The production of synthetic rubber and butadiene is prohibited, and all facilities for producing butadiene at the Hüls, Ludwigshafen, and Leverkusen plants are to be removed or destroyed. The production of styrene is limited to 20,000 tons per year. The production of petroleum, oil, and lubricants directly or indirectly from coal or brown coal by the Bergius hydrogenation process, the Fischer-Tropsch synthesis, or analogous processes also is prohibited except, temporarily, to the extent inseparable from the production of hydrocarbon waxes for the manufacture of synthetic fatty acids for the production of detergents. Production of synthetic waxes is to cease by December 31, 1949, and the 2 Fischer-Tropsch plants engaged in this are to be removed or destroyed at that time. All other Fischer-Tropsch plants are to be removed or destroyed immediately, as are all Bergius plants except that at Wesseling, which is to be retained for refining natural petroleum, for hydrogenating heavy residues from such refining, and for the synthesis of NH_3 and MeOH.

2524. ———. Company Formed in South Africa to Make Petrol From Coal. Vol. 49, No. 26, 1950, p. 46.

South African Coal, Oil & Gas Corp. has been formed in Pretoria to synthesize liquid petroleum products from coal. Erection of the plant, including O_2 manufacture, gasification, synthesis, oil-treatment units, boiler houses, and other units, will be thrown open to private contractors' bids. The Government has guaranteed up to £13,000,000 ($36,400,000). More than £20,000,000 is expected to be needed. The coal to be used is that from the Vredefort district. Production from the plant is not likely for 3 yr.; initial output will include about 1,000,000 bbl. of gasoline per yr.

2525. ———. Refinery to Be Rebuilt. Vol. 49, No. 48, 1951, p. 69.

Reconstruction and expansion into a modern refinery of the war-damaged facilities of Ruhrchemie A.-G. at Oberhausen-Holten has been approved. The new plant will be built around existing distillation and cracking units, and a reformer will be added for improving motor-fuel quality. The completed plant will be able to process about 5,000 bbl. per day, with a cracking capacity of about 2,000 bbl. Koch Engineering Co. of Wichita, Kans., is to build the cracking plant. Another project is the new plant of about 2,000 bbl. per day capacity to be erected at Muelheim on Ruhr by Ruhrbau, G. m. b. H., a company jointly organized by Braunkohle Benzin A.-G. and the Stinnes group. Parts of a shut-down shale-oil retorting plant at Balingen in Wuerttemberg will be used. It is planned to add possibly another 2,000 bbl. per day capacity, as well as cracking units.

2526. ———. Synthesis Plant in Africa. Vol. 49, No. 48, 1951, pp. 70–71.

Construction of the coal-to-oil gasoline-synthesis plant recently announced by the South African Coal, Oil & Gas Corp. Ltd., will be started soon by the M. W. Kellogg Co. The plant will be adjacent to the Vaal River, near Coalbrook in the Orange Free State, about 40 miles south of Johannesburg. The project is an integrated plant, which embraces the opening of virgin coal deposits, construction of aboveground gasification facilities to transform coal to synthesis gas, and the complete synthesis plant to produce liquid hydrocarbons. Kellogg's Synthol process will be utilized. It has been thoroughly developed and tested in the company pilot plant. The Coalbrook coal to be used as the raw material occurs at an average depth of 400 ft., with seams ranging in thickness from 10–20 ft. It is mined at a pithead cost equivalent to less than $1.00 per ton. Operations will be adjusted to produce maximum gasoline and diesel oil rather than chemicals.

OJI, G. *See* abs. **1897, 1898, 1899.**

OKAMURA, T., AND OGAWA, S. Magnetic Behavior of Magnetite at Low Temperatures. II. *See* abs. **2299.**

OKETANI, S. *See* abs. **3439, 3440, 3440a.**

OKUNA, T. *See* abs. **2501.**

2527. OLMER, F. [Reduction of Iron Oxides by Carbon Monoxide in the Presence of Certain Natural Impurities.] Compt. rend., vol. 206, 1938, pp. 353–355; Chem. Abs., vol. 32, 1938, p. 2447.

Although CO is unstable at 20°–1,000°, the velocity of the reaction $2CO=CO_2+C$ is very small in the absence of a catalyst. In the presence of Fe_2O_3 above 350°, it occurs rapidly either alone or accompanied by reduction of the Fe_2O_3, the velocity being proportional to the mass of the catalyst. Fe alone acts similarly. Similar experiments with Fe_2O_3, containing a phosphate or aluminate show that P_2O_5 and Al_2O_3 hinder the catalytic action of the Fe (or Fe_2O_3).

2528. ———. [Reduction of Iron Oxides in the Presence of Foreign Substances.] Rev. mét., vol. 38, 1941, pp. 129–134; Chem. Abs., vol. 36, 1942, p. 6931.

Reduction of Fe compounds was studied by photographically recording pressure drop of a constant volume of a reducing gas, after adsorption of H_2O and CO_2 formed during the reaction. The powdered sample was reduced in a fused SiO_2 chamber in a resistance furnace, regulated by an auxiliary nichrome-wound furnace. Reduction of Fe_2O_3 with H_2 begins around 325° and continues until pure Fe is formed, without intermediate formation of FeO. For an oxide simply dried at 300°, reduction begins at 240°; for an oxide that has been calcined at 1,300°, at least 400° is required. In the first case, Fe_3O_4 is formed at 300°; in the second, no Fe_3O_4 is formed. The decomposition of CO in the presence of different Fe compounds was studied to determine catalytic reactions, if any. No decomposition takes place with CO lower than 45%. For greater CO concentrations than 55%, catalysis is very pronounced. Fe_2O_3, Fe_3O_4, and cementite have no catalytic effect on the decomposition of CO. No FeO is produecd by CO reduction. Catalysis of CO decomposition with about 20 metals and oxides was studied. Cu, Pb, Zn, and Sn oxides are reduced quantitatively; oxides of W and Mo only partly even at 1,000°; Al_2O_3 and Cr_2O_3 are unaffected. Only oxides of Fe, Co, and Ni show a pronounced drop in gas pressure and a heavy C deposit; only these are decomposition catalysts. Experiments were conducted to show the relation between catalytic properties and magnetism of metals. The catalytic effect is believed to be connected with surface absorption, which depends on the radius of curvature of catalyst particles. The velocity of catalysis by Fe increases up to 580°. It appears that the reduced Fe is in a state of very fine division, and, at 580° these particles agglomerate; this increases the radius of curva-

ture. Dilution of the powdered Fe with an inert substance prevents agglomeration and preserves catalytic activity independently of temperature.

2529. ———. Decomposition of Carbon Monoxide by Ferromagnetic Metals. Jour. Phys. Chem., vol. 46, 1942, pp. 405–414; Chem. Abs., vol. 36, 1942, p. 3092.

Catalytic decomposition of CO at temperatures below 1,000° is limited to Fe, Ni, and Co, though there is no apparent relation between catalytic activity and magnetic properties. The activity is due to the metals, and not to their compounds, since there is no decomposition outside of the range at which the metallic phase exists. The activity curve for the pure metal passes through a maximum at 580°–590°, owing to agglomeration of the particles of the catalyst, thereby reducing their effective surface. At higher temperatures the speed of reatcion rises again and then drops toward zero as the temperature is approached at which CO is stable. If the catalyst is mixed with an inert substance that will prevent agglomeration, there is no loss in activity beyond 590°.

2530. ———. Reduction of Fe_2O_3 by Hydrogen. Jour. Phys. Chem., vol. 47, 1943, pp. 317–325; Chem. Abs., vol. 37, 1943, p. 6184.

Kinetic method developed by Olmer (abs. **2528**) is applied.

2530a. ONDA, K. Effect of an Electric Field on the Synthesis of Hydrocarbons. I. Effect of Volta e. II. Effect of Various Reaction Temperatures. Jour. Soc. Chem. Ind. (Japan), vol. 47, 1944, pp. 641–643, 643–644; Chem. Abs., vol. 46, 1952, p. 7,032.

I. Synthesis was performed with a Co–kieselguhr catalyst. The mean molecular weight of the oil obtained increased with increasing voltage. The I value was independent of the voltage up to 6,000 volts but decreased at 8,000 volts. HCHO formation increased with increasing voltage. The ratio of CO reacted to that of H_2 increases with increasing voltage. II. The mean molecular weight decreased with rising temperature. The I value of the oil was independent of the temperature. HCHO formation increased with temperature.

O'NEILL, W. E. *See* abs. **44.**

OPITZ, W. *See* abs. **1991.**

ORCHIN, M. *See* abs. **888, 3122, 3275a, 3650, 3651, 3652, 3653, 3654, 3655, 3655a, 3655b, 3656, 3656a, 3656b, 3656c.**

2530b. ORCHIN, M., AND SCHROEDER, W. C. Hydroformylation. Unit Processes in Organic Synthesis, by P. H. Groggins. McGraw-Hill Book Co., New York, 4th ed., 1952, chap. IX, pp. 555–595.

Review.

2531. ORIEL, J. A. Report on Visit to Oil Targets in the Ruhr and Hanover Areas. Nat. Petrol. News, vol. 37, 1945, R, pp. 926, 928, 930; TIIC Rept. 3; CIOS Rept. XXIII–16, 1945, 23 pp; TOM Reel 198; PB 282.

Plant to use the Oxo process was virtually completed at the Fischer-Tropsch installation at Holten when the war ended. This plant was to treat C_{12}–C_{17} olefins, converting them first to aldehydes by passing them, together with S-free water containing 39 parts of CO to 45 parts of H_2 over the ordinary Fischer-Tropsch catalyst, the temperature in the 1st stage being 135° and the pressure 150 atm., the temperatures being controlled by means of steam pressure. The process was intermittent, each cycle taking 20 min. The Fischer-Tropsch catalyst consisted of 100 parts Co; 5, Th; 8, Mg; and 180–200, kieselguhr. A suggested Fe catalyst was to consist of 100 parts Fe; 2.5–4, Cu; 10, lime; and 15, Kieselguhr; it was made from nitrates by precipitation with CO_2. The aldehydes after distillation were then passed together with pure H_2 over a Ni catalyst to convert them into alcohols. The temperature was 180° and the pressure the same as for the 1st reaction. The alcohols were to be used for making sulfonic soaps. The development work included the dehydrogenation of C_{16}–C_{18} cuts from Fischer-Tropsch operations to olefins for use in the Oxo process. The catalyst in this case was ThO_2 and Cr_2O_3. Describes method of preparing this catalyst.

2532. ORLOV, G. [Preparation of Ethylene From Carbon Monoxide and Hydrogen.] Ber. deut. chem. Gesell., vol. 42, 1909, pp. 893–895; Jour. Russian Phys.-Chem. Soc., vol. 40, 1908, pp. 1588–1590; Chem. Zentralb., 1909, I, p. 735; Chem. Abs., vol. 3, 1909, p. 1400.

Coke, in pieces the size of hazelnuts, was soaked in $Ni(NO_3)_2$, dried, and ignited. It was then treated in the same manner with $PdCl_2$ and was finally reduced in a Cu tube by means of MeOH vapor. When a mixture of H_2 and CO is placed over the prepared coke at 95°–100°, the issuing gas consists of CO, $H_2C_2H_4$, and air; CH_4 is not formed. When CO_2 is substituted for CO, neither C_2H_4 nor CH_4 is obtained, but at higher temperatures, or in contact with reduced Ni alone, both of these gases are produced.

2533. ORMANDY, W. R. Oil From Coal. Jour. Inst. Fuel, vol. 7, 1933, pp. 71–79; Chem. Abs., vol. 28, 1934, p. 3873.

Review of the production of oil from coal by: (1) Straight distillation over a wide range of temperatures; (2) direct hydrogenation; (3) the distillation of coal and the conversion of the coke into water gas, which is, in turn, converted to oils.

2534. ORMANDY, W. R., AND BURNS, J. Production of Oil From British Coal. Trans. Inst. Marine Eng., vol. 45, 1933, pp. 239–254; Petrol. Times, vol. 30, 1933, pp. 551–552, 579–581, 607–608; Colliery Guard., vol. 147, 1933, pp. 749–751; Chem. Abs., vol. 28, 1934, p. 620.

Quality of oils from coal is discussed with reference to price competition with petroleum. The production of oil from coal is considered under the headings (1) distillation with variation in temperature, (2) hydrogenation, and (3) distillation of coal and conversion of coke into water gas, which by catalytic reactions is converted into a wide range of products. Compares fuel-oil and coal-oil mixtures. Discusses Cunard process of using finely divided coal suspended in oil.

OROCHKO, D. I. *See* abs. **2169.**

2535. ORSONI, B. [Utilization of Synthetic Ammonia Plant for Production of Methanol.] Chimica e industria (Milan), vol. 29, 1947, pp. 137–139; British Abs., 1949, B, I, p. 199.

Details of the preparation of the reaction-gas mixture and of the necessary adaptation of the NH_3 plant equipment to the synthesis of MeOH. The method of preparation of the gas mixture depends on the process in operation for making NH_3. If the H_2 is obtained from water gas, this need be only partly converted to eliminate S as H_2S. The required CO: H_2 ratio can be attained by regulating the steam. A small amount of residual CO_2 helps to promote the synthesis of MeOH, thus economizing in water for washing the gas mixture. The water may contain 0.6–0.7 cc. CO_2 per $m.^3$ This offers an advantage over the requirements of NH_3 synthesis. When the CO, CO_2, and H_2 content of the gases reaches about 70–75% in the catalytic cycle, the residual gas must be freed from N_2 and CH_4, preferably by fractionation in the NH_3 plant. This involves the consumption of about 0.25 kw.-hr. per kg. of MeOH, but it can be avoided if O_2, which is always available in an NH_3 plant, is used for the production of water gas (about 0.5 $m.^3$ O_2 is required per kg. of MeOH). For pressures of 2.5–25 atm., steel pipes must be plated

(against corrosion by CO) with Zn and other surfaces with Sn; 6% Cr–V–Mo or Cr–Ni steel should be used when higher pressures are applied.

2536. OSBORNE, R. M. Adsorption of Low-Boiling Hydrocarbons by Activated Carbon. FIAT Tech. Bull. T–34, May 1, 1947, 2 pp.

Carboraffin, which is made from sawdust, activated by $ZnCl_2$, and powdered, is 1 of the several active carbons mentioned in FIAT Final Report 863, and manufactured by the I. G. Farbenindustrie, Leverkusen. It is said to have good adsorptive capacities for low boiling hydrocarbons. A carbon based upon the Carboraffin type with similar adsorption isotherms has now been developed into an active carbon capable of being fluidized and used in a continuous adsorption process. The exact method of manufacture has not been disclosed. On an industrial scale, there have been no developments on the preparation of active carbons that show selectivity for chemical types of hydrocarbons, although on a laboratory scale, where the time factor is not essential, some work has been done. It is almost certain that the presence of metals does not increase the selectivity of a given activated carbon for a particular type of hydrocarbon. Presents some of the physical properties and constants of active carbons developed by the Lurgi Co.

2537. ———. Extraction of Fatty Acids From Dilute Aqueous Solutions From the Fischer Process. FIAT Tech. Bull. T–35, May 1, 1947, 1 p.

Hoesch Benzin plant at Dortmund has been recovering the oxygenated products in the water layer condensed from the Fischer-Tropsch process. This plant operated at medium pressure (7 atm.) with the Co catalyst at 200° and treated about 150 $m.^3$ of the condensation H_2O per day. The solution 1st made alkaline to prevent corrosion, was distilled to give an approximately 30% alcohol solution in the overhead; the alcohols range from ethyl to octyl. The ethyl, propyl, and butyl alcohols were separated, and the higher alcohols were sold to the lacquer trade. The bottoms of the distillation were acidified with H_2SO_4 to a pH of 5, and the free fatty acids, corresponding to about 0.4% of the total primary synthesis product, were extracted with naphtha. About 200% naphtha based on the water was circulated. This extracted only the C_4 and higher acids. The recovered acids, amounting to about 1 ton per day, found use in boring oil. Degussa developed a method of extracting lower fatty acids from dilute solutions using ethyl acetate.

2538. OSBORNE, T. M. Coal-Gasification Unit Completed at Missouri Gas-Synthesis Plant. Southern Power and Ind., vol. 67, No. 7, 1949, pp. 72–73; Chem. Abs., vol. 43, 1949, p. 6393.

New plant for the production of synthesis gas by the steam and O_2 gasification of powdered coal is described briefly. This gas will be washed and cooled and then passed through electrical precipitators to remove dust before being compressed and purified.

OSHIMA, T. *See* abs. **1892, 1915.**

2539. OSHIMA, Y. High-Pressure Chemical Industries in Japan. Trans. World Power Conf., Chem. Eng. Cong., 1936, 10 pp.; Chem. Abs., vol. 31, 1937, p. 3167.

Development and present status of the synthetic MeOH and NH_3 and compressed gas industries are discussed briefly with special emphasis on plant capacity, economics, and regulatory measures.

2540. OSTERMEIER, L. [Use of the Residual Gas From the Fischer-Tropsch Gasoline-Synthesis Process as City Gas.] Gas u. Wasserfach, vol. 81, 1938, pp. 52–57; British Chem. Abs., 1938, B, p. 243; Chem. Abs., vol. 32, 1938, p. 3126.

High purity of the residual gas from the Fischer-Tropsch process is an important factor in considering its use for city gas, but this is partly balanced by its high content of inerts, especially CO_2 and high specific gravity. This gas may be converted into city gas by washing out CO_2, preferably with a solution containing a mixture of K and Na carbonate or by detoxification (removal of CO) before removing CO_2. In either case the density and inert content will be reduced to permissible limits, and a mixture of treated and untreated gas may be used, with or without other normal manufactured gases. The combination of synthesis-gas manufacture with the use of the residual gas would seem to be favorable for large gas works in Germany.

2541. OSTERRIETH, J. R., AND DECHAMPS, G. Production of Organic Compounds From Coke-Oven Gas. Gas Jour., vol. 201, 1933, pp. 202–206; Gas World, vol. 98, No. 2531, coking sec., 1933, pp. 14–17; Chem. Abs., vol. 27, 1933, p. 1736.

Commercial methods for producing MeOH and the higher alcohols from the constituents of coke-oven gas.

2542. OSTWALD, W. [Snythetic Fuels.] Motorwagen, vol. 28, 1925, pp. 565–567.

Bergius and Badische processes.

2543. ———. Motor Fuels From Cheap Materials. Oil Gas Jour., vol. 24, No. 38, 1926, p. 136; Chem. Abs., vol. 20, 1926, p. 2572.

Discussion of the production of synthetic motor fuels by the Mittasch, Fischer, Zelinsky, and Bergius processes. A synthetic fuel containing Fe carbonyl as an antidetonating component is not as poisonous as $Pb(C_2H_5)_4$, but when used in engines, it causes the valves to become incrusted quickly.

2544. ———. [Influence of German Gasoline Chemistry Upon American Refinery Technology.] Kraftstoff, vol. 16, 1940, pp. 271–273; Chem. Abs., vol. 35, 1941, p. 8268.

Present developments are traced to I. G. Farbenindustrie A.-G., high-pressure hydrogenation, and Fischer low-pressure synthesis. Shows schematic interrelations of the various processes.

2545. OTA, N. Water Gas by the Reaction of Methane and Carbon Dioxide. I. Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 284–290; Chem. Abs., vol. 43, 1949, p. 1944.

Equivalent mixture of CH_4 and CO_2 under atmospheric pressure was passed through a layer of catalyst at 700°–800° to obtain CO and H_2. Catalysts composed of Ni and various oxides and carriers in different ratio were used, and, among those tried, 1 containing Ni, MgO, and kieselguhr in the ratio 1:1:4 gave the best yield of $CO+H_2$ at 700° with the least formation of C on the catalyst.

2546. ———. Water Gas by the Reaction of Methane and Carbon Dioxide. II. Methods of Preventing Carbon Formation on the Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 284–290; Chem. Abs., vol. 43, 1949, p. 1944.

Formation of C on catalysts can be prevented not only by selecting a suitable catalyst but by (*a*) elevating the reaction temperature, (*b*) taking excess CO_2, or (*c*) adding H_2O to the reacting gas. Thus, when 30% excess CO_2 is used with the CH_4, the reaction proceeds smoothly at 800° with a Ni-kieselguhr catalyst without any other admixture. Similar results were obtained with a gas having 30% H_2O (based on CH_4) at 700° or 10% H_2O at 800°. By adding H_2O, the amount of CH_4 decomposed is increased.

OTTO, K. V. *See* abs. **1206.**

OTTS, K. *See* abs. **2740.**

OWENS, M. L. *See* abs. **2094.**

P

PACE, B. S. *See* abs. **810.**

2547. PACE, J., AND TAYLOR, H. S. Velocities of Adsorption of Hydrogen and Deuterium on Hydrogenation Catalysts. Jour. Chem. Phys., vol. 2, 1934, pp. 578–580; Chem. Abs., vol. 28, 1934, p. 6606.

Velocities of adsorption of H_2^1 and of H_2^2 are identical on Cr_2O_3, $ZnO–Cr_2O_3$ and Ni supported on kieselguhr, at 110°, 132°, and 184°. This process is, therefore, independent of the difference in zero-point energies, of the rate at which the gas molecules strike the surface, and of an activated migration.

PACHECO, J. R. *See* abs. **2137, 2917.**

2548. PADOVANI, C. [Progress in Production and Synthesis of Fuels.] Giorn. chim. ind. applicata, vol. 7, 1925, pp. 202–210; Chem. Abs., vol. 20, 1926, p. 3225.

Topics considered are: Benzine from petroleum, benzine from sources other than petroleum, light oils from solid fuels, indirect hydrogenation of C, fluidification of C by various chemical processes, liquid fuels from vegetable substances, synthetic petroleum.

2549. ———. Direct and Indirect Use of Methane as Motor Fuel. Proc. World Petrol. Cong., vol. 2, 1933, pp. 795–798; British Chem. Abs., 1934, B, p. 996.

Possibility of using compressed CH_4 as motor fuel, or of converting it into liquid fuel, for example, by direct thermal treatment or by conversion into a mixture of CO and H_2, which would then serve as the raw material for the synthesis of alcohols or light hydrocarbons, is discussed with particular reference to conditions in Italy.

2550. ———. [Treatment of Combustile Gases.] Jour. usines gaz, vol. 58, 1934, pp. 2–7; Chaleur et ind., vol. 15, 1934, pp. 461–468; Chem. Abs., vol. 28, 1934, p. 3872.

Lecture reviewing experiments on the conversion of CO, CO_2, and H_2 to CH_4. By the use of pressures around 10 atm., temperature below 400°, yields of 85–90% in the reaction $CO+3\ H_2=CH_4+H_2O$ can be obtained by the use of a complex (Ni-containing) catalyzer resistant to the effects of normal industrial gas. CO_2 is formed in a side reaction; no C is separated out. The process is important for the manufacture of nontoxic gas of high heating value from inferior fuels. A loss in the reaction of some 25% of the total heating value can be partly recovered. Reviews application of reverse reaction at 800°–900°.

2551. ———. [Conversion of Methane Into Liquid Fuels.] Kraftstoff, vol. 18, 1942, pp. 81–85; Brennstoff-Chem., vol. 23, 1942, p. 207; Chem. Zentralb., 1942, II, p. 971; Chem. Abs., vol. 37, 1943, p. 5217.

Gas mixture from the catalytic conversion of CH_4 according to the equation: $2\ CH_4+O_2=2\ CO+4\ H_2+17.4$ cal. is directly suitable for the synthesis of hydrocarbons by the Fischer-Tropsch process or for MeOH, the latter of which only is of interest to Italy at the present time. The main difficulties in the 1st stage of CH_4 conversion are the lack of suitable mechanically and thermally resistant catalysts, the problem of temperature regulation and the avoidance of side reactions, particularly in the preheating of the gases. The process, as developed, comprises, in addition to the preparation of the catalyst, the special conditions essential for the preheating of the reaction gases before their entrance into the reaction zone, the maximum temperature about 950°. The permissible velocity is about 500 $m.^3$ of CH_4 per hr. per $m.^3$ of catalyst. From 1 $m.^3$ of 95% CH_4, about 1.1 kg. of MeOH (98–99%) can be obtained with a consumption of 0.493 $m.^3$ of O_2 and 0.9 kw.-hr., corresponding to the use of 2.85 $m.^3$ of synthesis gas (65.2% H_2 and 32.1% of CO), 0.493 $m.^3$ of O_2, and 0.10 kw.-hr. The economy of the process is discussed, particularly as regards the supplies of CH_4. With the existence of larger amounts of CH_4, the MeOH process would offer the best solution. It is possible also that the benzine synthesis would be economically successful. The chemical conversion of CH_4 is at present made difficult by the relatively small amounts available, the uncertainty of the amount of reserves, and the present necessity of making quick use of the available supplies and, if necessary, moving the plants from one place to another.

2552. ———. [Evaluation of Italian Solid Fuels.] Chim. ind. agr. biol., vol. 18, 1942, pp. 79–84; Chem. Zentralb., 1942, II, p. 849; Chem. Abs., vol. 37, 1943, p. 5218.

Coal fields in Italy are usually small, widely separated, and of low value. An endeavor has been made to use the poorer coals for local chemical industry in special furnaces or gas producers. Low-temperature carbonization has replaced direct combustion when tar yields and coke properties are satisfactory. When the semicoke is unsatisfactory, the coal is gasified in producers, with tar recovery. A special demand has been noted for producers that give a mixture of CO and H_2 suitable for synthesis. There is a great need for the erection of Fischer plants using Italian brown coal.

———. *See* abs. **2106.**

2553. PADOVANI, C., AND BAYAN, S. [Reduction of Ferric Oxide With Mixtures of Carbon Monoxide and Hydrogen.] Ann. chim. applicata, vol. 24, 1934, pp. 394–409; Chem. Abs., vol. 29, 1935, p. 419.

Influence of time of contact on the reduction of Fe_2O_3 made from calcined siderite, by a mixture of CO and H_2, in the same proportions as in water gas, has been studied. A phase of complete combustion was noted, which is independent of the velocity or time of contact, within the limits used (temperature 950°), and which ends abruptly when a definite percentage (44.8) of the available O_2 from the Fe_2O_3 is consumed.

2554. PADOVANI, C., AND FRANCHETTI, P. [Reactions of Methane With Mixtures of Steam and Carbon Dioxide.] Inst. Ind. Chem. Fuels, Polytechnicum, Milan, vol. 4, 1932–33, pp. 173–191; Chem. Abs., vol. 29, 1935, p. 1229.

Mixtures of CH_4, CO_2, and H_2O are passed over Ni catalysts, with or without Cu or Al_2O_3 at temperatures from 650° to 1,200°, and principally at 850°. The CO and H_2 formed are measured. The results obtained are compared with those of Fischer and Tropsch (*see* abs. **1025**), and Hawk, Golden, Storch, and Fieldner (*see* abs. **1370**).

2555. ———. [Incomplete Oxidation of Methane With Oxygen and Air.] Giorn. chim. ind. applicata, vol. 15, 1933, pp. 429–432; Chem. Abs., vol. 28, 1934, p. 2853.

Reaction $CH_4+\frac{1}{2}O_2\rightarrow CO+2H_2+8$ cal. is influenced markedly by the presence of catalysts such as Ni; for example, at 850°–950° with a space velocity of 500, virtually equilibrium conditions were obtained. At 900°, less than 1% CH_4 remained in the reaction product. CH_4 from petroleum cracking, as well as from illuminating gas, was used. With reduced cost of O_2, the above reaction may become of interest in preparing H_2, NH_3 and alcohols.

2556. ———. [Methane Synthesis From a Mixture of Carbon Monoxide and Hydrogen.] Acqua e Gas, vol. 24, 1935, pp. 57–61; Chem. Zentralb., 1936, I, p. 478.

Synthesis of CH_4 under about 10–12 atm. pressure from a synthetic mixture of CO and H_2 (obtained by the gasification of brown coal with O_2 at low tempera-

tures) can be attained up to about 90% at 330° over a Ni catalyst deposited on kieselguhr and activated with Al and Mn at a space velocity of 1,040 and almost complete at lower space velocity. By using illuminating gas to which H_2 had been added, poisoning of the catalyst gradually took place, but after regeneration, it resumed operation so that finally 27% of the CO was converted into CH_4. A partial substitution of the Ni by a natural siderite gave good results with the illuminating gas+H_2. With illuminating gas alone, however, destruction took place through separation of C. A Ni catalyst on active C with illuminating gas+H_2 gave good results, but without H_2 it failed rapidly. High pressures (85–104 atm.) caused the catalyst to fail quickly and promoted the deposition of C.

2557. ———. [Synthesis of Methane From Mixtures of Carbon Monoxide and Hydrogen.] Atti cong. nazl. chim. pura applicata, 5th Cong., Rome, 1935, part II, 1936, pp. 818–828; Chem. Zentralb., 1937, I, p. 2307; Chem. Abs., vol. 31, 1937, p. 7393.

Experiments with various catalyzers containing Ni, Mn, Al, Fe, and Mg all tend to show the superiority of Ni as the catalyzer base.

2558. PADOVANI, C., AND GIORDANO, I. [Production of Gas With High Hydrogen and Low Carbon Monoxide Contents by the Action of Steam on Carbon.] Acqua e Gas, vol. 9, 1931, pp. 65–81; Chim. et ind., vol. 26, 1931, p. 1064; Chem. Abs., vol. 26, 1932, p. 1417.

Theoretically, the reaction of the production of H_2 is $C+2H_2O=CO_2+2H_2-19$ cal.; but, in practice, the process is carried out in 2 stages according to $C+H_2O=CO+H_2-29$ cal. and $CO+H_2+H_2O=CO_2+2H_2+10$ cal., the second stage being carried out at 400°–500° in presence of a catalyst. From a theoretical application of the law of mass action to the equilibria $CO_2+C\rightleftarrows 2CO$ and $CO+H_2O\rightleftarrows CO_2+H_2$ and a study of the ratios $CO:H_2$ and $(H_2O+H_2):H_2$ (the 1st measuring the impurity of the H_2 produced and the 2d the excess of undecomposed steam), considerable divergence was found between theoretical results and those obtained in practice, which is attributed to the thickness and nature of the layer of coke and to the treatment to which it was subjected during the coking process. Methods also were studied of increasing the reactivity of the C: (1) By addition of catalysts (chiefly alkali or alkaline earth salts, or oxides of Fe, Cr, or Mn); (2) by using coke (or more exactly semicoke) prepared under special carbonization conditions. The experimental set-up used in the investigation is described.

2559. PADOVANI, C., AND LOTTERI, A. [Reaction Velocities at Low Temperatures in the Water-Gas Equilibrium.] Studi ric. comb., vol. 6, 1936–1937; Jour. Soc. Chem. Ind., vol. 56, 1937, pp. 391–395T; British Coal Utilization and Research Assoc., Monthly Bull., vol. 2, 1938, No. 11, abs. 2342; British Chem. Abs., 1938, B, p. 13; Chem. Abs., vol. 32, 1938, p. 1170.

Composition of the feed was H_2, 46.5; CO, 52.5; N_2, 1.0%; trace of O_2; and no CO_2 or C_nH_m. The catalyst had an Fe_2O_3 basis (commercial). The apparatus is shown. The temperature of the reaction chamber was kept at 400° and that of the preheater was carried at 400°, 520°, and 580° at atmospheric pressure, and a $H_2C:CO$ ratio of 1.87 was used. The velocity coefficient k_1 for the reaction $CO+H_2\rightarrow CO_2+H_2$ was calculated from: $k_1dt=dx/(ax^2+bx+c)$; where t=reaction time and x concentration of CO. At preheater temperatures of 400°, 520°, and 580° the values of k_1 obtained were 0.00509, 0.00732, and 0.00860, respectively. Experiments on the effect of pressure showed that the highest yields lie between 10 and 20 atm. The effect or $H_2O:CO$ ratio was investigated, and it was shown that in order to obtain absolute yields above 90% at 400° a large excess of H_2O is necessary (ratios of 3–4 and space velocities not greater than 300–400). Experiments also are reported for catalytic temperatures of 300°, 350°, 400°, 450°, and 500° with equalized preheater temperature. The variation of k_1 as a function of temperature could be expressed by $k_1=9.387T^2\times 10^{-7}-5.919T\times 10^{-4}+0.09384$. With a $H_2O:CO$ ratio of 2, high yields are possible only at 450°–500°. With space velocities of about 500, yields of 75–80% can be realized. At 350°–400°, yields of 30–60% only are possible with space velocities between 300 and 500, and at 300° the reaction velocity is definitely too low.

2560. PADOVANI, C., AND SALVI, G. [Oxidation of Paraffin.] Riv. combustibili, vol. 2, 1948, pp. 231–244; Fuel Abs., 1949, No. 2, p. 931; Chem. Abs., vol. 43, 1949, p. 4000.

Some doubtful factors in this process have been studied and improvements and simplifications applied especially in the separation of the oxidation products. A commercial crystallized paraffin, m. p. 50°–52°, was taken as the raw material. The optimum temperature of reaction was found to lie between 130° and 135°. Although the reaction is exothermic, heat had to be applied at certain stages of the reaction to compensate for heat lost by dispersion. Best results were obtained with a $KMnO_4$ catalyst (0.2–0.5%). At the end of the process this catalyst had combined to 80% with the water-soluble fatty acids. 15% of O_2 mixed with the air used as oxidizing agent reduced the reaction period from 16–9 hr., the amount of air required from 480–250 l., and the oxy acids in the final products from 7 to 4%. Al and oxidized Al were found to be the best construction materials for the pilot plant equipment, since they darkened the color of the products least and appeared to have a slight accelerating effect. Whereas the Germans separated the oxidized products by saponification and removed the unsaponifiable matter by distillation under pressure, selective solution was adopted as being simpler and more economical. Two solvents were tested in the laboratory, isopropanol and MeOH–H_2O. Chromatographic separation also was tried, but difficulties were encountered.

PALEARI, C. *See* abs. **2706b.**

2561. PALFRAY, —. [Catalytic Hydrogenation Under High Pressures.] Cours conf., No. 1320, March 1945, 18 pp.; Chaleur et ind., vol. 28, 1947, p. 8D.

Study of the catalytic fixation of H_2 on unsaturated bonds, in particular of the synthesis of MeOH and the manufacture of synthetic gasoline. Light or heavy hydrocarbons are converted into light gasoline or lubricants.

PALM, J. W. *See* abs. **3726.**

PALMER, H. F. *See* abs. **3218.**

PANINA, A. M. *See* abs. **1592.**

PANNING, G. *See* abs. **3137.**

PANTAZOPLOS, G. *See* abs. **888.**

PANTAZOPLOS, P. *See* abs. **888.**

2562. PARANJPE, V. G., COHEN, M, BEVER, M. B., AND FLOE, C. F. Iron–Nitrogen System. Jour. Metals, vol. 188, No. 2, Trans., 1950, pp. 261–267; Chem. Abs., vol. 44, 1950, p. 3423.

Fe–N system was investigated by X-ray diffraction measurements and a controlled nitrogenizing method. The latter is an innovation and depends on the relation between the nitrogenizing power of an NH_3–H_2 mixture and the N content of the Fe–N alloy produced. Clarifies several controversial features of the Fe–N phase diagram.

2563. PARDUN, H. [Dependence of the Yield of Fatty Acid Upon the Stage of Oxidation of Aliphatic Hydrocarbons.] Fette u. Seifen, vol. 48, 1941, pp. 397–403; Chem. Abs., vol. 37, 1943, p. 2918.

Fischer-Tropsch slack wax was oxidized in an apparatus at a constant temperature (±1°) and with a uni-

form current of air. In various experiments 600 l. of air per hr. was blown through 6,000 gm. of slack wax for 1–9 hr. in the presence of 30 gm. Mn stearate as catalyst and at temperatures of 100°–160°. At different stages of oxidation (when the acid numbers were 20, 40, 60, 80, etc.), 40-gm. portions were removed and analyzed for unsaponifiable, fatty acids, OH acids, and nonvolatile soluble acids. From these data and from yields of nonvolatile oxidate obtained in blank runs, interpolation formulas were derived that could be used to calculate the course of oxidation for practical purposes and especially to determine the most favorable stage of oxidation.

2564. PARDUN, H. [Edible Fat From Coal.] Seifen-Öle-Fette-Wachse, vol. 74, 1948, pp. 25–27, 49–52; Chem. Abs., vol. 42, 1948, p. 8364.

Review of production of fats by the Fischer-Tropsch hydrocarbon synthesis, oxidation of hydrocarbons to fatty acids and their separation, esterification, and refining of crude triglycerides.

2565. ———. [Distribution of the Fatty Acids Formed by the Oxidation of Paraffins in the Fischer-Tropsch Process.] Fette u. Seifen, vol. 52, 1950. pp. 290–295; Chem. Abs., vol. 44, 1950, p. 10352.

Influence of the degree of oxidation on the distribution of the fatty acids formed in the Fischer-Tropsch process was investigated by oxidizing samples of a paraffin fraction $b_{.13}$ 168°–233° at temperatures of 110°, 120°, 130°, and 140° so as to yield products of acid numbers 10, 20, 40, and 80. The fatty acids were isolated as the Me esters, fractionated, hydrolyzed and analyzed. The distribution of the fatty acids formed a maximum in all cases. With decrease in degree of oxidation this maximum migrates toward fatty acids of higher molecular weight. It is probable that the primary reaction takes place at the end of the paraffin chain, and that the higher-molecular compounds formed first are split further on continuing oxidation.

2566. PARDUN, H., AND KUCHINKA, R. [Influence of the Amount of Air Upon the Oxidation of Paraffin Hydrocarbons.] Fette u. Seifen, vol. 49, 1942, pp. 441–446; Brennstoff-Chem., vol. 23, 1942, p. 208; Ind. Chemist, vol. 21, 1945, p. 447; Chem. Abs., vol. 37, 1943, p. 5697.

To determine the optimal amount of air for oxidation of aliphatic hydrocarbons to acids in liquid phase, a Fischer-Tropsch-Gatsch substrate was oxidized at temperatures 100°–160° with 0.05–1 l. of air per gm. per hr. until an acid No. of 50 was attained. At each temperature, the rate of oxidation rises until a limiting value is reached and then remains constant. The applicable equation is: 1 gm. $D=at-b$, where D=l. of air per gm. of substrate per hr., a=0.03, b for maximum rapidity=4.3, for maximum yield of acids=4.6. The temperature coefficient for 110°–140° is virtually constant at 2.52. Above this temperature it falls to 0.80–1.70.

2567. PARIS, A. [Mild Oxidation of Methane Under Pressure.] Chim. et ind., Special No., April 1934, pp. 411–420; Brennstoff-Chem., vol. 15, 1934, p. 413; Chem. Abs., vol. 28, 1934, p. 5806.

Investigation into the optimum conditions for formation of MeOH and CH_2O when working in a closed cycle. The possibility of isolating appreciable quantities of the principal oxidation product of CH_4 (MeOH) by raising the total pressure while at the same time remaining far enough from the limits of inflammability of CH_4–O_2 mixtures, seems to be due only to the selective increase in the rate of the reaction $CH_4+0.5\ O_2=CH_3OH$, relative to all the other reactions possible. This possibility is still further increased, and for the same reason but to a much greater extent, by increasing the ratio of CH_4 pressure to O_2 pressure. Temperature has but a very slight effect on the yields, the optimum detected at 450° being due to the fact that oxidation of MeOH starts long before that of CH_4 and that toward 500° it proceeds at an increasingly rapid rate. Industrial application can be conceived only by utilizing intensive circulation to compensate the low conversion resulting from the necessarily small O_2 content of the mixture.

2568. PARIS, A. [Metal Carbonyls.] L'Industrie chimique, vol. 38, May 1951, pp. 125–131.

Reviews preparation, structure, and applications of metal carbonyls. Under applications the promotion of the Oxo reaction by carbonylation, the synthesis of saturated acids from olefins and from olefinic acids from acetylenes (carboxylation), direct synthesis of alcohols from olefins, and direct synthesis of acids from alcohols are mentioned briefly.

2569. PARKER, A. Fuel Research Board: Its Objects and Achievements. Jour. Inst. Fuel, vol. 17, 1944, p. 90.

Outline of the work of the Coal Survey and its value to industry and a brief review of several researches that have been carried out at the Fuel Research Station, including the hydrogenation of coal, tar, creosote, etc. and hydrocarbon synthesis by the Fischer-Tropsch process.

2570. ———. Oil and Chemicals From Coal. Inst. Fuel, Wartime Bull., June 1944, pp. 161–163; Gas Jour., vol. 243, 1944, pp. 439, 441, 467–468; Colliery Guard., vol. 168, 1944, pp. 409–412, 445–447; Chem. Abs., vol. 38, 1944, p. 5,060.

Chemical products from carbonization represent 7% of the thermal energy of the coal but are 16% of the total value of the products. Various processes that may be used to increase these % include hydrogenation, low-temperature carbonization, Fischer-Tropsch, and MeOH synthesis. Reviews present uses and demands of various classes of chemical products from coal.

2571. ———. Coal, Science, and the Future. Chem. and Ind., vol. 23, 1945, pp. 234–239.

Paper read before the London Section, Society of the Chemical Industry. Some remarks were made in connection with the competitive prospects of petroleum and coal and products derived from them. The processes of synthesizing gasoline from coal either by catalytic hydrogenation or by way of the formation of H_2 and CO were discussed. Some estimates also were made of the possibilities of underground gasification of coal.

2572. ———. Oil-From-Coal Processes in Germany. Inst. Fuel (London) Bull., June 1947, pp. 128–129; Colliery Guard., vol. 174, 1947, p. 176; Gas World, vol. 126, 1947, p. 191, coking sec. pp. 11–12; Chem. Abs., vol. 41, 1947, p. 5282.

German plants for the hydrogenation of coal reached a capacity of 4,000,000 tons/yr. in 1944, with the greatest recorded production about 3,500,000 tons, a very considerable expansion over the prewar capacity. There was no great expansion in capacity of Fischer-Tropsch plants, which had a combined capacity of 740,000 tons/yr. and actual production of slightly more than 570,000 tons at the maximum. Natural oil resources reached 2,000,000 tons/yr., and 7,000,000 tons were imported from Rumania, etc. The hydrogenation process gives good yields of aviation and motor fuel, while the Fischer-Tropsch process produces some motor fuel of lower quality, high-quality diesel oil, and oils and waxes, which are excellent starting materials for various fats and chemicals. German costs for gasoline were >1 s. per imperial gal., and British costs would be more than 2 times as great; however, the process might be economical in some of the British dominions where lower-cost coal is available.

———. *See* abs. **2602.**

PARKER, A. M. B. *See* abs. **2119.**

2573. PARKS, G. S. Thermal Data on Organic Compounds. I. Heat Capacities and Free Energies of Methanol, Ethyl Alcohol, and *n*-Butyl Alcohol. Jour. Am. Chem. Soc., vol. 47, 1925, pp. 338–345; Chem. Abs., vol. 19, 1925, p. 1,085.

Specific heats of crystalline and liquid MeOH, EtOH, and BuOH were measured in an aneroid calorimeter with Cu block as a thermostat from liquid-air temperature to 25°. The accuracy was 0.5%. MeOH has a 2d crystalline form with a transition at 161.1° K. Its heat of transition is 4.4 cal./gm. at 161.1° K. Its specific heat at 168.3° K., 0.40 cal./gm. Its heat of fusion at 175.3° is 23.7.

2574. PARKS, G. S., AND HOFFMAN, H. M. Free Energies of Some Organic Compounds. Chemical Catalog Co., New York, 1932, pp. 113–123.

3 methods for developing the free-energy equation for the reaction $CO+2H_2=CH_3OH$ (g) are reviewed: (1) The application of the 3d law of thermodynamics to the available thermal data; (2) direct measurement of the equilibrium constant at 1 or more temperatures; (3) calculation based on measurements of equilibria in the methyl formate reactions. The 1st method is considered the most accurate, and the equation adopted is: $\Delta F°_{298}=-17{,}660+17.5T\ ln\ T-0.0136T^2-57.2T$.

2575. PARRAVANO, N. [Some Economic Aspects of the Synthesis of Alcohols.] Chim. et ind., Special No., April 1934, pp. 125–134; Chem. Abs., vol. 28, 1934, p. 5803.

Address discussing the following phases of the problem: Production of gases for synthesis from water gas or from whole gas with catalystic conversion of CO; production from gas obtained from O_2 generators; production by means of the gasification of lean fuels by O_2; production from natural gas and from petroleum refinery gases; and synthesis from saturated and from unsaturated hydrocarbons.

2576. PARRY, V. F., WAGNER, E. O., KOTH, A. W., AND GOODMAN, J. B. Gasification of Subbituminous Coal and Lignite in Externally Heated Retorts. Ind. Eng. Chem., vol. 40, 1948, pp. 627–641; Chem. Abs., vol. 42, 1948, p. 3929.

During the war the Bureau of Mines conducted experimental work on 2 pilot plants for gasification of low-grade fuels. The experimental data resulting from operation of the externally heated alloy retorts for a total of 3,500 hr. are summarized in graphs and tables, and the fundamental theories of gasification and heat transfer are discussed. The theory of the annular retort and mechanism of gasification therein are presented. It is shown that $CO+H_2$ can be made at rates of 65–70 ft.^{3} per hr. per ft.^{2} of heated surface in retorts heated to 1,900° F. The performance of various processes for production of $CO+H_2$ is compared on the basis of ft.^{3} per hr. per ft.^{2} of fuel-bed area. The Lurgi and Winkler generators, respectively, make 1,000–8,600 ft.^{3} of $CO+H_2$ per ft.^{2}, while externally heated processes make 1,000–2,300 ft.^{3} Various grades of water gas having H_2: CO ratios ranging from 1.9–10 were made in the pilot plants, but it is indicated that lowest-cost gases and highest efficiency and capacity are attained when making gases of 2.0: 2.5 H_2: CO ratio. The performances of 3 externally heated processes, the Didier-Bubiag, the Freiberger, and the annular retort, are reported with operating data. The Didier-Bubiag process was operated in Germany and supplied about 7% of the synthesis gas converted to liquid fuel by the Fischer-Tropsch process. This retort employs refractory chambers and each unit makes about 17,500 ft.^{3} of gas per hr. at an efficiency of about 78%. The 48-in. diameter annular alloy retort at Grand Forks has about the same capacity and has a present indicated efficiency of 71%. Calculations given show that the efficiency of externally heated continuous retorts should be about 80% when equipped with heat-recovery devices. In considering the economics of externally heated retorts, it is shown that the cost of alloy is about $0.01 per 1,000 ft.^{3} of $CO+H_2$, assuming that a 0.25-in.-thick alloy plate will have an average life of 10,000 hr. at 1,900° F. It is therefore indicated that, when making $CO+H_2$ at a rate of 70 cu. ft./hr./sq. ft. in the externally heated retort, the equivalent cost of O_2 to make the same gas in an internally heated process would be $0.03–$0.05 per 1,000 ft.^{3}

2577. PARRY, V. F., GERNES, A. C., WAGNER, E. O., GOODMAN, J. B., AND KOTH, A. W. Gasification of Lignite and Subbituminous Coal, Progress Report, 1945–46. Bureau of Mines Rept. of Investigations 4128, 1947, 68 pp.

Details of the design, construction and operation of 2 pilot plants for gasifying low-rank fuels. The work was part of a program to make reducing gases from lignite for beneficiation of low-grade Fe ores. The results of the work proved that the composition of water gases derived from low-rank fuels could be varied over a wide range. By changing the concentration of steam and the temperature around the retort, water gases having H_2: CO ratios of 2.15: 5.43 were obtained in the larger plant and ratios of 10.0 in the smaller. The indicated overall efficiency of gasification was 72%, when it is assumed that producer gas and steam for the process can be generated at efficiencies of 80–85%, respectively.

2578. PARTINGTON, J. R., AND SHILLING, W. G. Water-Gas Equilibrium. Jour. Soc. Chem. Ind. (London), vol. 44, 1925, pp. 149–150T, 242T; Chaleur et ind., vol. 7, 1926, p. 683; Chem. Abs., vol. 19, 1925, pp. 1769, 2267.

To determine the value of K in the equation $([CO_2]\times[H_2])/([CO]\times[H_2O])=K$, the value −0.4647 has been selected for the integration constant in the equation $\log K=-(2226/T)+1.077\ \log T-0.0_3898T+0.0_6133T^2+C$. Values for K for each 100° interval from 1,100° abs. to 1,800° abs. are given. The equation and curve presented represent the most reliable data at present available. Previous equations were based on inaccurate specific-heat data.

2579. ———. Calculations on the Water-Gas Equilibrium. Jour. Soc. Chem. Ind. (London), vol. 51, 1932, pp. 82T, 222T; Ind. Eng. Chem., vol. 24, 1932, pp. 591–593; Chem. Abs., vol. 26, 1932, pp. 2575, 3172.

Bryant's criticisms (*see* abs. **396**) of their original paper (abs. **2578**) are based on a mathematical error in tabulation, which was corrected. Bryant's reply is included.

2580. PASCAL, P. [Catalytic Hydrogenation—Synthesis of Methanol.] Tech. moderne, vol. 17, 1925, pp. 449–456; Chem. Abs., vol. 19, 1925, p. 2990.

Review of preparation of H_2, synthesis of MeOH, hardening of fats, hydrogenation of aromatic hydrocarbons, berginization, and cracking.

2581. ———. Fuel Problem. [Coordination of the Three Most Important Synthesis Processes: Fischer Synthesis, Hydrogenation and Methylation.] Tech. moderne, vol. 28, 1936, pp. 393–397; Brennstoff-Chem., vol. 18, 1937, pp. 347–348.

Description of the Fischer-Tropsch synthesis, the Bergius hydrogenation, and the Michot-Dupont methylation processes. It is suggested that a complete coordination of the 3 processes be made, as follows, in order to increase the yields of synthetic gasoline from brown coal and peat: Methylating low-temperature carbonization with fractionation and removal of aromatics; hydrogenation of the heavy liquid residues; gasification and Fischer treatment of the semicoke. This would give maximum yield and quality of gasoline and low capital and operating costs and eliminate coke

and byproducts, and at the same time it would supply aromatics for enriching natural products of low octane index. Example: Ordinary low-temperature carbonization of lignite would yield only 19 l. of gasoline b. 250°, whereas low-temperature methylation would give 50 l. per ton; by hydrogenating the heavy-tar residue an estimated 95 l. per ton would be given, and the gasification of the coke residue to synthesis gas and treatment by the Fischer process would increase the yield to a total of about 200 l. per ton of gasoline of an aromatic-aliphatic nature. Michot-Dupont process further discussed in abs. **2582.**

2582. ———. [Michot-Dupont Process for Low-Temperature Carbonization of Coal.] Tech. moderne, vol. 28, 1936, pp. 833–839; Teer u. Bitumen, vol. 35, 1937, pp. 38–39.

Ground coal is uniformly moistened with 2% aqueous Ca acetate, mixed with Fe filings and Na_2CO_3 and distilled in a continuous horizontal retort. A tar containing phenols 0.9, aromatic compounds 73, saturated hydrocarbons 18, and unsaturated hydrocarbons 8% is obtained, as compared with a normal tar containing 40.2, 43.0, 11.0, and 5.8%, respectively.

2583. PASCAL, P., AND BOTOLESEN, E. [Methane Synthesis From Carbon Monoxide and Water Vapor.] Jour. usines gaz, vol. 54, 1930, pp. 467–468; Compt. rend., vol. 191, 1930, pp. 186–187; Chem. Abs., vol. 24, 1930, p. 5282.

When a mixture of CO and H_2O vapor in excess is passed over $NiCO_3$, prepared from $Ni(NO_3)_2$ by precipitation with $MgCO_3$ and forming by heating to 700°, the superposition of 2 limited reactions is observed, the first starting at 250° and yielding CH_4 quantitatively to 275°, above which temperature the second reaction, giving CO_2 and H_2, begins. This reaction is appreciable at 300°, and at 750° the production of CH_4 is completely eliminated. At the higher temperatures the % production of CO and H_2 increases while that of CO_2 and CH_4 diminishes.

2584. PASCHKE, M. [Gas Production with Use of Oxygen by the Thyssen-Galocsy Process.] Stahl u. Eisen, vol. 60, 1940, pp. 934–935; Chem. Zentralb., 1941, I, p. 602; Chem. Abs., vol. 36, 1942, p. 2705.

Thyssen-Galocsy producer for the production of water gas or synthesis gas from coal or coke by the action of O_2, and steam is diagrammatically described.

PASTONESI, G. *See* abs. **2391, 2392.**

2585. PATART, G. [Synthesis of Methanol by the Reduction of Carbon Monoxide.] Compt. rend., vol. 179, 1924, pp. 1330–1332; Chem. Abs., vol. 19, 1925, p. 814.

Mixture of CO and H_2, 1:2, by vol., was circulated in a closed system for 3 hr. Pure ZnO, granular or suspended on asbestos, was used as a catalyst at 400°–420° and 150–259 atm. In a portion of the system cooled to 20° a liquid composed almost entirely of H_2O and MeOH collected. At the end of the run the volume of CO and H_2 remaining was about 1:1. Gives complete analyses of the gas mixtures before and after the experiment.

2586. ———. [Industrial Production of Methanol by Catalytic Synthesis Under Pressure.] Bull. soc. encour. ind. nat., vol. 137, 1925, pp. 141–173; Chem. Abs., vol. 19, 1925, p. 2026.

This lecture gives a detailed description of the theory and operation of the catalytic synthesis of MeOH from CO and H_2 and serves as a basis for a paper by Lormand in Industrial and Engineering Chemistry (abs. **2141**) descriptive of Patart's process.

2587. ———. [New Field of Catalysis Under High Pressure. Commercial Synthesis of Methanol.] Chim. et ind., vol. 13, 1925, pp. 179–185; Chem. Abs., vol. 19, 1925, p. 1556.

Fuller account is given of the experiments than appeared in Compt. rend., vol. 179, 1924, pp. 1330–1332 (abs. **2585**). A small-scale plant erected in 1922 is described. The mixture of water gas and H_2 is compressed to 500 atm., freed from oily impurities in a scrubber, and passed through the catalyst chamber. On leaving this, the MeOH produced is condensed by water cooling and the gases are returned to the process. The condensate is a greenish, turbid liquid, owing to the presence of salts of Zn, Cu, and Fe, the 1st derived from the catalyst and the last 2 from the apparatus, and amounting to 0.5 gm. in 154 cc. The liquid after distillation yields 80% of its original volume of MeOH with traces of acids, higher alcohols, and NH_3 but no acetone or formaldehyde, the remainder being water. Fe, Ni, and Co must be excluded as at temperatures above 300° they catalyze other reactions such as $2\,CO=CO_2+C$ and $CO+3H_2=CH_4+H_2O$. They cannot therefore, be used in the heating elements of the catalyst chamber. No gas purification such as is necessary in the synthesis of NH_3 is required. It is estimated that 100 l. of MeOH can be produced from 300 $m.^3$ of water gas at a cost of 25–35 gold francs.

2588. ———. [Commercial Transformation of Coal Into Technical Organic Products.] Chim. et ind., vol. 16, 1926, pp. 713–729; Chem. Abs., vol. 21, 1927, p. 639.

Discussion of the advantages and possibilities of Patart's process for the production of MeOH from CO and H_2 (abs. **2585, 2586, 2587**), which also can give higher alcohols under suitable conditions. In using coal as a raw material, most economical and efficient operation is obtained by first distilling for gas and then gasifying with steam to produce water gas, and the process could readily be installed in connection with gas works.

2589. ———. Industrial Transformation of Bituminous Coal into Organic Technical Products. Proc. Internat. Conf. Bituminous Coal, 1926, pp. 132–160; Tech. Eng. News M. I. T., vol. 8, December 1926, pp. 260–262; Fuel, vol. 6, 1927, pp. 160–170; Chem. Abs., vol. 21, 1927, p. 2371.

General discussion of the high-pressure synthesis of alcohols from water gas, including consideration of the effect of inerts in the reaction gas. The cost of production of MeOH under present U. S. conditions is estimated at $0.20 per gal.

———. *See* abs. **122.**

PATSCHEKE, G. *See* abs. **3374.**

2590. PAUL, H. [Economic and Thermal Efficiency of Fischer-Tropsch Synthesis.] Chemie-Ing. Tech., vol. 21, 1949, p. 110; British Abs., 1949, B, I, p. 560.

Thermal efficiency of the synthesis at low pressure is about 44 and that at medium pressure 38–41% corresponding with a consumption of 3.8–4.1 kg. of fuel per kg of product. Reviews range of byproducts.

2591. PAUL, H., AND TRAMM, H. [Fischer-Tropsch Synthesis for Coal Improvement and Power Generation.] Erdöl u. Kohle, vol. 2, 1949, pp. 229–237; Chem. Abs., vol. 43, 1949, p. 7,212.

Emphasizes importance of the Fischer-Tropsch synthesis in German economy. Application of the Ruhrchemie process will make it possible for Fischer-Tropsch plants to contribute greatly to gas supply and to satisfy peak gas requirements for industrial and home consumption. The large production of valuable raw materials for the manufacture of soap, sulfonated alcohols, waxes, etc., is an essential element for German recovery.

2592. PAULING, L. Nature of the Interatomic Forces in Metals. I. Phys. Rev., vol. 54, 1938, pp. 899–904; Chem. Abs., vol. 33, 1939, p. 1205.

It has been generally assumed that in the transition elements (Fe, Co, Ni, Cu) the 3*d* shell is filled with 10

electrons or is nearly filled, and that the *d* electrons make no significant contribution to the cohesive force in metals. Evidence is now presented showing that about half of the *d* orbitals (2.56 of the total of 5) are involved in bond formation, and that the number of covalent bonds resonating among the available interatomic positions increases from 1 to nearly 6 in the sequence K, Ca, Sc, Ti, V, Cr; remains nearly constant from Cr to Ni; and begins to decrease with Cu. The remaining 2.44 *d* orbitals, with very small interatomic overlapping, are occupied by nonbonding electrons, which are mainly responsible for the ferromagnetic and paramagnetic properties of the metals. This point of view provides a qualitative explanation of many properties of the transition metals, such as interatomic distance, characteristic temperature, hardness, compressibility, and coefficient of thermal expansion, and it accounts satisfactorily for the observed values of the atomic saturation magnetic moments of the ferromagnetic elements, Fe, Co, Ni, and their alloys. It also provides a reason for the occurrence of the positive exchange integrals, which give rise to ferromagnetism.

2593. ———. Nature of the Interatomic Forces in Metals. II. Atomic Radii and Interatomic Distances in Metals. Jour. Am. Chem. Soc., vol. 69, 1947, pp. 542–553; Chem. Abs., vol. 41, 1947, p. 5772.

Concept that the metallic bond is equivalent to resonating covalent bonds permits the formation of a system of atomic radii that can be used to calculate interatomic distances in metals and intermetallic compounds and to interpret observed interatomic distances in terms of the electronic structures of the crystals. An equation is developed to express the change in covalent radius (metallic radius) of an atom with change in bond number, or in coordination number, if the valence remains constant; the stabilizing, bond-shortening effect of the resonance of shared-electron-pair bonds among alternative positions also is taken into consideration. This equation is applied to the empirical interatomic-distance data for the elementary metals to obtain a nearly complete set of single-bond radii. Cr, Mn, and Sn exist in metals in 2 forms: A small, high-valent form and a larger, low-valent form. Both kinds of Mn atoms coexist in α– and in β–Mn. In many metals, each atom is attached to some of its neighbors by strong bonds and to others by much weaker bonds. An extreme case is β–W, in which there are straight strings of strongly bonded atoms; similar strings also are present in the α–U structure. The use of the radii is illustrated by application to the *structure of cementite* and *AuSn*.

2594. PAVCEK, P. L. Production of Fatty Acids From Byproducts of the Fischer-Tropsch Process. CIOS Rept. XXVIII–35, 1945, 3 pp., PB 4,291; TOM Reel 198.

Paraffins produced by the Fischer-Tropsch process (m. p. 50°–55° and consisting of C_{20}–C_{26} hydrocarbons) are oxidized with air at 130°–150°, using $KMnO_4$ as catalyst in Al towers. Oxidation is not complete and the Mn salts of the fatty acids must be separated from the unreacted paraffin by means of alcohol and C_6H_6. After neutralization with NaOH or Na_2CO_3, the crude soaps are steam-distilled at 250°. The lower fatty acids, such as formic, acetic, propionic, and butyric, come off immediately and the hydroxy acids are converted to unsaturated acids. Keto acids also are removed at this point by the Hader process. The olefinic and saturated acids remaining as the Na salts from the above distillation are set free with HNO_3, and the $NaNO_3$ is removed. The free acids are steam distilled by the Wecker method of forcing water into the hot fat. This method avoids polymerization and keto acid formation and high-grade fatty acids are obtained. The fatty acids are esterified with glycerol (made from propylene) to form soaps or edible triglycerides. Oppau and Witten utilize 20,000 tons/yr. of paraffin, the Märkische Seifenindustrie uses even larger quantities. The overall yield of fatty acids is about 50%. The C_6–H_{10} alcohols obtained as byproducts form excellent plasticizers when esterified with phthalic anhydride (abs. **186**).

2595. ———. Research on Synthetic Fats at University of Leipzig. PB Rept. 25,677, 1945, 2 pp.

Report chiefly concerns the research work done by Dr. K. Thomas on the utilization and metabolism of synthetic fatty acids produced by Märkische Seifenfabrik in Witten, Ruhr. Thomas found that these synthetic fats were only partly utilized by the bodies of both humans and dogs.

2596. PAVLYUCHENKO, M. M. [Fundamental Equation of Topochemical Reactions That Are Not Catalyzed by the Solid Reaction Product.] Jour. Phys. Chem. (U. S. S. R.), vol. 23, 1949, pp. 809–812; Chem. Abs., vol. 43, 1949, p. 8820.

If a reaction that has started on a crystal face is propagated at equal rates along the surface and normal to it, the rate of v of reaction is proportional to t^2. If the reaction spreads over the surface more rapidly than it penetrates into the crsytal, v is maximum at $t=0$; t is time.

2597. ———. [Reactions Involving Solids in the Absence of Any Catalytic Action of the Reaction Products.] Jour. Phys. Chem. (U. S. S. R.), vol. 23, 1949, pp. 800–808; Chem. Abs., vol. 43, 1949, p. 8820.

The corners of a cube are its most reactive points. If the reaction starts from the corners and proceeds along the diagonals of the cube, the area of the reactive surfaces increases; this explains the usual autocatalytic acceleration of reactions involving solids. The theory is applicable also to reactions starting at crystal edges. In both instances, the rate of reaction passes through a maximum.

2598. PEARSON, B. M. [Petrol Synthesis From Methane. The Hydrocol Process.] Ann. mines et carburants, Oct. 15, 1946; Gas Times, vol. 50, 1947, pp. 104–105.

Describes process, its development, and advantages. Gives operating principles, describes a commercial test-scale plant, and discusses a project for a large-scale plant.

2599. PEASE, R. N. Catalytic Combination of Ethylene and Hydrogen in the Presence of Metallic Copper. I. Measurements of Reaction Velocity and Adsorption Isotherms at 0° and 20°. Jour. Am. Chem. Soc., vol. 45, 1923, pp. 1196–1210; Chem. Abs., vol. 17, 1923, p. 2220.

Kinetics of the catalytic combination of H_2 and C_2H_4 have been studied at 0° and 20° in the presence of Cu. The reaction velocity and adsorption isotherms have been determined. Within limits, the velocity increases with the H_2 concentration but decreases as the C_2H_4 concentration increases. The temperature coefficient of the reaction velocity/10° rise between 0° and 20° is 1.62, indicating that diffusion does not play a dominant part.

2600. PEASE, R. N., AND CHESEBRO, P. R. Equilibrium in the Reaction $CH_4+2H_2O \rightleftharpoons CO_2+4H_2$. Jour. Am. Chem. Soc., vol. 50, 1928, pp. 1464–1469; Chem. Abs., vol. 22, 1928, p. 2139.

Reaction $CH_4+2H_2O \rightleftharpoons CO_2+4H_2$ has been studied at 500° and atmospheric pressure. Equilibrium was approached from both sides and the value of the constant found to be 0.037 (partial pressures being expressed in atmospheres) at 505°. This is in excellent agreement with the value calculated from Lewis and Randall's free-energy equations and thus supports in particular their equation for CH_4 in the low temperature region. It is pointed out that the reactions CH_4+

$H_2O \rightleftharpoons CO+3H_2$ and $CO_2+H_2 \rightleftharpoons CO+H_2O$ also are to be taken into account at higher temperatures. Equilibrium constants at 500°, 600°, and 700° are given for reference. Attention is called to the CH_4–steam reactions as a source of H_2 and of H_2–CO mixtures.

2601. PEASE, R. N., AND STEWART, L. Catalytic Activity and Adsorptive Power of Supported Iron, Cobalt, Nickel, Copper, and Silver. Jour. Am. Chem. Soc., vol. 49, 1927, pp. 2783–2787; Chem. Abs., vol. 22, 1928, p. 345.

Samples from a uniform supply of diatomite brick were impregnated with solutions of the nitrates of Fe, Co, Ni, Cu, and Ag, in the proportions of 1 gm.-atom of metal per 100 gm. of dry brick, in order to insure that the differences in catalytic activity of the supported catalysts thus prepared might be due only to the specific properties of the metal in question. The apparatus, the static method of measuring the catalytic activity of these catalysts for the hydrogenation of C_2H_4, and the method of measuring the adsorption of H_2 and C_2H_4 were the same as previously described in abs. **2599**. Co and Ni caused instantaneous hydrogenation of C_2H_4 at −20°; Fe was moderately active at 0°, Cu at 50°, and Ag at 100°. Much more H_2 was adsorbed by Ni and Co than by the other metals, and more C_2H_4 by Fe. Reaction velocity measurements with Ag at 100° and Cu show that the rate is proportional to the H_2, and independent of the C_2H_4 concentration. With Fe at 0°, excess H_2 increases the rate, while excess C_2H_4 has little effect. An association, rather than a dissociation theory of catalytic hydrogenation, is indicated.

2602. PECK, E. B., AND PARKER, A. Production of Synthesis Gas From Powdered Brown Coal or Coke at H. Koppers G. m. b. H., Essen. CIOS Rept. XXVIII-36, 1945, 4 pp., PB 417; TOM Reel 198; British Abs., 1946, B, I, p. 159.

Cost estimates for the production of 10^6 m.^{3} of synthesis gas per hr. Flow sheets for (*a*) the conversion of coke-oven gas into synthesis gas, and (*b*) low-temperature carbonization, followed by gasification of bituminous coal.

PEERLES, W. C. *See* abs. **1440, 1441, 1442, 1443, 1444, 1445, 1446, 1447, 1448, 1449, 1449a.**

PEPPER, W. P. *See* abs. **141.**

PERKINS, P. D. *See* abs. **6.**

2603. PERNOUX, E. [Examination Under the Electron Microscope of Some Kieselguhrs Utilized as Catalyst Supports.] Compt. rend., vol. 228, 1949, pp. 1,646–1,647; Chem. Abs., vol. 43, 1949, p. 8,831.

About 50 samples of 4 different commercial kieselguhrs were examined under the electronic microscope: A crude Filter-Cel, an acid-treated Filter-Cel, an acid-treated Filter-Cel followed by treatment with 5% Na_2CO_3, and a crude Filter-Cel treated with 5% Na_2CO_3. A magnification of 6,000 was adopted. The micrographs are described but not illustrated. Taking account of the fact that the kieselguhrs are made up of 95% of hydrated amorphous silica to which are added some silicates and various impurities (Al_2O_3 and Fe oxide), the following interpretations can be made. The acid treatment of the crude product causes the superficial formation of a silica gel, which seals the pores. This silica is redissolved by treatment with 5% Na_2CO_3. The direct carbonate treatment of the initial product involves only a small part of the silica consisting of the most finely divided portions. The microscopic examination thus confirms the conclusions made by Teichner.

2604. ———. [Use of the Electron Microscope in the Study of Catalyst Supports.] Jour. chim. phys., vol. 47, 1950, p. 233; Chem. Abs., vol. 44, 1950, p. 7635.

Treatment of kieselguhr with HNO_3 and HCl caused the formation of a SiO_2 gel. The gel was completely removed by reaction with 5% Na_2CO_3. Alkali treatment of raw kieselguhr dissolved only the smallest particles. The results confirmed the conclusions drawn by Teichner (abs. **3362**).

———. *See* abs. **3363, 3363a.**

2605. PERRAULT, R. [Synthetic Production of Motor Fuels According to the Fischer Process.] Rev. indust., vol. 65, 1935, pp. 373–376; Chem. Zentralb., 1936, I, p. 2011; Chem. Abs., vol. 31, 1937, p. 5973.

Summarizes discussion of benzine synthesis by the method of Fischer and Tropsch.

2606. ———. [Some New Uses of Cobalt.] Génie civil, vol. 108, 1936, pp. 254–257; Chem. Abs., vol. 30, 1936, p. 7516.

Stellite and the newer alloys of Co with Be, Ti, and Al are mentioned. Some of the hard Co alloys in the form of frit are mixed with powdered diamond. Co is used as a catalyzer in the Fischer process for synthetic production of light oils, also for plating.

2607. PERRIN, M. [Evolution of Activity of Fischer-Tropsch Catalysts.] Compt. rend., vol. 224, 1947, pp. 342–343; Chem. Abs., vol. 41, 1947, p. 3739.

Fischer and Meyer (abs. **988**) observed that CO was completely hydrogenated to CH_4 in the presence of a fresh catalyst. Craxford (abs. **637**) attributed the hydrogenation to metallic Co, and the synthesis of higher hydrocarbons to Co carbide. Earlier it was observed that where the CO and H_2 were diluted with CH_4, condensable hydrocarbons were formed at once. Now it has been found that N_2 produces the same effect, and, in general, lowering the partial pressure of CO and H_2 inhibits the formation of CH_4 almost completely. Lowering of the synthesis temperature from 190° to 175°, as well as a reduction in the flow of the reactants, also reduces the necessary delay in the starting of the synthesis reaction. These observations indicate that the initial production of CH_4 is due to overheating the catalyst bed and that any method of preventing this temperature rise starts the hydrocarbon synthesis without the formation of excessive CH_4.

2608. ———. [Chemical Evolution of Fischer Catalysts During the Thermal Reducing Treatment.] Compt. rend., vol. 227, No. 8, 1948, pp. 476–478; Bull. soc. chim., 1949, No. 5–6, pp. 366–367; Chem. Abs., vol. 43, 1949, p. 26.

Ni catalysts on kieselguhr with small amounts of ThO_2 or Al_2O_3 were subjected to reducing tests in order to ascertain, as a function of time and temperature, the loss in weight and the amounts of H_2O and CO_2 set free. The catalyst, after drying, tested 26.3% of Ni, the transformation of which to the metallic state involved a loss of 7.2%. A rapid heating up to 450° in a stream of H_2 for 127 min. caused a loss in weight of 24.8%, and in N_2, 24%. The same catalyst calcined in air at 900° lost 26.4% of its weight. The brief treatment up to 450° had an almost identical result and was enough to eliminate almost the whole amount of CO_2 and H_2O in the basic carbonates and the other hydrated substances that made up the dried catalyst. With a slower treatment of gradual heating up to 450° during a period of 4 hr., the loss in weight was 28.5%. There was an increased reduction of the NiO. The H_2O and CO_2 set free measured, respectively, 21.4 and 4.85% of the initial weight, the deficit of 2.25% being CH_4, which was carried away in the stream of H_2. At the end of a series of operations at different temperatures and times, the weight of the catalyst had diminished 32.5–32.8%, a result very close to that obtained by calcination in air at 900°, including the total reduction of the NiO (26.4%+7.2%=33.6%). These empirical results, however, do not necessarily agree with general practice; many factors may modify the results. The rate of temperature increase, the length

of treatment, and the flow of H_2 affect the various chemical reactions involved such as dehydration, decarbonation, reduction of CO_2 to CH_4, and reduction of NiO. The same parameters must likewise influence the formation of hydrated combinations between the silica of the kieselguhr, the Al_2O_3, and the oxides of the heavy metals, as these combinations are formed very easily under the conditions of preparation and reduction of Fischer catalysts.

2609. ———. [Loss in Weight of a Fischer Nickel Catalyst During Reduction.] Bull. soc. chim., 1949, No. 5–6, pp. 366–367.

Fischer Ni catalysts were heated to 450° in streams of N_2 and H_2; the losses in weight were virtually the same. A very slow reaction was observed at 220°, probably corresponding to a structural change in the catalyst. For a total loss of 28.5% of the initial weight of the catalyst, 21.4% was represented by H_2O and 4.85% by CO_2. The deficit of 2.25% was logically attributed to a slow reduction of CO_2 into CH_4, which dissolved in the H_2 and thereby was not measurable. In reducing the catalyst by successive steps of temperature maintained until the weight of the catalyst became constant, it was found that at 120° the loss in weight was rapid and virtually complete in 2 hr.; at 210° the loss was rapid at the beginning and then slow for about 50 hr.; at 360° the loss occurred in about 5 hr. and likewise at 450°. The losses were respectively, 9.4, 12.6, 9.1, and 1.7.

2610. ———. [Thermal-Reduction Treatment of Fischer Catalysts.] Jour. chim. phys., vol. 47, 1950, pp. 262–268; Chem. Abs., vol. 44, 1950, p. 7638.

Catalyst containing 26.3% Ni, small amounts of Mn, and Al with kieselguhr as support was studied. The total loss in weight and the amounts of H_2O and CO_2 formed were determined during successive reductions at 120°, 225°, 360°, and 450°. The total loss in weight was 32.5% and consisted of H_2O, 26.36; CO_2, 3.24; and presumable CH_4, 2.90%. All of the CO_2 evolved was formed at or below 225°.

———. *See* abs. **779, 2743, 2744, 3229, 3426, 3427, 3428.**

2611. PERRUCHE, L. [Synthetic Foods.] La Nature, No. 3146, 1947, p. 327.

Brief review of the manufacture of synthetic fats from Fischer-Tropsch paraffin.

2612. PERRY, C. W. German Chemical Engineering. A Survey 1935–45. Chem. Eng. Progress, vol. 43, No. 12; Trans. Am. Inst. Chem. Eng., 1947, pp. 659–666.

2613. PERRY, C. W. Evolution of the Petrochemical Industry. Oil Gas Jour., vol. 48, No. 21, 1949, pp. 66, 67, 82, 84, 87, 88.

Comprehensive summary of the petrochemical industry is presented, and the important sources of petroleum chemicals are reviewed. The possibilities in the production of oxygenated chemical byproducts of the Fischer-Tropsch synthesis are discussed.

2614. PERRY, G. T. Fuels and Lubricants From Sources Other Than Petroleum. Canadian Chem. Process Ind., vol. 32, 1948, pp. 624–629.

Review of the production of fuels and lubricants by the hydrogenation of coal and by synthesis from natural and water gas. It is concluded that Canada can be made independent of outside sources of crude-oil supplies by utilizing coal resources lying within its geographical boundaries, using either the Hydrocol or the Synthine process.

PERRY, H. *See* abs. **810a.**

2615. PERRY, H., COREY, R. C., AND ELLIOTT, M. A. Continuous Gasification of Pulverized Coal With Oxygen and Steam by the Vortex Principle. Trans. Am. Soc. Mech. Eng., vol. 72, No. 5, 1950, pp. 599–610; Chem. Abs., vol. 44, 1950, p. 7510.

This report presents the preliminary results of a Bureau of Mines investigation of the gasification of pulverized coal by steam–O_2 mixtures in a vortex reactor. The theory of the vortex is explained, the basic principles of reactor design is set forth, and an illustrative example of their application is given. A method of calculating the composition of the gas produced in this reactor is advanced and has been checked experimentally. The C conversion and the limits of operation have been found to be closely related to the type and uniformity of the coal distribution. A method of improving the operation of the equipment and the quality of the gas by a change in the type of coal distributor from the conical to the spinning-plate form appears to offer considerable advantages.

PERRY, L. R. *See* abs. **1105.**

PERSSON, O. *See* abs. **1385.**

2616. PERTIERRA, J. M. Errors in the Determination of Gas Temperatures With Thermocouples. Ion, vol. 10, 1950, pp. 395–401; Chem. Abs., vol. 45, 1951, p. 1861.

Discrepancies in gas temperature measurement with thermocouples and methods for elimination of the errors due to radiation are reviewed.

———. *See* abs. **419.**

2617. PETCH, N. J. Positions of the Carbon Atoms in Austenite. Jour. Iron Steel Inst. (London), vol. 145, 1942, pp. 111P–128P; Chem. Abs., vol. 36, 1942, p. 6477.

X-ray powder photographs of austenite show that the possible positions for C are at the centers of the unit cells and at the midpoints of the edges. Discusses theories of the structure.

2618. ———. Interpretation of the Crystal Structure of Cementite. Jour. Iron Steel Inst. (London), vol. 149, 1944, pp. 143P–150P; Chem. Abs., vol. 38, 1944, p. 4891.

Cementite is essentially a framework of close-packed Fe atoms with the small C atoms in the largest interstices held in place by metallic bonding. The lattice parameters of cementite have a small but systematic and definite decrease with increasing quenching temperature. Variation in the Fe : C ratio is the explanation of the lattice parameter variation. The most possible variation in composition is by omission of C atoms to a limited extent. 9 refs.

———. *See* abs. **2120.**

2619. PETERS, —. [Treatment of Kogasin.] TOM Reel 170, frames 415–419, July 18, 1939.

Catalytic cracking is superior to thermal cracking under pressure. Since cracking catalysts polymerize easily, they should be used first for polymerization and then for cracking. Si–Al as well as H_3PO_4 catalysts were being considered.

2620. PETERS, K. [Progress in the Improving and Utilizing of Coal.] Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 552–568.

General survey, including the benzine synthesis from coal and water gas.

———. *See* abs. **994, 995, 996, 997, 1034, 1035.**

2620a. PETERS, K., AND KAPPELMACHER, E. Conversion of Hydrocarbons to Carbon Monoxide–Hydrogen Mixtures. Brenstoff-Chem., vol. 33, 1952, pp. 296–307; Chem. Abs., vol. 47, 1953, p. 290.

Thermodynamic calculations were made for CH_4 splitting with air, steam and CO_2 over the entire temperature range of practical interest and the exact theoretical cracked-gas composition determined corresponding to the practically important CO–H_2 mixtures.

Ni catalysts were prepared with which these reactions were studied on a laboratory scale, with good agreement between theoretical and experimental results. Catalytic splitting of CH_4 is more rapid with air or O than with CO_2 and steam. The experiments gave some light as to the reaction mechanism and assisted in minimizing soot formation. Soot formation can be reduced by lowering the partial pressure of the hydrocarbons by adding an excess of steam, dilution with inert gases, or by the use of a catalyst of higher activity and selectivity. The results are presented in tabular form and in graphs so the theoretical conditions can be determined for any desired cracked gas composition. Since the thermodynamic final state is dependent only on the temperature and the atomic relation C : H : O : N in the reactants, these results are applicable to all cracking of solid liquid and gaseous fuels with air, O_2, steam and CO_2 as gasification media.

2621. PETERS, K., AND KÜSTER, H. [Water-Gas Equilibrium Under the Influence of Electric Discharges at Diminished Pressure.] Ztschr. physik. Chem., vol. 148, 1930, A, pp. 284–303; Brennstoff-Chem., vol. 11, 1930, pp. 171–172; Ges. Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 279–299; Chem. Abs., vol. 24, 1930, p. 4708.

Mixtures of CO and H_2 reacted during electrical discharge at diminished pressure according to the equation $CO_2+H_2=H_2O+CO-10.4$ cal. The yield increased with current density. No marked displacement of the equilibrium was noted between 20 and 60 mm. Hg. The yield remained constant up to a rate of flow of 710 l. per hr. The average temperature in the discharge tube was 300°, while that of the discharge stream was about 800°–1,000°. For mixtures rich in CO_2 the calculated equilibrium temperatures were up to 1,000° higher than the temperatures of the discharge stream, indicating pronounced electrical effects.

2622. PETERS, K., AND MEYER, K. [Thermal Formation of Acetylene From Methane.] Brennstoff-Chem., vol. 10, 1929, pp. 324–329; Chem. Abs., vol. 24, 1930, p. 484.

Possible reactions are: (1) $2CH_4 \rightarrow C_2H_2+3H_2-91$ cal.; (2) $2CH_4 \rightarrow 2C+4H_2-41$ cal.; (3) $2CH_4 \rightarrow 1/3(C_6H_6)+3H_2-42$ cal. Reaction (1) is favored by high temperature and low pressure. Reaction (2) can be suppressed by short heating time. The apparatus consisted of a glass globe with 3 tubulures, 2 of which, being coincident with the globe diameter, served to admit the gas and electric current for heating a W spiral in the center of the globe. Reaction gases were drawn off by the 3d tubulure. With a heating zone 20 mm. long (3 mm. wire) at 3,000° and CH_4 at 50 mm. pressure passed at the rate of 30 l. per hr., 66.5% of the CH_4 was converted into C_2H_2, no C_6H_6 being formed. The heating time was 0.0001 sec. These were the most favorable conditions found for reaction (1).

2623. PETERS, K., AND PRANSCHKE, A. [Decomposition of Methane With Carbon Dioxide and Water Vapor in the Electric Discharge.] Brennstoff-Chem., vol. 11, 1930, pp. 473–476; Ges. Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 271–279; Chem. Abs., vol. 25, 1931, p. 645.

At 5,000–6,000 v. in the discharge tube previously described and with rates of gas flow to 800 l. per hr., CH_4–H_2O and CH_4–CO_2 mixtures have been almost completely decomposed to CO and O_2. Separation of C did not occur, but at intermediate voltages a large part of the CH_4 formed C_2H_2. Tabulated data show that by varying the proportions of the mixture used, variations over a wide limit are possible in the resulting gas. Curves show the relationships between current density, CH_4 content, and the production of CO and C_2H_2.

2624. PETERS, K., AND WINZER, K. [Cracking of Kogasin.] Brennstoff-Chem., vol. 17, 1936, pp. 429–430; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 503–505.

Cracking of Kogasin II upon graphite is compared with that upon Pt (abs. **1035**); the yields are similar.

2625. ———. [Preparation of Light Naphtha From Kogasin II by Cracking.] Brenstoff-Chem., vol. 17, 1936, pp. 301–306; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 506–516; Coal Carbonisation, vol. 2, 1936, p. 205; Chem. Abs., vol. 31, 1937, p. 1992.

Cracking at 465°–570° and pressures to 100 atm. has been studied at throughputs up to 150 cc. oil/min. Cracking was assisted by H_3PO_4 catalyst. The proportion of gaseous to liquid products varied between 1 : 2 and 1 : 6 up to 530° and at 560° attained 1 : 1, as compared with cracking at atmospheric pressure in a Pythagoras tube up to 740° where proportions ranged 2 : 1–6 : 1. Pressure cracking yielded unsaturated compounds in smaller amount, the naphtha obtained, however, being highly unsaturated. Treatment with C_2H_4 in the presence of H_3PO_4 catalyst did not improve the octane number, although C_2H_4 did.

2626. PETERSEN, W. [Effect of Phenol Content of Flotation Agents in Treatment of Coal Fines.] Bergbau Arch., vol. 8, 1948, pp. 88–103; British Abs., November 1948, B, I, p. 580.

Tar-oil fractions for flotation should contain 4–5% of phenols to promote frothing. Part of the phenols can be supplied by addition of limited amounts of ammoniacal spent liquor containing about 1.8 gm. of phenols/l. Still greater economy of tar oil can be achieved by addition of pine oil. Paraffin is inferior to tar oils unless improved by frothing agents. A synthetic Fischer-Tropsch oil fraction containing no phenols, but 0.7% of saponifiable constituents, when tested in progressively increasing amounts, was comparable initially with tar oils, but its efficiency was not maintained at higher concentrations.

2627. PETERSON, S. F. Utilizing Natural Gas Would Aid United States Oil Supply. Oil Weekly, vol. 113, No. 9, 1944, pp. 22, 32; Petrol. Refiner, vol. 23, 1944, p. 145.

It is suggested that the Government could develop application of Fischer-Tropsch process to make synthetic oil from natural gas, thus increasing the liquid-fuel supply and conserving domestic petroleum reserves, rather than giving so much attention to foreign oil fields.

2628. Petroleum (London). Synthetic Fuels in Germany. I. Introduction. Vol. 9, 1946, pp. 74, 93.

Before the war the trend in fuel synthesis was toward the Fischer-Tropsch process, but during the war the Bergius hydrogenation process gained interest. Of the total oil production of 6,180,000 tons in 1943 from all sources, 3,088,000 tons was from Bergius hydrogenation and only 368,000 tons was produced by the Fischer-Tropsch process. Also, attention had been paid to increasing production rather than developing new processes during the war. No evidence has been found of developments that would make either of the processes more attractive economically. The use of pressures above atmospheric and the use of Fe catalysts and processes working in several stages had been investigated in connection with the Fischer-Tropsch process, but extensive plant application has not been established. As regards the use of pressure, drawings were obtained of vessels designed to operate at 10 atm. pressure. The principal feature is the methods used to dissipate the exothermic heat of reaction. Some useful information was obtained regarding operation in stages and recycling. Of particular interest is the Oxo process. Of importance, too, in the production of aviation fuel is the Dehydrierung-Hoch-Druck process, which catalytically dehydrogenates naphthenes to aro-

matics at 50 atm. and 500°. In this way, the yield of aromatized gasoline is said to be 65% of the feed.

2629. ———. Synthetic Fuels in Germany. II. Hydrogenation. Vol. 9, 1946, pp. 102, 109.

General review of 15 German hydrogenation plants with an annual production capacity of 3,700,000 tons of finished product. Tabulated summary.

2630. ———. Synthetic Fuels in Germany. III. Fischer-Tropsch Process, Lubricating Oils and Acetylene. Vol. 9, 1946, p. 158.

Brief review of the products from the Fischer-Tropsch synthesis, with a description of the Carrieres-Kuhlmann plant at Harnes, France (abs. **1262** and **3038**) and of the Oxo process of the Ruhrchemie at Holten (abs. **1363**, **1478**, and **2177**).

2631. ———. Synthetic Fuels in Germany. III (2). Fischer-Tropsch Process, Lubricating Oils and Acetylene. Vol. 9, 1946, p. 191.

2 processes are described briefly: That of the Kuhlmann Co. at Lestaque, France (capacity 25 tons per day) and a pilot plant at Harnes, France. To produce 1 ton of lubricant, the 1st process requires 600 kg Fischer-Tropsch gas oil, 600 of benzol, and 160 of dichlorethane. The gas oil is chlorinated at 90°–100° and is mixed with a benzol-dichlorethane mixture in the presence of $AlCl_3$ at 70° and then raised to 110°. The mixing time is 6 hr.; 10% of $AlCl_3$ is used. The liquid product is stripped of the uncombined benzol, allowed to settle, the $AlCl_3$ sludge is removed by water washing, and the washed oil is blended with gas oil to lower its viscosity and is used as a general machine-lubricating oil where a high-grade oil is unnecessary. The upper layer, after decantation, is clay-treated and distilled, the overhead product (20%) is sent back for reprocessing, the upper side stream product (30%) being used as a transformer oil. The bottoms make a high-grade steam-cylinder oil (20%), which can be used at superheat temperatures up to 350°; 30% of turbine oil also is obtained. The oils formed consist of polybenzenes with long paraffinic chains attached; this structure gives the oils a high viscosity index and a low pour point. The properties of some of the oils are shown in a table. In the 2d process the raw material is Fischer-Tropsch gasoline of as high olefin content as possible. This is mixed with 3% of $AlCl_3$ and remains in contact with it for 5 hr. at room temperature. On standing, 2 layers separate, the lower contains a heavy polymer bound chemically with the $AlCl_3$. It is treated with NaOH and washed with H_2O, leaving a lubricating oil. The upper layer contains paraffinic gasoline and free polymer, the former being removed by steam stripping, the remaining oil is clay-treated and filtered and a gas oil, a light lubricating oil for cold service, and a heavy lubricating oil suitable for ordinary lubrication is prepared. The latter can be hydrogenated at 100 atm. and 200° over the normal Fischer-Tropsch catalyst to produce a substance similar to vaseline. The above oils suffer from poor oiliness and ready oxidation. Properties of 4 oils are given in a table. The article concludes with a description of underground lubricating-oil plants.

2632. ———. Synthetic Plan for India. Vol. 13, 1950, p. 121.

Synthetic petroleum plant, expected to begin production in 1951, is to be built at Orissa, on the east coast of India. The project, prepared by experts of the National Petroleum Institute of Paris, is sponsored by an Indian industrialist, B. Patniak. It is anticipated that the cost of production of petrol will be below the present market price of petrol from crude oil.

2633. PETROLEUM ENGINEER. Synthetic Fuels Made From Dry Gas. Vol. 18, No. 2, 1946, p. 64.

A 10-bbl. per day experimental synthetic oil pilot plant is operating on natural gas at the Baton Rouge plant of the Standard Oil of New Jersey. The technique was developed before and after the war, was used to produce 100-octane aviation gasoline during the war and is now being tested in the production of fuel for automotive equipment of all kinds. These synthetic fuels are now being made from natural gas, but the process is applicable to coal as well and when perfected can serve to extend liquid fuel supplies indefinitely.

2634. ———. New Sulfur-Recovery Process. Vol. 23, No. 2, 1951, pp. C44, C47.

Girdler S-recovery process from H_2S gases is based on a modification of the original Claus process. Reaction is carried out in 2 stages:

$$(1)\ H_2S+3/2O_2\rightarrow SO_2+H_2O;$$

$$(2)\ 2H_2S+SO_2\rightarrow 3S+2H_2O.$$

The process is described by aid of a flow diagram. Up to 95% of the S in H_2S-carrying gas may be recovered. If used in combination with a Girbotol gas purification plant, the utility requirements of the S-recovery plant are minor.

2635. PETROLEUM PRESS SERVICE. Economics of the Fischer-Tropsch Process. Vol. 4, 1937, pp. 448–450.

2636. ———. German Developments. Vol. 5, 1938, pp. 301–304.

It is reported that at the end of 1937 Germany had 4 Fischer-Tropsch plants with a total capacity of 250,000 tons per yr.

2637. ———. Progress in Germany. Vol. 5, 1938, pp. 61–64.

As far as light motor fuel is concerned, the progress made, although falling short of earlier predictions, is estimated to be rapid enough to ensure virtual independence of imports within the next year or two. As regards heavier oils, which represent over ½ of the total requirements, there appears to be no prospect of self-sufficiency being attained in the near future.

2638. ———. New German Plants. Vol. 6, 1939, p. 529.

Plant of Krupp-Treibstoffwerk G. m. b. H. at Essen, which obtains its raw material from coal by low-temperature carbonization by the Krupp-Lurgi process, commenced production of primary product at the end of 1938, and a plant at Deschowitz has been recently completed for the Gräflich Schaffgottsche Benzin G. m. b. H. of the Silesian coal industry.

2639. ———. Soviet Germany—Oil-From-Coal Plans. Vol. 17, 1950, pp. 235–236; Fuel Abs., vol. 8, No. 6, 1950, abs. 4608.

Production of synthetic fuels in the Soviet zone of Germany is planned to reach 840,000 metric tons in 1950, and to rise to 1,260,000 tons in 1955 under a new 5-year plan. Based on lignite, this production meets the zone's requirements of automotive fuels, and has provided small quantities for export to Western Germany. All main plants have passed to U. S. S. R. ownership. Eastern Germany is the only part of Europe where there are fewer commercial motor vehicles than in 1938.

2640. PETROLEUM PROCESSING. Government Research on Synthine Process. Vol. 2, 1947, p. 172.

Some comments are made on the recent report to Congress by the Secretary of the Interior on the Synthetic Liquid Fuels Act. There is little question, it is stated, that the Bureau's work constitutes one of the largest present research programs in the field of synthetic liquid fuels, and that there is little doubt that the program will yield important data, especially if extended at least in time. Proper cooperation with industry and avoidance of unnecessary duplicative work

could make this program an outstanding example of Government research in applied fields of science.

2641. ———. Is $30,000,000 More Needed for the Liquid Fuels Program? Vol. 2, July 1947, p. 560.

Editorial criticisms of the Bureau of Mines program. No fault is found with the purpose back of the research program, which is to secure data on methods of producing liquid fuels synthetically, including processes, equipment, and costs, but rather with the manner in which the program is being carried out. It is thought that the Bureau has been far too wasteful and extravagant in its expenditures; too much money has gone for permanent-type laboratories, plants, and offices built to last a lifetime instead of for the length of the program. It also is said that the Bureau attempts to operate on too large a scale; equally reliable cost and operating data for the purpose of the present program could be obtained from laboratory and pilot-plant studies without the expense of installing large demonstration plants. Furthermore, the Bureau too often entirely ignores the advice of its petroleum-industry advisory committee and does not cooperate in a program that would correlate with the established research programs of the oil companies. Some method of obtaining closer control and assuring coordination with the needs of industry should be set up. The solution, perhaps, is an advisory board composed of representatives of industry, the Armed Services, and the Bureau and empowered to actually direct the course of the program. Commenting in Petroleum Processing (vol. 2, July 1947, p. 558) Eugene Ayres, Gulf Research & Development Co., and a member of the Industry Advisory Committee, says that such criticism comes from misunderstanding of the way in which the work is conducted, and that the program of the Bureau has satisfied the specification as set forth by the Advisory Committee.

2642. ———. Oil-Company Synthetic Fuels and Lubes Show Good Records in Navy Tests. Vol. 2, No. 1, 1947, pp. 37–39, 42–44.

Included among the fuels recently tested by the U. S. Navy at Annapolis in actual performance in gasoline and high-speed diesel automotive engines, were the following synthetic fuels and lubricants: The Texas Co.—gasoline and diesel fuel made from natural gas by the Hydrocol process; synthetic lubricating oil prepared by blending a highly refined mineral oil with an ester type synthetic oil of low viscosity. The Union Oil Co. of California—gasoline made from Colorado shale and diesel oil manufactured from shale oil. Standard Oil Development Co.—gasoline and diesel fuel made from natural gas in the modified Fischer-Tropsch unit at Baton Rouge employing the fluid catalyst technique. The Carbide & Carbon Chemicals Corp.—synthetic lubricating oil synthesized from natural gas or other hydrocarbon gases similar to a Society Automotive Engineers 30 grade. The chemical nature or method of manufacture is not yet disclosed. The gasoline and diesel engines powered and lubricated by synthetic products were put through performance tests described by the Navy as highly satisfactory. Liquid fuels made from coal by the Fischer-Tropsch process gave true similarity of performance in the experimental gas turbine to Navy-specification diesel fuel under optimum operating conditions. In gasoline engines the 80-octane synthetic fuel was equal to or better than normal petroleum gasoline. Further studies are to be made in the laboratory and in actual service. Properties of each of the gasolines, diesel fuels, and lubricating oils are tabulated.

2643. ———. Shall Government Permanently Engage in Liquid Fuels Research? Vol. 2, 1947, p. 160.

This editorial criticizes the Bureau of Mines for attempting to extend the synthetic liquid fuels program beyond its originally specified term of 5 yr. Government funds should not be spent on research that duplicates that being carried on by the oil companies, and that the latter are better equipped to do than the Bureau. Government research in connection with the development of liquid fuels should be confined to the assay and analysis of the low-grade coal deposits and the oil-shale beds for their potential value as source material for synthetic fuels when needed some time in the distant future. The use of either of these raw materials in the commercial production of substitute fuels will call for excavating, conveying, and handling solid materials, and, in the case of shale, disposal of solid wastes, on a huge scale. Studies of methods to be applied here and the economics involved are beyond the scope of research and development work of any individual oil company. At present such work is only a small part of the Bureau of Mines program, but it could be expanded and emphasized. It would correlate but not duplicate the studies of actual processing techniques, which some of the oil companies have been engaged in for several years.

2644. ———. Cancellation of Stanolind's Synthine Plant. Vol. 3, No. 10, 1948, p. 926.

Announcement was recently made by the Stanolind Co. that plans for the erection of a synthine plant at Garden City, Kans., were being canceled because of rising costs of construction and difficulty in obtaining materials. From the viewpoint of the petroleum industry, this occurrence may have unfortunate repercussions in that it weakens the industry's recent arguments that it can stand on its own feet in regard to building synthetic fuels plants and that there was no need for Government entry into competition with private industry in setting up a synthetic fuels industry. If the economics on which the Stanolind decision was based are universally applicable, it would appear that the petroleum industry is in no financial position to construct a large-scale synthetic fuels industry in the immediate future. The need for such an industry at the present time is somewhat debatable, but it is highly likely that sooner or later it will actually be needed for national security; the decision to erect one should not be left to Government forces with possible eventual Government control of the entire petroleum industry. Although this cancellation is a small matter commercially, it should not be seized upon as a sign of petroleum-industry weakness, which it certainly is not.

2645. ———. Gas-Synthesis Plant. Vol. 5, No. 9, 1950, pp. 946–947.

Major construction work has been completed on the Bureau of Mines gas-synthesis demonstration plant at Louisiana, Mo., which will convert coal into liquid fuels by a modified Fischer-Tropsch process. The plant, of 80–100-bbl. per day capacity, was built at a cost of $4,915,000. It is expected to begin integrated operations early next year. Modifications of the German Fischer-Tropsch process include improvements in the method of producing and purifying the synthesis gas, the use of a rugged, granular, synthetic-NH_3 type Fe catalyst, and the use of a fluidized-bed, internally cooled converter. The synthesis gas will be obtained by gasifying pulverized coal ranging from anthracite to lignite with O_2 and superheated steam. O_2 for the process will be extracted from the air at temperatures of more than 300° F. below zero in a Linde-Fränkl unit; it will be 98% pure. The gasification unit is briefly described. It will use about 28 tons of coal, 24 of O_2, and 35 of superheated steam to produce 2,000,000 ft.^{3} of raw synthesis gas daily. It is already demonstrated that a gas of normal composition (41% CO, 38% H_2, 16% CO_2, and 5% N_2 and impurities) can be produced. As an auxiliary source of synthesis gas, a 7-ft.-diameter Kerpely producer modified to operate continuously with coke and O_2 has been installed. Anticipated daily

production will be 55–60 bbl. of 75-octane gasoline, 10–12 bbl. of 80-octane diesel oil, and about 12 bbl. of heavy oils and waxes suitable for cracking stock. Process-flow diagram of the plant is shown.

2646. PETROLEUM REFINER. Hydrocol Process. Vol. 26, No. 4, 1947, p. 240. Process Handbook Section.

Description, with flowsheet of the Hydrocol process as licensed by the Texaco Development Corp.

2647. ———. Need for Synthetic Fuels. Vol. 27, No. 3, 1948, pp. 141, 143.

Summary of the current possibilities and developments in Government participation in the synthetic fuels program.

2647a. ———. Lukuga Synthetics Plant Possibility for Congo. Vol. 31, No. 8, 1952, p. 62.

Possibility of establishing a synthetic oil plant in the Belgian Congo by the Lukuga Coal Syndicate has already passed the study stage. Several hundred ton of coal have been shipped from the Lukuga Basin to Belgium for testing to determine its adaptability for transformation into gas and to choose the most appropriate method of gasification. The syndicate was organized in 1950 to study the possibility of establishing a synthetic fuels plant in the Belgian Congo. The Congo has coal deposits but no known oil resources.

2648. PETROLEUM TIMES. New Synthetic Oil Processes in Germany. Vol. 48, 1944, p. 28.

Reference to recent work described by Dr. F. Fischer. Mention of new raw materials for manufacturing synthesis gas and of work with new and more effective catalysts. Increasing the octane number of synthetic oils has received attention. The synthesis of carbohydrates as found in nature is visualized.

2649. ———. Chemical Derivatives of Coal and Home Refining of Petroleum. Vol. 49, 1945, p. 1078.

Excerpts from a report of a nonparty technical committee of 4 fuel technologists to draw up a policy for fuel utilization. Encouragement should be given to the extension of the chemical utilization of raw materials derived from coal. In the United States a synthetic organic chemical industry is being developed, which has no parallel in England, and the latter country has clearly lagged behind other nations in its researches on chemicals derived from petroleum and coal. It is urged that a Fischer-Tropsch plant should be erected for intensive study on the same lines as the coal-hydrogenation plant erected by the Imperial Chemical Institute. The British Coal Utilization and Research Association is starting work on chemical utilization problems, and its work should be encouraged.

2650. ———. Synthetic Motor-Fuel Production. Vol. 51, 1947, pp. 613 and 614.

Synthetic motor fuel is now being produced in the Soviet zone of Germany at the monthly rate of 80,000 tons, or nearly as much as was obtained during the early part of the war from the synthetic gasoline plants now under Russian control. These consist mainly of the Leuna and Brabag Works. The machinery for the Oswiecim plant being brought to Poland as German reparations is being assembled. When the plant goes on stream at the end of 1948, its output should be about 20,000 tons of synthetic gasoline per yr. The Peat Institute of Russia has worked out a scheme for the complete utilization of peat burned in power stations. The process consists in treating the peat chemically by means of gasification before sending it to the power station. The power station receives excellent gaseous fuel, and what remains of the peat after the treatment is used to make synthetic gasoline. The process of complete utilization of peat reduces capital expenditure on synthetic gasoline production by 20%, cost of the product by 18%, and peat consumption in power stations by 30–35%.

2651. ———. Oil Production in South Africa. Vol. 52, 1948, p. 989; Ind. Chem., vol. 24, 1948, p. 715.

In Government Gazette, October 9, 1948, announcement was made of license issued to Anglo Transvaal Consolidated Investment Co., Ltd., for manufacture of liquid fuels and oils from coal. The plant is to have an approximate capacity of 76,000,000 gal. of liquid fuel and oil per yr. It will operate a process for catalytic conversion of synthetic gases from carbon-bearing material into petroleumlike hydrocarbons. Production is to begin within 4 yr. The authorized capital of the company will not exceed £13,000,000.

2652. ———. Synthetic Alcohol by New "Esso" Process. Vol. 53, No. 1342, Jan. 14, 1949, p. 43.

Commercial production of iso-octyl alcohol has been announced by Esso Standard Oil Co. The process involves reaction of a selected gasoline fraction with H_2 and CO at pressures up to 3,000 p. s. i. Although iso-octyl, as such, has possibilities as a resin solvent and antifoaming agent, its principal value is as intermediate or raw material for other chemicals. It can be converted to wetting agents, or to metallic salts that make effective paint driers.

2653. PETROV, A. D. [Formation of Petroleum of the Naphthene Type. Transformation of Aliphatic Acids Into Hydrocarbons Under High Pressure.] Jour. Russian Phys.-Chem. Soc., vol. 61, 1929, pp. 1849–1859; Ber. deut. chem. Gesell., vol. 63B, 1930, pp. 75–84; British Chem. Abs., 1930, A, p. 322; Chem. Abs., vol. 24, 1930, p. 2696.

By cracking lactic acid in the presence of lime and H_2O, an oil was obtained identical with that obtained by the hydrolysis of cellulose and differing from Fischer's Synthol chiefly in containing less alcohol. Treatment with H_2SO_4 gave hydrocarbons identical with the corresponding Synthin fractions. Fischer and Schrader have found that lactic acid is the chief product in the hydrolysis of cellulose.

2654. ———. [Synthesis of Motor Fuel From Carbon Monoxide and Hydrogen.] Jour. Appl. Chem. (U. S. S. R.), vol. 5, 1932, pp. 274–284; Chem. Abs., vol. 26, 1932, p. 4932.

Review.

2655. ———. [Synthetic Liquid Fuel and Its Importance for the Ural-Kuznetzkii Basin.] Acad. Sci. Petrograd, 1932, 143 pp.; Chem. Abs., vol. 27, 1933, p. 1135.

Discussion of coal liquefaction, low-temperature carbonization and cracking of low-temperature carbonization tar, synthesis of hydrocarbons from CO and H_2, condensation of olefins from coke-oven plants and cracked gases, cracking of CH_4, condensation of C_2H_2 hydrogenation of naphthalene and other components present in tars, synthetic liquid fuel by fermentation and its byproducts, combined synthetic hydrocarbon and fermentation plants, properties of mixtures containing benzene, gasoline, and alcohol as motor fuels, and automobiles with gas producers using charcoal.

2656. ———. [Gases Obtained in Low- and High-Temperature Carbonization as Raw Material for Commercial Organic Synthesis.] Khim. Tverdogo Topliva, vol. 6, 1935, pp. 82–92; Chem. Abs., vol. 29, 1935, p. 7616.

Review with 28 refs.

2657. ———. [Synthesis of Gasoline From Gases.] Khim. Tverdogo Topliva, vol. 8, 1937, pp. 981–996; Uspekhi Khim., vol. 6, 1937, pp. 1509–1525; Chem. Zentralb., 1938, II, p. 631; Chem. Abs., vol. 32, 1938, p. 5187.

Comprehensive review, with 65 refs.

2658. PETROV, A. D., AND VITTIKH, M. V. [Snythesis and Properties of Isoparaffinic Hydrocarbons of the

Composition C_{13}–C_{24}.] Bull. acad. sci. U. R. S. S., Classe sci. chim. 1944, English summary, pp. 238–242; Chem. Abs., vol. 39, 1945, p. 1618.

Pr hexyl ketone was treated with CH_2: $CHCH_2MgCl$ to yield hexylpropylallylcarbinol, b_7 116°–118°, d_{20}^{20} 0.8482, n_D^{15} 1.4535: dehydration over Al_2O_3 gave a mixture of 4–propyl–1,3–decadiene and 4–propyl–1,4–decadiene, b_6 85°–88°; hydrogenation over Pt black gave 4–propyldecane, b. 214.5°–215.5°, d_{20}^{20} 0.7716, n_D^{20} 1.4354. Dihexyl ketone treated with BuMgBr gave 7–butyl–7–tridecanol, b_{10} 163°–165°, d_{20}^{20} 0.8350, n_D^{20} 1.4489, which was dehydrated by boiling with I to yield an isomeric hydrocarbon mixture, b_9 140°–147°; hydrogenation of the latter over Ni oxide at 240°–250° gave 7-butyltridecane, b_{12} 147°–148°, d_{20}^{20} 0.7793, n_D^{20} 1.4355. Crude methyldioctylcarbinol (admixed with some olefin) was prepared from EtOAc and C_8H_{17} MgBr; this was dehydrated by boiling with I to yield 9-methylheptadecene, boiling at 169°–174° (no pressure given), d_4^{20} 0.7916, n_D^{20} 1.4472, freezing point 26.5°; hydrogenation of the latter over Ni gave 9-methylheptadecane, b_{10} 172°–174°, d_4^{20} 0.7810, n_D^{20} 1.4388. C_8H_{17} MgBr and dihexyl ketone gave 7–hexyl–7–pentadecanol, b_7 196°–197°, d_{20}^{20} 0.8420, n_D^{20} 1.4519; dehydration with I gave an isomer mixture b_7 181.5°–183°; hydrogenation of the mixture over Ni oxide at 220°–250° gave 7–hexylpentadecane, $b_{9.5}$ 182°–183°, d_{20}^{20} 0.7923, n_D^{20} 1.4419. Et caprylate and C_8H_{17} MgBr gave a mixture of 9–heptyl–9–heptadecanol and its dehydration product (pure alcohol b_9 230°–231°, d_{20}^{20} 0.8470, n_D^{20} 1.4538); after the usual dehydration the olefin mixture b_9 206°–212° was hydrogenated over Ni at 250° to yield 9–heptylheptadecane, b_8 210°, d_{20}^{20} 0.8009, n_D^{20} 1.4465. The C_{17}, C_{21}, and C_{24} compounds have cetane numbers near 100 and have satisfactorily low melting points in the continued study of compounds having good antidetonating properties.

PETROVA, L. V. *See* abs. **804.**

PETROVA, N. Y. *See* abs. **279, 281, 282.**

2659. PETTY, M. Scanning Washington's Oil Horizon. Petrol. Eng., vol. 18, No. 12, 1947, p. 14.

Military leaders apparently have become convinced that development of a synthetic fuel industry in the United States, capable of producing 1,000,000 bbl. per day of synthetic oil, is the only sure way of attaining the self-sufficiency required by national defense. As the result of recent conferences between officials of the Interior Department and of the Army and Navy, a plant-construction program, costing several hundred million dollars, may be submitted at the next session of Congress. The program probably will call for building 4 synthetic plants, each with a capacity of 25,000–30,000 bbl. per day to make liquid fuels by retorting oil shale, by hydrogenation of coal, and by the Fischer-Tropsch process using natural gas and coal. Preliminary to this, the Bureau of Mines, at the request of the military, has launched an immediate survey for suitable locations for synthetic plants with a capacity of 1,000,000 bbl. per day. As an indication of the task ahead in making the Nation self-sustaining in synthetic liquid-fuel resources in the face of a natural petroleum shortage in the not too distant future, it was recently pointed out by W. G. Greenman, Director of Naval Petroleum Reserves, that to provide 1,500,000 bbl. of synthetic fuel per day (500,000 bbl. from each of shale, coal, and gas, using the Fischer-Tropsch process for the latter two cases), the following would be needed: total plants, 65 (15 for shale, 25 for each of coal and gas); steel, 9,500,000 tons; construction costs, $4,300,000; mine costs, $650,000,000; and staff for plant operations and mining, 148,000 men. It is estimated by the Bureau of Mines that synthetic plants smaller than those contemplated by the military would be nearly competitive with petroleum refineries; for a 10,000-bbl. per day plant producing motor fuel from subbituminous coal at $1.50 per ton the net cost would be 8.7 cents per gal. while a 20,000-bbl. shale oil plant could make synthetic crude oil for $1.92 per bbl., exclusive of profit and interest on the investment.

2660. PEUSEL, —. Lubricants and Surface Protection in the Metal Industry. TOM Reel 53, February 1945, frames 62–95.

Discusses some important developments in the field of lubricants. The starting material is Kogasin, obtained as a product of the Fischer-Tropsch synthesis and hydrogenated into Mepasin. It was found that a derivative of this, Mepasin sulfonamido acetic acid, had outstanding qualities as a lubricant in metal working, both for cutting, drilling, and milling and for hot and cold shaping, deep drawing of wire, etc. The product is used as an emulsion, both because the lubricating effect is not affected and savings are made, and because this greatly reduced the danger of plant fires. There is presented during the discussion what appears to be a relatively new theory of film formation, lubricating effect, and adhesion to metal. The theory involves molecular polarity, formation of supermolecular structures in the nature of liquid colloidal crystals, the interplay of surface forces, and other novel hypotheses that appear to be solidly grounded and highly illuminating. It is claimed that the new Mepasin derivatives actually make pretreatment of metal blanks in deep-drawing operations unnecessary.

2661. PEW, J. E., AND DOTTERWEICH, F. H. Maximum Hydrocarbon Utilization With Natural Gas as a Chemical Raw Material. Petrol. Refiner, vol. 23, No. 4, 1944, pp. 130–134; Gas, vol. 20, No. 4, 1944, pp. 14–16, 19–20; Chem. Abs., vol. 38, 1944, p. 2475.

Known natural-gas reserves are estimated to be sufficient for at least 30 yr. and large quantities of natural gas are still being wasted. The liquid constituents of natural gas now serve as a source for chemicals, including aviation gasoline and solvents. Expansion is possible in this respect. Dry natural gas can be used for many purposes; it can readily be reformed to water gas, and about 50% of the emergency synthetic NH_3 is made with H_2 from this source. The Fischer-Tropsch process can produce liquid hydrocarbons from this re-formed natural gas, but it is probable that this process will only be operated at remote points where pipelines are not available. It is estimated that 4.2 gal. of liquid products are recoverable from 1,000 ft.^{3} of dry natural gas.

2662. ———. Science in Natural Gas. Gas Age, vol. 949, 1944, pp. 19–21, 62, 64, 66. Petrol. Refiner, vol. 23, December 1944, pp. 92–96; Nat. Petrol. News, vol. 37, No. 1, 1945, pp. R–11, 12, 14, 79; Am. Gas Assoc. Monthly, vol. 27, 1945, pp. 103–106, 148.

Combination of the Fischer-Tropsch process and the natural gas-steam reaction to produce liquid hydrocarbon fractions on a favorable economic basis could result in an enormous amount of natural gas being used, thereby depleting our natural-gas reserves. The operation of pilot plants indicates a favorable economic conversion with plans for at least 1 commercial plant underway.

PFLEGLING, —. *See* abs. **2878.**

2663. PHILIPPOVICH, A. [Decomposition of CO With and Without Catalysts.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 37–43.

Review of literature.

PHILLIPS, J. R. *See* abs. **576.**

2664. PHILLIPSON, G. A. Coke-Oven Managers Association Presidential Address. Gas World, vol. 125, No. 3248, supp., 1946, pp. 10–14.

It is proposed to make use of central coal-carbonizing plants interconnected by gas grids and then installing synthesis plants operating on both gas and coke, which-

ever should be in excess supply at any time, thereby increasing the benefits derived from full-capacity operation of the carbonizing plants.

PHINNEY, J. A. *See* abs. **2834, 2835.**

2665. PHRAGMEN, G. [Stability of Cementite and the Various Forms of Carbon.] Jernkontorets Ann., vol. 114, 1930, pp. 431–442; Chem. Abs., vol. 25, 1931, p. 271.

Critical review of the literature. Conclusion: The evidence indicates that cementite becomes stable at higher temperatures.

———. *See* abs. **3669.**

2666. PICHLER, H. [Coal as a Source of Raw Materials.] Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 734–737; Chem. Abs., vol. 26, 1932, p. 3899.

2667. ———. [Progress in the Field of Coal Utilization.] Ztschr. Ver. deut. Ing., vol. 74, 1930, pp. 720–722; Ges. Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 594–604; Chem. Abs., vol. 24, 1930, p. 3879.

Discusses chemical improvement of coal, especially from the viewpoint of producing liquid fuel.

2668. ———. [Effect of Pressure on the Conversion of Water Gas.] Brennstoff-Chem., vol. 12, 1931, p. 235.

Paper presented at the meeting of the Verein Deutscher Chemiker in Vienna, May 1931. Increased pressure hinders the gasification of carbonaceous substances with steam, owing to the masking of the surface by inert gases. If this inactivity is prevented by means of increased temperature or by the addition of alkali, a secondary formation of hydrocarbons occurs through the action of the nascent H_2 on the C present. Increased pressure in the catalytic hydrogenation of CO favors the deposit of high-molecular products on the catalyst. Thus the catalyst activity deteriorates much fasten than at 1 atm. pressure. At higher pressures acid-containing products take the place of the hydrocarbons. Diminished pressure is unfavorable for the formation of hydrocarbons since for the same amount of conversion larger amounts of catalyst are necessary. The nature and the speed of CH_4 cracking with CO_2 or steam is strongly influenced by pressure. At 1/100 atm. and 500°–600° all of the CH_4 is converted into CO and H_2, whereas at atmospheric pressure a temperature of 900°–1,000° is required. The speed of reaction increases in proportion to the diminution in pressure.

2669. ———. [Influence of Pressure on Several Conversions of Water Gas.] Ztschr. angew. Chem., vol. 44, 1931, p. 472.

Paper presented before the Fachgruppe für Brennstoff and Mineralölchemie in May 1931.

2670. ———. [Synthesis of Gasoline at 200° C. and Atmospheric Pressure.] Ztschr. Ver. deut. Ing., vol. 79, 1935, pp. 883–885; Coal Carbonisation, vol. 1, 1935, pp. 101–103.

In the Fischer-Tropsch process, Fe, Co, and Ni are found to be the best catalysts for the conversion of CO–H_2 into hydrocarbons. Their action probably involves the temporary formation of carbides. However, to obtain the best results, it has been found necessary to employ combinations with other metals in specific amounts. Thus far the best yields have been obtained with a Co–Th–Cu–kieselguhr catalyst precipitated with soda under defined conditions. This yielded 105–110 and even over 120 gm. of liquid hydrocarbons per $m.^3$ of gases in a single pass, and maintained 80% of this yield after 60 days, during which period the catalyst absorbed up to 150% of its weight of hard paraffin. After appropriate regeneration the catalyst can be used again. The synthesis proceeds at about 200° C. and atmospheric pressure; about 75% of the original gas is converted. Complete conversion results in the liberation of about 600 kgcal. per $m.^3$ of gas or about 20% of the heat of combustion, therefore, the removal of the heat is an important problem and is solved by circulation of oil through the contact chamber and a steam generator for utilization of the heat extracted. The mixture of gases for the synthesis of gasoline consists of CO and H_2 in the ratio of 1 : 2. If unsaturates are desired in the products, a higher proportion of CO is used. The S content of the synthesis gas should not exceed 0.2 gm. per 100 cu.m. The products of synthesis from a 29 : 58=CO : H_2 mixture with Co catalyst, in weight %, consisted of gasol, 4% (boiling below 30°); gasoline or Kogasin I, 62% (boiling at 30°–200°); oil or Kogasin II (boiling above 200°); solid paraffin from oil, 7% (m. p. 50°); hard paraffin from catalyst, 4% (m. p. 70°–80° or more). The gasoline is low in antiknock properties; the octane No. of the 30°–180° C. Kogasin fraction is 67 with 0.5 cc. of $PbEt_4$ per l. and 71.5 with 1 cc. per l. The Kogasin II is an excellent diesel fuel. The synthetic paraffin is of specially high purity. An increased yield of gasoline can be obtained by subjecting the higher boiling Kogasin II to cracking by the usual methods of petroleum technology. The unsaturated hydrocarbons in the synthesis products can be varied by altering the composition of the initial gas and the catalyst; they are important as the raw materials for the manufacture of pure higher alcohols or esters. For the manufacture of lubricating oils (1) the fractions containing olefins are treated with 5% by weight of $AlCl_3$, (2) the high-boiling fractions low in olefins are chlorinated and then converted to Cl-free viscous oil by activated Al_2O_3, (3) chlorinated Kogasin with aromatic hydrocarbons is condensed in presence of $AlCl_3$. Such lubricants combine a favorable viscosity index with a low setting point (—42° C. compared with —16° C.) for a commercial winter oil.

2671. ———. [Working Up Fischer-Tropsch Products.] Brennstoff-Chem., vol. 16, 1935, pp. 404–406; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 481–486; Chem. Abs.. vol. 30, 1936, p. 3980.

Synthetic-paraffin oil boiling at over 250° has been converted at 500°–600° and atmospheric pressure without carrier gas, in one step, into gaseous olefins and volatile unsaturated and aromatic hydrocarbons with 75% yields. The remainder consisted of saturated gaseous hydrocarbons, unconverted paraffins, and aromatic tar. Below 500°, conversion was small. Above 600°, yields of gaseous olefins predominated. Example: 20% olefins at 550° and 0.4 sec. reaction time in small tubes, 60% at 700° and 0.14 sec.

2672. ———. [Discovery and Synthesis of New Paraffins of Very High Molecular Weight.] Brennstoff-Chem., vol. 19, 1938, pp. 226–230; Petrol. Ztschr., vol. 34, No. 38, 1938, pp. 1–5; Chem. Abs., vol. 33, 1939, p. 120.

In preliminary pressure hydrogenations with noble-metal catalysts, mixtures of 1 : 2 CO : H^2 heated to 140° in contact with reduced Ru oxide at 150 atm., while paraffins accumulate upon the catalyst. These are completely soluble only in boiling ether, C_6H_6, or toluene and are separated with boiling toluene or xylene into fractions, the highest m. 120°–132°. Repeated hydrogenation is made with 3 gm. catalyst in a heated-steel tube with continuous flow of the gas mixture exhausted at 1 l./hr. and starting at 15 atm. and 140°, the temperature is increased 10° each 24 hr. Conversion begins at 160°, with 7% contraction in gas volume at 180°, increasing to 24% at 240°. The solid and liquid reaction products, melting clear at 111°, are recovered in maximum yield at over 70% contraction at optimum conditions of 200° and 100 atm. At 50–100 atm., over 90% of the O_2 in the CO forms H_2O; only below 50 atm. and above 200° are appreciable amounts of CO_2 formed. Small amounts of fatty acids are

formed with the reaction H_2O. No decrease in catalyst activity is observed in 26 wk. of continuous use. The oil-free solid paraffins constitute 60–70% of the product by the butanone method and m. 118°–119°. Of these, 13% are insoluble in boiling C_6H_6 and m. 126°–128°. The 53% soluble in boiling C_6H_6, m. 113°. Subsequent extraction of the Ru catalyst with boiling toluene yields a paraffin m. 132°. All the paraffins recovered, recrystallized, and washed with MeOH and distilled ether have the composition C_nH_{2n+2}. Determination of molecular weight by boiling point elevation, mostly in toluene, show a range of 2,100–8,000, or 170–670 C atoms, for the 5 paraffins m. 123.5°–131.5° extracted from the catalyst. These are situated upon the upper extension of the hyperbolic C atom: melting point curve of *n*–paraffins. The 1:1 addition of kieselguhr to the Ru is without effect. At atmospheric pressure, Pt produces no solid or liquid products, whereas Os and the remaining noble metals, beginning at 215°, produce small amounts of gaseous hydrocarbons other than CH_4 becoming inactive at 315° to produce only CH_4. Under pressure, considerable yields are obtained with Rh and Os, the first giving contractions similar to Ru but with O-containing compounds, the latter reaching an activity at 220° to produce gaseous hydrocarbons. Pt is even less active while only traces of hydrocarbons are obtained with Pd and Ir.

2673. ———. Lecture and Discussion on Iron Catalysts for the Middle-Pressure Synthesis, Sept. 9, 1940. TOM Reel 101; Transl. on TOM Reel 244, 21 pp.

In general, it has been found that the best catalysts are those prepared by precipitation of ferric nitrate solutions with Na_2CO_3 or NH_3; they are designated normal Fe catalysts. They must be inducted before use, and the best method, therefore, appears to be that of passing pure CO at lower pressures and higher temperatures than are used in the following synthesis and at a high gas velocity, for example: 1/10 atm., 255°–325°, and 400 l. of CO gas/kg. Fe/hr. The induction period is terminated when the formation of CO_2 has passed through a maximum and has reached a more or less constant minimum value, generally in about 25 hr. With a catalyst thus inducted, a synthesis pressure of 15 atm., a temperature of 235°, and a synthesis gas composition of 3 CO : 2 H_2, maximum yields of 130–160 gm./N $m.^3$ of gas can be obtained. An Fe catalyst made and operated as above had a life of 1½ yr. without regeneration at a temperature of 260°; it still gave a yield of 140 gm./N $m.^3$ The ideal synthesis gas was produced by passing CO_2 and steam over hot coke according to the equation $5\ C+4\ H_2O+CO_2=6\ CO+4\ H_2$. The CO_2 for the conversion is obtained by scrubbing the end gases from the synthesis process. Addition of small amounts of alkali (0.5–5% K_2CO_3) to the Fe catalyst has no important effect on the total yield of products but does change their quality, an increase in the paraffins and oxygenated products and a decrease in the liquid and gasol hydrocarbons with increasing alkali contents. The lifetime of the catalyst also is longer at a low alkali content (1% K_2CO_3 or other alkaline salt) than it is at a higher content. It was found that treatment of the catalyst with H_2 either before induction with CO or between the induction period and the synthesis proper offers no improvement in the activity of the catalyst. Some increase in the activity and a better stability of the catalyst does, however, result by interrupting the synthesis and treating with H_2; this must be done before the catalyst has deteriorated to a great extent. The use of kieselguhr as carrier in the Fe catalyst is detrimental to its activity unless added after alkalization. As regards mechanism of the induction process, it is assumed that the primary reaction is the reduction of the ferric oxide into ferromagnetic Fe_3O_4, which, at the low temperature and pressure of the induction, is converted directly into carbide by action of the CO without going through the FeO phase. In presence of 100% CO induction gas and at the low pressures and high CO velocities used during the induction, the CO_2 is rapidly removed from the catalyst and the carbide remains stable without oxidation. The action of CO on the Fe catalyst is 3-fold: the reduction process differs from the H_2 reduction, the CO deposits free C on the catalyst thus loosening the crystal lattice and making more surface available for the reaction, and carbides are formed. With a $CO+H_2$ mixture, liquid and solid hydrocarbons are forming on the catalyst surface and preventing the activating gases from coming in contact with the catalyst. Some description is given of the products of the middle-pressure synthesis. The Fe catalysts are not only superior to the Co catalysts because of their cheapness, but also for the cheaper apparatus required and the more stable lifetime that they exhibit. The antiknock properties of the benzine made with the Fe catalyst are better than those made with the Co catalyst, and the unsaturated gasol hydrocarbons can be used to greater advantage for production of high-quality benzine. Fe catalysts have the disadvantage of working at higher temperatures, hence greater steam pressure, if cooling is done with H_2O. Furthermore, they have a greater tendency to form C than do the Co catalysts. This report includes the only published data on induction methods for Fe catalysts. The documents translated are: PG–21559–NID; PG–21574–NID (lecture by Dr. Pichler); PG–21581–NID (recent investigations); and PG–21577–NID (behavior of Fe catalysts where operated with H_2-rich synthesis gas.)

2674. ———. [Town Gas in Conjunction With Kogasin Synthesis.] Brennstoff-Chem., vol. 22, 1941, pp. 244–248; British Chem. Abs., 1942, I, p. 218B; Chem. Abs., vol. 36, 1942, p. 6329.

Possibility of obtaining town's gas of specified properties, for example, calorific value 4,200–4,600 kcal./$m.^3$, d. 0.4–0.5, and Ott number 60–100, by mixing residual gas from the Fischer-Tropsch hydrocarbon synthesis process with water gas in suitable proportions, converting CO into H_2 and CO_2, and removing CO_2, is discussed theoretically. The effects on the composition of the town gas obtained of changing the CO : H_2 ratio of the synthesis gas, the type of synthesis catalyst employed, and the presence of CO_2, N_2, and CH_4 in the synthesis gas are illustrated by examples.

2675. ———. [Formation and Decomposition of Formic Acid and Formates.] Brennstoff-Chem., vol. 24, 1943, pp. 27–31; Chem. Abs., vol. 37, 1943, p. 6644.

Review with over 50 refs., most of which are incorporated in this bibliography. From experiments conducted by the author, it is found that under suitable conditions of pressure, temperature and catalysts, it is possible to synthesize a relatively high % of free HCOOH from CO and H_2O or CO_2 and H_2. The production of sugar is a possibility.

2676. ———. [Reaction of Carbon Dioxide During Hydrogenation.] Brennstoff-Chem., vol. 24, 1943, pp. 39–40; Chem. Zentralb., 1943, I, p. 2556; British Chem. Abs., 1944, B, p. 194; Chem. Abs., vol. 37, 1943, p. 6526.

In the Fischer-Tropsch synthesis, CO_2 does not react in the presence of CO; atomic H is assumed to be necessary for the hydrogenation of CO_2. Only little chemisorbed H_2 is present on the catalyst surface during the formation of higher hydrocarbons. The hydrogenation of CO_2 does not follow the same course as that of CO. HCOOH may be considered the first intermediate product in the hydrogenation of CO_2 and it is converted isomerically into dioxymethylene. The next stage is CHOH with liberation of H_2O from which

CH_4 or MeOH is formed according to the reaction conditions.

2677. ———. Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. Bureau of Mines Special Rept., June 1947, 159 pp.

Comprehensive review of the development of the Fischer-Tropsch hydrocarbon synthesis at the Kaiser Wilhelm Institut für Kohlenforschung, and of the most-important work connected therewith. Consideration is given to the historical background; the normal pressure synthesis, its catalysts, and products; medium-pressure synthesis with Co and Fe catalysts and its products; modifications of these processes, such as hot gas recycle, liquid-phase catalyst suspension process, oil recycle; high-pressure synthesis of paraffin with Ru catalysts; isosynthesis in presence of oxide catalysts (ThO_2); and mechanism of the hydrogenation process.

2678. ———. [Development of Gasoline Synthesis in the United States. Hydrocol Process.] Brennstoff-Chem., vol. 30, 1949, pp. 105–109; Chem. Abs., vol. 43, 1949, p. 7664.

Development of the Fischer-Tropsch process in the United States is reviewed. Stress is laid on the use of a fluidized catalyst (alkalized Fe) and the use of a highly efficient external heat exchanger to remove the heat of reaction; this avoids the use of numerous small internally cooled catalyst chambers as in Germany. This catalyst is poisoned by S but is not affected by the formation of small amounts of C, although excessive amounts of C reduce its efficiency. The gasoline consists of a mixture of primary gasoline and polymerization gasoline. The C_3–C_4 fraction is nearly 100% saturated. The gasoline has an octane number of about 80 motor method. Brief reference is made to costs, and a simplified flow sheet is given.

2678a. ———. Fischer-Tropsch and Related Processes for Synthesis of Hydrocarbons by Hydrogenation of Carbon Monoxide. Advances in Catalysis, Academic Press, Inc., New York, 1952, vol. 4, pp. 271–341.

2678b. ———. [Review of 25 Years Research on the Fischer-Tropsch Synthesis and Related Processes With Especial Attention to the Reaction Mechanism Involved.] Brennstoff-Chem., vol. 33, 1952, pp. 289–296; Chem. Abs., vol. 47, 1953, p. 290.

Review, with 44 refs.

———. *See* abs. **872, 999, 1000, 1001, 1002, 1003, 1004, 1005, 1006, 1007, 1008, 1009, 1010, 1011, 1036, 1037, 1038, 1039, 1040, 1041, 1048, 1837.**

2679. Pichler, H., and Buffleb, H. [Behavior of Ruthenium Catalysts in Synthesis of Paraffin Hydrocarbons of High Molecular Weight.] Brennstoff-Chem., vol. 21, 1940, pp. 273–280; Chem. Zentralb., 1941, I, p. 1118; Chem. Abs., vol. 36, 1942, p. 2253.

Activity of the catalyst was the same whether it was first reduced with H_2 or with $2H_2+CO$ at atmospheric pressure, or was reduced directly with synthesis gas under pressure without pretreatment. The normal gas rate used was 5 l. per hr. with 3 gm. of Ru; with falling gas rate, the conversion into liquid and solid hydrocarbons rose to approximately the theoretical value. The yield per hr. reached a maximum (300–350 gm. per l. of catalyst space) at a gas rate of 10 l. per hr. per gm. of Ru. Data on the variation of the yield with temperature and pressure are tabulated. Yields remained approximately constant over 200 days' operation at 195° per 100 atm., and thereafter slowly diminished; after 560 days, when the temperature had been raised to 215°, the yield was 140 gm. per $m.^3$, that is, only 10% less than the initial value. Addition of alkali (K_2CO_3) to the catalyst had little influence on its activity or on the ratio of liquid to solid hydrocarbons in the product. Addition of H_3PO_4 or phosphates did not improve the catalyst. By carrying out the synthesis with a Ru catalyst suspended in H_2O at 150°, a high proportion of paraffins of high melting point, insoluble in boiling C_6H_6, was obtained. Briefly discusses the mechanism of the reaction.

2680. ———. [Properties of Some Solid Paraffins Produced From Carbon Monoxide and Hydrogen at High Pressures on Ruthenium Catalysts, With Special Reference to the Previously Unknown Highest Melting Constituents.] Brennstoff-Chem., vol. 21, 1940, pp. 285–288; Chem. Zentralb., 1941, I, p. 119; Chem. Abs., vol. 35, 1941, p. 7365.

Paraffins were fractionated by means of solvents and the ultimate analysis, mean molecular weight, melting range, density, and viscosity of each fraction were determined. The dependence of melting point and viscosity on molecular weight is shown graphically. The highest melting fraction (132°–134°) had a mean molecular weight of 23,000 and d^{20} 0.980. A comparison of paraffins formed on the Ru catalysts with those from medium pressure synthesis on Co catalysts showed that the former have the higher melting range. The production of such paraffins has not been possible so far by any other process.

2681. ———. [Synthesis of Paraffin Wax on Ruthenium Catalysts at Pressures up to 1,000 Atmospheres.] Brennstoff-Chem., vol. 21, 1940, pp. 257–264; Chem. Zentralb., 1941, I, p. 850; Chem. Abs., vol. 36, 1942, p. 2253.

Gas mixture ($CO+2H_2$) was passed over the catalyst (3 gm. of Ru) at a rate corresponding with 1 l. (normal temperature and pressure) of resultant gas per hr. At 140° the conversion of CO into hydrocarbons rose from nil at 15 atm. to 18% at 100 atm. and 54% at 1,000 atm. (36% of liquid and solid hydrocarbons); at 180° the conversion rose from 11% at 15 atm. to 70% at 100 atm. and 91% at 1,000 atm. (72% of liquid and solid hydrocarbons). At 100 atm. about 65% and at 1,000 atm. about 75% of the liquid and solid hydrocarbons consisted of paraffin waxes of melting point up to 134°. At 200° per 100 atm. and half the above rate of gas passage, yields of 190 gm. per $m.^3$ (normal temperature and pressure) of initial gas, that is, 91% of theory, were obtained. The yields of liquid and solid hydrocarbons varied only slightly with temperature over the range 190°–240°; at higher temperature, especially above 300°, the formation of CH_4+CO_2 became marked. Mixtures of CO_2 and H_2 interacted over a Ru catalyst at lower temperature than $CO+2H_2$ but only CH_4 and H_2O were formed. The presence of CO_2 did not affect the interaction of CO and H_2.

2682. ———. [Synthesis of Free Formic Acid From Carbon Monoxide and Water.] Brennstoff-Chem., vol. 23, 1942, pp. 73–77; Chem. Age, vol. 53, 1945, pp. 463–468; Chem. Abs., vol. 36, 1942, p. 4474.

Formation of formic acid through the direct action of CO and H_2O under pressures up to 2,000 was investigated. At each temperature, a definite state of equilibrium exists between the concentration of liquid formic acid and CO pressures. Certain mineral acids and salts (Cu_2SO_4, $CuCl_2$) and especially H_2S and H_3PO_4 are suited as catalysts. The salts under the conditions of the reaction are reduced to the mineral acids. The optimum conditions for formic acid synthesis are determined.

2683. Pichler, H., and Merkel, H. Chemical and Thermomagnetic Studies on Iron Catalysts for the Snythesis of Hydrocarbons. Bureau of Mines Tech. Paper 718, 1949, 108 pp.; TOM Reel 259, frames 129–328; FIAT Reel CC–259.

Literature review of the mechanism of the synthesis reaction by way of heterogeneous catalysis, on carbide formation in the treatment of Fe catalysts with CO, and on the thermomagnetic method of studying the carburization of Fe. The composition of Fe catalysts

at various stages of pretreatment and snythesis was determined by chemical and thermomagnetic analysis. The latter method revealed the almost complete transformation of Cu-free Fe catalysts, carburized at 325°, to a ferromagnetic higher Fe carbide (Fe_2C) with a Curie point of 265°. Carburization of Cu-promoted (20% Cu) Fe catalysts at 220°–230° yielded not only the Curie point 265° carbide but also a second ferromagnetic Fe carbide whose Curie point was 380°. Of these 2 carbides, the first is the more thermally stable; it reverts to Fe_3C above 400°, whereas the second carbide is unstable above 300°, being ultimately converted to cementite and free Fe above that temperature. The higher Fe carbides formed during carburization were stable during the synthesis. During carburization at 325° and during subsequent medium-pressure synthesis; the Curie point 265° carbide was virtually the only carbide present. After carbide-oxide equilibrium was established, active catalysts maintained their carbide content unchanged. A decrease in catalytic activity was marked by a drop in the carbide content and by an increase in the O content. Fe catalysts with a high Cu content consisted of approximately equal amounts of Curie point 265° and Curie point 380° carbide during operation at atmospheric pressure. These carbided catalysts gave almost quantitative conversion of the CO in water gas with liquid and solid hydrocarbons as the principal products. When a catalyst thus carbided was operated at medium pressure, the maximum synthesis temperature dropped from 220° to 205° for the same conversion capacity. This increase in activity probably was due to the presence of the Curie point 380° carbide, which characterizes atmospheric pressure synthesis. When the synthesis proceeded at a lower temperature, no formation of free C appeared during carburization and synthesis. At the end of the pretreatment process, carbide formation and conversion capacity had reached their maximum values and no further C appeared. (*See* abs. **2239.**)

2684. ———. [Chemical and Magnetochemical Investigations of Iron Catalysts Used in Fischer-Tropsch Snythesis. I.] Brennstoff-Chem., vol. 31, 1950, pp. 1–9; Bureau of Mines Tech. Paper 718, 1949, pp. 16–45; Chem. Abs., vol. 44, 1950, p. 3696.

Composition of Fe catalysts used in medium-pressure syntheses was studied by means of acid decomposition. The activity of the catalysts increased with increasing formation of carbide during carburization. In synthesis, the large amount of carbide present after pretreatment decreased during the 1st days of operation to 0.2–0.4 gm. of carbidic C per 10 gm. Fe in an active catalyst. There was a corresponding increase in the O content to 0.1–0.2 gm. per 10 gm. Fe. The catalysts maintained this carbide-oxide equilibrium for months. Acid decomposition of catalysts whose activity had decreased (contraction less than 40%) showed, at most, 0.1 gm. carbidic C per 10 gm. Fe and a correspondingly high O content. (*See* abs. **2683.**)

2685. ———. [Chemical and Magnetochemical Investigation of Iron Catalyst Used in Fischer-Tropsch Synthesis. II. Magnetochemical Investigations.] Brennstoff-Chem., vol. 31, 1950, pp. 33–42; Chem. Abs., vol. 44, 1950, p. 4223.

Two Fe carbides, both having the formula Fe_2C, appear in various stages in the preparation and use of Fe catalysts for hydrocarbon synthesis. The more stable form has a Curie point of 265°; the less stable, 380° (there may even be a 3d form with a Curie point near the latter). Determinations of the C content of such carbides by the acid method give only 50% of the value determined by hydrogenation with H_2. In acid decomposition, ½ of the C is liberated in free form. In normal-pressure synthesis at 220°–230°, the 2 Fe carbides are present in equivalent amounts. In medium pressure syntheses with Cu-free catalysts, formed at temperatures above 250°, the 265° Curie-point carbide appears to predominate. However, if the normal pressure mixture of the 2 carbides is used, the synthesis temperature can be lowered from 220° to 200° for equal throughputs, and this catalyst activity is well maintained. Low temperatures of carbide formation and increased Cu content favor the formation of Fe_2C with the 380° Curie point; with an Fe: Cu ratio of 5:1 and a temperature below 200°, this is the predominant carbide. An amount of Fe_3O_4 corresponding to the specific equilibrium conditions is always found in the catalyst. The carbide Fe_3C has not been found as a primary C reaction product in active catalysts. While formation of the Fe_2C is a necessary condition for an active catalyst, and the activity of the catalyst is parallel to the Fe_2C content, the physical structure of the catalyst also is important. The possible role of intermediate reactions in hydrocarbon synthesis is discussed. (*See* abs. **2683.**)

2686. Pichler, H., and Reder, R. [Formation of Methanol in the Partial Oxidation of Methane and Ethylene Under High Pressure.] Angew. Chem., vol. 46, 1933, pp. 161–165; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 318–326; Chem. Abs., vol. 27, 1933, p. 2671.

Yield of MeOH increases with increasing pressure and decreasing O_2 content of the starting products. With a ratio of CH_4 or C_2H_4: O_2 of 10:1, about 7% of the theoretical yield was obtained. If the initial O_2 content is below 1%, the partial combustion forms mainly MeOH. The formation of MeOH was favored by the presence of H_2O vapor and CO_2, but decreased in the presence of metallic catalysts. Optimum temperatures for the start of the reactions were found for CH_4 but not for C_2H_4. Apparatus is described for gas reactions at high pressures (400 atm.). For practical purposes the reaction could be carried out either at very high pressures or by recirculation of the stripped reaction products with low O_2 concentrations, or by a combination of both. 10 literature refs.

2687. Pichler, H., and Walenda, H. [Formation of Iron Carbonyl in the Action of Carbon Monoxide Upon Steel.] Brennstoff-Chem., vol. 21, 1940, pp. 133–141; Chem. Abs., vol. 35, 1941, p. 3207.

Literature is reviewed in work arising from projected use of CO and H_2 with alloy steels at 300° and 1,000 atm. The heat of formation of liquid $Fe(CO)_5$ in the equilibrium $Fe+5\ CO=Fe(CO)_5$ was determined as +53.7 kgcal. per mol. at constant volume. Theoretical and actual temperature-pressure relations were determined by use of filings of 0.15–0.30 mm. low-C steel containing S and P in 48-hr. tests with still and flowing CO, containing 10% N_2, at 100°–250° and 300 atm. starting pressure. Maximum action in the tests occurred at 270 atm. and 200° in 2 days in still gas. Equilibrium concentrations of gaseous $Fe(CO)_5$ decreased sharply from 5% to 0.01% with increasing temperature. Tests with alloy steels at 200° and 300 atm. showed the 14.2 and 24.4 Cr steels to suffer no weight losses, while a 2.8% Si steel and one containing 1.22% Cb lost 2–3%. Similar tests at 450 atm. of Cr 14.2 and Ni 0.72% gave no weight loss, but steel containing Cr, 3.18; Mo, 0.64; W, 0.6; and V, 0.12% lost 5–8%. Large and small steel filings, containing 5.0% Ni, lost 10 and 30%, respectively, the carbonyl analysis showing no preferential Ni. Steel of 2.46% Mn lost over 5%. Steel of 2.3% V or 1.22 Cb lost 5–8% and one of 5.3 Al lost 1–1.5%. In tests of nearly 17 days at 6 l. per hr. with rods 40 x 6 mm. diam. in flowing 100% CO at 1,000 atm. and 200°, low-C steel lost 2% in weight. After heat-treatment its loss was around 7%. Gray cast iron lost around 75%, retaining its dimensions with a reduction in apparent density from 7.1 to 2.0 and increasing in C from 2.9 to 16% instead of

the expected 10–11%. Metallographic sections showed residual skeletons of phosphide eutectic and ferrite residue. Two series of tests with rods in 100% CO and CO containing 60% H_2 and 10% N_2 at 1,000 atm. and 200° showed that steel of 3.18% Cr plus small amounts Mo, Si, W, and V lost weight but increased Cr and Si reduced the loss; mixed gas attacked these alloy steels less; steels of 14–28% Cr were unattacked by either gas; steel of Cr 18, Ni 8.9, and Ti 0.53% gained weight; steels of 2.8–4.3% Si were attacked strongly, but 15% Si greatly reduced attack; steels of 5–23% Ni were attacked strongly at the lower Ni; steels of 2.5–13.5% Mn were attacked less at higher Mn; a 0.4–0.6% Mo steel was attacked strongly by mixed gas; low Cr–Mo–V steels were attacked strongly by both gases as were steels of 2.3% V and 1.22–3.5% Cb. 26 refs.

2688. PICHLER, H., AND ZIESECKE, K. H. [High-Pressure Hydrogenation of Carbon Monoxide Preferably to Isoparaffinic Hydrocarbons. (Isosynthesis). I.] Brennstoff-Chem., vol. 30, 1949, pp. 13–22; Fuel Abs., 1949, No. 2,913.

Isosynthesis is defined as the high-pressure hydrogenation of CO at pressures exceeding 30 atm., preferably between 300 and 600 atm., and about 450°. ThO_2 has been found to be the best simple catalyst. ZrO_2, CeO_2, and, to a much less extent, Al_2O_3 are suitable also. Gaseous and liquid hydrocarbons are formed in which, for example, the C_4 hydrocarbons are 80–90% of a branched nature. If the pressure is too high (above 600 atm.) and the temperature too low (below 400°), considerable quantities of compounds containing O_2 (most of all MeOH, isobutanol, and dimethyl ether) are formed. At 600 atm. and 450° with ThO_2 catalyst, a yield of about 154 gm. was obtained, which consisted of 34.5% liquid products, 29.3% iso–C_4, 14.7% C_3 and *n*–C_4, and 18.2% C, and C_2 hydrocarbons beside dimethylether. By working in several stages, the yield at moderate pressures could be considerably increased. In circulation experiments the $CO : H_2$ working ratio could be widely shifted in the direction of H_2 consumption.

2689. ———. [High-Pressure Hydrogenation of Carbon Monoxide, Especially to Isoparaffin Hydrocarbons. (Isosynthesis). II. Tests on Composite Catalysts and the Conversion of Dimethylether.] Brennstoff-Chem., vol. 30, 1949, pp. 60–68, 81–84; TOM Reel 279, item 13, frames 789–931.

In the continual development of isosynthesis catalysts, a number of composite catalysts were subjected to thorough investigation. It was found that by adding ZnO to ThO_2 the yield of liquid hydrocarbons was increased, and by adding Al_2O_3 the isobutane yield was increased. The yield of isobutane was especially high when 3% K_2CO_3 was added to the aluminum precipitate of a ThO_2+20% Al_2O_3 catalyst. At 300 atm. and 450°, the yield was about 85 gm. per N $m.^3$ of pure gas, or 51% of the hydrocarbons produced. When an alkali-free (ThO_2+20% Al_2O_3) catalyst was used at 600 atm. and 450°, 130 gm. of liquid hydrocarbons plus gasol per N $m.^3$ of CO–H_2 mixture were obtained. The yield consisted of 61 gm. of isobutane and 56 gm. of liquid hydrocarbons. With the correct amount of $ZnO : Al_2O_3$, it was possible to replace some of the ThO_2. However, the space-time yield was not obtained. A 4-month, large-scale laboratory test with (ThO_2+20% Al_2O_3) catalyst demonstrated the long life and the regenerabiilty of the isosynthesis catalyst. Some investigation was made of the occurrence of dimethylether in the isosynthesis reaction, particularly with ThO_2. It was found that considerable amounts of isobutane could be produced.

2690. ———. Isosynthesis. Bureau of Mines Bull. 488, 1950, 39 pp.

This bulletin is a translation and revision of the original German paper describing an investigation of the synthesis of branched-chain hydrocarbons. The paper contains data on the development of the catalyst for the isosynthesis, on the effect of temperature and pressure of operation, and on the composition of the products of the reaction. Experimental evidence and speculations concerning the mechanism of the isosynthesis are discussed. The original paper appears on TOM microfilm reel 279, item 13, frames 789–931. (*See* abs. **2688, 2689.**)

2691. ———. Isosynthesis Process. Oil Gas Jour., vol. 49, No. 15, 1950, pp. 92, 95, 107–108.

Summary in English of the paper reported in abs. **2688**, abs. **2689**, and abs. **2690.**

2692. PICHLER, H., ZIESECKE, K. H., AND TITZENTHALER, E. [Composition of Hydrocarbons From Isosynthesis.] Brennstoff-Chem., vol. 30, 1949, pp. 333–347; Chem. Abs., vol. 44, 1950, p. 815.

Benzine fraction was found to consist predominantly of branched paraffins and naphthenes. The principal synthesis products boiling up to 100° were methylbutane, 2–methylpentane, 2,3–dimethylbutane, 2,4–dimethylpentane, 2–methylhexane, 3–methylhexane, 2,3–dimethylpentane, methylcyclopentane, dimethylcyclopentane, and methylcyclohexane. Small amounts of unbranched paraffinic and naphthenic hydrocarbons were found as well as examples of the quaternary C-atom, neohexane, and homologous heptanes. The olefin and aromatic contents increased with the boiling point. More olefins were formed at low synthesis temperature, 375°, than at the higher, 425°. The octane number, motor method, of the primary benzine was about 80 and could be increased about 12 units with 0.08% by vol. of $PbEt_4$. By the addition of alkylated isobutane and $PbEt_4$, the octane number could be increased to approximately 100.

2693. PICHLER, H., ZIESECKE, K. H., AND TRAEGER, B. [Oxygenated Compounds, Particularly Alcohols, From Isosynthesis.] Brennstoff-Chem., vol. 31, 1950, pp. 361–374.

Purpose of this work was to investigate the oxygenated compounds formed on isosynthesis catalysts and to establish how their composition depends upon the various catalyst additions, the synthesis temperature, and the pressure. In preparing the products, the synthesis conditions were, in part, intentionally chosen so that fewer hydrocarbons and more oxygenated compounds would be formed. In order to investigate the synthesis products, which were obtained through distillation, it was necessary to separate the oxygenated compounds from the hydrocarbons. This was first attempted by selective solution, but it did not succeed. It was necessary to convert the alcohols into their boric acid and phthalic acid esters, which were then easily separated from the hydrocarbons. The most suitable way to isolate the alcohols boiling up to 160° from the isosynthesis mixture was to separate the nonalcohols through azeotropic distillation with MeOH. The alcohols isolated in this way were fractionally distilled afterwards and characterized on the basis of their physical properties. Aldehydes and ketones, as well as acids and esters, have been determined by their chemical characteristics. The dehydration necessary for precise characterization of alcohols can be well-accomplished by extractive distillation with carbon tetrachloride. The composition of the isosynthesis products shows, that under the reaction conditions by which oxygenated compounds are formed, the alcohols are of the same type as those formed on oxide catalysts in the synthesis of MeOH and higher alcohols. MeOH and isobutanol were found as the chief components besides small amounts of ethanol and propanol as well as traces of isopropanol and tertiary

butanol. The higher alcohols investigated (up to C_7) showed almost exclusively α-branchings. The carbonyl compounds formed in relatively small amounts consisted especially of isobutyraldehyde. The ester fraction was very small. The acid content made up about half of the ester fraction, and isobutyric acid was the chief acid component. Addition of alkali favored up to a certain extent the formation of higher alcohols. ZnO added to the ThO_2 catalyst increased the higher alcohol content. Addition of Al_2O_3 strongly reduced the formation of alcohols at far lower synthesis temperatures than normal, apparently through dehydration, and ethers, in part, appeared as byproducts. An increase in pressure effected an increase in the amount of alcohols, probably because of the prevention of dehydration. Hereby, somewhat greater amounts of alcohols, usually present only in traces, have been formed. Increase in temperature favored dehydration, in fact, the straight-chain alcohols decreased in amount less than the branched and the primary decreased less than the secondary or even the tertiary alcohols. The amount decreased further with decreasing C number. A flow diagram is presented that explains the formation of the oxygenated compounds in the catalytic hydrogenation of CO. A comparison of the oxygenated compounds and the hydrocarbons from isosynthesis makes it appear that alcohols are the probable primary products from which by dehydration and hydrogenation the corresponding aliphatic hydrocarbons are formed.

2694. Pickles, A. T., and Sucksmith, W. Magnetic Study of the 2-Phase Iron–Nickel Alloys. Proc. Roy. Soc. (London), vol. 175, 1940, A, pp. 331–344; Chem. Abs., vol. 34, 1940, p. 5811.

Measurements of magnetic saturation intensity of annealed Fe–Ni alloys were used to demonstrate the existence of a 2-phase field in the Fe-rich part of the system. The phase boundaries were determined at temperatures above 450°, and the relation of the equilibrium phase diagram to the thermal hysteresis observed under normal rates of temperature change was studied. At temperatures less than 850°, the diffusion processes take place very slowly in the Fe–Ni alloy, nevertheless, at 525°, annealing for even 12 hr. leads to a considerable breakdown of the single-phase alloys.

2695. Hoselitz, K., and Sucksmith, W. Magnetic Study of the 2-Phase Iron–Nickel Alloy. II. Proc. Roy. Soc. (London), vol. 181, 1943, A, pp. 303–313; Chem. Abs., vol. 37, 1943, p. 6232.

Earlier method for using the magnetic saturation intensity of annealed Fe–Ni alloys for the determination of the equilibruim phase boundaries is extended. Lower temperatures are examined. The mechanism and kinetics of phase changes are studied. High magnetic fields are employed (16,000 gauss). Various heat treatments are described, being carried out down to 325°. The phase diagram of the system is accurately determined as 525°–325°. The mechanism of the phase segregation from the single phase α state has been studied. Contrary to the usual case, one of the phases crystallies out in its equilibrium concentration while the residue of the alloy progressively and uniformly approaches equilibrium composition. The rate of attainment of equilibrium was determined. It is considered that the lower practical limit of temperature where the equilibrium diagram can be studied by annealing experiments has been reached.

2696. Pier, M. [Hydrogenation and Synthesis.] Oel u. Kohle, vol. 1, 1933, pp. 47–53; Chem. Zentralb., 1934, I, p. 2524; Chem. Abs., vol. 29, 1935, p. 6727.

Fundamental principles of the MeOH synthesis and the hydrogenation of coal and mineral oils are represented with the aid of diagrams.

2697. ———. [Leuna Gasoline.] Automobiltech. Ztschr., vol. 36, 1933, pp. 159–160; Chem. Abs., vol. 27, 1933, p. 4384.

Short review of the hydrogenation process of the I. G. Farbenindustrie, covering the preparation of NH_3, MeOH, gasoline, etc.

2698. ———. [Synthetic Motor Fuels and Oils.] Oel u. Kohle Erdoel Teer, vol. 13, 1937, pp. 622–624; Brennstoff-Chem., vol. 18, 1937, p. 402; Chem. Abs., vol. 31, 1937, p. 8874.

Review of the Bergius and the Fischer-Tropsch processes.

2699. ———. [Gasoline From Coal, Tar, and Petroleum. Development of the German Fuel Situation.] Oel u. Kohle, vol. 38, 1942, pp. 1445–1448; Chem. Abs., vol. 37, 1943, p. 6842.

Historical discussion.

———. *See* abs. **1494, 1495.**

2700. Pierce, C., Wiley, J. W., and Smith, R. N. Capillarity and Surface Area of Charcoal. Jour. Phys. and Colloid Chem., vol. 53, 1949, pp. 669–683.

Evidence in support of the view that adsorption by charcoal is due to capillary condensation chiefly rather than to formation of a surface layer, as in nonporous adsorbents. The forces causing capillary condensation at low pressures are of the same type as those that cause multilayer adsorption on a plane surface, but because of the effects of opposite walls they are stronger at a distance of several molecular diameters from the substrate than is found for a plane surface. If capillary condensation occurs, it is not possible to determine the surface area of a porous solid from an adsorption isotherm, and the commonly accepted values are much too large. In capillaries a few molecular diameters in width, the Kelvin equation is not applicable. Retentivity is greater for slightly activated samples than for more highly activated ones.

2701. Pierre, H. [Spontaneous Adhesion of Nascent Iron.] Compt. rend., vol. 229, 1949, pp. 203–205; Chem. Abs., vol. 43, 1949, p. 8322.

Low-temperature reduction of powdered Fe minerals yields Fe that has a strong tendency to agglomerate, whereas nonferromagnetic metals do not behave this way. The attraction between grains of Fe to give agglomerates is due to a weak external magnetic field possessed by each grain and is enhanced by the breakdown of crystalline structure during the reduction.

2702. Piganiol, M. [Synthesis of Molecules With Lubricant Properties.] Bull. soc. chim., vol. 10, 1943, pp. 301–310; Petrol. Refiner, vol. 24, No. 5, May 1945, pp. 111–116; Chem. Abs., vol. 38, 1944, p. 2481; vol. 39, 1945, p. 2864.

Review of the theories of lubrication and the possible sources of suitable raw materials for the production of lubricating oils. One of the best sources seems to be those heavy fractions (200°–300° C.) of synthetic hydrocarbons from Fischer-Tropsch process designated as Kogasin, which are rich enough in higher olefins to be converted into excellent oils by polymerization.

———. *See* abs. **759.**

2703. Pignot, A. [Catalytic Process for Preparation of a Methane-Rich Fuel Gas from Manufactured Gas.] Ind. Petrol., vol. 9, No. 36, 1941, pp. 29–35; Chem. Zentralb., 1943, I, pp. 471–472; Chem. Abs., vol. 38, 1944, p. 3111.

This process is based on the transformation of CO according to the equation $CO+3H_2=CH_4+H_2O$. In this way a fuel gas having a heating value of 6,000–7,000 kcal. per $m.^3$ can be prepared from manufactured gas, which is a mixture of coal gas and blue gas from coke. Calculations are presented for a plant capable of handling 200 $m.^3$ of manufactured gas per hr.

2703a. Pines, H. Isomerization of Alkanes. Advances in Catalysis, Academic Press, Inc., New York, 1948, vol. I, pp. 201–256.

Isomerization of butanes, pentanes, hexanes, heptanes, and higher alkanes are discussed. 45 refs. are given.

2704. PINGAULT, P. [Formation and Decomposition of Cementite.] Compt. rend., vol. 191, 1930, pp. 1007–1008; Chem. Abs., vol. 25, 1931, p. 1193.

Pure cementite, prepared by the action of NaCN upon Fe filings at 650°, was heated in a vacuum at various temperatures and subjected to the attack of HNO_3 (d., 1.2). After 10 hr. at 1,000° only faint traces of graphite could be found. After 1 hr. at 1.075° the cementite was agglomerated, and distinct traces of graphite were found. After 1 hr. at 1,175° the cementite was transformed partly into metallic globules having the microscopic characteristics of gray-cast Fe and partly into a powder, containing much graphite. Below 1,000°, therefore, the pure cementite may be considered very stable, but, as soon as the melting temperature of cast Fe is approached, the decomposition of the cementite becomes rapid. In forming cementite from pure Fe and NaCN in the absence of air, it was found that the cementation of the Fe was negligible at temperatures of 600°–650° and 850°–900°. The same results were obtained in pure and in commercial NaCN. Different results obtained in the presence of air are believed to be due to the carbonizing action of the decomposition products of the NaCN.

2705. ———. [Equilibrium Between Iron–Iron Carbide–Oxygen.] Compt. rend., vol. 192, 1931, pp. 45–47; Chem. Abs., vol. 25, 1931, p. 1727.

Fe–C–O diagram is completed by determining the curve representing the equilibrium between Fe and Fe_3C in mixtures of CO and CO_2. In the apparatus used the gas was passed continuously through a closed circuit. The 50-cc. samples were analyzed chemically with an accuracy of more than 0.5%. The Fe was used in the form of fine wire, which made it possible with a small weight of material to fill the whole tube and obtained a rather large reaction surface. The experiments were carried out at atmospheric pressure. To insure having no false equilibrium due to passive resistance, Fe was carburized in a mixture rich in CO and decarburized in a mixture rich in CO_2. Analysis showed that the 2 methods gave the same results at the same temperature. When a mixture of Fe and C was kept in a limited quantity of O_2 the results varied with the temperature: Above 740° Fe_3C was formed, and CO_2 in the gaseous phase varied from 0–28%; between 740° and 700°, the proportion of CO_2 was 28–42%, and Fe_3C was oxidized to Fe and CO; below 700° the content of CO_2 became high enough to oxidize Fe. The following calculations were made: Between 700° and 1,000°, $CO_2+Fe_3C \rightleftharpoons 3Fe+2CO-14.5$ cal.; $3Fe+C \rightleftharpoons FeC-27.5$ cal.

2706. ———. [Cementite.] Ann. chim., vol. 20, 1933, pp. 371–438; Chem. Abs., vol. 28, 1934, p. 3040.

Cementite (Fe_3C, 6.65–6.70%) containing 0.05% of free C was prepared by heating Fe with NaCN at 600°–650°; it also may be prepared by electrolysis of fused NaCN with Fe electrodes or by passing coal gas or CH_4 over Fe at 850°–975°. Fe_3C reduced by H_2 has a density at 0° of 7.30, is not attacked by H_2 under atmospheric pressure at 450°, is thermodynamically unstable at ordinary temperatures, and begins to decompose near the melting point of cast Fe. The equilibria in the system Fe–Fe_3C–O_2 have been studied at 830°–1,000°.

———. *See* abs. **472.**

PINKEL, I. I. *See* abs. **3295.**

2706a. PINO, P. [Uses of the Oxo Synthesis as a Laboratory Method for the Synthesis of Certain Aldehydic Compounds.] Gazz. chim. ital., vol. 81, 1951, pp. 625–634; Chem. Abs., vol. 46, 1952, p. 7,079.

Advantages offered by the Oxo synthesis in organic chemistry are shown by the results obtained in the preparation of aldehydes by the reaction of olefins with CO and H_2. The method is relatively rapid and gives better yields than can be obtained by classic organic syntheses.

———. *See* abs. **2393, 2401, 2401a, 2401b.**

2706b. PINO, P., AND PALEARI, C. [Synthesis of Anilides From Unsaturated Compounds, Carbon Monoxide, and Aniline.] Gazz. chim. ital., vol. 81, 1951, pp. 646–653; Chem. Abs., vol. 46, 1952, p. 7,063.

Synthesis of anilides is analogous to that of Oxo synthesis. As in Oxo synthesis and syntheses of esters $HCo(CO)_4$ may be the actual catalyst of the reaction of unsaturated compounds, CO, and aniline. For a given temperature and pressure, the rate of absorption of CO in the formation of anilides is intermediate between that for Oxo synthesis and that for the synthesis of esters.

2706c. PINO, P., ERCOLE, R., AND MANTICA, E. [Synthesis of Esters From Olefins, Alcohols, and Carbon Monoxide.] Gazz. chim. ital., vol. 81, 1951, pp. 635–645; Chem. Abs., vol. 46, 1952, p. 7,062.

Reactions between cyclohexene and various primary, secondary, and tertiary alcohols were studied to gain information on the range of applicability of this method of synthesis and to explain its mechanism. The work indicates that the synthesis of esters from olefins, CO and alcohols is a slower reaction than the Oxo synthesis. The mechanism probably involves scission of the addition compound of Co hydrocarbonyl and olefin by the alcohol.

PIONTELLI, R. *See* abs. **2394.**

2707. PIRSON, M. [Production of Gasoline From Coal.] Rev. ind. minerale, No. 394, 1937, pp. 249–263; Chem. Abs., vol. 31, 1937, p. 5538.

Development of the process of coal hydrogenation is reviewed. The net cost of motor fuel produced by this process, or by the Fischer-Tropsch process, is estimated as approximately 20 pf. per l. It is claimed that the synthetic motor-fuel industry could not exist without Government subsidies, but development of processes would be important in case of war.

PISARZHEVSKAYA, N. P. *See* abs. **2890.**

2708. PITAVAL, R. [Hydrogenation in France.] Echo mines et met., 1938, p. 487; Coal Carbonisation, vol. 5, 1939, p. 49.

Output of the older French plants for the manufacture of synthetic petrol is to be augmented by several new establishments, the annual output of which is apparently to range 30,000–100,000 tons of petrol. Apart from importation of petrol, the importation of crude petroleum for refining and for the hydrogenation of residues will continue to be normal practice, but the synthetic manufacture is to be developed to meet emergencies. The national resources of coal and lignite do not permit such development as in Germany, where the present production of nearly 1,000,000 tons of synthetic petrol per yr. is to be quintupled within the next 3 yr.

PITZER, K. S. *See* abs. **3589.**

PIZZO, M. *See* abs. **748.**

PLANTS, K. D. *See* abs. **3305a.**

PLATE, A. F. *See* abs. **1705, 1706.**

2709. PLATONOV, M. S., TOMILOV, V. I., AND TUR, E. V. [Catalytic Properties of Rhenium. VI. The Decomposition of Methanol Over Rhenium.] Jour. Gen. Chem. (U. S. S. R.), vol. 7, 1937, pp. 1803–1804; Chem. Abs., vol. 31, 1937, p. 8341.

When MeOH is passed over ordinary Re catalyst, it is completely decomposed and almost no CH_2O is obtained. If the catalyst is partly poisoned by H_2S or As_2O_3, good yields of CH_2O result.

2710. PLOTNIKOV, V. A., AND IVANOV, K. N. [Decomposition of Methanol in Presence of the Zinc–Chrome Catalyzer.] Jour. Chem. Ind. (U. S. S. R.), vol 6, 1929, pp. 940–943; Chem. Abs., vol. 24, 1930, p. 3984.

In the synthesis of MeOH from water gas, the reaction is reversible, and the most active catalyzers favor MeOH decomposition as well as its synthesis. A study is made of the decomposing action of the catalyzer $ZnO–Cr_2O_3$ at ordinary atmospheric pressure on the MeOH already formed. The molecular proportion of ZnO to Cr_2O_3 was 10 : 1. The catalyzer was precipitated on Fe-free asbestos to increase its surface. The precipitation should be effected by Na_2CO_3 from the solutions of the nitrates of the metals; when precipitating by NH_3, the catalyzer obtained is considerably less active. After the precipitation, the carbonates are reduced by H_2. Care must be taken to avoid excessive rise of temperature during the preparation of the catalyzer. The proportion of pure catalyzer to asbestos was 1 : 1, the total weight of both being 9.5 gm. *Apparatus.*—The MeOH from a burette entered a V-shaped glass tube heated in an oil bath to 150° where it evaporated and its vapors passed into a decomposition apparatus where they were first heated, then filtered through the catalyzer. The products obtained were cooled to liquefy and separate the undecomposed MeOH, the volume of which was measured in a burette, and the gases were collected in gasometers filed with acidified H_2O. *Influence of temperature and speed.*—The first bubbles of decomposition gas appear at 240°–250°; with increase in temperature their quantity gradually increases and becomes particularly noticeable at 275°–280°; at 300° the decomposition is already very intensive. It was found most convenient to pursue the investigation at 325°, the speed of passing in MeOH being 0.125 gm. per min. At a greater rate of speed and at a higher temperature, for example, 335°–350°, a change takes place in the character of the decomposition and of the catalyzer itself, the MeOH decomposing 5 times faster than at 320°–325° while noncondensable white gases are emitted; these vapors are products of HCHO polymerization, whereas the condensed product is trioxymethylene; the catalyzer blackens and a gray ring of volatilized Zn is formed, Zn being reduced at about 340°–350°. Under normal conditions of speed and temperature the condensate consists chiefly of MeOH, whereas the gases consist of H_2, CO, and CO_2. *Stability of catalyzer.*—In agreement with the findings of Smith and Hawk (abs. **3210**) and contrary to the statements of Taylor and Kistiakovskii (abs. **3336**) and of P. V. Zimakov (Jour. Chem. Ind. (Russia), vol. 5, 1928, p. 1072), the CO_2 formed does not act as catalyzer poison, although it is strongly absorbed by the catalyzer. The catalyzer is very stable and after 57 hr. of uninterrupted work shows no sign of fatigue.

2711. ———. [Synthesis of Methanol From Carbon Monoxide and Hydrogen Under Pressure.] Jour. Chem. Ind. (U. S. S. R.), vol. 7, 1930, pp. 1136–1145; Chem. Zentralb., 1931, I, p. 2143; Chem. Abs, vol 25, 1931, p. 4218.

Object of the investigation was the preparation of MeOH from CO and H_2 under high pressure with the use of catalysts. The synthesis was carried out in a circulating system with a pressure decreasing from 170 atm. in an apparatus presenting no novel mechanical features. The activity of Zn–Cr catalyst begins at 315°–320° and attains a practical speed of condensation at 330°. The highest activity was displayed by Zn–Cr in the proportion of 4 : 1, while any decrease in Cr reduced the efficiency of the catalyst. The results obtained with various thicknesses of the layers of catalyst do not show any regularity, from which is inferred that such changes, besides influencing the speed of condensation, also affect the character of the process. Dilution of the reacting gas mixtures with H_2 reduces the speed of reaction. Increase of temperature accelerates the general course of the process: At 360° CH_4 predominates, while at 400° higher hydrocarbons take its place. The Zn–Cr catalyst becomes readily poisoned. Precipitated on asbestos, it seems to possess a more highly active surface, tending also to an excessive formation of higher hydrocarbons. ZnO is less active than Zn–Cr. Addition of UO_2 to ZnO does not change the activity of the latter. All catalysts containing Zn tend to the formation of gaseous products, such as CH_4 and higher hydrocarbons with separation of H_2O and contamination of the gases with CO_2. Some CO is reduced to C with formation of soot. The liquid condensate consisted of oil and water layers, the former comprising up to 10% of the bulk. The aqueous layer contained up to 12% of MeOH, 15% EtOH, MeCOEt, and iso–BuCHO. With a Cu catalyst obtained by precipitation of $Cu(NO_3)_2$ and reduction to Cu, the activity begins at 280°, drops at higher temperatures, and becomes again stable at 305°–310°. Addition of 5% of Ag increases the activity of Cu, while addition of Zn–Cr increases the activity very highly, the reaction beginning at 240°. Of all the composite catalysts containing 3 elements, $Cu–ZnO–Cr_2O_3$ in the proportion of 91 : 8 : 1 proved most active, supporting the reaction with enough speed at 250°. Precipitation of a mixed solution of all 3 salts and subsequent reduction of the hydroxides produces a much more active catalyst than a mixture of separately prepared metals. Increase of temperature speeds up the process, while dilution of the reacting gas with H_2 reduces the speed. The Cu catalyst with decreased temperature tends to increase the formation of liquid products, however, without any oil. The condensate contains 85% MeOH, EtOH, and H_2O, while the gas is mostly CH_4. No formation of free C was observed. At 250°–265°, the process proceeds to complete conversion of CO. In these tests under the condition of falling pressure, the yield based on CO reached up to 70% when the condensate contained about 85% of MeOH.

2712. ———. [Methanol Catalyzers.] Jour. Gen. Chem. (U. S. S. R.), vol. 1, 1931, pp. 826–844; Chem. Zentralb., 1932, II, p. 1393; Chem. Abs., vol. 26, 1932, p. 3774.

Synthesis of MeOH from CO and H_2 was studied at pressures up to 162 atm., with high speed of reaction gases through the apparatus and temperatures up to 320°, in the presence of various catalysts. Cu is a weak catalyst for MeOH; ZnO possesses good activity, but at high speed of gas flow mostly hydrocarbons are formed in its presence; Cr_2O_3 promotes the reaction: $2CO+2H_2=CH_4+CO_2$. The addition of ZnO to Cu produces no appreciable effect, while the addition of Cr_2O_3 to Cu has a decided favorable effect on the catalysis of MeOH. Like ZnO, Cr_2O_3 becomes ineffective at high speed of reacting gases, and instead of MeOH, hydrocarbons are produced. The combination of Cu, ZnO, and Cr_2O_3 forms an active MeOH catalyst.

2713. ———. [Pyrophoric Character of Some Copper Catalysts for Methanol Synthesis.] Jour. Gen. Chem. (U. S. S. R.), vol. 4, 1934, pp. 1003–1005; Mem. Inst. Chem., Ukrain. Acad. Sci., vol. 1, 1934, pp. 127–131; Chem. Abs., vol. 29, 1935, p. 2062.

Admixture of 2% ZnO or Cr_2O_3 increases the stability of the Cu dispersion formed during the process of its reduction from CuO. The ability, on contact with air, to form spontaneously centers of oxidation and the extension of this process is associated with the presence on the surfaces of adsorbed H_2 in the active state. The preparation obtained by reduction with CO is similar to that from H_2. The pyrophoric process converts the Cu principally to Cu_2O.

2714. PLOTNIKOV, V. A., AND KAGANOVA, E. M. [Decomposition of Methanol in Presence of Copper Cata-

lysts.] Jour. Chem. Ind. (U. S. S. R.), vol. 7, 1930, pp. 672–674; Chem. Abs., vol. 26, 1932, p. 81.

Pure Cu as catalyst is very active, but the degree of activity and stability of the catalyst vary with the kind of initial material: a catalyst prepared by reduction of Kahlbaum CuO wire loses its activity when heated 15 min. to 300°, while that obtained from Merck's CuO granules can stand 3 hr. at 350° without injury. 94% molecular CuO+6% molecular V_2O_5 reduced at 200° 3.5 hr. by H_2 gives a highly efficient catalyst, effecting 100% decomposition at 230°–240°, but, besides H_2 and CO, CO_2 and CH_4 are generated; for synthesis this catalyst cannot, therefore, be of use. Activation of catalysts by addition of ZnO and Cr_2O_3 gives the best results with 90% molecular CuO, 8% molecular ZnO, and 2% molecular Cr_2O_2. Increase in Cr_2O_3 effects a decrease in activity; 100% decomposition was obtained at 200°–210° with CO_2 and CH_4 amounting to about 1% each. Addition of Cd to this catalyst lowers its efficiency to a negligible quantity.

2715. Plotnikov, V. A., and Pospekhov, D. A. [Hydrogen Adsorption on Methanol Catalysts.] Mem. Inst. Chem., Ukrain. Acad. Sci., vol. 1, 1934, pp. 153–167 (in German, pp. 169–170); Chem. Abs., vol. 29, 1935, p. 7741.

H_2 adsorption was studied on a Cu–ZnO–Cr_2O_3 catalyst reduced in H_2 at 200°–300° and still containing bound water. In the range 200°–300, a higher temperature of evacuation increases subsequent H_2 adsorption (removal of more adsorbed H_2O). Successive adsorption and desorption lead to a greater mass of adsorbed gas each time. Saturation is reached only above 1 atm. The catalyst evacuated at 300° (anhydrous) shows lower but completely reversible adsorption. Fatigue is held to be due to dehydration. Adsorption is greater in catalysts rich in ZnO–Cr_2O_3; these also show fatigue most rapidly. No direct simple relation exists between the adsorption of H_2 and the activity at a given temperature. The effect of the temperature of evacuation on the H_2 adsorption is very slight for a 91% Cu catalyst, only 10% from 225° to 300°, but very great for catalysts of lower Cu content, 2.5 times from 225° to 290° for a 60% Cu catalyst. Heat of adsorption is about 1,500 cal. per mol. of H_2.

2716. Plotnikov, V. A., Ivanov, K. N., and Pospekhov, D. A. [Complex Catalysts for the Synthesis of Methanol.] Jour. Chem. Ind., (U. S. S. R.), vol. 8, 1931, pp. 472–478; Chem. Abs., vol. 25, 1931, p. 5139.

Study of the catalytic synthesis of MeOH from CO and H_2 was continued. The possibilities of further activation of the complex catalyst Cu–ZnO_2–Cr_2O_3, the catalytic action of the individual components, and their substitution were investigated. The procedure was the same as that in the former experiments; the reaction was carried on again under the conditions of falling pressure, which begins with the inception of the reaction at a certain temperature. Conclusions.—Cu alone is a poor catalyst; Cr_2O_3 alone is more energetic than Cu, effecting the reaction at 265°, the main reaction proceeding thus: $2CO+2H_2=CH_4+CO_2$. Addition of ZnO to Cu somewhat increases the activity and so does the addition of Cr_2O_3, but the temperature of reaction is reduced to 265°–285°, with formation of a considerable amount of MeOH. Addition of both ZnO and Cr_2O_3 doubles the activity and the conversion of CO into MeOH, as compared with Cu containing only either ZnO or Cr_2O_3. The effect of the combination of ZnO and Cr_2O_3 with Cu does not constitute a simple sum of their influences as individual components. The complex catalyst Cu–ZnO–Cr_2O_3 is considered as a system in which the individual influences of the components are merged to create a specific MeOH catalyst. Addition of Na_2CO_3, Ag, and MgO led to impairment of the activity of Cu–ZnO–Cr_2O_3 and the reaction products.

2717. ———. [Synthesis of Methanol in Presence of Copper, Zinc Oxide, and Chromic Oxide Catalysts.] Jour. Chem. Ind. (U. S. S. R.), vol. 8, 1931, pp. 119–126; Chem. Abs., vol. 25, 1931, p. 5661.

Results of experiments show that the optimum proportions of ZnO: Cr_2O_3 with respect to activity are 11:1; to reach the highest activity they have to constitute 30% of the catalyst. Conversion of CO into combustible liquids (mostly MeOH) is highest at ZnO: Cr_2O_3=8:1 and 60–70% Cu, but the quality of the products is highest at 55% Cu. The velocity of the reaction increases with excess of H_2; the yield of MeOH and other combustible liquids also is increased, and the % CO_2 is decreased. The best temperature is 265°; above 280° the quality of the products of reaction is lowered considerably; below 250° the velocity is too low. The maximum of CO conversion, that of activity of the catalyst, and that of its stability, do not coincide. The stability is increased by addition of Na_2SiO_3 but the catalytic qualities are lowered.

Podgurski, H. H. *See* abs. **2010.**

2717a. Podgurski, H. H., and Emmett, P. H. Adsorption Studies on Iron. Am. Chem. Soc., 121st Meeting abs., March–April, 1952, p. 29–N.

Adsorption characteristics of various Fe catalysts and Fe samples for H_2 and CO have been evaluated from 10^{-2} to 700 mm. Hg pressure between —195° and —200°. No evidence could be found on bulk Fe catalysts for the "solubility" effect noted by Beeck and coworkers for H_2 in thin metal films of Fe and Ni between —195° and 0°. On no surface studied was the activated adsorption of H_2 at —195° sufficient in quantity to cover the free Fe surface with a layer of H atoms; however, for a singly promoted Fe catalyst (2–10% Al_2O_3), the rapid adsorption of H_2 at —195° was equivalent to adsorption as atoms on about ⅔ of the "free Fe surface". Type B activated adsorption of H_2 on promoted Fe catalysts at and >100° is very pressure-sensitive, and at a pressure of 10^{-2} mm. Hg apparently becomes very small relative to Type A adsorption (chemisorbed at —78°). The chemisorption of CO at —195° to —78°, which seems to be satisfactory for measuring the free Fe surface of catalysts and thin evaporated Fe films, covers only about 10% of the surface of very pure Fe wire, Fe powder from the reduction of pure Fe_2O_3, and Fe powder from Fe carbonyl. The ratio of Type B H_2 adsorption to Type A appeared to increase as the ratio of promoter to Fe content was increased in synthetic NH_3 catalysts.

2718. Podgurski, H. H., Kummer, J. T., DeWitt, T. W., and Emmett, P. H. Preparation, Stability, and Adsorptive Properties of the Carbides of Iron. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 5382–5388.

Hägg Fe_2C can be formed by carbiding finely divided Fe catalysts with a hydrocarbon such as propane, butane, or pentane equally as well as carbiding with CO. The carbiding process using a hydrocarbon is not accompanied by a lay-down of free C or by any strong exothermicity. The samples of Fe_2C formed by using butane as a carbiding gas still contain a little residual Fe after the carbiding reaction at 300° apparently comes to an end. Only about 7.5% C seems capable of being incorporated by this procedure in the catalyst employed. It is possible to form hexagonal Fe_2C by carefully carbiding an Fe synthetic NH_3 catalyst at about 215° with CO, even though the catalyst does not contain Cu. CO is still chemisorbed by a partly carbided Fe catalyst at —195°, —78.5°, and —46°, indicating that the carbiding proceeds through the formation of nuclei of carbide rather than by the formation of a smooth layer of carbide over the catalyst surface. The formation of carbide eliminates most of the chemisorption of CO at 100° and 200°. It also eliminates the chemisorption of H_2 in the temperature

range —78.5° to 0°. On the other hand, it has little effect on the higher temperature type of H_2 adsorption occurring at and above 100° until the catalyst samples are almost completely converted to Fe_2C. The energy of activation for carbiding Fe with CO to form Fe_2C is about 32.5 kg.-cal. per mol.

PODUROVSKAYA, O. M. *See* abs. **1653.**

POLL, A. *See* abs. **642.**

POLLCHIK, M. *See* abs. **2100, 2101, 2103a.**

POLLEY, M. H. *See* abs. **1771.**

POLOZHINTSEVA, E. *See* abs. **2775.**

2719. POMEY, J. [Cementation With Carbon and With Nitrogen.] Rev. Mét., vol. 47, 1950, pp. 637–657, 727–738; Chem. Abs., vol. 45, 1951, p. 1929.

Comprehensive review of the latest knowledge of cementation phenomena, giving a review of theories explaining the equilibrium of γ-iron in mixtures of CO, CO_2, CH_4, H_2 in different concentrations followed by their individual analysis. It is held that H_2 is adsorbed during preheating, becomes dissociated on the surface of γ-iron, and decomposes CO, forming nascent C, which alloys with Fe. Influence of type of C on the carburization phenomena was investigated by placing low-C steel specimens embedded either in graphite or in amorphous C in a furnace filled with a carburizing atmosphere and heating at a carburizing temperature. Specimens placed in amorphous C were properly carburized, and those in graphite did not show any case. Formation of graphite in carburized case should be avoided on this account, and curves are given to show temperature leading to formation of graphite and amorphous C. Sugar and cellulose do not produce any graphite on carburization, but polynuclear aromatic compounds such as naphthalene, anthracene, or picene produce macromols on carbonizing, carrying on their periphery C atoms partly composed of graphite. The mechanism of graphite formation is illustrated. Aliphatic hydrocarbons dissociate on pyrolysis into H_2 and free radicals which can recombine with each other or with H_2, C_2H_4 being the principal radical. A maximum C concentration of 0.85% produced by CH_4 can be increased to 1.15% C by using less stable C_2H_6 or C_2H_4 in concentration under 5% or, preferably, 0.5–3.5% C_3H_8. Diffusion phenomena are extensively investigated mathematically, and an equation is developed.

2720. POMEY, J., COUDRAY, R., AND GOUTEL, F. [Kinetics of the Decomposition of Austenite of the Alloy Iron–Carbon–Nitrogen.] Compt. rend., vol. 230, 1950, pp. 2298–3000; Chem. Abs., vol. 44, 1950, p. 10641.

Study of the isothermal decomposition in the alloy Fe–C–N obtained by gaseous cementation of Fe wire and homogenization shows that N_2 has a considerable retarding effect both on the rate of germination of α–Fe and on the rate of linear crystallization.

2721. POMEY, J., GOUTEL, F., MOULIN, J., AND COUDRAY, R. [Thermomagnetic Transformation of the Iron–Carbon–Nitrogen Alloys.] Compt. rend., vol. 230, 1950, pp. 2196–2198; Chem. Abs., vol. 44, 1950, p. 10641.

Fe–C–N alloys containing up to 1.5 N_2 and 1.25% C were prepared by cementation of 0.5-mm. wires of mild steel heated to 810° in a mixture of CO_2, H_2, and acetonitrile for N_2 content up to 0.6% and a slight addition of NH_3 for N_2 contents 0.6–1.5%. These alloys showed the reversible thermomagnetic transformations of austenite in cementite Fe_3C and nitride Fe_4N. This eutectoid transformation begins at 595°, as in the Fe–N alloys, but it is completed at a lower temperature than the Fe–N and Fe–C alloys.

PONGRACZ, A. *See* abs. **3373.**

PORAI-KOSHITS, E. A. *See* abs. **3414.**

PORTER, D. J. *See* abs. **2178.**

2722. PORTER, H. C. Coal as an Auxiliary Source of Gasoline Supply. Chem. and Eng. News, vol. 22, 1944, p. 904.

In connection with a possible shortage of petroleum and natural gas, the possibility is discussed of obtaining gasoline through the conversion of coal into water gas and thence into gasoline by the Fischer-Tropsch process. An estimation is given of the costs in the coal process, and a comparison is made with the cost of gasoline produced in a refinery.

2723. POSPEKHOV, D. A. [Properties of Methyl Alcohol Catalyst.] Mem. Inst. Chem., Ukrain. Acad. Sci., vol. 2, 1935, pp. 157–173; Chem. Abs., vol. 30, 1936, p. 5734.

Catalyst (60 : 35.6 : 4.4 = Cu : ZnO : Cr_2O_3) is highly active for 1 : 2 CO : H_2 mixtures at 192°–230° per 100 atm. At high rates of flow and at 200°–300° the ZnO undergoes reduction, yielding Cr_2O_3 impregnated with brass; the condensate contains little MeOH, the yields of which rise with diminishing rates of flow. The results suggest that a higher Cu content is indicated, in order to prevent local overheating of the catalyst, with its consequent inactivation.

2724. ———. [Role of Copper in Methyl Alcohol Catalysts.] Mem. Inst. Chem. Ukrain. Acad. Sci., vol. 3, 1936, pp. 533–540; Jour. Chem. Ind. (U. S. S. R.), vol. 14, 1937, pp. 173–176; British Chem. Abs., 1937, B, p. 646; Chem. Abs., vol. 31, 1937, p. 4265.

Cu–ZnO–Cr_2O_3 = 60 : 35.6 : 4.4 gives good yields of MeOH from CO and H_2 at 230°, but is rapidly inactivated. Cu–ZnO–Cr_2O_3 = 82 : 16 : 2 is stable but gives higher alcohols in addition to MeOH. Satisfactory results were obtained with a 1 : 1 mixture of the 2 catalysts, with an initial contact temperature of 200°.

2725. ———. [Synthesis of Methanol at Low Pressure.] Jour. Chem. Ind. (U. S. S. R.), vol. 14, 1937, pp. 24–28; Mem. Inst. Chem., Ukrain. Acad. Sci., vol. 3, 1936, pp. 403–412, in German pp. 412–413; Chem. Abs., vol. 31, 1937, pp. 2165, 5755.

Catalyst 60 Cu : 35.6 ZnO : 4.4 Cr_2O_3 is very active, but it rapidly loses activity when it works above 200°. If the pressure is 40–30 atm., yields of 0.51–0.63 l. of MeOH per hr. per kg. of catalyst are obtained, and the catalyst retains its activity. At higher pressures, larger yields are obtained but catalytic activity drops. The ratio of CO : H_2 can be varied greatly without effect on the process.

2726. ———. [Copper–Zinc–Chromium Catalysts for Methanol Synthesis.] Mem. Inst. Chem., Ukrain. Acad. Sci., vol. 5, 1938, pp. 507–515; Chem. Abs., vol. 33, 1939, p. 5608.

Review of the literature and patents dealing with Cu–ZnO–Cr_2O_3 catalysts for MeOH synthesis, with 43 refs.

2727. ———. [Mechanism of Catalytic Syntheses From Hydrogen and Carbon Monoxide. (Preliminary Report).] Sbornik Nauch.-Issledovatel. Rabot Kiev. Tekh. Inst. Kozhevenno-Obuvnoi Prom., vol. 3, 1940, pp. 261–267; Khim. Referat. Zhur., vol. 4, No. 5, 1941, p. 12; Chem. Abs., vol. 37, 1943, p. 5569.

It is postulated that the primary process of catalytic transformations of the mixture of CO and H_2 consists of the hydration of CO, and of its condensation with the formation of the lower oxides. The properties of the known oxides of C belonging to several homologous series (cyclic structures also are possible) are given. It is expected that the hydration of these oxides forms compounds with the same C lattice.

2728. ———. [Choice of Catalysts for the Synthesis of Methanol From Carbon Monoxide and Hydrogen.] Jour. Appl. Chem. (U. S. S. R.), vol. 20, 1947, pp. 769–772; Chem. Abs., vol. 42, 1948, p. 5410.

Choice of a catalyst for synthesis under high pressure on the basis of its behavior in the decomposition of MeOH under atmospheric pressure is unjustified.

2729. ———. [Comparative Characteristics of Catalysts Used in Synthesis of Methanol.] Jour. Appl. Chem. (U. S. S. R.), vol. 20, 1947, pp. 1182–1184; Fuel Abs., 1948, abs. 4013.

Results of an experimental evaluation of 16 different catalytic compositions described in the literature for the synthesis of MeOH from CO and H_2 are tabulated. A Cu–Zn–Cr_2O_3 catalyst is preferred.

———. *See* abs. **2715, 2716, 2717.**

2730. POSPEKHOV, D. A., AND SHOKOL, A. A. [Effect of Alkali Upon Copper Catalysts for Methanol.] Mem. Inst. Chem., Ukrain. Acad. Sci., vol. 4, 1937, pp. 205–212, in German, pp. 212–213; Chem. Abs., vol. 32, 1938, p. 3244.

Catalysts 60 Cu : 35.6 ZnO : 4.4 Cr_2O_3 and 16 ZnO : Cr_2O_3 : 82 Cu containing 0.1–5 mol. % KOH were used in MeOH synthesis from CO_2 and H_2. The catalysts showed great activity at pressures up to 100 atm. and at an initial temperature of 200°. The product consisted chiefly of MeOH and EtOH (22.3% by weight). By increasing the volume speeds the yield of EtOH is increased and MeOH is decreased. The catalyst 82 Cu : 16 ZnO : Cr_2O_3 is more suited for EtOH formation and is more stable.

2731. POSTLETHWAITE, J. P., BARDGETT, H., AND BONDY, H. F. Inspection of Krupp-Lurgi Plants for the Carbonization of Coal at Low Temperatures. BIOS Final Report 616, 1946, 41 pp.; PB 46,390.

Krupp plants at Wanne Eickel and Velsen are described. The coke from the former plant was used for gas generation in the adjoining Fischer-Tropsch plant. Of the 10 Fischer-Tropsch generators, 2 operated on low-temperature coke and 8 on high-temperature coke. The coke was particularly suitable for the production of water gas as the ratio H_2 : CO was 1.4 : 1, as compared with 1.2 : 1 in the case of high-temperature coke. The tail gases from the Fischer-Tropsch plant were used to heat the low-temperature retorts. The gasoline obtained by scrubbing the low-temperature gas was mixed with that obtained from the Fischer-Tropsch plant and helped to raise the octane number.

POUILLARD, E. *See* abs. **2272.**

2732. POURBAIX, M. [Heterogeneous Catalysis of Reactions Between Gases, on Reactions Between Gases and Nongaseous Substances, and on the Poisoning of Catalysts.] Bull. soc. belge ing. ind., 1934, pp. 783–817; Chem. Abs., vol. 29, 1935, p. 402.

With the help of the Nernst approximation formula equilibrium calculations are presented for the reaction of O_2, H_2, N_2, Cl_2, and S_2 with metals to form, respectively, oxides, hydrides, nitrides chlorides, and sulfides; the reactoin of H_2O, CO_2, and SO_3 with metal oxides to form hydrates, carbonates, and sulfates, respectively; and of O_2 with metal sulfides to form sulfates and oxides, respectively. Values for the heats of these various reactions are tabulated for many metals. Similarly, equilibrium calculations are presented for the reduction of metal oxides by H_2, CO, and hydrocarbons; particular attention is paid to the reduction of ZnO. The poisoning of catalysts is considered from the standpoint of the partial pressures or ratios of partial pressures of various reactants necessary to convert the catalyst into some noncatalytic compound.

2733. POWELL, A. R. Future Possibilities in Methods of Gas Manufacture. Transcript of Federal Power Commission hearings, June 1946, 46 pp.

A comprehensive review of methods and their economic possibilities. It is concluded that the future raw materials for the manufacture of gas in the northeastern part of the United States will continue to be chiefly bituminous coal and heavy fuel oil. High-temperature carbonization will continue to be carried out predominantly in byproduct coke ovens. This process is characterized by relatively high investment cost per unit of gas made, and by high operating credits from coke, tar, and other products. Costs will be decreased by the development of new byproducts, the upgrading and discovery of new uses for present product, increasing capacity and thermal efficiency of present equipment, and cheaper plant construction. The location of high-temperature carbonization plants near the point of gas consumption is more economical than their placement at the coal mine. Low-temperature carbonization of coal has no future interest largely because of low operating credits and a low yield of gas. The carburetted water-gas process using chiefly coke and heavy fuel oil will remain the major method of manufacturing gas for many years to come. The most important potential improvement is an increase in the thermal efficiency owing to the use of O_2 which can now be produced at a reasonable price. Producer gas, because of its low heating value and despite its high thermal efficiency and low cost of manufacture, has no future. Complete gasification processes as recently developed in Germany (Bubiag-Didier, Pintsch-Hillebrand, Schmalfeldt-Wintershall, Winkler, Lurgi, and Thyssen-Galocsy) are not suitable for use in this country. The most promising principle appears to be the complete gasification of powdered coal suspended in a stream of O_2 and steam (an H. Koppers development). Underground gasification as practiced in Russia has little prospect of success in the United States. The manufacture of oil gas, of liquefied petroleum gases, or re-formed natural gas has only limited possibilities locally.

2734. ———. German Developments in the Production of Synthetic Liquid Fuels. Coal Technol., vol. 1, No. 3, August 1946, 6 pp.; Am. Inst. Min. Eng., Tech. Pub. 2096.

Summary of the more important information obtained by the Combined Intelligence Objectives Subcommittee in its investigation of German synthetic liquid fuels activities. A brief description of each of the 2 general processes for synthetic fuel production—the Bergius and the Fischer-Tropsch—with special mention of the more important new developments. Of the peak production of oil fuel of about 1,200,000 metric tons per month, about 29% was synthetic liquid fuel, and, of the 347,000 tons per month of synthetic fuel, 14% was made by the Fischer synthesis and 86% by hydrogenation of coal and tar. The general impression gained by the Technical Oil Mission was that the engineering design of the plants and the operating techniques were neither economical nor efficient and, by American standards, should have produced a much greater quantity of oil than they did.

2735. ———. Gas Manufacture From Fuels Other Than Coal. Gas World, vol. 127, 1947, pp. 116–121; Gas Times, vol. 52, 1947, pp. 164, 167–168, 233–234, 237, 292–294; Gas, vol. 23, July 1947, pp. 75–76.

Discussion of the oil-gas process, carburetted water gas, liquefied petroleum gas, oil carbonization, cracking of bunker C oil, and the Fischer-Tropsch process, the latter from its possible application to the manufacture of gas in conjunction with the manufacture of synthetic oil and the utilization of off-peak water gas to make synthetic oil. Previous economic calculations are reviewed and conclusions drawn. In view of the economic situation and the fact that much development work remains to be done on the conversion of coal into gasoline and gas, the scheme of making gas in conjunction with manufacture of synthetic gasoline does not appear to be an immediate practical possibility. Also the probabilities of utilizing off-peak water-gas equipment for the production of products other than gas are remote. Furthermore, the capital investment in a

Fischer-Tropsch plant is far greater than in the water-gas plant used to make the synthesis gas, so we would have the incongruity of building an expensive plant for part-time operation to keep a less expensive plant in full-time operation.

———. *See* abs. **98, 1329, 1330.**

2736. POWELL, H. M., AND EWENS, R. V. G. Crystal Structure of Iron Enneacarbonyl. Jour. Chem. Soc., vol. 61, 1939, pp. 286–292; Chem. Abs., vol. 33, 1939, p. 3651.

Crystal structure of Fe enneacarbonyl, $Fe_2(CO)_9$, prepared by the method of Dewar and Jones (abs. **700**) was derived by a Patterson and Fournier analysis differing from that of Brill (abs. **354**) and of Sidgwick and Bailey (abs. **3184**). Each Fe atom is linked to 3 terminal carbonyl groups and the 2 Fe atoms are joined by 3>C=O bridges. Data are based on single crystal oscillation and zero-layer-line Weissenberg photographs about the *a* and *c* axes of thin, hexagonal, crystal plates. The unit cell contains 2 mol., a=6.45, c=15.98 Å., density=2.08. The space group is $C\ 6_3/m$. The interatomic distances are: Fe–Fe, 2.46, Fe–C (in C≡O), 1.9; Fe–C (in C=O), is 1.8; C≡O is 1.15; and C=O is 1.3 Å. Angle between (OC)–Fe bond is 94°; between Fe–C bonds, 78°; and between bonds of >C=O, 87°. The structure simultaneously fixes the molecular formula of the compound as $Fe_2(CO)_9$, as no direct molecular-weight determination is available. Its magnetic properties are discussed.

2737. POWER, H. H. Petroleum Substitutes: Past and Present Research, Development, and Economics. Petrol. Eng., vol. 18, No. 5, 1947, pp. 70, 72, 75, 78, 80, 82, 84.

Review of the literature on the production of liquid fuels from the hydrogenation of coal, from coal carbonization, from oil shale, from tar sands, and from the Fischer-Tropsch synthesis, with 25 refs. Special emphasis is placed on the economics of the various processes and the discussion on costs is summarized in the table given below.

Process	Est. reserves in U. S.		Size of plant, bbl. gasoline per day	Total investment, million dollars	Investment cost per bbl. gasoline per day, dollars	Operating costs, including depreciation	
	Bbl. oil, billion	Bbl. gasoline, billion				Per bbl. oil, dollars	Per gal. gasoline, cents
Coal hydrogenation		3,100	1,750	50	28,500		[1] 15.5–22.6.
Coal carbonization		322	1,000	4	4,000	0.94	[2] 10.
Oil shale	100		500–540	5.8–5.9	11,600–16,700	1.75–2.00	9.7–10.7.
Tar sands	[3] 275		3,000	8	2,670	.75	(Compete with gasoline from crude oil.)
Fischer-Tropsch:							
European process using coal		4,000	6,000	45.6	7,600		[1] 19.2.
European process using natural gas		15	6,000	28.5	4,750		[4] 8.8.
Future American process using coal		4,000					[5] 6.0.
Future American process using natural gas		15	6,000	20	3,330		[4] 5.25.

[1] Coal at $2.75 per ton
[2] Coal at $1.55 per ton.
[3] Total in Western Hemisphere.
[4] Natural gas at $0.05 per M cu. ft.
[5] Coal at $2.00 per ton.

PRANSCHKE, A. *See* abs. **2623.**

PRATJE, W. *See* abs. **3052, 3053.**

2738. PRATT, T. W. Aromatic Adsorption Index for the Estimation of Surface Area and Catalytic Activity. Petrol. Processing, vol. 2, 1947, p. 946.

Paper presented at the 27th annual American Petroleum Institute meeting in Chicago. The aromatic adsorption index provides a means for rapidly and simply detecting changes in the catalytic surface available and changes in activity owing to the destruction of catalytic surface either by heat or steam. Detailed procedure for the determination of the aromatic adsorption index, as well as experimental data and correlations concerning the effect of variables upon the value, are given, and the steps to be taken in determining the index are described. Correlations of the aromatic adsorption index with activity for type "A" and other synthetic catalysts show the estimated activity of a given sample can be expected to be within + or −2% (conversion) of the true activity. In most cases correlations for catalysts from the same source used in different units under different conditions will be accurate enough for the estimation of activity.

2739. PRAX, Y. Synthetic Methanol. Chem. and Ind., No. 34, Aug. 23, 1947, p. 525.

Since 1945, a pilot plant for the synthesis of MeOH by the Lacotte process has been operating at Decazeville, France, by the Société Aveyronnaise de Methanol. The process uses wood as the raw material, and the gas retort, using steam and O_2 injection and operating at about 500°, yields a gas containing, by vol., 30% CO_2, 21% CO, 42% H_2, 3% CH_4, and 4% N_2. CO_2 is removed by water washing at a pressure of 30 kg. per cm.^{2}, leaving a gas containing 30% CO and 60% H_2 with less than 10% of inert gases. To produce MeOH the gas is passed at a pressure of 650 kg. per cm.^{2} and a rate of 750 m.^{3} per hr. over a catalyst consisting of a mixture of Zn and Cr deposited on active charcoal. The temperature in the catalyst tubes is about 425°.

2740. PRCHLÍK, J., AND OTTA, K. [Determination of Low Concentrations of Carbon Monoxide in Flue Gases by the Combustion Method.] Paliva a voda, vol. 30, 1950, pp. 218–219; Chem. Abs., vol. 44, 1950, p. 11059.

I_2O_5 method has disadvantages: I_2O_5 is hygroscopic; it is very difficult to determine when I_2O_5 is exhausted; the method consumes considerable time; it is difficult to obtain reliable results when CO is above 0.1%. To obviate the mentioned difficulties, the authors designed gas absorption apparatus using a modified combustion method. The flue gases are measured in a 1,000-ml. gas burette containing saturated Na_2S as confining liquid. The gases enter a scrubber with 30% KOH to remove CO_2 and safety wash bottle with 0.005 N $Ba(OH)_2$ and then are led over granular refractory material 3–10 mm. in size in a Mars-tube furnace held at about 900°. The products of combustion, with formed CO_2, are absorbed in a series of 3 washing bottles, each one containing 20 ml. 0.005 N $Ba(OH)_2$. After the run, the excess of $Ba(OH)_2$ is titrated back with 0.005 N oxalic acid to phenolphthalein (0.2 gm. phenolphthalein in 100 ml. 70% EtOH). Before actual determination, the apparatus is flushed with 300 ml.

CO-free air. During the run the gas is bubbled through the tube furnace at a rate of 1–2 bubbles per sec. Ba $(OH)_2$ is titrated back to the first disappearance of color. The sum of the 3 wash bottle titrations gives the total CO content in flue gases. The mixing of Ba $(OH)_2$ during titration is accomplished with CO-free air. The accuracy is ±0.002%; the range, 0.002–0.5%; and the time required, 2 hr.

2741. PRETTRE, M. [Methane: Reagent for Hydrocarbon Synthesis.] Conf. réunion soc. belge étude pétrole, dérivés et succédanés, Brussels, 1947, 16 pp.; Rev. inst. franç. pétrole et Ann. combustibles liquides, vol. 2, 1947, pp. 131–140, 195–200; Jour. Inst. Petrol., vol. 33, 1947, p. 308A; Chem. Abs., vol. 42, 1948, p. 6084.

Two aspects of the kinetics of contact catalysis are examined: Adsorption and reactions in the adsorbed phase. By interrupting a normal catalytic reaction, cooling the catalyst zone in the presence of the reactants and transferring the cold catalyst, with exclusion of air, to a special apparatus (not described), it is possible to study the gases given off on desorption as the temperature rises, the most loosely adsorbed products being evolved first. A study of the catalyst in the course of catalytic cracking with hydrogenation showed a high concentration of CH_4, although none of this material was present in the feed and only a small amount in the product. It is, therefore, concluded that the adsorbed phase has a high concentration of CH_3, CH_2, and CH radicals; the isomerization process can thus be considered as being one of methylation. In seeking to find a reaction in which the role of CH_4 could be experimentally demonstrated, thermodynamic considerations pointed to the Fischer-Tropsch synthesis as being one in which this effect ought to be evident at atmospheric pressure. Experimental addition of CH_4 to synthesis gas shows that it participates in the reaction. The use of CH_4 decreases the induction period of the Fischer-Tropsch catalyst (during which large quantities of CH_4 are normally produced); a similar effect is obtained by the dilution of the synthesis gas with an inert material, such as N_2. It is considered that the large initial formation of CH_4 normally observed is due to the heating up of fresh catalyst; if the temperature is kept low, then condensable aliphatic hydrocarbons can be obtained almost immediately.

2742. ———. [Conditions for Utilizing Surface-Area Measurements by Adsorption in the Study of Adsorbents, Catalysts, and Their Constituents.] Jour. chim. phys., vol. 47, 1950, pp. 99–103; Chem. Abs., vol. 44, 1950, p. 7615.

Surface-area measurements by low-temperature gas adsorption are useful in studying adsorbents and catalysts. However, in comparing surface area and catalytic activity, cognizance must be taken of the many variables such as catalyst composition, temperature, time of evacuation, and nature of prior chemical treatment that may cause marked variation in the activity per unit surface area.

———. *See* abs. **779.**

2743. PRETTRE, M., EICHNER, C., AND PERRIN, M. Catalytic Oxidation of Methane to Carbon Monoxide and Hydrogen. Trans. Faraday Soc., vol. 42, 1946, pp. 335–340; Chem. Abs., vol. 41, 1947, p. 2225.

Controlled catalytic oxidation of CH_4 to CO and H_2 usually is represented by the equation: $CH_4+\frac{1}{2}\ O_2=CO+2H_2$. Experiment shows, however, that in practice, at temperatures up to 1,500° K, conversion yields corresponding with the values of the equilibrium constants for the above reaction are never obtained. The oxidation results from an initial reaction of complete combustion of part of the CH_4, $CH_4+2O_2=CO_2+2H_2O$, which consumes all the O_2. The residual CH_4, amounting to approximately ¾ of that originally taken, then reduces the water vapor and CO_2: $CH_4+H_2O=CO+3H_2$ and $CH_4+CO_2=2CO+2H_2$. Since these equilibria do not give good yields in the absence of a large excess of oxidants, except at fairly high temperatures, it is necessary to effect catalysis at above 850°, or even 900°, to obtain a product containing not more than traces of CH_4. (*See* abs. **779.**)

2744. ———. [Participation of Methane in Synthesis Reactions and in the Conversion of Aliphatic Hydrocarbons.] Compt. rend., vol. 224, 1947, pp. 278–279; Chem. Abs., vol. 41, 1947, p. 3739.

It is evident from the results of experiments performed with a catalyst of reduced Ni base on kieselguhr under ordinary pressure and at a space velocity of 100 and using various mixtures of CO, H_2, and CH_4, that with all the mixtures analyzing at least 50% of CH_4, this gas is consumed in various amounts, small at 190° but increasing until at 175° nearly 1 vol. of it is consumed for each 2 vol. of CO in spite of an excess of H_2 in the mixture of reagents. The work summed up in this paper demonstrates that in the presence of suitable catalysts, CH_4 participates in the Fischer-synthesis reaction and in the conversion of aliphatic chains.

2745. PREUNER, G. [Equilibrium Between Iron, Ferrosoferric Oxide, Hydrogen, and Water Vapor.] Ztschr. physik. Chem., vol. 47, 1904, pp. 385–417; Jour. Chem. Soc., 1904, II, p. 317.

According to the equation $3\ Fe+4\ H_2O \rightleftharpoons Fe_3O_4+4\ H_2$, p_1/p_2, where p_1 is the water vapor pressure after equilibrium has been reached and p_2 the H_2 pressure under the same conditions, should be a constant for a given temperature. This was found to be the case at 3 temperatures, 900°, 1,025° and 1,150°, the mean values of p_1/p_2 being 0.69, 0.78, and 0.86, respectively. In these experiments, p_1 was varied between 8.8 and 49.3 mm. The heat effect of the reaction $3\ Fe+4\ H_2O=Fe_3O_4+4\ H_2$, obtained by inserting the values of the equilibrium constants in van't Hoff's equation, is calculated to be 11,900 cal. at 960°, while calculations from calorimetric data give 42,890 cal. When used in calculating the heat of formation of ferrosoferric oxide, the value 11,900 cal. gives a result much more in harmony with Baur and Glaessner's work than does the value of 42,890 cal.

PRIBYTKOVA, N. A. *See* abs. **2916.**

2746. PRICHARD, C. R., AND HINSHELWOOD, C. N. Interaction of Hydrogen and Carbon Dioxide on the Surface of Platinum. Jour. Chem. Soc., vol. 127, 1925, pp. 806–811; Chem. Abs., vol. 19, 1925, p. 3411.

At 1,000°, when the pressure of CO_2 is kept constant, the rate of formation of CO increases almost linearly with the pressure of H_2 at least up to 300 mm. At constant H_2 pressure, the rate of reaction is at first proportional to the pressure of CO_2 and then passes through a maximum when the pressure of CO_2 is approximately double that of H_2. Large pressures of CO_2 have a greater retarding influence on account of its relatively strong adsorption by the catalyst. CO has a slight retarding influence. When the reacting gases are in equimolecular proportions, the pressure of each being 100 mm., the course of the reaction is very nearly unimolecular; but this result is to some extent a coincidence. A simple mechanism, which accounts for most of the observed facts, is that reaction occurs when H_2 and CO_2 become adsorbed adjacent to each other on an active part of the surface. It must be assumed also, that the fraction of the active surface covered by CO_2 increases from 0° to 400 mm., while the adsorption of H_2 at these points left free from CO_2 is never very great so that the zone of reaction is in that portion of the H_2 adsorption isotherm where adsorption is more or less directly proportional to pressure.

2747. PRIESTLY, J. J. Technical and Economic Aspects of Liquid Purification. Gas Jour., vol. 265, 1951, pp. 611–616, 618; Gas World, Coking Sec., vol. 133, April 7, 1951, pp. 6–15.

Further discussion of the Manchester liquid purification process, which depends on the following reactions:

(*a*) (i) $H_2S+(NH_4)_2CO_3=NH_4HCO_3+NH_4HS$
(ii) $H_2S+NH_4HCO_3=NH_4HS+H_2O+CO_2$
(*b*) $3\ NH_4HS+Fe_2O_3=Fe_2S_3+3\ NH_4OH$
(*c*) $2\ Fe_2S_3+2\ O_3=2\ Fe_2O_3+6\ S$

The process is quite similar to the American Ferrox process and the German Gluud process. Some approximate costs of liquid purification to 100 grains per ft.^{3} are given and compared with oxide boxes as follows, respectively:

Gross cost, d. per 1,000 ft.^{3} of gas	0.79	0.92
Net cost, d. per 1,000 ft.^{3} of gas	[1].54	.47
Gross cost, £ per ton of S	12.9	8.1
Net cost, £ per ton of S	[1]8.6	4.2

[1] S credited at £4 5 s. per ton.

2748. PRING, J. N. Direct Union of Carbon and Hydrogen at High Temperatures. Proc. Chem. Soc., vol. 26, 1910, p. 55; Jour. Chem. Soc., vol. 97, 1910, pp. 498–511; Chem. Abs., vol. 4, 1910, p. 2111.

Continuation of previous work by Pring and Hutton (abs. **2752**). C and H_2 combine at all temperatures above 1,100°. At 1,200° reaction is very slow without a catalyst and estimation of the exact equilibrium value of CH_4 is uncertain. 0.35% CH_4 was obtained after 22 hr. at 1,200°. At 1,500°, an equilibrium value of 0.17% CH_4 was obtained after 2 hr. When the C contained a surface deposit of Pt, 0.56% CH_4 was obtained at 1,200° and 0.30% at 1,500°. Above 1,550°, the % of CH_4 rises with temperature. C_2H_2 changes quickly into CH_4 and C_2H_4 above 1,500°, and the CH_4 formed is comparatively stable. In the decomposition of C_2H_2 at 1,200°–1,400°, C_2H_4 forms and is found to persist. This appears to preclude the possibility of CH_4 arising secondarily as no traces of C_2H_4 were found. The presence of CO seems to have no effect in the synthesis or decomposition of CH_4 at any temperature employed.

2749. PRING, J. N., AND FAIRLIE, D. M. Methane Equilibrium. Proc. Chem. Soc., vol. 27, 1911, p. 305; Jour. Chem. Soc., vol. 101, 1912, pp. 91–103; Chem. Abs., vol. 6, 1912, p. 953.

Reaction between C and H_2 was investigated at high gaseous pressures in order to find the equilibrium values at high temperatures, and to learn the effects of pressure upon the synthesis $C+2H_2=CH_4$. The high pressure greatly hastens attainment of the equilibrium value, even in the absence of a catalyst; disturbance of the equilibrium due to formation of C_2H_4 was greatly diminished by the rapid cooling caused by the water-cooled steel walls of the reaction vessel. The experiments up to 100 atm. were carried out in a pressure furnace, while for those from 100–200 atm. a new form of furnace of smaller capacity was constructed. With pressures between 30 and 50 atm., equilibrium was reached in about 2 hr. at 1,200°–1,300°, and in 15 min. at 1,400°, either with or without a catalyst. At 200 atm. the reaction was still more rapid. This indicates that finely divided C would at still higher pressures unite with H_2 with extreme rapidity, since the reaction is exothermic, thus the method might be used for preparing CH_4 on a large scale. CH_4 is the only saturated hydrocarbon formed between 1,100° and 2,100° with pressures up to 200 atm. In the experiments between 10 and 200 atm., the values of the ratio of the partial pressures of CH_4 and of H_2 were constant, when the same modificaton of C was used. At 1,200°, 0.24% and at 1,500°, 0.07% of CH_4 is in equilibrium with H_2 and graphite. For amorphous C the corresponding values are 0.36 and 0.21% for the metastable equilibrium. Thus, the change of free energy of the transformation of C into graphite increases rapidly between 1,200° and 1,600°. The mean specific heat of amorphous C thus, is higher than that of graphite between 0° and 1,200°. The values of the equilibrium constants obtained in this work will probably give, by calculation, more accurate values of the relative specific heats of C and graphite and of C, H_2, and CH_4 at these high temperatures than could be obtained by any direct measurements.

2750. ———. Synthesis of Hydrocarbons at High Temperatures. Proc. Chem. Soc., vol. 27, 1911, p. 217; Jour. Chem. Soc., vol. 99, 1911, pp. 1796–1811; Chem. Abs., vol. 6, 1912, p. 629.

When pure C in the form of a rod is electrically heated in an atmosphere of H_2 at 1,200°, CH_4 and C_2H_4 are formed, the rate of formation of C_2H_4 being about 0.01 that of the CH_4. No C_2H_2 could be detected. Measurements made of the rate at which C_2H_2 and C_2H_4 react with H_2 to give CH_4 show that enough time was not allowed in the above experiments for any large interaction of C_2H_4 and C_2H_2 with H_2 to occur, so that the formation of the hydrocarbons must have been direct. At 1,400° and at pressures 10–40 cm. CH_4 and C_2H_2 are obtained, the ratio of their rate of formation being about 10:1. At 1,650° CH_4, C_2H_4, and C_2H_2 are obtained; and, as at higher temperatures, the quantity of C_2H_4 is about twice that of the C_2H_2. Pd in contact with the C assists catalytically the formation of CH_4 to the same degree as Pt, while Si has no appreciable effect. As the presence of a highly charged electric field makes no difference in the rate of formation of CH_4 at 1,200°–1,600°, no complication is produced in the reaction by ionization from heated C. The formation of C_2H_4, which has not before been observed at these temperatures, can be detected at 1,200° and 1,400°; it is comparable with the CH_4 formed.

2751. ———. Synthesis of Hydrocarbons at High Temperatures and High Pressures. 8th Internat. Cong. Appl. Chem., vol. 21, 1912, p. 65; Chem. Abs., vol. 6, 1912, p. 3363.

Apparatus is a modified form of the pressure furnace used previously (abs. **2750**). The main reaction studied: $C+2H_2=CH_4$. Below 1,000° C and H_2 at 1 atm. react so slowly, even in the presence of Pt as catalyst, that equilibrium values are not reached within any reasonably time. H_2 was brought into contact with a C rod heated to 1,100°–1,600° by passing an electric current through it. The containing walls of the Ni-steel reaction vessel (750 cc.) were H_2O-cooled. The CH_4, yielded at any given temperature of the C rod, corresponded to the equilibrium value for this temperature since CH_4 does not decompose in the colder regions of the apparatus. Furthermore, the amount of C_2H_4 formed as a by-product at temperature below 1,500° is so slight that the reaction $C_2H_4+2H_2=2CH_4$, which takes place in the cooler parts does not appreciably affect results. C_2H_2 first becomes noticeable (0.001%) at 1,650°. Various grades of C and graphite were tried. The Sodeau apparatus was used in analyzing the products. Amorphous C gave higher % CH_4 than graphite. Upon long heating of the former the values dropped owing to the gradual change into graphite. Partly purified amorphous C heated 3 hr. at 1,275°, H_2 at 100 atm., gave equilibrium values: 21.5% CH_4, 0.25% CO, and 0.002% C_2H_4. Pt-coated amorphous C, preliminarily purified in Cl_2, after 2.5 hr. at 1,100°, 20 atm., gave 6.35% CH_4 and 1.1% CO. Acheson graphite, 1,200°, 2.5 hr., 105 atm., 17.5% CH_4 and no CO. Other graphites, 1.6–4.7% CH_4. At 1,200°–1,300° and at 30–50 atm., equilibrium is reached in about 2 hr.; above 1,400°, in about 15 min. The reaction velocity at 200 atm. exceeds by far that at 1 atm. The results are in

agreement with the mass action law. At 1 atm. the equilibrium value of CH_4, in presence of graphite, is 0.24% at 1,200° and 0.07% at 1,500°. With amorphous metastable C the values are 0.36% at 1,200° and 0.18% at 1,500°. At n atm., the CH_4 pressure is n times that at 1 atm. From the data obtained, the authors calculate approximately the heat of reaction for changing amorphous C into graphite, to be 1,480 cal. at 1,200°; 1,950 at 1,300°; 2,450 at 1,400°; and 3,200 at 1,550°. It follows that the mean specific heat of amorphous C above 1,100° is higher than that of graphite, and the difference increased rapidly with the temperature. No saturated hydrocarbon other than CH_4 was produced in any of the experiments.

2752. Pring, J. N., and Hutton, R. S. Direct Union of Carbon and Hydrogen at High Temperatures. Jour. Chem. Soc., vol. 89, 1906, pp. 1591–1601; Proc. Chem. Soc., vol. 22, 1906, p. 260; Chem. Abs., vol. 1, 1907, pp. 178, 550.

Purest C rods on being heated in H_2 gave about 0.25% CH_4 at 1,200°–1,350°, 0.4% at 1,700°, and about 1% at 2,700°. (*See* Bone and Jerdan, Jour. Chem. Soc., vol. 71, 1897, p. 41; vol. 79, 1901, p. 1042.) Traces of C_2H_2 were formed at 1,700°, measurable quantities at 1,800°, 0.88% at 2,000°, 3.35–4.2% at 2,500°, and 2.75–3.03% at 2,700°.

2753. Pritzer, G. G. Production of Synthetic Lubricating Oil by Condensation and Polymerization. Nat. Petrol. News, vol. 38, 1946, pp. 606, 608, 610, 612; Petrol. Processing, vol. 1, 1946, pp. 58–59, 61–64.

General survey of literature and patents on the production of synthetic lubricants. One of the most highly developed processes is the thermal or catalytic polymerization or condensation of unsaturated olefinic hydrocarbons such as C_2H_4. C_2H_2 is catalytically reduced to C_2H_4 and this is polymerized to lubricating oil. Olefins from the Fischer-Tropsch process are used as raw materials. The silent electric treatment of various hydrocarbons and fatty materials also results in the production of lubricating oil.

2754. Privalov, S. I., Chaukavin, M. K., Zueva, V. P., and Ogarkov, N. P. [Synthesis of Gas Suitable for Cementation Operations.] Vestnik metallopromyshlennesti, vol. 19, No. 1, 1939, pp. 85–91; Chem. Abs., vol. 34, 1940, p. 1286.

Gas suitable for cementation of steel was prepared by synthesizing CH_4 from CO, CO_2, and H_2 in the presence of a catalyst comprising pumice stone impregnated with a solution of $Ni(NO_3)_2$ containing 15% powdered Cr_2O_3 and reduced with H_2 at 350°. The life of the catalyst was indefinite provided the temperature did not exceed 500°–600° and its surface remained clean. The temperature in the retort was maintained at 400°. If the starting gas has 4–5 times as much H_2 as $CO+CO_2$, the resulting gas did not have to be scrubbed of the CO_2.

2754a. Probst, R. E., Meyerson, S., and Seelig, H. S. Adsorption and Reaction of Carbon Monoxide on Promoted-Iron Catalysts. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 2115–2116.

In a study of the adsorption of CO on Fe catalysts, it was found that chemical reactions occur that produce Fe pentacarbonyl and CO_2. The adsorption apparatus was of conventional design and was operated at constant pressure. The Fe catalyst was of the usual type used for the synthesis of hydrocarbons from CO and H_2. It consisted of mill scale in powdered form finer than 100 mesh, promoted with 0.5 wt. % K_2O. After reduction with H_2 at 340° under 250 p. s. i., the catalyst was degassed at 450° until a pressure of 1.5×10^{-6} mm. was obtained. The gas used contained 98.4 vol. % CO, 0.1 CO_2, 0.7 H_2, and 0.8 N_2. Four adsorption isotherms were measured at 0°, 25°, 65°, and 108° at 280 mm. pressure. After 144 hr. analysis was made of the gas in the adsorption cell revealing Fe pentacarbonyl and large amounts of CO_2. The results indicate that, at temperatures as low as 25°, CO will react with reduced Fe to form $Fe(CO)_5$. The CO_2 could have been produced by the Fe–catalyzed conversion of CO to C and CO_2. It is also possible that the CO_2, and presumably Fe carbide, were produced by the decomposition of $Fe(CO)_5$.

2755. Procopiu, S., and Farcas, T. [Ferromagnetic Curie Point of Thin Layers of Electrolytic Nickel.] Compt. rend., vol. 198, 1934, pp. 1983–1985; Chem. Abs., vol 28, 1934, p. 4642.

Curie point of 3 such layers 80–400μ thick averaged 370°, as compared with 355°, the average for 3 layers 4–40μ thick. The difference is attributed to the greater internal pressure of the thinner layers increasing the number of particles surrounding each magnetic atom (abs. **1395, 2779**).

Proctor, R. A. *See* abs. **2318.**

Prokhorova, Z. M. *See* abs. **280.**

2756. Proteus. Synthetic Gasoline by the Fischer Process. Gas World, vol. 105, 1936, pp. 362–363.

Review of the principles, products, and economic aspects of the Fischer process.

Pruett, H. T. *See* abs. **649.**

Prziza, O. *See* abs. **1012.**

2757. Pshenitsyn, N. N., Sidorov, N. V., and Sternina, D. G. [Ultrasonic Treatment of the Catalyst for Ammonia Synthesis.] Jour. Appl. Chem. (U. S. S. R.), vol. 13, 1940, pp. 76–78 (in German, p. 78); Chem. Abs., vol. 34, 1940, p. 8189.

Treatment of the $Fe_3O_4+3\%$ $Al_2O_3+1.5\%$ K_2O catalyst with a sound of frequency 555 kilohertz did not increase its activity in NH_3 synthesis under a pressure of 300 atm. Describes apparatus used for the treatment.

Puff, H. *See* abs. **1648a.**

2758. Pursglove, J. Will Coal Help to Meet the Future Ueeds for Gaseous and Liquid Fuels? Petrol. Refiner, vol. 26, No. 11, 1947, pp. 198, 200, 202; Min. Cong. Jour., vol. 34, 1948, pp. 22–24.

Paper presented to the American Gas Association Meeting in Cleveland at a general discussion of the synthesis of oil from coal by the modified Fischer-Tropsch process about to be practiced at the plant of the Pittsburgh Consolidated Coal Co.

2758a. ———. Economic Coal Conversion, Is It Possible? Ohio State Univ., Eng. Expt. News, vol. 23, Oct. 1951, pp. 7, 8, 37–40.

Paper was given at the Second Annual Ohio Mineral Ind. Conf., Oct. 5, 1951. Bergius and Fischer-Tropsch processes are discussed. They are considered to be uneconomic under present United States conditions. The Pittsburgh Consolidated Coal Co., has developed a process by which partial conversion of coal will yield a char residue suitable for boiler fuel and 30–40 gal. of liquid fuel and 1,000 cu. ft. of high-B. t. u. gas per ton. Plant cost will be 10% that of a hydrogenation plant and 15% of a Fischer-Tropsch plant. Chemicals and ash-free C will be produced in the hydrogenation plant rather than gasoline or gas.

2759. Putnam, G. L., and Kobe, K. A. Hydrocarbons From Carbides. Chem. Rev., vol. 20, 1937, pp. 131–143; Chem. Abs., vol. 31, 1937, p. 3867.

Review, with 78 refs., deals with the classification of the carbides and with their preparation and reactions.

Puzitskiĭ, K. V. *See* abs. **792, 799, 800, 801, 802a, 802c.**

2760. PYHALA, E. [Franz Fischer Method for Synthetic Gasoline Manufacture in Germany.] Teknillinen Aikakauslehti, vol. 25, 1935, pp. 396–397; Chem. Abs., vol. 30, 1936, p. 1203.

Methods have been developed for removing the S from water gas, and catalysts that give yields up to 70% of the theoretical have been discovered. Estimates show that a factory with a yearly capacity of 25,000 tons could work economically, two-thirds of its output being gasoline and the rest byproducts.

PYRCIOCH, E. J. *See* abs. **3573a.**

PYZHEV, V. *See* abs. **3368.**

Q

QUIGGLE, D. *See* abs. **1098, 1104.**

2761. QUILL, L. L. Chemistry and Metallurgy of Miscellaneous Materials. Thermodynamics. McGraw-Hill Book Co., New York, N. Y., 1950, 329 pp.; Chem. Abs., vol. 44, 1950, p. 5694.

QUINKE, F. *See* abs. **2306.**

2762. QUIRK, R. N. Combined Intelligence Objective Subcommittee Investigation of Ruhr Synthetic Oil Plants. Preliminary Progress Report. TIIC Rept. 17, 1945, 9 pp. PB 17; Nat. Petrol. News, vol. 37, No. 45, 1945, pp. R 861–864.

Brief description of the conditions and work at several plants interested in synthetic oils, etc. Brief summary of the technical work carried on, such as preparation and purification of synthesis gas; catalyst ovens; catalysts; method of operation of the process; the Oxo process for treating C_{12}–C_{17} olefins to produce aldehydes; coal hydrogenation; the Pott-Broche process and the use of pitch; vapor-phase hydrogenation; the D. H. D. process for dehydrogenating naphthenes; use of propane and butane; carbonization and gasification; Lurgi pressure gasification process; Krupp-Lurgi low-temperature carbonization process; brown-coal low-temperature carbonization by the so-called "Spülgas" process; coke ovens; hard-coal tar and brown-coal tar.

R

2763. RACINE, J. [Study of the Reducing Properties of Methane.] Compt. rend., vol. 220, 1945, pp. 823–825; Chem. Abs., vol. 40, 1946, p. 3672.

Reduction of some metallic oxides by CH_4 was studied at temperatures up to 1,100°. The following were reduced: CuO, ZnO, CdO, HgO, PbO_2, Cr_2O_3, MoO_3, NiO, WO_3. The following were not reduced: MgO, CaO, Al_2O_3. MnO is converted to a carbide at 800°. C_2H_2 appears at 825°. Fe_2O_3 is reduced to an unidentified oxide at 400°, and to Fe at 800°; a carbide is formed at 1,050°. C_2H_2 is formed at 800°; C is deposited at 1,000°. Co_2O_3 is reduced to CoO at 450°, and to Co at 800°; a carbide is formed at 1,000°.

2763a. RADANČEVIĆ, M. [Synthesis-Gas Production by Partial Oxidation of Methane.] Nafta (Yugoslavia), vol. 3, No. 12, 1952, pp. 5–11; Fuel Abs., vol. 12, No. 2, 1952, abs. 1485; Chem. Abs., vol. 46, 1952, p. 11,636.

Experiments on synthesis-gas production by partial oxidation of CH_4 over catalysts containing various amounts of Ni on SiO_2 gel are described. Catalysts were prepared by impregnating SiO_2 gel of 2-mm. size with $Ni(NO_3)_2.6\ H_2O$ solutions, drying several hours, calcining 1 hr. at 500° in an air stream, and reducing in pure H_2 30 min. at 500°. Catalytic conversions have been carried out in an electric-tube reactor containing 25.4–29.4 cc. catalyst. The optimum conditions for the reaction were: Inlet gas rate, 1.12 liter per min., O_2: CH_4 mol. ratio 0.6 and a temperature of 850°. The optimum amount of Ni on the carrier was 3.2%, a further increase of Ni on the carrier giving no better yields of synthesis gas. Equilibrium conditions from available thermal data have been calculated and presented.

2764. RADEMACHER, H. [Wintershall-Schmalfeldt Process for Gasifying Crude Brown Coal.] Feuerungstech., vol. 28, 1940, pp. 85–86; Chem. Abs., vol. 35, 1941, p. 6091.

Wintershall-Schmalfeldt process, based on the use of friable raw brown coal, gasifies the small fuel in a circulating stream of synthesis gas charged with the vapor produced by the drying. The combination of synthesis-gas manufacture with drying in suspension, without intermediate separation of dust, is one characteristic feature. Another is heating of the circulating gas stream by regenerators, which are themselves heated by the combustion air being preheated to a high temperature, 1,300° C. This is necessary to cover the heat requirements of the water-gas reaction and to maintain temperatures high enough for gasification, making possible high outputs and the production of gas low in CH_4. An illustration shows the general arrangement of the plant.

2765. RAIKES, H. R. Liquid Fuel From Coal. South African Ind. Chem., vol. 3, 1949, pp. 82–89; British Abs., 1949, B, I, p. 852.

Reviews proposed production of liquid fuel from coal deposits at Vredefort, Orange Free State, by a modified Fischer-Tropsch process. The water requirements of the plant, estimated at 7×10^6 gas. per day, are high in relation to the local supply. The location of other liquid-fuel plants in catchment areas with a rainfall higher than that of Vaal Basin, is discussed with reference to the water supply and the amount and quality of the coal reserves.

RAINEAU, A. *See* abs. **110, 111, 112.**

2766. RALPH, H. D. Importance of Domestic Industry Stressed in O'Mahoney Report. Oil Gas Jour., vol. 45, No. 40, 1947, pp. 38–39.

According to the final report of the Senate Petroleum Resources Committee, the first principle of American petroleum policy should be to sustain our domestic supply of petroleum and to maintain the American system of competitive free enterprise at home and abroad. The Nation faces 2 alternatives: (1) To await with hope the discovery of enough petroleum within our boundaries to satisfy our future military requirements, and meanwhile to depend upon foreign oil and trust that war will not cut off our imports; or (2) to take steps to guarantee an adequate domestic supply by promoting the search for new deposits of petroleum within the United States itself and the continental shelf and to continue the present program looking to the manufacture of synthetic liquid fuels to supplement our domestic crude supply. Government facilities can be utilized to promote research in the manufacture of snythetic liquid fuels, but without permitting Government competition with private industry. The committee recommends "bold steps" in the direction of synthetic production as being the answer to national defense and to fears that we are running out of oil, and points out that natural gas, shale, coal, and lignite are available in huge quantities and can be liquefied at costs not too far above that of refining crude petroleum.

2767. RAMMLER, E. [Semicoke for Gasification.] Gas- u. Wasserfach, vol. 80, 1937, pp. 683–691; British Chem. Abs. 1937, B, p. 1153.

Reviews properties of semicokes from coal and brown coal, and gives the results of gasification trials. Good yields of producer gas of net calorific value 1,300–1,400 kcal./m.^{3} were obtained, the brown coal product being rather more reactive than coke from coal. Brown coal semicoke also can be used via water gas as a source of H_2 for hydrogenation purposes or of Fischer-Tropsch synthesis gas.

2768. ———. [Utilization of Low-Temperature Coke From Brown Coal and Bituminous Coal.] Gas- u. Wasserfach, vol. 18, 1942, pp. 437–444; British Chem. Abs., 1943, B. I, p. 270; Chem. Abs., vol. 37, 1943, p. 5848.

Application to synthesis gas production is foreshadowed.

RAMPTON, H. C. *See* abs. **1505.**

2769. RANDALL, M., AND GERARD, F. W. Synthesis of Methane From Carbon Dioxide and Hydrogen. Ind. Eng. Chem., vol. 20, 1928, pp. 1335–1340; Chem. Abs., vol. 23, 1929, p. 814.

Equilibrium for the reaction $CO_2+4H_2 \rightleftharpoons CH_4+2H_2O$ was determined by the dynamic method at atmospheric pressure and at temperatures 322°–392.5°. The catalysts used were supported Ni catalysts, both unpromoted and promoted by ceria. Space velocities 6–12 were used. Equilibrium was approached from both sides. In studying the forward reaction, ratios of H_2: CO_2 of 4 and 2.3 were used. The free-energy equation that fits the data for this reaction is $\Delta F^\circ = -35{,}093+12.38\ T\ln T-0.00415T^2-0.000000025T^3-39.91T$. This equation gives $\Delta H^\circ_{298.1}+ -38{,}401$ cal. and $\Delta F^\circ_{298.1}= -26{,}339$ cal. An observed deposition of C during some of the experiments is accounted for by assuming reaction is thermodynamically possible under experimental conditions prevailing.

2770. RANDALL, M., AND MOHAMMAD, A. Synthesis and Free Energy of Methane. Ind. Eng. Chem., vol. 21, 1929, pp. 1048–1052; Chem. Abs., vol. 24, 1930, p. 333.

Equilibrium in the formation of CH_4 from graphite and H_2 and in the reverse reaction was determined at high temperatures, 1,024°–1,237°. The catalyst was reduced Ni with ceria as a promoter. The free energy and heat of reaction of CH_4 calculated from the experiments agree with the values found from the indirect measurements of Randall and Gerard (abs. **2769**). $\Delta F^\circ_{298.1}= -11.573$ cal. and $\Delta H^\circ_{298.1}= -16{,}963$ cal. $\Delta F^\circ= -14{,}343+11.1\ T\ln T\ -0.0081T^2+0.0000006T^3 -51.591T$. Compares and discusses results of other workers at different temperatures.

2771. RANDALL, M., AND SHIFFLER, W. H. Deposition of Carbon in the Reaction Between Carbon Dioxide and Hydrogen. Ind. Eng. Chem., vol. 21, 1929, p. 941; Chem. Abs., vol. 24, 1930, p. 333.

New equation: $CO_2(g)+2H_2O(g)=C(\text{graphitic})+2H_2O$ is offered as a possible explanation for the results presented by Randall and Gerard (abs. **2769**) although the mechanism of the reaction may involve a series of reactions.

RAO, B. C. S. *See* abs. **256a.**

2771a. RAPOPORT, I. B. [Synthetic Motor Fuel From Carbon Monoxide and Water.] Paliva, vol. 31, 1951, pp. 328–337; Chem. Abs., vol. 46, 1952, p. 11,632.

Review of synthesis of motor fuel from CO and H_2O, including reaction temperatures, pressures, and catalysts, as well as physical properties and analysis of products formed.

2772. RAPOPORT, I. B., AND BLYUDOV, A. P. [Methane Synthesis.] Khim. Tverdogo Topliva, vol. 5, 1934, pp. 625–632; Chem. Abs., vol. 29, 1935, p. 2905.

CH_4 synthesis is effective, using CO and H_2 over a Ni catalyst at 250° at 270° the conversion of CO is 99%. A Ni-Mn catalyst permits of carrying out the reaction at 200°–204°. A considerable amount of CO_2 is formed when the temperature is raised to 250°–280°. A Ni–Mn–Al catalyst at the above temperature promotes the simultaneous formation of CO_2 and CH_4. Mo catalyst promotes CH_4 formation at 350°–400°; this reaction slows down and a considerable amount of CO_2 is produced when the above temperature is exceeded. Addition of Al_2O_3 has almost no effect on the yield of various products. The operations are described in detail, and analytical data are tabulated.

2773. RAPOPORT, I. B., AND LANG, A. [Genesis of Catalyst Skeletons.] Jour. Appl. Chem. (U. S. S. R.), vol. 11, 1938, pp. 1056–1062 (in French, p. 1063); Foreign Petrol. Technol., vol. 7, 1939, pp. 13–26; Chem. Abs., vol. 33, 1939, p. 4115.

Properties of catalyst skeletons, which were obtained by the treatment of alloy (Ni–Co–Al or Ni–Al) with an alkali to remove most of Al, were investigated. The catalyst skeletons are more stable against poisoning with S-containing organic compounds than the precipitated catalysts (oxides). The hydrogenation of caprylene, octyl alcohol, cyclopentanone and 1, 3, 4-xylenol in a current of H_2 at 190°–195° disclosed that the Ni–Co–Al catalyst skeleton is a very active hydrogenation catalyst. The dehydrogenation of cyclohexane and methylcyclohexane over the above catalyst proceeded very effectively at 180°–200°, with pressure or without it. The best products were obtained at 240°–260° but the reaction, in this case, was accompanied by a decomposition reaction. At temperature above 260° (280°–320°), the surface of the catalyst was gradually covered with a C film and the catalyst completely lost its activity. The catalyst cannot be reactivated in the usual manner. The loss of activity is explained by the recrystallation of the crystal lattice of the catalyst skeleton at high temperature. Therefore, the isomerization reaction in the presence of the catalyst skeleton would not proceed to a great extent because: (1) The catalyst rapidly loses its activity at 270°–280° and (2) at this temperature the main reaction is the decomposition reaction. Thus, the catalyst skeletons prepared from Ni–Co–Al and Ni–Al alloys are similar to the precipitated catalysts (oxides) in respect to hydrogenation, dehydrogenation, and isomerization reactions, but the first catalysts are less affected by S-containing organic compounds.

RAPOPORT, I. B., AND POLOZHINTSEVA, E. Synthesis of Hydrocarbons From Carbon Oxide and Hydrogen Over Alloyed Catalysts. II. *See* abs. **2775.**

2774. RAPOPORT, I. B., BLYUDOV, A. P., SHEVYAKOVA, L., AND FRANTZUZ, E. [Gasoline Synthesis From Carbon Monoxide and Hydrogen at Atmospheric Pressure. I.] Khim. Tverdogo Topliva, vol. 6, 1935, pp. 221–235; Chem. Zentralb., 1936, II, p. 3967; Chem. Abs., vol. 29, 1935, p. 7617.

Of the catalysts Ni–Mn, Ni–Mn–Al, Ni–Mn–Cu, Ni–Mn–Cr., Ni–Th–Hg, Co–Th, and Co–Mn, the most active were Co–Th, Co–Mn, Ni–Mn–Cr, and Ni–Mn–Al. The method of preparation of the catalyst greatly affects its activity. The reaction temperature is very important to the life of the catalyst. A high temperature yields less solid hydrocarbons, which are deposited on the catalyst. The best temperature is that at which 7–10% CH_4 is formed. The presence of small amounts of NH_3 in the reaction gas increases the yield of gasoline, particularly with catalysts precipitated on fuller's earth. Asbestos carrier yields the best catalysts. 12 refs.

2775. RAPOPORT, I. B., AND POLOZHINTSEVA, E. [Synthesis of Hydrocarbons From Carbon Oxide and Hydrogen Over Alloyed Catalysts. II.] Khim. Tverdogo

Topliva, vol. 9, 1938, pp. 64–70; Foreign Petrol. Technol., vol. 6, 1938, pp. 215–246, 293–304; Oil Gas Jour., vol. 38, No. 20, 1939, pp. 52–54; Chem. Abs., vol. 32, 1938, p. 9446.

Gas mixture, an average composition CO, 31.7; H_2, 63.08; CO_2, 0.05; O_2, 0.2; and N_2, 4.97%, after purification and drying was passed into a quartz tube filled with a catalyst, then into a graduated receiver cooled with ice, on to a charcoal scrubber, and then into a gasometer. A portion of the gas was withdrawn for the analysis. The quartz tube was kept at 165°–220°. Ni–Al, Co–Al, and Co–Si catalysts were used in the powdered and granular forms. The Ni–Al catalyst reduced in the H_2 atmosphere at 350° yielded 140 cc. per $m.^3$ (of gas) of hydrocarbon under the optimal conditions: vol. velocity 166 at 170°. The Co–Al catalyst, reduced with H_2 in the NH_3 atm. at 220°, yielded 175 cc. per $m.^3$ (of gas) hydrocarbon at 200° and vol. velocity of 83. The Co–Si catalyst, reduced as the Co–Al catalyst, yielded 109.6 cc. per $m.^3$ (of gas) hydrocarbon at 220° and vol. velocity of 59. All the above data are given for the catalysts in the granular form; the yield of hydrocarbon using powdered catalysts was somewhat lower.

2776. RASMUSON, A. [Production of High-Purity Oxygen and Its Uses in Chemical Industry.] Tek. Tid., vol. 78, 1948, pp. 155–159; British Abs., 1948, B, I, p. 390.

Modern German and American processes for the manufacture of O_2 by fractionation of liquid air are described. The Linde-Fränkl plant, using a Fränkl corrugated Al heat exchanger, provides O_2 of 98% purity at a cost of 0.64 kw.-hr. per $m.^3$; the American plant using a Collins tubular heat exchanger, provides O_2 of 99.5% purity at a cost of 0.5 kw.-hr. per $m.^3$ The main outlet for this cheap O_2 is in the manufacture of synthetic fuel gases. Water gas is made from lignite, steam, and O_2 in a Winkler generator or from coke breeze in a Thyssen-Galocsy generator. The American Hydrocol process utilizes O_2 for the partial combustion of natural gas to yield liquid petroleum fuels. The use of O_2 also is being considered for the underground gasification of coal.

2777. RATCLIFF, J. D. All the Gas We Need. Collier's, Nov. 24, 1945, p. 16.

Pilot plant, built by Hydrocarbon Research, Inc., for the production of gasoline from natural gas by the Fischer-Tropsch process, has operated so successfully that a $15,000,000 commercial plant is to be constructed this year at Carthage, East Texas. This plant when completed will produce 5,000 bbl. of 80-octane gasoline, 1,000 bbl. of Diesel oil, and 200,000 lb. of crude alcohols per day. The plant will consume 65,000,000 $ft.^3$ of gas and 40,000,000 cu. ft. of O_2 per day. The process as developed obtains the necessary synthesis gas in the right proportions of $CO : 2H_2$ by burning CH_4, natural gas, with O_2. The O_2 for the process is produced, it is said, for $0.05 per 1,000 cu. ft., this low cost being made possible by utilizing the exothermic heat from the Fischer converter in heat exchange relation to produce the power for operating the compressors and other equipment in the O_2 plant. It is expected that the cost of the gasoline will compete with that produced from petroleum.

2778. RAVIZZA, G. [Refinery Gas as a Source of Methane.] Atti III° convegno naz. metano, vol. 2, 1941, pp. 301–305; Chem. Zentralb., 1942, II, p. 1988; Chem. Abs., vol. 38, 1944, p. 3460.

Dependent upon raw material used and the methods of refining, refinery gases have a variable composition but consist predominantly of CH_4 and contain no hydrocarbons with more than 6 C atoms. Cracked gases contain, relatively, many unsaturated hydrocarbons, and hydrogenated gases virtually none. Modern processes for treating refinery gases are discussed. Gas with S removed, freed from gasoline, butane, and propane, consists essentially of CH_4 and can either be compressed and used as fuel gas or used for the preparation of H_2. The economic fundamentals of getting CH_4 from refinery gas are discussed.

2778a. RAY, J. N. Possible Synthetic Petrol Industry in India. Jour. Indian Chem. Soc., vol. 28, 1951, pp. 53–58; British Abs., 1951, B. I, p. 1052.

It is concluded from a survey of the suitability of the coal resources of India that the production of synthetic fuels from coal would not be an entirely uneconomical process.

2779. RAY-CHAUDHURI, D. P. [Displacement of the Curie Point for Nickel by Pressure.] Ztschr. Physik, vol. 71, 1931, pp. 473–477; Chem. Abs., vol. 26, 1932, p. 3154.

In the Curie point of a Ni wire under tension agreement with the Heisenberg theory of ferromagnetism is found. There is agreement between the curves of temperature against temperature coefficient of resistance and against extension, and there also is similarity with the curve obtained between temperature and specific heat for a ferromagnetic substance.

RAYET, R. *See* abs. **1647.**

RAYNOR, G. V. *See* abs. **1517.**

READ, A. A. *See* abs. **88, 89.**

RÉANT, R. *See* abs. **62.**

REDER, R. *See* abs. **1038, 1039, 2686.**

2780. REED, F. H. Chemical Aspects of Coal Utilization. Univ. Illinois Eng. Exp. Sta., Short Course in Coal Utilization, Circ. 31, 1937, pp. 159–175; Coal-Heat, vol. 32, No. 3, 1937, pp. 56–60; Chem. Abs., vol. 32, 1938, p. 6027.

Review dealing mainly with coal as a chemical raw material and as a source for liquid fuels. Discusses 3 general methods for producing liquid fuels from coal: (1) Carbonization or destructive distillation, (2) direct liquefaction through destructive hydrogenation (Bergius process), (3) synthesis from the products of coal and coke gasification (Fischer process). Hydrogenation of coal seems to be preferred at present over the Fischer synthesis from CO and H_2. It is not probable that commercial production will be undertaken in the United States until the cost of motor fuels from petroleum approaches the cost of making these fuels by synthetic means.

2781. ———. Synthetic Liquid Fuels. Opinion and Comment, University of Illinois Bureau of Economic and Business Research, May 1948; Mines Mag., Colorado, vol. 38, September 1948, pp. 23–25, 34, 36; October 1948, pp. 23, 24.

Review covering developments in the United States with some consideration of the plant requirements in establishing a synthetic fuels industry. Also presents cost estimates.

2782. REED, R. M., AND ERIKSEN, A. Hydrogen and Synthesis-Gas Production. Petrol. Processing, vol. 3, No. 10, 1948, pp. 1011–1016; Petrol. Eng., vol. 20, No. 1, October 1948, pp. 278, 280, 282, 284, 290; Gas, vol. 24, No. 10, 1948, pp. 53–56; California Oil World, vol. 41, No. 16, 1948, pp. 3, 5, 7, 9, 11; Chem. Abs., vol. 42, 1948, p. 9097.

Paper presented before the California Natural Gasoline Association, August 5, 1948. Reviews status of the hydrocarbon-steam process for manufacturing H_2 and mixtures of H_2 and other gases for various purposes, from natural gas, light hydrocarbons, and steam. Gives an account of the application of the process to the hydrogenation of various petroleum materials, the synthesis of NH_3, the production of high-purity H_2 and $CO–H_2$ mixtures by the Girbotol methods for use in

fuel synthesis processes, and for producing gas mixtures suitable for supplementing manufactured gas.

REED, W. A. *See* abs. **2110.**

2783. REFINER. Synthetic Lubricating Oils by Transformation of Chlorinated Hydrocarbons. Vol. 16, 1937, pp. 92–93.

Suitable paraffin wax is obtained from petroleum from low temperature carbonization of coal tar, lignite tars, or directly from waxy products of the Fischer-Tropsch synthesis. Chlorination is carried out by passing Cl gas at maximum temperature through melted wax with I as catalyst.

2784. REGNER, A. Magnetometric Determination of the Curie Points. Jour. Iron Steel Inst. (London), Advance Copy, No. 6, 1930, 22 pp.; Chem. Abs., vol. 24, 1930, p. 5695.

A low-frequency magnetometer and 2 high-frequency magnetometers suitable for detecting transformation points in steel are fully described. These instruments gave clear indications of the A_2 point and cementite changes both at 60° and 210°. Irregularities were observed at the temperature of the pearlitic change.

2785. REICH, S., AND SERPEK, H. O. [Some Reactions of Calcium Hydride.] Helv. chim. acta, vol. 3, 1920, pp. 138–144; Chem. Abs., vol. 14, 1920, p. 1302.

Pure dry CO is passed over Ca hydride heated to a dark-red heat converting more than 16% of the CO into CH_2O. CH_4 also was produced.

2786. REICHL, E. H. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, 128 pp.; PB 22,841; TOM Reel 200.

Contains information on location and production of 9 commercial Fischer-Tropsch plants in Germany; data on the supply and preparation of the Co catalyst; economic and operating data of large-scale commercial operations; development of the middle-pressure units; gas recycle operation; products from Fischer-Tropsch plants; adsorption of hydrocarbons on activated C; development work performed by the several organizations interested in the Fischer-Tropsch operations; the Synol process; synthesis of high-melting point waxes; isosynthesis; isobutanol synthesis; low-pressure MeOH synthesis; and the Oxo synthesis.

2787. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Location and Production of Commercial Fischer-Tropsch Plants in Germany. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 11–15; PB 22,841; TOM Reel 200.

Distribution of low-pressure and medium-pressure capacity among Fischer-Tropsch plants

German Fischer-Tropsch plants

(Based on actual production for 1942)

Operator	Location	Capacity		1,000 tons per mo. ave. mo. prod.				Low-pressure operation, tons per year	Medium-pressure operation, tons per year	Total tons per year
		Tons per year	Percent	Gasoline	Diesel fuel	Waxand kogasin	Lube oil			
Ruhrchemie	Oberhausen, Holten, Ruhr	72,000	12.0	2.1	0.8	1.4	1.2	18,088	44,545	62,633
Gewerkschaft "Viktor"	Castrop-Rauxel, Ruhr	40,000	6.8	1.5	1.0	.8	-------	37,699	----------	37,699
Rheinpreussen	Moers-Meerbeck, Ruhr	70,000	11.8	2.8	2.1	1.1	.2	67,212	----------	67,212
Krupp-Benzin [1]	Wanne-Eickel, Ruhr	60,000	10.2	2.2	1.1	1.7	-------	48,300	11,857	60,187
Hoesch-Benzin	Dortmund, Ruhr	47,000	7.9	.5	1.2	2.0	.2	----------	46,044	46,044
Braunkohle-Benzin	Ruhland, Saxony	170,000	29.2	8.4	2.5	3.1	-------	164,606	----------	164,606
Essener-Benzin	Bergkamen, Ruhr	80,000	13.6	4.1	1.8	.8	-------	79,974	----------	79,974
Schaffgotsch Benzin	Deschowitz, Silesia	40,000	6.8	.7	.8	1.8	-------	----------	26,374	26,374
Wintershall	Lutzkendorf, Saxony	[2] 70,000	1.7	.2	.1	.7	-------	11,468	----------	11,468
		12,000	----------	----------	----------	----------	----------	----------	----------	----------
Total		591,000	100.0	22.5	11.4	13.4	1.6	427,377	128,820	556,197
Percent		----------	----------	46.1	23.3	27.4	3.2	76.8	23.2	100.0

[1] In this plant, the 1st stage operates at low pressure; the 2d stage at medium pressure.
[2] Under construction.

Product distribution of Fischer-Tropsch units, tons per year (1941)

Plant	Gasol	Gasoline	Kogasin	Diesel fuel	Paraffin (Gatsch)	Hard wax	Other products not sold directly	Total	Net sale value RM per year	Sale value pf. per kg.
Ruhrchemie	8,988	20,616	----------	8,454	----------	----------	14,855	52,913	13,504,550	25.40
Viktor	4,471	18,167	3,358	7,395	2,927	833	24	37,175	9,788,611	26.30
Rheinpreussen	7,379	34,191	6,656	16,394	5,093	1,408	----------	71,122	20,467,303	28.70
Krupp	4,657	25,531	----------	11,467	5,575	2,500	8,645	58,375	16,987,486	19.20
Hoesch	3,591	9,523	3,749	15,287	5,788	351	6,110	44,055	12,114,410	27.99
Brabag	8,421	77,955	----------	31,845	9,812	3,230	8,864	140,177	42,141,536	30.20
Essener	10,415	32,574	4,767	17,007	6,199	1,351	----------	72,312	20,677,082	28.50
Schaffgotsch	1,557	6,035	56	5,320	4,441	1,441	1,640	20,490	5,798,738	29.15
Wintershall	5	3,388	838	631	503	195	----------	5,561	1,685,762	30.31
Total	49,484	227,980	19,424	113,800	40,388	11,309	40,138	502,175	143,345,478	28.4 (ave.)
Percent	9.81	45.57	3.86	22.50	8.00	2.55	8.00	100.0		
Bbl. per day (7.5 lb. per gal.)	948	4,380	372	2,175	755	216	770	9,620		

License fee to Ruhrchemie was 1% of the net sales value of the products or 1,433,454 RM per yr. or 2.85 RM per ton.

Prices for different Fischer-Tropsch products were:
Gasol 22–26.6 pf. per kg.
Gasoline 25.7–31.5 pf. per kg.
Diesel oil 23.0–27.0 pf per kg.
Paraffin gatsch 20.5–25.0 pf. per kg.
Special waxes 56.0–92.0 pf. per kg.

2788. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Supply and Preparation of Cobalt Catalyst. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 15–18; PB 22,841; TOM Reel 200.

All existing plants were operated with the standard Ruhrchemie Co–ThO_2–MgO–kieselguhr (100 : 5 : 10 : 200) catalyst, which was supplied from 3 plants: Ruhrchemie (Ruhr); Brabag (Saxony); and Wintershall (Silesia), with respective capacities of 100, 65, and 35 oven fillings per mo., each roughly 1 ton. The overall Co consumption was 85–95 tons per yr., the loss in synthesis and in reworking being for Ruhrchemie 4.0 and 4.0%, respectively, and for Brabag 1.0 and 1.5%, respectively. The Co resources were barely enough to keep all plants running, Finland being the only source of supply. The method of preparation of the catalyst had not been changed since 1938 except for an improved drying apparatus, which not only dried the filter cake but shaped the catalyst with a minimum of abrasion loss in handling. It consisted of a drum, the outside surface of which was indented to form the molds, the filter cake being pressed on to it to give small (3-mm.) cylinders. The drum rotated slowly (0.1 r. p. m.), and hot gases passing through it dried the catalyst particles before they could reach the bottom, where having contracted slightly during drying, they dropped out by gravity. This method made it possible to use a softer kieselguhr, pretreated at 700° instead of 1,000°, which gave a more active catalyst.

2789. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Production Data From Commercial Large-Scale Operation. Cost of New Fischer-Tropsch Plants. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 18–21, 28; PB 22,841; TOM Reel 200.

Figures on the cost of Fischer synthesis plants according to Lurgi (basis 100,000 tons/yr.) are as follows: For a plant including the synthesis and recovery of products with the newest Fe catalyst using gas recycle and staging—400 RM/ton/yr./product; complete unit including gas generator—900 RM/ton/yr./product. According to I. G. Farbenindustrie (basis, 180,000 tons/yr.), for a plant including synthesis and recovery of products with Co catalyst and multiple stage operation without gas recycle—290 RM/ton/yr./product; complete unit including generator (coke basis)—590 RM/ton/yr./product; complete unit including conversion (natural-gas basis)—500 RM/ton/yr./product. On the basis of 100,000 tons/yr. the cost of the complete unit (coke basis) becomes 615 RM/ton/yr./product. Average monthly production data from the balance sheet of Brabag in 1943 are as follows:

(1) *Gas production:*

Total synthesis gas produced	116,736,300 m.³ per mo.
CO + 2 H_2 in gas	79%
Yield of gas from brown-coal briquets	1,107 m.³ per ton

(2) *Synthesis:*

(*a*) Production: Kondensatoel.

	6,306.1 tons per mo.—52%
Primary gasoline	5,842.0 tons per mo.—48%
Liquid products:	
Total	12.148.1 tons per mo.—100%
Pure gasol	2,836.7 tons per mo.—23.2%
Total	14,989 tons per mo.
(*b*) Total yield per ton briquet	157. 2 kg.
(*c*) Total yield per m.³ gas	128. 4 gm.

(3) *Sales products* 14,762.8 tons per mo.

(4) *Financial statement:*

(*a*) *Cost breakdown—material cost:*	*RM per ton prod.*
Briquets (at RM 9.60 per ton)	60. 99
Outside coke (at RM 34 per ton)	20. 15
Grude coke (at RM 23 per ton)	4. 38
Raw coal (boilers) (at RM 2.4 per ton)	. 92
Outside power (at pf. 1.9 per kw.-hr.)	4. 04
Catalysts	9. 61
Charcoal purification	1. 20
Licenses	3. 12
Total	104. 41
Less credit for chemicals recovered	10. 21
Net total materials cost	94. 20

(*b*) *Other costs:*	*RM per tbn prod.*
Hourly wages	46. 80
Salaries	19. 23
Other costs	42. 10
Overhead	9. 28
5% capital interest (basis 165,000,000 RM)	45. 61
9% amortization (basis 149,000,000 RM)	74. 12
Total operating expense	331. 34
Sales	314. 17
Loss	17. 17

2790. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Medium-Pressure Fischer-Tropsch Units. 3-Stage Operation. Gas-Recycle Operation. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 23–27; PB 22, 841; TOM Reel 200.

In connection with the introduction of medium-pressure synthesis, it was found desirable to revise operations to produce liquid products with a maximum of olefins. The process used consisted in a combination of staging and gas recycle without substantial change in the operating temperature. It was found that considerable improvement could be made in the operation and the products by lowering the H_2 : CO ratio from the usual 2 : 1 to 1.94 : 1 then to 1.8 : 1 and 1.6 : 1. This resulted in improved liquid yields, higher olefin content, lower CH_4 formation, and higher average space velocity. The only apparent disadvantage was the decrease in the average catalyst life. Because of the low H_2 : CO ratio in the feed, a corresponding low ratio in the exit gas was obtained; therefore, since the ratio of consumption averages nearly 2.15 : 1, H_2 had to be added to convert the CO remaining from the first state in the second stage. To correct the ratio, H_2 in the form of converted water gas with a ratio of 3.79 : 1 was added. Even then the total conversion in the 2 stages was low. It was decided, therefore, to add a third stage, preceded by another addition of H_2. The favorable results of this operation with low H_2 : CO ratio led to adoption of an 8-stage operation in the 3 medium-pressure units at Hoesch, Ruhrchemie, and Lurgi. In spite of the general improvement in the operation, the olefin content of the products was still too low and finally was overcome by the use of gas recycle in the ratio of recycle gas to feed gas up to 3 : 1. The olefin content of the gasoline cut (200° end point) is about 70%, the Kogasin cut (200°–325°) about 45%. The temperature required to give adequate conversion is somewhat higher than in ordinary Co operation but does not exceed 225°, which can be reached with the existing steam-cooled reactors. The advantages derived from the above operation are: The shorter time required to bring the oven on stream; the increase in the yield per m³ of synthesis gas. Thus in the first stage above, the same yield may be reached as before in 2 stages; higher space velocity with a corresponding decrease in the number of ovens required; lower catalyst cost; less disturbance to the operation from variations in the feed gas composition; higher olefin concentration in the products. In general the application of recycle lowers the boiling point of the product toward lighter materials, but this may be corrected by raising the CO : H_2 ratio.

2791. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Adsorption of Hydrocarbons on Activated Carbon. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 31–34; PB 22, 841; TOM Reel 200.

Process used for recovery of the gasol fraction from the products of the Fischer-Tropsch synthesis by means of activated C is described with reference to a diagram. In operation, at least 4 adsorbers are required, each chamber being used successively for adsorption, drying, and cooling. The desorption after adsorption is performed with steam. The C used,

known as Supersorbon, is made from peat and activated by a $ZnCl_2$-steam treatment. The Lurgi Co. has developed a new C known as SK, which is activated with K_2S and is said to have about 2 times the capacity for low-boiling hydrocarbons as Supersorbon.

2792. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Development Work on the Fischer-Tropsch Process. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 35–69; PB 22, 841; TOM Reel 200.

Development work of Lurgi, Kaiser-Wilhelm Institute, Rheinpreussen, Ruhrchemie, Brabag, and I. G. Farbenindustrie on the Fischer-Tropsch process. Major attention was applied to the development of the Fe catalyst. Lurgi proposed 2 types of Fe catalysts: One precipitated on Si and operated at low temperature, 230°, designed to give a maximum of high-boiling-point product through polymerization; the second made from Lautmasse, a cheap product of the manufacture of Al from bauxite, impregnated with Cu and designed for the production of gasoline and olefins. Both operated with gas recycle; the product distribution of each was, respectively, gasoline 20 and 71%, Kogasin 20 and 20%, soft wax 15 and 9%, hard wax 45 and —%; the respective olefin content of the gasoline was 60 and 75% and of the Kogasin 45 and 60%. Kaiser Wilhelm Institute placed the research emphasis on the study of carbide formation in a precipitated Fe catalyst. Rheinpreussen likewise, and also on a catalyst based on Luxmasse with 0.15–5.0% K_2CO_3 and 0.0–3.0 Cu, which operated for 3.5 yr. and still gave 85% conversion at a space velocity of 80 and 113 gm. liquid product per m^3 of gas plus 32 gm. gasol. Ruhrchemie developed a precipitated Fe catalyst for wax production, which operated at low temperature, but an olefin producer did not get beyond laboratory stage. Brabag also developed Fe catalyst of the precipitated carrier type with emphasis on wax and olefin production, while I. G. Farbenindustrie studied the fused and sintered Fe (WK17) catalyst of NH_3 type and the effects of the reduction temperature, space velocity, and synthesis temperature on its productive capacity. Data of comparative tests of each of the above catalysts are presented. Reasonably good results were obtained from all. Attention also was paid to liquid-phase operation and 3 types of operation were tried: (*a*) Oel Kreislauf, the use of a solid catalyst bed with circulation of oil over the catalyst concurrently with the gas. It uses the fused Fe type NH_3 catalyst. The important features are the high space velocity, 200, and resulting high production from a given catalyst volume, 7.2 ton per 10 m^3. Olefin production is also high. The cost of a 100,000 ton per yr. plant is given as RM 57.2 per yr. per ton, as compared to RM 243 for the gas circulation process (I. F. Farbenindustrie), or RM 290 for a regular Fischer-Tropsch plant (Lurgi) with Fe catalyst and gas recycle. (*b*) Schaumfahrweise, suspension of the catalyst in the oil phase and dispersion of the catalyst with removal of the heat of reaction by circulating the slurry through an external cooler. Production of olefins and oxygenated products is high. (*c*) Static liquid phase, similar to (*b*), but the heat of reaction is removed by cooling tubes inserted in the liquid. This operation was regarded as highly promising. Some informtion is given concerning improvements in reactor designs, particularly the Krupp Taschenrohrofen at Wanne-Eickel, the Lurgi medium-pressure reactor, the I. G. Farbenindustrie medium-pressure reactor for the Synol plant, and the Rheinpreussen liquid-phase reactor.

2793. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. The Synol Process. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 72–92; PB 22,841; TOM Reel 200.

Development of the Synol process by I. G. Farbenindustrie is reported in detail. The process involves the direct synthesis of higher alcohols from CO and H_2 over a sintered Fe catalyst specially reduced by dry, pure H_2 at about 450° over a period of 50 hr. and medium pressure. The synthesis operation is performed at about 25 atm. and a temperature of 190°–225°. By raising the temperature, the same catalyst will produce a gasoline of 40–60% olefins with 65–75 octane number. With higher pressure, Fe carbonyl formation is considerable. The products consist almost wholly of straight-chain terminal alcohols, useful for making lubricating oils and detergents. Methods of separating the products are discussed at some length.

2794. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Isosynthesis. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 96–102; PB 22,841; TOM Reel 200.

Synthesis of low-boiling isoparaffins, as discovered in the laboratories of the Kaiser Wilhelm Institute, is a variation of the MeOH or the isobutyl synthesis. It operates at temperatures above those used in MeOH synthesis; although MeOH is believed to be an intermediate product. The upper temperature range is limited by the decomposition of CO at about 550°; this limit is constant for all pressures. The lower temperature limit is a function of the operating pressure; at 1,000 atm. the isosynthesis may be carried out at 400°; at 100 atm. a minimum of 450° is required. The kinetics of the synthesis is assumed to be as follows: (1) Formation of MeOH from CO and H_2; (2) dehydration of alcohol and immediate reaction with additional CO and H_2 to isobutylene and higher isoparaffins; (3) polymerization of isobutylene possibly followed by hydrogenation of alkylate, or formation of dimethylether from MeOH through addition of CO and H_2. At very high pressure the reaction proceeds as follows: $CH_3OH+CO+2\ H_2 \rightarrow CH_3OCH_3+H_2O$. The catalyst is pure ThO_2 or better combined with a dehydrating catalyst such as Al_2O_3; the % of Al_2O_3 based on ThO_2 varies 30–40%. A ThO_2–ZnO (1 : 1) catalyst does not give yields comparable to those with ThO_2–Al_2O_3; only 100 gm. per m.,[3] as compared to 130 gm. per m.[3] The ThO_2 catalysts are virtually insensitive to S poisoning and their long life is remarkable. The synthesis is carried out in a single pass with the feed gas containing CO–H_2 in the ratio 1 : 1.2; 70–75% conversion is obtained at average space velocities of about 1,350, 150 atm., and 450°. The products obtained are mostly low-boiling isoparaffins with isobutane the largest individual component.

2795. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Isobutanol Synthesis. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 103–108; PB 22,841; TOM Reel 200.

Isobutanol synthesis was a prewar I. G. Farbenindustrie development and was practiced for the production of isobutylene polymer (Oppanol) and isooctane. The high-boiling fractions were useful for production of detergents and lubricants. The isobutanol synthesis uses the same raw materials as the MeOH synthesis, virtually the same catalyst, and like pressures, about 240 atm. The catalyst in ZnO–Cr_2O_3–KOH (60 : 40 : 1 parts). The temperature used is about 430°. Compared with the MeOH synthesis, the output per catalyst volume is low since the main product MeOH is recycled to extinction; about 5–6 parts of MeOH are obtained for each part of isobutanol. The higher alcohols and ketones make up about 15% of the total product. An important part of the isoBuOH synthesis, which increases the yield of isoBuOH and utilizes one of the byproducts, is the reaction of isobutyron (diisopropyl ketone) with CH_2O to

give 2 mol. of isoBuOH. A detailed list of the compounds contained in the product is given to illustrate the complexity of the composition. Separation of the products from the synthesis is by fractional distillation.

2796. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Low-Pressure Methanol Synthesis. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 109–113; PB 22,841; TOM Reel 200.

This synthesis of MeOH is carried out at 30 atm., compared with usual operation at 250 atm. The work had been carried out on a laboratory scale and a pilot plant had been built. The process is as follows: A solution of Na metal in MeOH, 5.8 gm. in 100 gm., is charged to an autoclave and a pressure of 30 atm. set up by feeding CO. The temperature is maintained at 80°. The crude product, a mixture of MeOH and CH_3COOH, is separated from the catalyst salts by distillation and is then hydrogenated over a catalyst of Cu–Cr–Ba oxides at 175°–185°. The products of hydrogenation are separated by fractional distillation. Overall yields of 95% to MeOH are claimed.

2797. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. The Oxo Synthesis. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 114–128; PB 22,841; TOM Reel 200.

Oxo synthesis is a process for the production of alcohols by the action of olefins with 1 mol. each of CO and H_2 and subsequent hydrogenation of the resulting aldehyde. The process was developed by Ruhrchemie and I. G. Farbenindustrie and a plant was built at Holten but never operated. The information in this report is based on large-scale pilot-plant operation and laboratory work. The chemistry of the process was studied, and pure olefins of different types were subjected to the Oxo reaction and the products separated and analyzed. The compounds charged to the Oxo synthesis are known to be substantially terminal olefins, yet it was found that some of the products could have been formed only if a double bond shift had preceded the formation of the aldehyde. Tests with *n*–dodecylene–1 proved that from terminal normal olefins the Oxo synthesis yields branched alcohols, particularly 2–alkyl alcohols, whereby the yield decreases with increasing length of the sidechain. It was finally possible to prove that Co carbonyl was the catalyst responsible for the double bond shift. Fe carbonyl showed a similar effect but not the same activity, and Ni had no effect at all. Many materials were tested as feed for the synthesis; it appears that the reaction is applicable in principle to all monoolefins independent of origin, although synthetic olefins are preferred because of their higher purity. Compounds containing double bonds give unsatisfactory results. The customary catalyst is the CO–ThO_2–kieselguhr (100 : 1.5 : 200) applied as a slurry in the liquid feed in concentration of 3% by weight of the olefins. It does not contain MgO, because this encourages condensation of the aldehydes. One of the main problems in the process, as noted above, is the formation of Co carbonyl. The I. G. Farbenindustrie developed a Co–Cu catalyst that gave only a fraction of the carbonyl and was satisfactory for the first stage (aldehyde formation) but did not hydrogenate well. The catalyst is recovered from the reactants at the end of the operation by filtration and returned for further use. In a modification of the process, Co acetate is contacted with fatty acids in an autoclave to yield the Co salt, and this is introduced in solution into the feed to give a concentration of 0.02–0.05% of Co. This mixture is charged to the reactor where it passes over a solid Co catalyst bed (Co on pumice) and is finally freed from the Co in a special smaller reactor filled with plain pumice by being reduced with H_2 and deposited on the pumice. This reactor is purged of Co after several months by forming the carbonyl, which is again dissolved in oil and returned to the feed. The operating conditions for both the batch and the continuous processes and the fractionation of the products are described. The over-all cost of the final product is given as 0.60–0.65 RM per kg. of alcohol. Further development of the process probably will be toward continuous operation and better control of the synthesis, particularly the suppression or close control of the double bond shift to give clearly defined α-substituted alcohols of predetermined branching.

2798. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. BIOS Misc. Report 60, 1947, 128 pp.; PB 22,841.

This report is a reproduction of United States Naval Technical Mission in Europe Rept. 248–45, PB 22,841. It covers the Fischer-Tropsch process, the Synol process, synthesis of high melting point waxes, isosynthesis, isobutanol synthesis, low pressure MeOH synthesis, and the Oxo synthesis.

———. *See* abs. **1469.**

2799. REID, J. B. Recovery of Byproducts in High-Temperature Coking. British Coal Utilisation Research Assoc., Monthly Bull., vol. 9, No. 8, 1945, pp. 225–234.

Review with 46 refs. Reformation of coke-oven gas is directed principally to producing mixtures for hydrocarbon synthesis. The various reactions by which CH_4 can be converted are:

(1) $CH_4=C+2H_2-18$ kcal.
(2) CH_4+H_2O (vapor) $=CO+3H_2-49.5$ kcal.
(3) $CH_4+CO_2=2CO+2H_2-59.5$ kcal.
(4) $CH_4+\frac{1}{2}O_2=CO+2H_2+8.5$ kcal.

All the reactions require temperatures of about 1,200° C; at a lower temperature reaction (2) merges into the exothermic reaction: $CH_4+2H_2O=CO_2+4H_2$. 5 reformation processes, based on the above reactions and directed principally to producing gas mixtures of composition $CO:H_2=1:2$, have been developed: The Fischer process in which the CH_4-containing gas is passed with steam through coke in a water-gas generator, producing mixtures of H_2 and CO in the ratio of 2 : 1 when suitable adjustment is made of the gas: steam ratio and the lengths of gas and blow periods; the Linde process makes use of reaction (4) by which it is claimed that 90–95% of the CH_4 is converted giving a final gas mixture very near to $2H_2+CO$; the Kuhlmann process operates reaction (2) at hot inert surfaces, the gas and steam being the sole reactants, the resulting gas mixture being mainly H_2 and CO in the ratio of 4 : 1; the Koppers process, which is similar to Kuhlmann, in that it makes use of thermal reformation at hot surfaces with an efficiency of 90–95% as against 75% for the Kuhlmann process; the I. G. Farbenindustrie process is catalytic and is conducted at about 800° C. on a Ni catalyst, it depends on reactions (2) and (3) so that both CO_2 and steam are added to the gas mixture, and the product is H_2 and CO in a ratio of almost exactly 2 : 1.

2800. REINÄCKER, G. [Heterogeneous Catalysis and Atomic Structure.] Die Chemie, vol. 57, 1944, pp. 85–90; Chem. Abs., vol. 40, 1946, p. 4593.

Discussion, with 76 refs. The magnetocatalytic effects of Ni-Fe catalysts on the decomposition and hydrogenation of CO are of interest in connection with the change in catalytic activity above the Curie-point temperature. The change in activity that occurs at the Curie point is due to electronic changes.

2801. REINDERS, W. [Composition of Water Gas at Lower Temperatures.] Ztschr. physik. Chem., vol.

130, 1927, pp. 405–414; Chem. Abs., vol. 22, 1928, p. 860.

Mathematical treatment of the various equilibria among the components of water gas is given with a discussion of the Fischer synthesis of hydrocarbons from CO and H_2 and a probable explanation of the formation of CH_4.

REINHARD, O. *See* abs. **3245.**

REINOV, N. *See* abs. **65.**

2802. REIS, T. [Theoretical and Experimental Contributions to the Study of Fluid Catalyst Systems.] Bull. assoc. franç. techniciens pétrole, No. 76, 1949, pp. 3–44; U. O. P. Co. Lib. Bull., Oct. 5, 1949.

This article is composed of 3 parts. The 1st part discusses the theory of fluid catalysis and reviews the work of other investigators. Semiempirical formulas are introduced for making the following calculations: (*a*) The length of time the particles are in a reactor; (*b*) the loss of charge; (*c*) the distinction between aggregative and particulate fluidization; (*d*) the initial expansion of the solid particle bed; (*e*) the efficacy of fluidization; (*f*) the loss of charge in the case of horizontal or vertical flow of the dispersed suspensions. The 2d part describes a new experimental method for directly controlling the behavior of dispersed catalyst suspensions. The 3d part is devoted to new theoretical conceptions of fluidized systems.

REISEMANN, E. *See* abs. **137.**

2803. REISINGER, —. Report on the Synol Synthesis. TOM Reel 134, Rept. 283, May 2, 1941, 19 pp.

In the examination of catalysts for the reaction, the fused Fe catalyst WK17, Leuna NH_3 catalyst, gave the best results; the Oxo fraction, 230°–350°, of the primary products contained 25–35%, by weight, of alcohols. Fe precipitation catalysts with promoters were tried. The most active of these was the Fe–Al type, which, with a specific total yield of 84.3 gm. per N $m.^3$, gave 42.5% alcohol by weight, in the Oxo fraction. Also worthy of note are the catalysts Fe–Mn and Fe–Ni. The amount of promoter element should not exceed 1–3% for the best results. Experiments on the influence of temperature on the course of the synthesis showed that a maximum alcohol yield only can be obtained at low temperatures, 200°–240°, and with low gas conversions, 40% contraction. The chemical natures of the Fe catalyst primary products were determined by fractional distillation. The alcohol concentrations were found to increase with rising temperature continuously up to a maximum at 100°–180°, C_4–C_7, with a concentration of 30% alcohol, then decrease fast to 11%, rising again to a maximum at 300°–320°, approximately C_{15}. At still higher temperatures, virtually no alcohols were present. During distillation of the primary product, the acids contained in the product esterify corresponding amounts of alcohol. By deacidification of the products before the distillation starts, the alcohol contents in the fractions above 200° can be retained. A comparison is given on the composition of products obtained by the 2 methods. By heating the high-melting paraffins, 84° and more in air, varnishlike coatings of good qualities have been obtained.

2803a. REITLINGER, O. [Increasing the Efficiency of Catalysts for Gas Reactions.] Chem. Ing.-Tech., vol. 24, 1952, pp. 1–2; Chem. Abs., vol. 46, 1952, p. 3,681.

Catalysts are prepared by depositing powdered active catalytic materials on catalyst carrier by means of hydrated bonds. Preparation of an Fe_2O_3 catalyst is described in detail and data are presented for 6 examples as follows: Chlorination of CH_4 and C_2H_4, $C_2H_4+HCl \rightarrow C_2H_5Cl$, $C_2H_2+HCl \rightarrow C_2H_3Cl$, $2C_2H_2+3H_2O \rightarrow CH_3COCH_3+2H_2+CO_2$, and hydrogenation of CO.

2804. REITMEIER, R. E., ATWOOD, K., BENNETT, H. A., AND BAUGH, H. M. Production of Synthesis Gas by Reacting Light Hydrocarbons With Steam and Carbon Dioxide. Ind. Eng. Chem., vol. 40, 1948, pp. 620–626; Chem. Abs., vol. 42, 1948, p. 4328.

Study was made by the Girdler Corp. to establish the optimum conditions for the production of synthesis gas mixtures for the Fischer-Tropsch reaction, having a ratio of H_2: CO capable of being varied between 0.5 and 3 in the same equipment without running into difficulties brought about by the deposition of C, by controlling the temperature and the composition of the reactant. This study involved consideration of the equilibria when light hydrocarbons are reacted with steam and CO_2 and attempted to predict the conditions necessary to prevent C deposition. Calculation of the proper proportion of reactants to be introduced into the furnace for the production of the desired ratio was included. Following this, laboratory-scale experimental work was conducted to determine the possibility of approaching the conditions predicted. Finally the work was expanded to pilot-plant scale as a successful result of which a plant is being constructed at Bruceton for the Bureau of Mines. The paper presents curves and formulas that have been developed to facilitate the selection of conditions and reaction mixtures of light hydrocarbons, steam, and/or CO_2 to produce a synthesis gas having a wide range of compositions. Laboratory experimental data are given, which demonstrate that the conditions and compositions predicted by the curves can be closely approached in actual practice. Pilot-plant investigations also are described, which show that the process is commercially feasible.

REITSTOETTER, J. *See* abs. **3588.**

2805. REMBASHEVSKIĬ, A. G. [Enriching of Binary Gas Mixtures.] Trudy Leningrad. Khim. Tekhnol. Inst., No. 6, 1938, pp. 288–312; Khim. Referat. Zhur., vol. 1, No. 8–9, 1938, pp. 3–4; Chem. Abs., vol. 33, 1939, p. 9593.

Artificially prepared mixtures of CO and H_2 were passed through a layer of the cataylst [Ni obtained from $Ni(NO_3)_2$] at 200°, 240°, 280°, and 320°. For $CO:H_2=1:3$, the reaction $CO+3H_2 \rightleftarrows CH_4+H_2O$ reaches its maximum at 280° (92.8% CH_4, 8% H_2). The 1 : 1 and 1 : 2 mixtures yield less CH_4, and C is deposited from the side reaction $2CO \rightleftarrows CO_2+C$. No advantages were obtained from the substitution of Co for Ni. The maximum CH_4 formation took place at a higher temperature. The use of Fe–Zn, and of a specially prepared Fe catalyst gave unsatisfactory results. To obtain the $CO:H_2=1:3$ binary gas mixture, half of the gas, free from H_2S and from CO_2, was passed at 450°–500° through a converter, Fe oxide with the oxides of Cr, Mg and other metals as catalysts. The CO is oxidized by water vapor according to $CO+H_2O \rightleftarrows CO_2+H_2+10{,}000$ kcal. After removing the CO_2, both gases are mixed, dried, and passed over the catalyst. Experiment with binary peat gases gave a product with a 4,500 kcal. heat capacity, and an 80.43% yield. Analogous results were obtained from the 1 : 1 mixtures, but the 1 : 3 mixture reaction was faster, and it took place at a lower temperature. The best catalyst was Ni–Al_2O_3 (stable to contact contamination). Prepared water gas was passed through the catalyst at 250°–280° with an increasing velocity until the heat capacity of the final product was below 4,000 kcal./ $m.^3$. The reaction yield increased with the velocity and decreased with the increase of the heat capacity of the final product. A temperature increase, in the 250°–280° region, for the same heat capacity of the final product caused a decrease of the yield and an increase of the velocity. It was calculated that a 100,000 $m.^3$/ hr. enriching of the gases to 3,000, 3,600, 4,500, and

5,800 kcal./m.³ is commercially profitable only if the products are used close to the production plant.

REMEIKA, J. P. *See* abs. **1136.**

2806. RENNEKAMP, F. [Composition of Fat Acids in a Fat Obtained From Oxidation Products of Synthetic Paraffin.] Ztschr. physiol. Chem., vol. 259, 1939, pp. 235–244; Chem Zentralb., 1939, II, p. 3061; Chem. Abs., vol. 33, 1939, p. 7605.

Synthetic fat contained all the fat acids from C_8 to C_{22} with about equal quantities of odd and even numbers of C atoms. It melts at 27°–29°, has I No. 4.2, acid No. 0, saponification No. 231, and unsaponifiable 0.3%. The Me esters were fractionated and some of the acids isolated pure from the fractions.

2807. RENZI, E. [Industrial Utilization of Methane.] Atti III° convegno naz. metano, vol. 2, 1941, pp. 293–296; Chem. Zentralb., 1942, II, p. 1989; Chem. Abs., vol. 38, 1944, p. 3108.

Applications discussed are: Decomposition of CH_4 above 900° with catalysts into H_2 and lampblack, and utilization of the lampblack for making printer's ink, etc.; decomposition of the H_2, for example, for synthesizing NH_3 or liquid motor fuels; transformation of CH_4 and H_2O vapor at 900° with Ni catalyst to CO_2 and H_2; transformation of CO_2 in gas producers according to $C+CO_2=2$ CO–37 cal.; use of the CO and H_2 for the synthesis of hydrocarbons or MeOH; preparation of a mixture of C_2H_4, C_2H_2 and H_2 by treatment of CH_4 with a spark discharge; transformation of the mixture at 200°–250° at normal pressure with Ni catalyst into benzine.

2808. REPPE, —. New Syntheses of Acrylic Acid. Modern Plastics, vol. 23, No. 3, 1945, pp. 162–165, 210; Chem. Abs., vol. 40, 1946, p. 1449.

Translation of a captured German report by the above author, obtained under auspices of U. S. War Department. Metal carbonyls promote reaction between C_2H_2 or olefins, CO and H_2O, alcohols, or other compounds containing labile H. Cyclopropenones or cyclopropanones probably form as intermediates by interaction between C_2H_2 or olefin and CO. These intermediates hydrolyze or alcoholyze to the corresponding acids or esters. Acrylic esters or amides are obtained from C_2H_2, CO, and alcohol or amine with Ni and NiI_2 catalyst at 150°. Similarly, olefins with CO and alcohols give almost quantitative yields of saturated carboxylic acid esters. α–olefins yield a mixture of straight chain and α–Me substituted acid esters. The Oxo synthesis of aldehydes also is explained as owing to hydrogenolysis of a cyclopropanone intermediate. $Ni(CO)_4$ (0.25 mol.) added dropwise to a mixture of EtOH (1 mol.) and concentrated HCl (0.5 mol.) saturated with C_2H_2 gives $CH_2:CHCO_2Et$ virtually quantitatively. Similarly other alcohols give the corresponding acrylate esters, mercaptans give acrylic thio esters, amines give acrylic amides, and H_2O gives $CH_2:CHCO_2H$, all yields being substantially quantitative. Co carbonoyl, but not Fe carbonyl, may replace $Ni(CO)_4$ in this reaction. $NiCl_2$ solution resulting from the process is reclaimed by adding NH_3 in slight excess over the requirement to form $NiCl_2$ hexamine and treating with CO at 80° and 50–100 atm. to form $Ni(CO)_4$.

RESCORLA, A. R. *See* abs. **3082.**

2809. RESEARCH COUNCIL OF ALBERTA. Fischer-Tropsch Synthesis of Liquid Fuels. Annual Rept. 45, 1944.

In 1944 a project was begun concerned with the improvement and development of catalysts. Equipment was designed, erected, and tested to provide for water gas production and a battery of 6 catalyst testers. A start had been made on catalyst preparation, and it was expected that all equipment, testing and control methods, operating technique, and procedures would be completed and runs started by March 1945.

2810. ———. Natural-Gas Research. Annual Director's Rept. 47, 1945, pp. 14–15.

Study of the Fischer-Tropsch synthesis of gasoline and other liquid fuels was begun in 1944 (abs. **2809**) in cooperation with the Federal Bureau of Mines. The process is of interest as a possible source of liquid fuels from natural gas or coal since Alberta has large reserves of both of these natural resources. The work thus far is concerned mainly with a study of catalysts, and early in 1945 some static tests were carried out, the results of which are to be correlated with continuous tests now under way.

2811. RETTENMAIER, A. [Process and Raw Materials for Complete Gasification of Coal and Its Importance in Meeting Further Increased Gas Demands.] Gas u. Wasserfach, vol. 84, 1941, pp. 473–477; Chem. Abs., vol. 36, 1942, p. 5333.

Development of processes for the complete gasification of lignite is reviewed. 2 new processes have been developed for the gasification of bituminous coals by means of O_2 and steam, 1 using pulverized coal and the other, the Thyssen-Galocsy process, using lump coal. The latter process, described, gasifies noncoking coals in a shaft generator from which the slag is removed in molten form. The section of the generator resembles that of a blast furnace. To avoid hot spots in the combustion zone, a portion of the injected O_2 is mixed in a small precombustion chamber with some of the process gas or other suitable gas. Decomposition of the added steam is virtually complete at the high temperature employed. The resulting oxygas can be used for synthesis purposes or methanized to town gas. The technical problem of methanization using a Ni catalyst is now claimed to be solved. The efficiency of the Thyssen-Galocsy generator, including gas and tar, is about 90%, or, taking into account the energy required for the O_2 used, about 80%. Costs given.

2812. REVUE PÉTROLIFÈRE. [Substitute Motor Fuels, A Study of Hydrogenation Processes From the Economic Standpoint.] Feb. 8, 1930, p. 210.

Yields per ton of coal treated are given for various processes. The Bergius process yields 150 kg. of gasoline, 200 kg. of diesel or impregnating oil, 80 kg. of fuel oil, and 60 kg. of lubricating oil. The Patart, Badische Anilin u. Soda Fabrik, or Fischer-Tropsch methods give 400–600 kg. of MeOH, 200–600 kg. of liquid hydrocarbons, and recovery of the gases from coke manufacture, 5–10 kg. of C_6H_6, 5 kg. of EtOH, 5–7 kg. of MeOH. The Fischer process at ordinary temperature requires a very large plant. The apparatus for the production of synthetic MeOH, although less cumbersome, is not less costly.

REYERSON, L. H. *See* abs. **2328.**

REYNOLDS, D. A. *See* abs. **3213, 3214.**

2813. RHEAD, T. F. E., AND WHEELER, R. V. Effect of Temperature on the Equilibrium $2\ CO \rightleftharpoons CO_2+C$. Proc. Chem. Soc., vol. 26, 1910, p. 220; Jour. Chem. Soc., vol. 97, 1910, pp. 2178–2189; Chem. Abs., vol. 5, 1911, p. 641.

In an electric furnace constructed so that a given temperature could be maintained, without serious fluctuations, for several weeks, and with a N_2 jacket around the reaction tube to prevent diffusion of O_2, pure CO_2 was circulated over pure wood charcoal until the pressure became constant. The values obtained for the equilibrium are as follows: At 850°, by vol., 6.23% CO_2 and 93.77% CO; 900°, 2.22, 97.78; 950°, 1.32, 98.68; 1,000°, 0.59, 99.41; 1,050°, 0.37, 99.63; 1,100°, 0.15, 99.85; 1,200°, 0.06, 99.94. By means of the equation $(19{,}500/T)+\log_e C_1^2 \log_e C_2=k$ (from LeChatelier's equation for the equilibrium in gaseous systems), the following values for k, at the above series of temperatures were calculated: 20.01, 20.39, 20.24, 20.44, 20.32,

20.70, and 20.65. At 850°, the speed of reduction of CO_2 by C was found to be 116 times that of the reverse reaction. (*See* abs. **185**, **319**, **698**, and **3068**.)

2814. ———. Effect of Temperature and Pressure on the Equilibrium: 2 $CO=CO_2+C$. Jour Chem. Soc., vol. 99, 1911, pp. 1140–1153; Chem. Abs., vol. 5, 1911, p. 3644.

Authors have previously investigated this equilibrium at atmospheric pressure (abs. **2813**). Further measurements have now been made at 0.5–3 atm., in order to prove whether the expression $(N'-N)\ ln\ P$ in Le Chatelier's general equation for mobile equilibrium satisfies experiment in this particular case. The reaction vessel of quartz glass was heated in an electric resistance furnace wound with Pt wire. Temperatures ranged from 800°–1,100° and were measured by means of a Pt–PtRh thermocouple placed outside the quartz vessel. The equation $(38{,}055+2.02\ T-00031\ T_2)2\ T+ln\ P+In\ (C_1^2/C_2)=k$ was found to satisfy the data obtained. In this equation T is absolute temperature, P the pressure in atmosphere, C_1 and C_2 the fractional concentrates of CO and CO_2, respectively, and k a constant. Equilibrium was reached rapidly at the higher temperatures, but at 800° it was attained only after heating for more than 70 hr.

RHEINHEIMER, W. *See* abs. **1610.**

RI, T. *See* abs. **1489.**

2815. RICE, F. O. Attempts to Prepare the Methylene Radical by the Thermal Decomposition of Hydrocarbons. Jour. Am. Chem. Soc., vol. 61, 1939, p. 213; Chem. Abs., vol. 33, 1939, p. 1663.

Results indicate that trivalent C radicals are the primary products of organic dissociations, and even in the few cases, such as CH_2N_2 and CH_2: CO, in which CH_2 is the primary product, it passes readily into the trivalent state.

2816. RICHARDS, T. W., AND DAVIS, H. S. Heats of Combustion of Benzene, Toluene, Aliphatic Alcohols, Cyclohexanol, and Other Carbon Compounds. Jour. Am. Chem. Soc., vol. 42, 1920, pp. 1599–1617.

Heat of combustion of MeOH in 18°-cal. per gm. was found to be 5,326.

2817. RICHARDSON, R. E., AND OTHERS. Synthetic Emulsifying Agents, Wetting Agents, Detergents, and Soap Substitutes. PB 6,684, 1945, 38 pp.

Trade names, chemical composition, and manufacturing process for the products made by I. G. Farbenindustrie A.-G. Among the products mentioned are: Igepons and Igepals, alkyl–aryl–sulfonate-type detergents, made from Fischer-Tropsch oils, and Mersol emulsifiers.

RICHARDT, F. *See* abs. **1299.**

RICHTER, H. *See* abs. **1832**, **1833.**

RICHTER, M. *See* abs. **3089.**

2818. RIDEAL, E. K. Note on a Simple Molecule Mechanism for Heterogeneous Catalytic Reaction. Proc. Cambridge Phil. Soc., vol. 35, 1939, pp. 130–132.

Proposed mechanism involves 2 assumptions: (1) That surface catalytic reactions take place between a chemisorbed radical or atom and a molecule derived from the gas phase; (2) that in the interaction between the 2 species the covalent bond between the chemisorbed constituent and substrate either is not broken or is converted into the van der Waals bond.

2819. ———. Mechanism of Catalytic Hydrogenation. Chem. and Ind., 1943, pp. 335–338; Chem. Abs., vol. 38, 1944, p. 15.

An address on the development and extension of Sabatier's ideas by Rideal over the last 20 yr. is given. In agreement with Sabatier, and contrary to the views of H. S. Taylor, Rideal concludes that a metallic catalyst is covered with a monolayer of chemisorbed H_2, which is adsorbed without appreciable energy of activation. Further changes in H_2 retention with temperature are due to solution of H_2 in the metal, or activated diffusion. The methods of photoelectric thresholds, or better, the change in contact potential caused by the presence of a monolayer were used by Rideal to study the chemisorbed layer. The ortho-para H_2 conversion at a metallic surface is due to interaction between a chemisorbed and a van der Waals adsorbed species and, thus, can be used as an indicator for chemisorbed H atoms. This is an aid in explaining the mechanism of certain hydrogenation reactions. The theory of intermediate compound formation best explains such hydrocarbon catalysis reactions as the exchange of H and D in C_2H_4 and C_3H_6, and the migration of the double bond in higher olefins under conditions when exchange occurs. Although the mechanism by which H_2 is added across a double bond at the surface of Ni is as yet uncertain, present evidence favors the view that catalytic hydrogenation proceeds through the addition in 1 step of an undissociated molecule of H_2. Organometallic intermediate compounds explain also the catalytic cyclization reactions of heptane, octane, and the Fischer-Tropsch synthesis. The main reactions occurring in the latter are due to van der Waals adsorbed H_2 alone rather than chemisorbed H_2, which in this synthesis causes formation of large quantities of CH_4.

———. *See* abs. **643**, **808**, **1407**, **1519**, **1520**, **3510.**

2820. RIDEAL, E. K., AND TRAPNELL, B. M. W. [Adsorption of Hydrogen by Tungsten, and the Mechanism of Para-Hydrogen Conversion at Tungsten Surfaces.] Jour. chim. phys., vol. 47, 1950, pp. 126–138; Chem. Abs., vol. 44, 1950, p. 7118.

The adsorption of H_2 was measured over the temperature range −185° to 0° and pressure range 1.5×10^{-7} to 10^{-2} mm. on a film of W formed by evaporation of W atoms from a wire. The equilibrium adsorption changed very slowly with temperature and pressure, increasing only 9% at 0° for a 10^4 pressure increase and only 14% on dropping the temperature from 0° to −183° at 10^{-2} mm. If the surface area of the film is judged from the chemisorption of O_2, the measurement represents coverages in the range 60%–90%. The heats of adsorption calculated by the Clausius Clapeyron equations are 14, 11, 7, 3, and 2 kcal. per mole at coverages of 70, 75, 80, 85 and 90%, respectively. The data fit a Freundlich isotherm. Quantitative analysis of the data leads to the conclusion that the observed fall in heat of adsorption with coverage cannot be accounted for on the basis of simple electrostatic dipole-dipole repulsions. The data are consistent with the rate of interconversion of ortho-para H_2 observed by Eley and Rideal (abs. **808**) if it is assumed that this reaction is the result of alternate chemisorption and evaporation of H_2 mol. from a surface that is so extensively covered with H_2 as to have a low heat of desorption of H_2 mol.

2821. RIEDEL, H. G. [Status of Scientific Knowledge and Technical Development in the Field of Tar Processing, Extraction and Synthesis.] Bergbau-u. Energiewirtsch., vol. 2, 1949, pp. 243–250; Chem. Zentralb., 1950, II, p. 1765.

Subjects discussed are: Preparation of low-temperature tars, their processing, extraction, and hydrogenation, and the Fischer-Tropsch process.

2822. RIEDL, R. [Gas Developments in Czechoslovakia.] Rev. gén. gaz, vol. 69, No. 3, p. 73; Coke and Gas, vol. 9, 1947, p. 350.

Summary of a detailed study of the production of gas by the Lurgi process and of the development of the Czech gas industry within the 2-year plan provided by nationalization. Typical analyses are given of gas

obtained by treatment of a Czech lignite. A Lurgi producer, dealing with 8–20 mm. lignite and rate at 3,000–4,000 $m.^3$ of gas/hr., produced 700 $m.^3$ of gas and 80 kg. of tar/metric ton of lignite and requires/$m.^3$ of gas: O_2, 0.19 $m.^3$ at 22 atm.; steam, 1.25 kg. at 25 atm.; electric energy, 0.16 kw.-hr.; and water 0.06 $m.^3$ Three Lurgi producers at the Stalin works near Möst have been in service since 1945 and appear to have given no difficulty in operation. A map shows the development of the Czech gas industry.

2823. ———. [Manufacture of Synthetic Liquid Fuels.] Paliva a voda, vol. 27, May 20, 1947, p. 74; Fuel Abs., vol. 2, No. 3, 1947, p. 41; Chem. Abs., vol. 42, 1948, p. 5199.

The author stresses the interest for the manufacture of artificial motor fuel even in those countries that possess their own naphtha sources. Two basic manufacturing methods, Fischer-Tropsch and Bergius, and a schematic manufacturing method at the Stalin works are described.

RIEDLER, G. *See* abs. **3578.**

RIEHL, N. *See* abs. **1234.**

RIES, H. E. *See* abs. **1625a.**

RIESZ, C. H. *See* abs. **1957, 1958, 1959.**

2824. RIESZ, C. H., LISTER, F., SMITH, L. G., AND KOMAREWSKY, V. I. Catalysts for Hydrocarbon Synthesis. Ind. Eng. Chem., vol. 40, 1948, pp. 718–722; Chem. Abs., vol. 42, 1948, p. 4325.

Hydrocarbon synthesis catalysts are regarded as complex-action catalysts, combining hydrogenation and polymerization. Although complicated by carrier and promoter effects, the above was substantiated by preparation of 2-component catalysts containing Co, Ni, or Fe for the hydrogenating action; ThO_2, SiO_2, Al_2O_3, or ZnO as polymerization components. Co–ThO_2, Co–SiO_2, and Co–Al_2O_3, were particularly active catalysts, optimum liquid formation occurring when the metal content of the catalyst was 75% by weight. Ni catalysts formed excessive amounts of gaseous hydrocarbons, but Fe catalysts were relatively inactive in the absence of elevated pressure.

RIGAMONTI, R. *See* abs. **2395, 2396, 2397.**

2825. RIKLES, B. [Liquid and Solid Hydrocarbons From Natural Gas—the Fischer-Tropsch Process in Argentina.] Bol. inst. sudamer. petrol. (Montevideo), vol. 2, 1947, pp. 543–593; British Abs., 1949, B, I, p. 37.

Review with 88 refs.

2826. RILEY, H. L. (Chairman). Chemicals From Coal in the North of England. Coal-Processing Industries Report. Chem. Age, vol. 53, 1945, pp. 565–568.

Objectives to be considered are the development of the tar distillation industry and the extraction of C_2H_4 from coke-oven gas. The statement is made that the Northeast provides one of the most suitable areas in the country for large-scale trials of the Fischer-Tropsch process. The County of Durham, with its large coke-producing units and potential reservoirs of surplus gas, is eminently well-placed for this research work, and the products made by the Fischer-Tropsch process may be linked with those from the C_2H_4 extraction plan.

2827. ———. Carbides, Nitrides, and Carbonitrides of Iron. Quart. Revs. (London), vol. 3, 1949, pp. 160–172; Chem. Abs., vol. 43, 1949, p. 7361.

Review with 64 refs.

RIOTT, J. P. *See* abs. **2881.**

2828. RISENFELD, E. H. [Significance of the Fischer Synthesis (Hydrogenation of Carbon Monoxide) in the Domestic Manufacture of Benzene and Lubricating Oil in Sweden.] Tek. Tid., vol. 66, Uppl. A–C, Kemi, 1936, pp. 89–98; Chem. Abs., vol. 31, 1937, p. 3665.

Fischer-synthesis process, in contrast with the Bergström and the Bergius processes, offers the only possibility for the production of liquid hydrocarbons in Sweden, for which only wood, peat, or charcoal is available as the raw material.

RITCHIE, A. W. *See* abs. **179, 180.**

2829. RITMAN, E. L. Carbohydrates and Related Constituents of Plant Tissues as a Supplement to Coal and Petroleum. Trans. World Power Conf., Fuel Conf., Sec. A–3, Paper 8, 1947, 7 pp.; Chem. Abs., vol. 42, 1948, p. 736.

Best method of converting carbohydrates and related constituents of plant tissues to fuel appears to be the fermentation of a suspension containing dissolved carbohydrates. It is probable that 3 $m.^3$ or more pure CH_4, mixed with CO_2 in ratio of about 7 CH_4: 3 CO_2, can be produced per 24 hr. per $m.^3$ of tank vol. The gas mixture is very suitable for the Fischer-Tropsch synthesis.

RITTER, H. *See* abs. **1206.**

2830. RIVETT, D. Oil Production From Coal From an Australian Viewpoint. Petrol. Times, vol. 38, 1937, pp. 629–633; Engineering, vol. 144, 1937, pp. 748–749; Iron and Coal Trades Rev., vol. 136, 1938, pp. 653–654; Brennstoff-u. Wärmewirt., vol. 20, 1938, pp. 87–92; British Chem. Abs., 1938, B, p. 129.

Economic possibilities of establishing, in Australia, plants for producing gasoline from coal by direct hydrogenation or by the Fischer process have been investigated by a Government committee. The scheme was received unfavorably.

2831. ROBELL, J., AND DEWLING, W. L. E. Methanol Synthesis at the I. G. Farbenindustrie A.-G. Plant at Oppau; FIAT Rept. 888, 1946, 14 pp.; PB 47,864; TOM Reel 240.

Presents information on process and equipment design of the MeOH synthesis plant at Oppau, and reviews the latest developments achieved by I. G. Farbenindustrie A.-G. in the art of MeOH synthesis. The equipment is described, and operating data are presented in some detail. In general, the process is similar to that used in the United States. Analysis of the feed gas at the entrance to the converter is as follows: CO, 18.4; H_2, 67.2; CO_2, 0.7; CH_4, 0.6; and inerts 13.1%. The maximum operating temperature in the catalyst bed is 360°–390°; the usual operating pressure, 250–260 atm. Approximately 3,000 $m.^3$ of fresh feed are required per ton of crude MeOH produced; the circulation rate approximately 100,000 $m.^3$ per hr. With the new type of converter described the conversion per pass is 12–16% of the CO fed, the yield of MeOH on the basis of the CO fed being approximately 72% and on the H_2, 62%. The catalyst for MeOH synthesis has the following composition: 26–30 Cr_2O_3, 59–64 ZnO, 1–1.5 graphite, and 9–10% H_2O. The method of preparation and reduction is described. Its normal life is 6–12 months. The following utilities are required per ton of crude MeOH: Electricity 25 kw.-hr., steam 0.3 ton, cooling water 130 $m.^3$, and labor 1.54 man-hours.

2832. ROBERTS, E. C. Precementitic Carbides in Tempered Martensite. Jour. Metals, vol. 188, 1950, Trans., p. 1210.

The 3d stage of tempering quenched steel is the development of cementite from an intermediate, which makes its appearance in the 1st stage. This is not a transition precipitate but a distinct entity with no coherence existing between the carbide and the matrix. It forms faster in quenched martensite than does cementite, and its growth to larger particle size than

early Fe_3C must mean that the latter grows as a result of a competitive process.

2833. ROBERTS, G. Production of Liquid Hydrocarbons and Chemicals From Natural Gas. Oil Gas Jour., vol. 46, No. 26, 1947, p. 40; Petrol. Processing, vol. 2, 1947, pp. 905–906.

Abstract of paper presented at the meeting of the Independent Natural Gas Association of America. Synthetic gasoline from natural gas now is competitive economically with gasoline from crude oil, and if crude oil were to rise approximately $1.00 per bbl., gasoline from coal would then be competitive with petroleum gasoline. Gasoline from coal may become a reality by 1950. Commercial use of the synthesis process will give great impetus to the organic chemical industry. In this connection, the work now being planned for the plant of the Stanolind Oil & Gas Co. at Hugoton is described. Application of the fluid technique to operation of the synthesis process is discussed.

2834. ROBERTS, G., AND PHINNEY, J. A. Manufacture of Synthetic Gasoline Nearing Commercial Application in United States. Oil Gas Jour., vol. 45, No. 45, 1947, pp. 72–73, 139–141; Petrol. Processing, vol. 2, 1947, p. 312; World Petrol., vol. 18, No. 7, 1947, pp. 46–49; Chem. Abs., vol. 41, 1947, p. 4286.

Paper presented at the American Society of Mechanical Engineers meeting, Tulsa, Okla. An outline is given of the engineering aspects of the commercial synthetic gasoline plants in Germany and of the proposed plants in the United States. It is shown by actual construction data how superior the American engineering techniques are to those of Germany. The investment cost for commercial synthesis plants in Germany was about $7,500–$8,000 per daily bbl. of product, as compared with $3,000–$3,500 in America. In a commercial plant of American design, 6 reactors, each of approximately 3,400 cu. ft. vol., would be required to produce 6,000 bbl. per day of synthetic oil, whereas, by the German technique, about 300 reactor units, each of approximately 950 cu. ft. vol., would be required.

2835. ———. Power-Plant Services for Synthetic Gasoline Manufacture. Power Plant Eng., vol. 51, No. 8, 1947, pp. 108–111; Chem Abs., vol. 41, 1947, p. 7073.

German and American methods for the production of synthetic gasoline are outlined. 2 American methods, 1 using CH_4 with steam and CO_2, and the other CH_4 and O_2 under pressure, are considered. Certain engineering problems are cited. Describes projected plant.

2836. ROBERTS, G., AND SCHULTZ, P. R. Production of Liquid Fuels From Coal and Oil Shale. Oil Gas Jour., vol. 48, No. 19, 1949, pp. 116–125; Petroleum Technol., vol. I, No. 9, 1949, Sec. 1, pp. 24–30.

An economic analysis of comparative costs of liquid fuels from natural gas, oil shale, and coal based on present-day production methods. As a basis for comparison, 5 different raw materials are investigated: Wyoming crude oil, natural gas, oil shale, Indiana bituminous coal, and Montana subbituminous coal. Total direct costs of liquid fuels expressed as cents per gal. of equivalent gasoline are calculated. To the direct costs are added depreciation and tax charges, a major part of the costs of an oil operation. The factual analysis shows that manufacturing costs in bituminous coal, with reference only to Fischer-Tropsch operation, and shale operations would be approximately 80% higher than that made from crude oil, whereas that from subbituminous coal would cost about 125% more. Coal hydrogenation is ruled out. Comparisons of direct cost plus 14% per yr. on the investment show $0.122 for Wyoming crude, $0.15 for natural gas, $0.225 for oil shale, $0.225 for Indiana bituminous coal, and $0.276 for Montana subbituminous coal. It is believed that application of several process improvements now under investigation in the synthesis from coal might lower the cost to a level only $0.05–$0.06 per gal. above present costs of gasoline from petroleum, and that further research might make synthesis nearly competitive.

2837. ———. Liquid Fuels From Coal and Oil Shale. Petrol. Refiner, vol. 29, No. 1, 1950, pp. 104–108.

As a result of an economic study, it is shown that, at present, liquid fuels from oil shale and coal cannot compete with those derived from crude petroleum. Natural gas as a raw material may or may not be competitive, depending on the relative locations of raw-material supply and product markets.

2838. ROBERTS, J. K. Adsorption of Hydrogen on Tungsten. Proc. Roy. Soc. (London), vol. 152, A, 1935, pp. 445–463; Chem. Abs., vol. 30, 1936, p. 1630.

Method is described for studying the adsorption of H_2 on a bare W surface, which depends on the fact that the accommodation coefficient for Ne is considerably greater for a surface covered with a film of adsorbed gas than for pure W. It is shown that on a clean W surface chemisorption of H_2 occurs very rapidly at temperatures as low as 79° K., saturation of the surface taking place at a partial pressure of 10^{-4} mm. or less. The heat of adsorption as measured on a single fine wire varies from 45,000 cal./mol. for the 1st H_2 mol. to 18,000 for the last portion becoming adsorbed. The amount of H_2 required to form a unimolecular layer is consistent with the adsorption of H as atoms. The film is stable for heating times of about 1 min. up to about 700° K. Calculations show the dipole moment/adsorbed atom to be 1.94×10^{-18} e. s. u. and the change in work function resulting from covering the surface with a complete film to be 5.2 v. The rapidly occurring chemisorption of H_2 on the W surface differs from the more slowly occurring activated adsorption. The accommodation coefficient of Ne at 79° K. is 0.32 on a W surface covered with a layer of chemisorbed H_2 compared to about 0.1 for bare W; at 295° K. the coefficients are, respectively, 0.17 and about 0.08.

2838a. ———. Kinetics of Adsorption With Interaction Between the Adsorbed Particles. Proc. Roy. Soc. (London), vol. A161, 1937, pp. 141–153; Chem. Abs., vol. 31, 1937, pp. 7,719–7,720.

Rate equations, which take into account interaction between adjacent adsorbed particles, are deduced for evaporation and condensation in adsorption both with and without molecular dissociation, and for the formation of a stable, immobile film following dissociation. The nature of the films formed is analyzed, and illustrated by the adsorption of H_2 on W.

———. *See* abs. **3720.**

ROBERTSON, A. *See* abs. **1408.**

ROBEY, R. F. *See* abs. **2325a.**

2839. ROBINET, P. [Hydropolymerization of Carbon Monoxide.] Chim. et ind., vol. 47, 1942, pp. 480–482; Chem. Zentralb., 1942, II, p. 1652; Chem. Abs., vol. 37, 1943, p. 6107.

Following reaction types occur in hydropolymerization of CO:
(1) $2CO+2H_2 \rightarrow CH_2(OH)CHOH_2$ $CH_2(OH)$ CH_2OH; (2) $2CO+4H_2 \rightarrow C_2H_4+2H_2O$; (3) $4CO+2H_2 \rightarrow C_2H_4+2CO_2$. The synthesis of higher hydrocarbons from water gas at normal pressures is regarded as a combination of (2) and (3). At higher pressures (1) takes place predominantly, with the formation of O-containing compounds. In the reaction mechanism proposed, H_2O is split off before condensation occurs. A primary complex is formed upon the catalyst. At normal pressure this complex decomposes into CH_4. Under the influence of condensing catalysts, an in-

crease in the complex occurs on certain active centers, and the reaction becomes strongly exothermic. If the growth of the complex is not stopped by the cleavage of H_2O or CO_2, the evolution of heat become so great that sudden decomposition of the complex takes place, so that all of the active centers can form only CH_4, H_2O, and CO_2. It is possible that the complex grows not only under the influence of CO and H_2, but under the influence of free radicals that originate simultaneously in other active centers. Thus, not a polymerization of radicals, as contemplated by Fischer, but a kind of copolymerization takes place upon the active centers.

ROBITSCHEK, F. O. *See* abs. **587.**

2840. ROBSON, G. W. Benzol Recovery by Active Carbon. Gas Jour., vol. 246, 1945, pp. 687, 689.

Active C plant at the Morpeth Gas Works is described. Its capacity is 400,000 cu. ft. of gas per day, using about 3 cwt. of C in the absorber. A complete cycle of operation has 3 periods: adsorbing, steaming, drying in the time ratio of 60 : 33 : 30. The efficiency of extraction is about 90%; this could be raised with careful chemical supervision. The over-all running costs are about 6 d. per gal. of benzol recovered.

ROCK. S. M. *See* abs. **1195.**

ROCKENBACK, L. P. *See* abs. **3306.**

2841. RODE, E. Y. [Iron Oxides and Their Reducibility With Hydrogen and Carbon.] Jour. Russian Phys.-Chem. Soc., vol. 62, 1930, pp. 1453–1466; Chem. Abs., vol. 25, 1931, p. 2628.

Heating curve of Fe_2O_3 has a conversion point at 745°, quite likely corresponding to a definite modification of Fe_2O_3. Beginning with 1,280° some irregularities are observed that probably have a connection with the beginning of loss of O_2. The temperature curve of reduction of Fe_2O_3 with H_2 has 2 kinks, probably corresponding to 2 steps in reduction, 1st to Fe_3O_4 and then to a lower oxide. There is no definite proof of formation of FeO as an intermediate product. Fe_2O_3 is more easily reduced with H_2 than Fe_3O_4. In reducing hydrated Fe oxides with H_2 the point where reduction begins could not be ascertained, because it lies in the region of decomposition of corresponding hydrates. If the products of reduction are cooled in H_2, they become pyrophoric when the heating temperature does not exceed 600°–650°. A higher heating temperature makes them nonpyrophoric. Reduction of Fe_2O_3 and hematite ore with C gives on the temperature curve 3 halts, probably corresponding to 3 consecutive stages of reduction to the metal. Here again Fe_2O_3 is more easily reduced than Fe_3O_4.

2842. RODILLON, G. [Formula Permitting the Unique Calculation of the Boiling Point of Normal Saturated Hydrocarbons C_nH_{2n+2} as a Function of the Number of Carbon Atoms in the Molecule.] Bull. soc. chim., 1950, pp. 839–840; Chem. Abs., vol. 45, 1951, p. 1824.

Following empirical formula was utilized: Log $T_n=(0.5145-0.00122n)$ log $N+P+1.303$, where T is the boiling point in °K. at 760 mm., n is the number of C atoms, and P is the weight % of C in the molecule. Tabular data were presented, which indicated that the results were accurate to 1°–3° for molecules containing 1–19 C atoms.

2843. ROELEN, O. [Temperature Control in Exothermic Gas Reactions.] Brennstoff-Chem., vol. 11, 1930, pp. 68–70; Ges. Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 577–583; Chem. Abs., vol. 25, 1931, p. 190.

Discussion containing some remarks on the effect of exothermic heat changes on the Fischer-Tropsch synthesis.

2844. ———. [Determination, Conversion, and Removal of Organically Combined Sulfur From Gas.] Brennstoff-Chem., vol. 12, 1931, pp. 305–312; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 466–480; Chem. Abs., vol 25, 1931, p. 5970.

Combustion methods of determination already proposed and modified give low results. Conversion into H_2S by means of various catalysts and types of apparatus becomes incomplete after a short time. CO and H_2S in contact with Fe at various temperatures form volatile S compounds not removable as H_2S from the gas. The catalyst so sulfurized then forms organic S compounds with purified gas even at temperatures as low as 300°. Maximum formation of organic S compounds on passing water gas or coke-oven gas, cracked with steam at high temperatures, over Fe wool occurred at 100°. None formed with CO-free gas or Al or Ag catalyst. The formation of $Fe\chi S$ as an intermediate in the formation of COS and CS_2 from H_2S and CO is suggested. For the production of gas low in organic S, coke-oven gas is passed through heated Fe-catalyst contact purifiers, after first passing through CH_4 cracking units where steam at high temperatures also decomposes part of the organic S compounds. Extensive bibliography.

2845. ———. [Manufacture of Magnesium-Containing Catalysts for the Gasoline Synthesis.] FIAT Reel K–25, Nov. 19, 1937, frames 3,827–3,828; PB 70,216: TOM Reel 292.

Direction for wholesale manufacture of Mg-containing catalysts, including a method for the manufacture of Co–Mg–Th–kieselguhr catalysts.

2846. ———. [Alkali Resistance of Kieselguhrs.] FIAT Reel K–29, 1938, frames 7,087–7,090; PB 70,218: TOM Reel 296.

It is established by tests that no causal connection exists between the alkali resistance and the catalytic usefulness of kieselguhrs. 1 table and 3 diagrams.

2847. ———. [Determination of Grit in Kieselguhr.] FIAT Reel K–29, 1938, frames 7,082–7,086; PB 70,218; TOM Reel, 296.

Schulze-Harkert washing method is the only one recommended for the determination of the heavy components. Directions are given for the analytical analysis of a specific type called kieselguhr 120.

2848. ———. [Determination of the Content of Free Metal in Cataylsts.] FIAT Reel K–20, frames 32–37, 1938; PB 70,211; TOM Reel 287.

Co catalysts are not reduced completely; unreduced oxide and carbonate remain. The determination of the proportion of reduced metal is based on the fact that only the reduced metal, when mixed with H_2SO_4, develops an equivalent amount of H_2, which is measured. By determination of the total amount of Co used, the proportion of reduced metal can be calculated. Care must be taken that the N_2 used for the catalyst is free from O_2 and that the H_2 adsorbed on the catalyst is sucked off beforehand in the vacuum. Details, with sketch of apparatus.

2849. ———. [Longevity of Catalysts.] FIAT Reel K–29, 1938, frames 7,030–7,031; PB 70,218; TOM Reel 296.

Successful test on the reactivation of a catalyst for the gasoline synthesis without pressure proves, in principle, the possibility of an extraordinary long catalyst life.

2850. ———. [Preparation of Catalysts.] FIAT Reel K–29, 1938, frames 7,189–7,193; PB 70,218; TOM Reel 296.

Review of the actual state of tests on the improvement in catalyst preparation in the form of an operating instruction for the preparation, especially of Th-free Co–Mg catalysts. 1 picture.

2851. ———. [Report on the Most Favorable Ratio in Cobalt–Kieselguhr Catalysts.] FIAT Reel K–25, May 2, 1938, frames 3,757–3,781; PB 70,216; TOM Reel 292.

Tests and table show that the ratio of 1 : 2 is the best in such catalysts. There is no obvious reason for changing this ratio. Consideration also is given to catalysts of Th–Co–kieselguhr and Th–Mg. Numerous tables and graphs.

2852. ———. [Catalysts for Fischer-Tropsch Synthesis.] FIAT Reel K–20, frames 340–348, Aug. 18, 1939; PB 70, 211; TOM Reel 287.

Development of the gasoline synthesis by the Fischer-Tropsch method is reviewed, and special stress is placed upon the production of a suitable catalyst as being the most important point in the economy of the process.

2853. ———. [Determination of Iron in Catalysts.] FIAT Reel K–29, 1939, frames 6,930–6,931; PB 70,218; TOM Reel 296.

For the determination of Fe in catalysts a 10% acetic acid is recommended as solvent. The determination is based on active Fe and not on the total Fe content.

2854. ———. [Development of Catalysts for the Fischer-Tropsch Synthesis.] FIAT Reel K–29, 1939, frames 6,959–6,967; PB 70,218; TOM Reel 296.

Survey of the history of the development of catalysts for the Fischer-Tropsch synthesis. The survey considers only the usual Fe and Co catalysts and does not give any new catalysts or methods.

2855. ———. [Iron Catalysts in the Gasoline Synthesis.] FIAT Reel K–29, 1939, frames 6,912–6,925; PB 70,218; TOM Reel 296.

Operating experiences with Fe catalysts under pressure in a single passage and in the circulating process are reviewed. 13 diagrams.

2856. ———. [New Method of Cooling Catalyst Furnaces for the Synthesis of Hydrocarbons.] FIAT Reel K–29, 1939, frames 6,936–6,940; PB 70,218; TOM Reel 296.

Reaction temperatures of certain catalysts, for example, Fe catalysts, are very high. The use of H_2O as coolant causes high pressure, therefore the cooling system must have corresponding dimensions. An appropriate fraction of the hydrocarbons prepared by the synthesis process is recommended as cooling medium. Later it is returned to the process.

2857. ———. [Paraffin Synthesis With a New Cobalt Catalyst.] FIAT Reel K–29, 1939, frames 6,941–6,944; PB 70,218; TOM Reel 296.

Description of a new Co catalyst, which gives a very high yield of paraffin, is given. The new catalyst has a very high density of Co and contains Mn as an activator.

2858. ———. [Sulfur Content in Solutions for the Preparation of Cobalt Catalysts.] FIAT Reel K–29, 1939, frames 6,987–6,988; PB 70,218; TOM Reel 296.

It is proved that a % of sulfate up to 8% in pure Co solutions in the preparation of Co catalysts does not reduce perceptibly the activity of the catalyst. In the technical operation, however, one has to take into account a certain Ca content in the Co solutions, which causes, in connection with the H_2SO_4, a plastering and consequently a deterioration of the contact. For this case, an activating washing with dilute alkali solution is recommended.

2859. ———. [Hydrocarbon Synthesis With Iron Catalysts.] TOM Reel 178, Sept. 13, 1940, frames 2,643–2,669; PB 97,330t; Bureau of Mines Transl. T–469, Dec. 29, 1948, 21 pp.; TOM Reel 279, frames 0,127–0,147.

Brief account of the development of Fe catalysts, their operation, as compared with Co catalysts, and some results obtained in pilot-plant operation. Results are tabulated.

2860. ———. [Ruhrchemie Oxo Synthesis.] FIAT Reel K–21, 1940, frames 610–673; PB 70,212; TOM Reel 288.

Reports included review of the possibilities of making higher fatty acids and alcohols from olefinic primary hydrocarbons by means of the Oxo synthesis. Different alcohols are examined as to their chemical-physical qualities. Description and flowsheet are given for the manufacture of fatty alcohols.

2861. ———. [Concentrated Cobalt Catalysts.]. FIAT Reel K–29, 1941, frames 7,296–7,301; PB 70,218; TOM Reel 296.

Composition of a catalyst with a high Co density for an increased production of paraffin with the most important data and an exact manufacturing direction.

2862. ———. [Oxo Synthesis Especially for Manufacturing Propyl Aldehyde.] FIAT Reel K–21, frames 1,140–1,146, Nov. 27, 1941; PB 70,212; TOM Reel 288.

A program is set up for the Oxo synthesis. The intention is to make determinations on the advantage of transforming the Co either into its colloidal or very finely distributed form or into carbonyl by previous operating processes.

2863. ———. [Catalysts for the Hydrogenation of Carbon Monoxide.] FIAT Reel K–29, 1943, frames 7,226–7,239; PB 70,218; TOM Reel 296.

Catalytic hydrogenation of CO is reviewed. It is established, above all, that the weakening of the catalyst under normal synthesis conditions during the first 6 months cannot be explained by coarsening changes in the structure.

2864. ———. [Calculation of the Yield in the Synthesis of Higher Hydrocarbons.] FIAT Reel K–29, 1944, frames 7,201–7,209; PB 70,218; TOM Reel 296.

Development of a simplified clear method for the calculation of the yield in synthesis of higher hydrocarbons. Includes formulas.

2865. ———. [Calculations of Gas Utilization and the Course of Synthesis During the Hydrogenation of Carbon Monoxide.] TOM Reel 49, July 1944, frames 470–523; Bureau of Mines Transl. T–420, November 1947, 65 pp.; TOM Reel 274, frames 1,205–1,270.

Gives the basis of a mathematical treatment of the computations of gas utilization during the hydrogenation of CO. The basic relationships between the amounts of raw materials and of the resulting products are explained. These fundamental relationships lead readily to convenient formulae that can be applied algebraically to any additional computations.

2866. ———. [Calculations of Yields in the Modern State of the Synthesis of Higher Hydrocarbons.] TOM Reel 49, August 1944, frames 524–532; Bureau of Mines Transl. T–421, November 1947, 12 pp.; TOM Reel 274, frames 1,271–1,282.

Continuation of the computations discussed in abs. **2865.**

2867. ———. [Iron Catalysts.] FIAT Reel K–29, 1944, frames 7,210–7,213; PB 70,218; TOM Reel 296.

Problems of the change from Co to Fe catalyst are discussed. A final result is not formulated.

2868. ———. [Calculation of Gas Consumption and Synthesis Course in the Hydrogenation of Carbon Monoxide.] TOM Reel 134, Navy 5811, Item Ib–3; Bureau of Mines Transl., February 1947, pp. 32–69.

Characteristic properties of a mixture of synthesis gas and reaction products, which describe the course of the synthesis, are discussed, and an appropriate nomenclature is suggested. On the basis of simple stoichiometry, a variety of relationships among these properties is derived. A numerical method for cal-

culation of the yield and related properties from gas analysis data is devised. Methods for testing the accuracy of calculations of the experimental data are developed.

2869. ———. [Calculation of Yield for Higher Hydrocarbons Based on Recent Methods.] TOM Reel 134, Navy 5811, Item Ib–4; Bureau of Mines Transl., February 1947, pp. 70–78.

Methods for calculating the yield and related properties, discussed in item Ib–3, are developed further and compared with the methods employed in Government research.

2870. ———. [Synthesis of Aldehydes and Derivatives From Olefins, Carbon Monoxide, and Hydrogen.] Angew. Chem., vol. 60, 1948, A, p. 62; British Abs., 1949, A, II, p. 3.

Reaction of olefins with CO and H_2 over Co or Fe, to give aldehydes containing 1 C atom more than the olefin, is described in detail. C_2H_4 with CO and H_2 in equivalent proportions, with a Co catalyst, at 115° and not less than 100 atm., gives 75% EtCHO. Byproducts include aldol condensation products and below 100°, $COEt_2$. Above 200°, C_2H_6 and PrOH are obtained over a Co–Cu catalyst. Only Fe may replace Co as catalyst. It should be introduced or generated in finely divided form. The actual catalysts are metal carbonyls, which may replace the metal, thus enabling lower reaction pressures to be used. Water gas may replace CO and H_2. Production of aldehydes is a general reaction of olefins. Higher olefins react best at 130°–150° and give less byproducts than does C_2H_4. Unsymmetrical olefins may give a mixture of 2 isomeric aldehydes, but steric factors may suppress the formation of 1 of them. Aldehydes, C_4–C_{24}, can be obtained from the olefins produced in the Fischer-Tropsch synthesis and can be reduced readily, without isolation, over similar Co catalysts to the corresponding alcohols. Derivatives of these products and their possible industrial applications are listed. C_2H_2 and water gas over Co at 140°–150° and 10 atm. give 120 gm. per $m.^3$ liquid products. Chiefly they are unsaturated secondary products of higher molecular weight. No experimental details.

2871. ———. [Cobalt and Nickel Catalysts for the Hydrogenation of Carbon Monoxide.] Angew. Chem., vol. 61, 1949, p. 448.

Paper presented at the annual meeting of the German Chemical Society in September 1949. The best method for producing highly active catalysts from Co is by precipitation of the carbonate from boiling nitrate solution upon kieselguhr. Newly roasted kieselguhr from finely divided crude kieselguhr with a minimum amount of impurities makes the best carrier. The particle size of the carrier influences the boiling properties of the products and the paraffin deposition on the catalyst. The 3 best activators for Co are Th, Mg, and Mn. Th and Mn promote the formation of high-molecular hydrocarbons and the deposition of paraffin on the catalyst, whereas Mg has the opposite effect. Further specific effects were determined. The technically best catalyst contains both Th and Mg. The highest activity, measured by the temperature, is shown by Mn with complete conversion already at 160°. Co oxide can, under the best conditions, be reduced below 250°; at 400° complete reduction occurs in 1 min. The mechanism of the poisoning of the catalyst by impurities was explained; it occurs only in the afterheating period of reduction, neither before nor after. The Co solution must contain no Cu, Fe, Al, and Ca. These metals are removed by wet regeneration. The temporary disabling of the catalyst because of paraffin deposition can be removed through destructive hydrogenation or extraction. C deposition was acknowledged as the reason for any remaining poisoning rather than recrystallization or the like. Dry regeneration by removing the deposited C by means of H_2 at 400° gave complete reactivation. Repeated dry regeneration produced operating periods of over 2 yr. without exhaustion of the catalyst. Highly active Co catalysts decompose CO at temperatures as low as 30°. Mg is able to activate Ni catalysts also. The first technical methanation was realized with a Ni–Mg–kieselguhr catalyst.

2872. ———. [Determination of Double Bonds and Their Terminal Constituents in Hydrocarbons by Ozonization and the Application of This Method to the Determination of the Olefin Distribution in Fischer-Tropsch Products.] Erdöl u. Kohle, vol. 3, 1950, p. 591.

Abstract of a paper presented at the 3d meeting of Die deutsche Gesellschaft für Mineralölwissenschaft und Kohlechemie. Olefinic double bonds can be determined by weight analysis by adding ozone and ascertaining the increase in weight. The method gives accurate and reliable values, in many cases even when the addition of halogens fails to work. Terminal double bonds were determined by cracking the ozonides obtained as previously and determining the formic acid produced. With Fischer-Tropsch products, the characteristic dependence of the α–olefin constituents upon the production conditions and the size of the molecules was established in this manner. The experimental results also support the theory for the range of molecules above C_8, whereby primary α–olefins are formed in the hydrogenation of CO and are finally partly isomerized.

2873. ———. [Synthesis of Methane in Connection With the Production and Utilization of City Gas.] Erdöl u. Kohle, vol. 3, No. 1, 1950, p. 10.

Paper presented at the 1949 meeting of Diedeutsche Gesellschaft für Mineraloelwissenschaft und Kohlechemie. The necessity of producing more city gas without increasing the amount of coke has led to attempts to bring the Fischer-Tropsch synthesis into city gas production. The synthesis can be so conducted that it produces directly a residual gas of city-gas quality, or the necessary heating value of the synthesis residual gas can be obtained by a special methanization. New Fe and Ni catalysts have been developed for the various possible ways of operating. CH_4 synthesis can now be conducted by choice from CO and H_2 with exclusive formation of H_2O or CO_2, from CO and steam with simultaneous conversion, or by any combination whatever of these 3 reactions. A new Ni–Mg catalyst methanizes the CO and CO_2 in coke oven gas quantitatively below 200° and at gas throughputs 10 times greater than the former technical Fischer-Tropsch synthesis. By means of a NiS catalyst it is now possible to desulfurize coke-oven gas to a synthesis gas purity. With these 2 new Ni catalysts methanization of city gas could be successfully realized at the storage tank in small automatic plants. By such means, the heating value is raised from about 4,400 to 6,000 kg.-cal. per $m.^3$ The gas is detoxicated at the same time and freed from all corroding constituents except hydrocyanic acid. The original tank plants for methanizing in Altenessen, 1942, have already been followed by others.

———. *See* abs. **341, 402, 1042, 1214, 1334, 1335, 3729.**

2874. Roelen, O., and Feisst, W. [Improved Method for the Determination of Sulfur in Gas.] Brennstoff-Chem., vol. 15, 1934, pp. 187–192; Chem. Abs., vol. 28, 1934, p. 6278.

Method of Heinrich and Petzold for the determination of total or organic combined S has been improved mechanically, to permit greatly increased throughput and absorption in alkaline H_2O_2. Apparatus for the

combustion method has been improved also. Typical comparative data for both old and new apparatus are given with demonstration of the decreasing organic S content of gases with storage. Completely purified gas also is shown to reacquire S from distribution systems. For comparative purposes, gas samples must be identical in time, place, and other sampling conditions. Extensive bibliography of S-determination methods, grouped according to absorption agents.

2875. ROELEN, O., AND HECKEL, H. [Most Favorable Cobalt–Kieselguhr Ratio in Cobalt Catalysts.] FIAT Reel K–29, 1938, frames 7,139–7,163; PB 70,218; TOM Reel 296.

As a result of an extensive examination and discussion, the Co-kieselguhr proportion 1 : 2 is indicated as virtually the most favorable under actual conditions. 6 tables and 8 diagrams.

2876. ———. [Influence of the Condition of the Kieselguhr on the Stability of the Catalyst.] FIAT Reel K–20, Sept. 12, 1939, frames 337–339; PB 70,211; TOM Reel 287.

After a discussion of the possible dependence of the catalyst stability on the condition of the kieselguhr, a method is described whereby the proportion of dust can be decreased considerably by sintering the kieselguhr with an Mg salt at 1,000°.

2877. ROELEN, O., AND HINTERMAIER, A. [Disintegration of the Catalyst in the Synthesis of Benzine.] Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 517–518; Chem. Abs., vol. 25, 1931, p. 3807.

An alkaline Cu-Fe catalyst exposed to water gas at 250° showed disintegration with increase in bulk volume. After 500 hr. its bulk density had fallen to about ¼ the original value. Thereafter it remained constant.

2878. ROELEN, O., AND PFLEGLING, —. [Synthesis of Hydrocarbons with Iron Catalysts.] FIAT Reel K–29, 1940, frames 7,240–7,241, 7,250–7,276; PB 70,218; TOM Reel 296.

Review of the development and use of Fe catalysts since 1913. Recent tests are discussed on the basis of extensive data. The output of Fe catalyst surpasses the output of Co catalyst, but more work needs to be done on its development. 16 tables.

2879. ROELEN, O., AND ROYEN, P. [Mechanism of Carbon Dioxide Formation on Catalysts of the Fischer-Tropsch Synthesis.] Erdöl u. Kohle, vol. 3, No. 1, 1950, p. 10.

Paper presented at the 1949 meeting of the die deutsche Gesellschaft für Mineraloelwissenschaft und Kohlechemie. It was already regarded in 1923, by Fischer and coworkers that CO_2 formation occurs on Fe catalysts of the hydrocarbon synthesis as a secondary reaction, which is identical with the known conversion of a mixture of CO and steam into CO_2 and H_2. Finally in 1949, H. Kölbel on the strength of newer investigations has replaced this view. According to older conceptions of Wieland in 1912, Fischer and Schrader in 1921 assumed that, by this conversion, CO and H_2O are together changed to formic acid, which then is split catalytically into CO and H_2. It is known that addition of alkali compounds, especially in the form of hydroxides and carbonates, to the Fe and Co catalysts of the Fischer synthesis intensify the conversion. Roelen and later independently Royen supposed that, in this case, a 2d mechanism is introduced consisting in an intermediate formation of potassium formate from potassium hydroxide and carbon monoxide, a reaction that technically serves for the production of formic acid. The potassium formate 1st formed is split on the catalyst by means of adsorbed water vapor hydrolytically into potassium hydroxide and free formic acid. Roelen has shown that sodium formate at 200°–230° in presence of active Fe or Co is decomposed by water vapor into CO_2 and H_2. He found that formic acid is converted by Fe catalysts and very quickly into H_2 and CO_2. In mutual tests, it was shown that these reactions occur also on alkalized Cu catalysts at 120°. It is further shown that catalysts of active C with a few % of alkali hydroxide plainly perform the conversion at 140°. By the conversion, the potassium hydroxide present on the catalyst goes over in great part into potassium formate. Catalysts which were impregnated with potassium hydroxide-potassium formate mixtures in the proportion formed by the conversion, showed by the treatment with water vapor of the same partial pressure as by the conversion tests, CO_2 and H_2 concentrations in the residual gas of the same magnitudes as in the conversion. It was shown, thus, that the formate mechanism with alkalized catalysts of the Fischer-Tropsch synthesis can supply an essential contribution to the conversion reaction. This determination is supported also by several physical-chemical observations.

2880. ROELEN, O., AND SCHENK, —. [Nickel-Containing Cobalt Catalysts.] FIAT Reel K–29, no date, frames 7,302–7,307; PB 70–218; TOM Reel 296.

Tests show that the partial replacement of Co by Ni in Co catalysts produces a deterioration of the grain solidity of the catalyst and that, in the synthesis, the gasification is higher, the boiling conditions easier, and the rate of saturation higher. Extending the Co stock by Ni is, therefore, of doubtful value for a large production.

2881. ROGERS, B. A., WENTZEL, K., AND RIOTT, J. P. Magnetic Methods for Determining Carbon in Steel. Trans. Am. Soc. Metals, vol. 29, 1941, pp. 969–983; Chem. Abs., vol. 36, 1942, p. 720.

Magnetic saturation and C content can be correlated accurately at 0.50–1.10% C. Samples containing more than 0.40% C were quenched from above 700°; other C contents required slow cooling. When both types of heat treatment were used, samples containing 0.10–1.10% C could be tested. The apparatus is described.

2882. ROGERS, L. J. Oil From Coal. Hydrogenation. Chem. Eng. and Min. Rev., vol. 23, 1931, pp. 373–380; Chem. Abs., vol. 25, 1931, p. 5272.

Brief description of the catalytic reduction of CO and the synthetic production of MeOH. The production of synthetic fuels is not recommended from an economic standpoint as an adjunct to a gas works.

2883. ROGERS, W. Reduction of Mixed Oxides. Copper and Zinc Oxides. Jour. Am. Chem. Soc., vol. 49, 1927, pp. 1432–1435; Chem. Abs., vol. 21, 1927, p. 2855.

In a mixture with CuO, ZnO is completely reduced by H_2 at 300°, a temperature far below that necessary for ZnO alone. A tentative explanation is offered.

2884. ROGINSKIĬ, S. Z. [Theory of Preparation of Catalysts. The Role of the Free Energy of the Processes of Preparation.] Jour. Phys. Chem. (U. S. S. R.), vol. 15, 1941, pp. 708–730; Chem. Abs., vol. 37, 1943, p. 821.

Roginskiĭ continues his development of a theory of catalyst surfaces. The active points are considered as points of supersaturation with respect to free energy. 4 types of such points are considered: A definitely distinct phase, local or general structural variations of a given phase, anomalous chemical composition of a phase, and, finally, the degree of dispersion of a phase. The free energy of such active centers and of the formation of such centers are discussed essentially according to Gibbs' technique. The supersaturation with respect to free energy is shown to be not only a thermodynamic precursor of formation of any type of deviation from equilibrium in a solid phase, but assures this formation kinetically. Also, in any process

of physical and chemical crystallization, along with the growth of supersaturation of the genetic reaction of a solid body, in the moment of its formation and thereafter, the content of any possible supersaturated formation in the above solid must increase constantly. This article is the introduction to a series of applications of the supersaturation theory to experimental data.

2885. ———. Theoretical Principles of the Preparation of Catalysts. I. Methods of Production and Regulation of Supersaturation. Jour. Appl. Chem. (U. S. S. R.), vol. 17, 1944, pp. 3–15 (English summary); Chem. Abs., vol. 39, 1945, p. 1350.

Theoretical discussion of physical and chemical principles that control supersaturation in the preparation and use of catalysts. Suitable selections must be made for preparation of specific catalyst masses.

2886. ———. [Theoretical Principles of the Preparation of Catalysts. II. Conditions for Utilization of Supersaturation of Reactions in the Preparation of Catalysts.] Jour. Appl. Chem. (U. S. S. R.), vol. 17, 1944, pp. 97–106; Chem. Abs., vol. 39, 1945, p. 1350.

Excess free energy, that is, supersaturation, of the reaction in the preparation of catalysts is the source of the catalytically active structures in the final product. A theoretical discussion shows that concentration and temperature are essential factors in the preparation of catalyst masses. The usual methods of catalyst preparation are classified and analyzed as to phase conditions in the course of topochemical reactions. A preliminary guide is indicated for selection of the interval during which the application of high supersaturation is most effective.

———. *See* abs. **703, 1709.**

2887. ROGINSKIĬ, S. Z., AND TSELLINSKAYA, T. F. Experimental Investigation of the Role of Supersaturation in the Preparation of Catalysts. Acta physicochim. U. R. S. S. vol. 19, 1944, pp. 225–247 (in English); Jour. Phys. Chem. (U. S. S. R.), vol. 18, 1944, pp. 477–492; Chem. Abs., vol. 39, 1945, p. 2447.

Pyrolytic decomposition of $NiCO_3$ is a centripetal topochemical reaction. The decomposition was affected in an apparatus in which the CO_2 pressure (pT) was controlled by freezing out CO_2 in a cryostat maintained at various temperatures. The supersaturation (A) of the genetic reaction is defined as $A=RT\ ln\ (pT/pT')$, in which pT is the equilibrium pressure of CO_2 at the surface of the solid. The decomposition of $NiCO_3$ is autocatalytic; the reaction velocity increases with increasing supersaturation. This decomposition is extremely rapid at CO_2 partial pressures of 10^{-4} to 10^{-2} mm. of Hg; near the equilibrium pressure the decomposition is slow. The rate constant varies exponently with the temperature. The apparent activation energies for the decomposition are 11,000 cal. per mol. for $\triangle F$=constant, 17,000 for $p_{co_2}=3\times10^{-3}$ mm., 15,000 for p=2 mm., and 11,000 for p=10 mm. Up to its maximum, the reaction velocity obeys an approximate quadratic law; hence the process involves primarily the development of formerly existing initiation centers, as is true for the decomposition of Ni formate (abs. **703**). The values of the reciprocals of the times needed to attain a definite degree of decomposition increase almost linearly with the supersaturation. A plot of velocity versus % of decomposition shows a maximum for each temperature and CO_2 pressure; this maximum is at 5–10% decomposition and is only slightly dependent on the experimental conditions. The H_2O content of the sample of $NiCO_3$ has a peculiar, and as yet unexplained, effect on the kinetics of the decomposition.

ROĬTER, V. A. *See* abs. **1164, 1165.**

2888. ROĬTER, V. A., AND GAUKHMAN, S. S. [Adsorption Properties of Differently Prepared Iron Catalysts of the Same Composition.] Ber. Pissarjewsky Inst. physik. Chem., Akad. Wiss. Ukr. S. S. R., vol. 12, 1940, pp. 3–11, in German 12–13; Chem. Abs., vol. 35, 1941, p. 2686.

Study was made of the nature of adsorption of H_2 and N_2 within the interval of −184° to +425° on 2Fe catalysts used in the synthesis of NH_3. The catalysts contained 98% Fe_2O_3 and 2% Al_2O_3. 1 of the catalysts was fused in an electric arc. 3 types of sorption of H_2 were observed; physical sorption at 184° and 2 types of activated sorption analogous to pure Fe and other promoted catalysts. With the fused catalyst there was activated sorption of N_2 at 250°–425° with measurable speed, but there was no measurable sorption of N_2 on the unfused catalyst. Measurements also were made of the kinetics of NH_3 synthesis (both catalysts were used). The catalytic activities are compared with the sorption characteristics.

2889. ROĬTER, V. A., GAUKHMAN, S. S., AND LEPERSON, M. [Investigation of the Adsorption of Hydrogen and Nitrogen on Iron–Molybdenum–Ammonia Catalysts.] Acta Physicochim. U. R. S. S., vol. 4, 1936, pp. 145–158; Chem. Abs., vol. 30, 1936, p. 3707.

Stable catalyst composed of 18.5% Mo, 74.1% Fe, and 7.4% Al_2O_3 was prepared by reduction at 450°. At 1 atm. its activity is the same as that of the unstable catalyst without Al_2O_3 but, at 150 atm., it is 8 times as great. At −183°, adsorption of H_2 is completely reversible. Above 0°, a slow "irreversible" adsorption begins, more marked for the still unfatigued and especially the promoted catalysts. N_2 shows only van der Waals reversible adsorption with Q=about 4,500 cal. at 25° for the unpromoted and 12,000 cal. for the Al_2O_3-promoted catalyst. The mechanism proposed by Emmett and Brunauer (abs. **823**) is criticized.

2890. ROĬTER, V. A., GAUKHMAN, S. S., PISARZHEVSKAYA, N. P., AND GVALIYA, T. M. [Kinetics and Mechanism of Catalytic Conversion of Carbon Monoxide.] Jour. Appl. Chem., U. S. S. R., vol. 18, 1945, pp. 439–449; U. O. P. Co. Survey Foreign Petroleum Literature Index May 31–June 7, 1946, pp. 3–8; Chem. Abs., vol. 40, 1946, p. 4593.

Reaction $CO+H_2O\rightleftharpoons CO_2+H_2+9.6$ kcal. was studied in the presence of K_2CO_3 on activated C and on technical Fe oxide catalyst of the type known as nitrogene. Data are reported on the effects of the space velocity, total pressure, and partial pressures of the components, and the kinetics and the mechanism of the process are discussed. The surface of the catalyst was determine by the method of Gaukhman and Roĭter (abs. **1164**). The results are explained by a new theory for the K carbon catalyst in which the following scheme of reactions is proposed: $2KOH+CO=K_2CO_3+H_2$; $K_2CO_3+H_2O=2KOH+CO_2$, with summary result: $CO+H_2O=H_2+CO_2$. In case of the Fe catalysts there is evidence for considerable effect of the following reaction sequence: $2CO=CO_2+C$; $C+2H_2O=CO_2+2H_2$.

ROLLEFSON, G. K. *See* abs. **1050.**

2891. ROLLEFSON, G. K., AND GARRISON, W. Iodine-Sensitized Decomposition of Methyl Alcohol. Jour. Am. Chem. Soc., vol. 62, 1940, pp. 588–590; Chem. Abs., vol. 34, 1940, p. 2784.

I-sensitized decomposition of MeOH has been studied at 325°. The net over-all reaction may be represented by the equation $3MeOH=2CH_4+CO+2H_2O$. This is the result of 2 parallel reactions, one an oxidation of the alcohol by I to CO, the other a reduction by HI to CH_4. These reactions are represented by equations $MeOH+2I=CO+4$ HI and $MeOH+2HI=CH_4+I_2+H_2O$. Tables are given for the distribution of I and for the amounts of CH_4 and CO present during the reaction.

2892. ROQUET, J. [Magnetic Properties of Magnetic Ferric Oxide.] Compt. rend., vol. 222, 1946, pp. 727–729; British Abs., 1946, I, A, p. 274.

Fe_2O_3 was heated to 700° and cooled in a magnetic field. Its specific permanent magnetization, σ, was measured. The Fe_2O_3 was heated again to 700°, which demagnetized it, and it was allowed to cool again in the same field. There was an increase in σ after each heating and cooling. The curve of σ against time t (the sum of the individual times during which the Fe_2O_3 was heated to 700°) tends toward a limit, σ_s, for t amounting to several days. X-ray analysis reveals no change in the crystalline structure. σ_s and the time required to attain it vary considerably from one sample to another. The susceptibility of the unheated Fe_2O_3 is 100×10^{-6}—200×10^{-6}. If X_t is the susceptibility after a short period of heating and X_s is that after heating long enough for the magnetization to reach the limit, X_t does not differ from X_s for a given sample by more than the experimental error and lies between 25×10^{-6} and 32×10^{-6}.

2893. ROSE, H. J. Secrets of German Fuel Technology. Min. and Met., vol. 27, 1946, pp. 106–108.

Brief review of German technical progress, as investigated by the Technical Industrial Intelligence Committee (TIIC), on coal treatment and synthetic fuel production.

2894. ———. New Chemical Processes Based on Coal and Their Significance. Crucible, vol. 32, October 1947, pp. 244, 246.

Paper read before the Pittsburgh section of the American Chemical Society. Approximately ½ of the world's coal reserves are in the United States and about 40% of the United States production has been in Pennsylvania. Coal constitutes 98.8% of the proved fuel reserves of the United States. It is, therefore, natural that coal should become the raw material for the production of gaseous and liquid fuels as well as chemicals. Some information was given on the Fischer-Tropsch and the Bergius processes for the production of gaseous and liquid fuels, and several new processes were briefly discussed for the production of chemicals from coal, such as acetylene chemistry, synthetic rubber, organic acids from coal oxidation, chemical methods for ash reduction, active C, ion-exchange mediums, waxes, and resins.

2895. ROSENDAHL, F. [Chemical Utilization of Coal.] Metallbörse, vol. 19, 1929, pp. 397–398, 455–456, 510–512, 622–624, 678–680, 733–735; Chem. Abs., vol. 23, 1929, p. 3557.

An attempt to cover in 1 article (1) the constitution of coal; (2) low- and high-temperature distillation of coal; (3) application of the gases for the synthesis of hydrocarbons and fertilizers; (4) liquid fuels: Benzene, alcohol, hydronaphthalene: (5) production of oils without coking. Conclusion: The direct utilization of coal for the production of valuable products is still an unsolved problem, but the new processes for combining CO, CO_2, and H_2 obtained from coal, low-temperature distillation, high-temperature distillation, and the indirect treatment of coal and its products by catalysts have already proved their worth.

2896. ———. [Carbon Monoxide and Hydrogen.] Montan. Rundschau, vol. 25, 1933, pp. 1–14; Petrol. Ztschr., vol. 29, No. 6, 1933, pp. 1–14; Chem. Abs., vol. 27, 1933, p. 1861.

Detailed historical review of the catalytic preparation of MeOH, hydrocarbons, etc., from CO and H_2 under high temperature and pressure.

2897. ———. [Manufacture of Hydrocarbons From Carbon Monoxide and Hydrogen.] Oel u. Kohle, vol. 36, 1940, pp. 340–349; Chem. Abs., vol. 35, 1941, p. 8251.

Review.

2898. ———. [Liquid Fuels From Coal.] Mineralöle, vol. 15, 1942, pp. 23, 61, 143.

Production of motor fuels by various processes of carbonization and by solvent extraction and hydrogenation is briefly described. The author then deals in greater detail with the processes for making Fischer-Tropsch synthesis gas (Koppers, Pintsch-Hillebrand, Wintershall-Schmalfeldt, Didier-Bubiag, Lurgi, and the reforming of waste synthesis gases either by cracking or by partial combustion). The paper concludes with a discussion of the Fischer-Tropsch process, with particular reference to the products and their treatment by dehydrogenation and polymerization along the lines adopted in the oil industry.

2899. ———. [Obtaining Fuel From Coal.] Allgem. Oel- u. Fett-Ztg., vol. 39, 1942, pp. 23–27, 61–65, 143–147; Asphalt Teer Strassenbautech., vol. 42, 1942, pp. 254–257, 288–292; Chem. Abs., vol. 37, 1943, p. 5219.

Review of synthesis processes. The subject is reviewed under the following headings: Coking, low-temperature carbonization, extraction of coal, hydrogenation and synthesis of hydrocarbons. The various processes used for synthesis of hydrocarbons are reviewed thoroughly.

2900. ———. [Production of Aviation Gasoline, With Particular Reference to American Processes.] Teer u. Bitumen, vol. 40, 1942, pp. 191–202; Chem. Abs., vol. 37, 1943, p. 6861.

Processes covering S-removal, production of isooctane and other antiknock constituents, isomerization, reforming, aromatization, polymerization, cracking and catalytic cracking, the Fischer-Tropsch and other syntheses are described briefly with some flow sheets and 27 refs. It is believed better from economic and practical standpoints to produce a motor operating on all fuels, even though it is now possible to make any desired fuel for any motor.

2901. ———. [Production of Synthetic Gas by Gaseous Transformation.] Ztschr. kompr. flüss. Gase, vol. 37, 1942, 117–122, 130–134; Chem. Zentralb., 1943, I, p. 1635; Chem. Abs., vol. 39, 1945, pp. 1280–1281.

Brief description of the various processes for the production of synthetic gas by the transformation of gaseous hydrocarbons and the production of high grade H_2 by the removal of CO from water gas.

2902. ———. [Manufacture of Fat Acids for Soap by Oxidation of High-Molecular Hydrocarbons.] Ztschr. kompr. flüss. Gase, vol. 38, 1943, pp. 25–30, 37–43, 49–57; Chem. Zentralb., 1944, I, p. 1149; Chem. Abs., vol. 39, 1945, p. 3445.

Oxidation of paraffins is discussed from the standpoint of basis for the process, raw materials, pretreatment of raw materials, oxidation with air and other oxidizing gases, equipment, removal of unsaponifiable (according to the patent literature), use of the fat acids in the soap industry, and for the manufacture of glycerides and fat alcohols.

ROSENFELD, L. *See* abs. **873, 874, 875, 876, 877, 878.**

2903. ROSENTHAL, H. [Manufacture of City Gas From Water Gas.] Gas- u. Wasserfach, vol. 78, 1935, pp. 436–438; Chem. Abs., vol. 29, 1935, p. 6397.

One $m.^3$ of water gas containing CO, 39; H_2, 51; CO_2+H_2S 6 and N_2 4% can be converted into 0.56 $m.^3$ of city gas, analyzing CO, 16; CH_4, 25; H_2, 46.2; CO_2, 5.5; and N_2, 7.3% by catalytic conversion with H_2O and methanation. Half of the water gas is mixed with steam, the CO_2 converted into CO and H_2 at approximately 500°, and the gas cooled in a waste-heat boiler and direct cooler to 50°, at which temperature H_2S is removed. Organic S is removed at about 180°, and

partial methanation, conversion of about 60% of the CO with 3 times as much H_2, is carried out at 380° with a Ni catalyst. Cost data are given for the various steps and over-all costs based on the use of blue gas from peat or brown coal.

2904. ———. [What Can the Gas Industry Contribute to the Four-Year Plan?] Gas-u. Wasserfach, vol. 80, 1937, pp. 103–106.

Discussion of the economic possibilities of utilizing the excess production capacity of German gas plants for the manufacture of liquid fuels by the Fischer-Tropsch process. It is calculated that the 80 largest gas plants, which ordinarily produce 90% of the fuel gas requirements, could gasify an extra 6,000,000 tons of coal and could thus supply the raw material for 1,000,000 tons of liquid fuel. The cost would be high until the Fischer-Tropsch installations could be written off in about 3 years, when the cost would then compete fairly well with world markets.

Ross, J. F. *See* abs. **424.**

2905. Rossi, G. [Methyl Alcohol.] Riv. catasto servizi tecn. erar, vol. 9, 1942, pp. 459–471; Chem. Zentralb., 1943, I, p. 2242; Chem. Abs., vol. 38, 1944, p. 4410.

Production of MeOH by the dry distillation of wood and its synthetic production from CO and H_2 are described. Properties and uses discussed.

2906. Rossini, F. D. Heat of Combustion of Methanol. Proc. Nat. Acad. Sci., United States, vol. 17, 1931, pp. 343–347; Chem. Abs., vol. 25, 1931, p. 4773.

With the same calorimetric apparatus and procedure that was used for H_2, CH_4, and CO, the heat of the reaction $CH_3OH\ (g)+3/2\ O_2\ (g)=CO_2\ (g)+2H_2O\ (l)$ was found to be 763.77±0.20 internat. kilojoules/mol. at 25°. By combining with this value the data of Fiock, Ginnings, and Holton on the heat of vaporization of CH_3OH, the heat of combustion of $CH_3OH\ (l)$ is computed to be 726.34±0.20 internat. kilojoules/mol. at 25°, or, with the factor 1.0004/4.185, 173.63±0.05 kg.-cal_{15}. The value obtained by Richards and Davis is about 1.5% lower than this, while that of Thomsen agrees with it within the assigned limits of error. In the present experiments CH_3OH was vaporized by a stream of dry air and burned in an excess of O_2. Tests were made to determine the purity of the reaction. No CO was found, and only negligible amounts of N oxides and HCHO.

2907. ———. Heats of Combustion of Methanol and Ethyl Alcohol. Bureau Standards Jour. Research, vol. 8, 1932, pp. 119–139; Chem. Abs., vol. 26, 1932, p. 2109.

Complete information as to apparatus and procedure is given. The heats of combustion of gaseous MeOH and EtOH, at saturation pressure, from their mixture with air, under a constant total pressure of 1 atm. to form gaseous CO_2 and liquid H_2O were found to be 763.68±0.20 for MeOH at 25° and 1407.50±0.40 for EtOH at 32.50°, in internat. kilojoules/mol. By combining with these data the heats of vaporization and correcting the data for EtOH to 25°, the heats of combustion of the alcohols, in the liquid state are, at 25° and a constant pressure of 1 atm., respectively: 726.25±0.20 and 1,366.31±0.40 internat. kilojoules, or 173.61±0.05 and 326.61±0.10 kg.-cal_{15}./mol.

———. *See* abs. **3589.**

2908. Roth, W. A. [Thermochemistry of Iron, Manganese, and Nickel.] Ztschr. angew. Chem., vol. 42, 1929, pp. 981–984; Arch. Eisenhüttenw., vol. 3, 1929, pp. 339–346; Chem. Abs., vol. 24, 1930, p. 291.

Heats of formation were determined with a calorimetric bomb, paraffin being used to start the reactions. The reaction products were carefully analyzed. Values found (in general slightly higher than those previously accepted) are given in calories: MnO 96.2; Mn_3O_4, 343.8; $MnCO_3$, 218.2; $MnO+CO_2$, 27.7; Mn_3C, 23; FeO, 64.0; Fe_3O_4, 265.7; Fe_2O_3, 197.6; $FeCO_3$, 171.7; $FeO+CO_2$, 13.4; Fe_3C, −5.4; $Fe(CO)_5$, 54.4; NiO, 58.6; Ni_3C, −9.2, all at constant volume. Values at constant pressure, also given, are similar but not identical.

2909. Roth, W. A., and Wienert, F. [Thermochemistry of Iron.] Arch. Eisenhüttenw., vol. 7, 1934, pp. 455–460; Chem. Abs., vol. 28, 1934, p. 2604.

Heats of formation of the Fe oxides were redetermined from pure synthetic materials; methods are described in detail. The heats of reaction, at 20.7°, were found to be: $Fe+\frac{1}{2}\ O_2=FeO+64.6_5\pm0.1_2$ kcal.; $3Fe+2\ O_2=Fe_3O_4+266.7_6\pm0.2_2$ kcal.; $2Fe+1\frac{1}{2}\ O_2=Fe_2O_3+195.1_9\pm0.2_0$ kcal.; $FeO+Fe_2O_3=Fe_3O_4+6.9_4\pm0.3_3$ kcal.; $Fe+1\frac{1}{2}\ Cl_2=FeCl_3+93.5_6\pm0.2_3$ kcal.; $Fe_2O_3+3Cl_2=2FeCl_3+1\frac{1}{2}O_2+8:07\pm0.4_4$ kcal. A comparison with older values is added.

2910. Röttig, —. [Aromatization of Straight-Chain Aliphatic Hydrocarbons From the Fischer-Tropsch Synthesis.] TOM Reel 138, Doc. 28, 13 pp.

Some reference is made to the ability of Cr_2O_3 to convert napthenic and aliphatic hydrocarbons into aromatics and to the possibility of depositing these catalysts on active C, pumice, Al_2O_3, and silica gel. Such metals as Ni, Co, Fe, Ta, etc., are mentioned as promoters. Preliminary treatment of the catalysts with CO_2, H_2S, PH_3 is said to increase their activity. Reference is made to the work of Huppke-Frey and Moldavskii-Kamuscher with multiple component catalysts. Calcined magnesite is stated to increase catalyst activity. It is possible by means of efficient fractionation columns to isolate C_5, C_6, C_7, and C_8 hydrocarbons from Fischer-Tropsch gasoline fractions. A flow sheet of a cyclization is shown. The economics of the process is discussed.

2911. ———. [New Experiences With Iron Catalysts for the Normal Pressure Synthesis.] Erdöl u. Kohle, vol. 3, No. 1, 1950, p. 10.

Paper presented at the 1949 meeting of Die deutsche Gesellschaft für Mineraloelwissenschaft und Kohlechemie. By using nonsupported Fe catalysts, it is possible in a straight 1-stage passage at temperatures of about 200° to attain a $CO+H_2$ conversion of 65–70%, corresponding to CO conversion of 85–95%. The gas charge per hr. amounts to 100 l. per vol. of catalyst. Water gas is the best gas to use, although the use of H_2-rich gas is possible. Especially favorable is the use of CO-rich gas. The catalysts must be extracted initially in periods of 4–6 days at the reaction temperature considered. Several new experiences in the extractions are presented. The operating time of such Fe catalysts is very high; at almost constant reaction temperature a life of 10,000–11,000 hr. is attained and this can be extended considerably by raising the temperature. CH_4 formatiou is essentially less than with Co catalysts. The proportion of hydrocarbons boiling above 320°, calculated on the total liquid yield, is 25–30% by weight as the average of a long operating period.

2912. Röttig, E. [New Substances With Spinel Structure.] Angew. Chem., vol. 62, 1950, p. 87.

$CuFe_5O_8$, analogous to $LiAl_5O_8$ and $LiFe_5O_8$, was made at 1,200° C. Its $\Theta=390°$ and $a=8.389\pm0.003$ Å. This is a spinel. $CuFe_2O_4$, made at 600°, has $\Theta=490°$ and is psuedo-tetragonal with $a=8.4_4$ Å, $c/a=0.97_5$. Mixtures of $CuFe_2O_4$ and $\frac{Cu+Fe}{2}\ Fe_2O_4$ have $\Theta=440°$ and a spinel structure with $a=8.377\pm0.003$ Å. $CuAl_5O_8$ is not quite cubic. $CuAl_2O_4$ and $CuCr_2O_4$ are not cubic, contrary to the literature. Li^+, Cu^+, or Ti^{4+} spinels could not be obtained. $LiFeTiO_4$ and $LiCrTiO_4$ are

spinels. $LiAlTiO_4$ is not cubic. $LiFeTiO_4$ is ferromagnetic with $\Theta=130°$.

ROUDEBUSH, B. *See* abs. **626.**

2912a. ROUSSEAU, P. E. South Africa's Oil-From-Coal Project. South African Min. and Eng. Jour., vol. 62, 1951, pp. 207–211, 255–259; Chem. Age, vol. 66, 1952, pp. 129–130.

An outline of the development work being planned and carried out in the production of oil from coal and of chemical byproducts by the South African Coal, Oil & Gas Corp. ("Sasol" project). The process to be employed, and found most suitable for South African low-grade coals, is a combination of American and German developments of the original Fischer-Tropsch method.

ROYEN, P. *See* abs. **2879.**

ROZENGART, M. I. *See* abs. **1706.**

ROZHDESTVENSKAYA, I. D. *See* abs. **3179.**

RUBANIK, M. Y. *See* abs. **932.**

2913. RUBANIK, M. Y., ZABOLOTSKIĬ, T. V., AND RUSOV, M. T. [Iron-Molybdenum Catalysts for the Synthesis of Ammonia.] Jour. Chem. Ind. (U. S. S. R.), vol. 14, 1937, pp. 484–485; Ber. Inst. physik. Chem., Akad. Wiss. Ukr. S. S. R., vol. 6, 1936, pp. 77–82; Chem. Abs., vol. 31, 1937, p. 5519.

Fe–Mo–Al_2O_3 catalysts are less active than **Fe–Al_2O_3** ones. Addition of Al_2O_3 to Fe–Mo catalyst causes them to retain their activity longer.

2914. RUBINFELD, J. [Liquefaction of Coal.] Allgem. österr. chem. u. tech.-Ztg., vol. 43, 1925, p. 151; Chem. Abs., vol. 20, 1926, p. 1313.

Brief discussion of 4 methods by which motor fuel can be produced: Low- and high-temperature carbonization of coal, Synthol process, Bergius process, and Badische process.

2915. RUBINSHTEIN, A. M. [Catalytic Hydrogenation in the Vapor Phase in Connection With the Degree of Dispersion of the Catalysts.] Bull. acad. sci. U. R. S. S., Classe sci. chim., 1940, No. 1, pp. 144–150 (in German, pp. 150–151); Chem. Abs., vol. 35, 1941, p. 3512.

Hydrogenation of C_6H_6 and CO in the presence of a **Ni–Al_2O_3** catalyst in which the dimensions of the Ni crystals varied 40–102 Å. was investigated. C_6H_6 was hydrogenated in an excess of H_2 at 155° and 175°, the velocity of the C_6H_6 stream was 3 cc. per hr., yielding 70.2–75.0% and 83.3–85.5%, respectively, C_6H_{12}. The highest yield was in the more disperse catalyst. The catalysts with Ni crystals greater than 65 Å. had little or no activity. The activation energy also varied within 3,100–10,450 cal. per mol. with the dispersity of Ni 49–102 Å. The mixture $CO+3\ H_2$ was hydrogenated at 230°–260° at various velocities of the mixture, 4.6–10.0 l. per hr., yielding CH_4; again the most disperse catalysts (49, 58 Å.) promoted best the transformation of CO into CH_4. Other catalysts had little or no activity. Presumably, all catalysts of the same chemical nature, metals, and oxides and having the same crystal system and cube as the above catalyst should have the same relation between activity and dispersity.

2916. RUBINSHTEIN, A. M., PRIBYTKOVA, N. A., KAZANSKIĬ, B. A., AND ZELINSKIĬ, N. D. [Catalysts for Benzine Synthesis From Carbon Monoxide and Hydrogen Which Do Not Require High-Temperature Reduction.] Bull. acad. sci. U. R. S. S., Classe sci. chim., 1941, pp. 41–48; Chem. Zentralb., 1942, II, p. 971; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 334; Chem. Abs., vol. 37, 1943, p. 5217.

Catalysts produced from $KAlFe(CN)_6$, $Ni^2Fe(CN)_6$, and $Co_2Fe(CN)_6$ by decomposition in a H_2 atmosphere yielded no liquid hydrocarbons under the experimental conditions, temperatures 230°–280° and space velocity of 18–50, but only catalyze CH_4 formation. A Co–Cu–Mn catalyzer, produced by precipitation with K_2CO_3 on kieselguhr, in a single experiment yielded 204 cc. benzine per $m.^3$ of gas, whereas a catalyst of similar composition prepared by igniting the nitrates was not as effective. The kieselguhr required no preliminary ignition or treatment with HCl or Na_2CO_3. A 2-stage synthesis with Co–Cu–Mn catalyst gave benzine yields of 160 cc. per $m.^3$ over a long time with space velocities of 100–120. With prolonged tests, lower catalyst activity was noted with intermittent than with continuous operation.

2917. RUBIO, F. B. L., AND PACHECO, J. R. [Mechanism of the Catalytic Process for the Synthesis of Hydrocarbons by the Fisher-Tropsch Process.] Ion, vol. 8, 1948, pp. 86–89; Chem. Abs., vol. 42, 1948, p. 5643.

Most active catalysts for the Fischer-Tropsch synthesis are Fe, Co, and Ni. Of these, **Fe** is probably the least active, but it has the advantage of being effective over a wide range of temperatures and is characterized by production of liquid hydrocarbons with CO_2 as byproduct. Co gives a product rich in olefins. Ni tends to produce CH_4 along with liquid and solid paraffins. Previous theories have attributed the catalytic action of these metals either to formation of CH_2 groups, with carbides of the metals acting as intermediates and polymerization of the CH_2 groups, or of higher alcohols with subsequent dehydration to olefins. According to a new theory, carbonyls of the metals are the primary active materials. The existence of a compound $[Fe(CO)_5]_4$ including long chains of CO groups is assumed. This is reduced to 2 mol. of C_8H_{18} and a **Fe** carbonyl of much lower CO content. After a number of reactions, with Fe_3C, C_3O_2, FeO, and Fe_2O_3 among the intermediate products, the lower carbonyl is reconverted to Fe. Overall reactions are: $18\ CO+4\ Fe \rightarrow [Fe_2(CO)_9]_2$; $[Fe_2(CO)_9]_2+2\ CO \rightarrow [Fe(CO)_5]_4$; $[Fe(CO)_5]_4+34\ H_2 \rightarrow 2\ C_8H_{18}+15\ H_2O+CO_2+3\ CO+4\ Fe+H_2$. The volumes of CO and H_2 to produce 1 mol. of C_8H_{18} are $10\ CO+17\ H_2$ instead of the previously given $8\ CO+17\ H_2$, and the theoretical yield of octane is only 188.4 gm. per $m.^3$ instead of 203.5. The presence of Fe carbides and oxides in the catalyst is consistent with this theory, but these compounds only represent stages in the regeneration of the metallic **Fe**. Hydrocarbon formation is by substitution of **H** for **O** in (CO_n) chains already formed. Polymerization of CH_2 groups is not inconsistent with this theory. The action of alkalies added to **Fe** catalyst may be either (1) removal of O from CO groups to give percarbonate, H then combining with C and the percarbonate being subsequently reduced, or (2) polymerization of CO to chains, which combine with Fe to give carbonyls.

RUCKES, W. L. *See* abs. **625.**

2918. RUER, R. [Iron–Carbon Alloys.] Ztschr. anorg. Chem., vol. 117, 1921, pp. 249–261; Chem. Abs., vol. 16, 1922, p. 702.

(1) *Solubility of cementite in molten iron.* A quenched melt of an Fe-C alloy containing 6.5% C showed a structure consisting entirely of cementite. Cementite is precipitated directly from the melt and is not formed by the reaction between 2 phases, 1 solid and the other liquid. The solubility curve of Fe_3C in molten Fe rises from the eutectic temperature to a maximum at 6.67% C corresponding to the compound Fe_3C. The melting point of Fe_3C in the metastable system Fe–C cannot be determined because Fe_3C dissociates at temperatures above 1,100°. The slope of the solubility curve of Fe_3C in the metastable system is less than that of graphite in the stable system because with increasing C content the suppression of the separation of graphite becomes more difficult. Small cubes of Swedish Fe containing 2.5–4% C and

no Mn were heated in a vacuum for 10 min. at temperatures 1,100°–1,150°. The velocity of the dissociation of Fe_3C on the surface of the cubes was higher than the velocity at the center; no explanation is offered.

(2) *Complete equilibrium between austenite, ferrite, and graphite corresponding to the pearlite equilibrium.* A sample of Fe containing 3.5% C and no Mn or Si was solidified slowly. After the solid had cooled to 1,000° it was heated to just above the eutectic temperature and again slowly solidified. After a repetition of this latter procedure, the sample was cooled to room temperature. Repeated heating and cooling curves for the sample were then made. The maximum temperature reached in each experiment was 772°. The first curve showed an arrest at 734° on heating and at 720° on cooling. The second curve showed arrests at 736° and 746° on heating and at 720° on cooling. The third curve showed arrests at 736° and 746° on heating and at 720° and 707° on cooling. All these arrests were recognized on subsequent heating and cooling curves up to the twelfth. The twelfth curve showed an arrest at 736° on heating and 712° on cooling. The arrest at 736° corresponds to the transformation of pearlite into austenite. The rate of cooling was so slow that Fe and graphite rather than Fe_3C precipitated from the austenite. The arrest at 746° corresponds in the stable system Fe–C to the solution of ferrite and graphite in austenite. The gradual disappearance of the 746° arrest from the heating curves is caused by the coalescence of the graphite particles into large masses, which, under the experimental conditions, would not dissolve in austenite. The double arrest on the cooling curves is not easily explained. The upper arrest at 718° cannot be attributed to the transformation in the stable system and the lower to the transformation in the metastable system because white cast Fe shows the austenite-pearlite transformation at 718°. The simultaneous precipitation of pearlite and the graphite eutectic may occur. Since the arrest at 746° ascribed to the transformation of the eutectic in the stable system lies 12° higher than the arrest at 734° ascribed to the transformation of pearlite in the metastable system, then the equilibrium temperature of the former transformation should occur 12° higher than the equilibrium temperature of the latter transformation, that is, at 721+12=733. A horizontal should be drawn across the Fe–C diagram from 0–100% C at 733° to represent the eutectic transformation in the stable system. The concentration of C in the eutectic in the stable system is 0.7%.

2919. ———. [Magnetic Transformations of the Ferromagnetic Metals.] Ztschr. anorg. Chem., vol. 165, 1927, pp. 142–148; Chem. Abs., vol. 22, 1928, p. 208.

Discrepancies between the results of Ruer and Bode (abs. **2921**) and Wever (abs. **3672** and **3673**) are discussed at length. It is claimed that one of Wever's investigations was made with Fe of insufficient purity, whereas in the other there is evidence of faulty technique. This explains the failure of Wever to observe the polymorphic transformation at 769° originally reported by Ruer and Bode.

2920. ———. [Magnetic Transformations of the Ferromagnetic Metals.] Ztschr. anorg. Chem., vol. 205, 1932, pp. 230–234; Chem. Abs., vol. 26, 1932, p. 3707.

Temperature–temperature-difference curves for exceptionally pure electrolytic Fe were recorded photographically. Both the heating and the cooling curves show sharp breaks at the magnetic transformation point as well as more pronounced ones at the β–γ transformation. Wever has questioned the idea advanced by Ruer and Bode that the magnetic transformation in pure Fe at 769° is a homogeneous phase change (abs. **2919**). The evidence, both experimental and theoretical, bearing on this point is reviewed.

2921. Ruer, R., and Bode, K. [Magnetic Transformations of Ferromagnetic Metals.] Stahl u. Eisen, vol. 45, 1925, pp. 1184–1189; Chem. Abs., vol. 20, 1926, p. 3426.

Experiments were made with a view to find a fixed point at 700°–800° for the purpose of calibrating thermocouples. 3 cooling curves and 1 heating curve for electrolytic Fe are given, that show an arrest point at 769°. Electrolytic Fe from the Langbein-Pfanhauser works showed the point at the same temperature. Kahlbaum Fe in rods gave the point on heating but not on cooling and gave results midway between those for electrolytic Fe and mild steel. The arrest is suppressed by impurities, but the impurity that is effective has not been identified. The heat set free at the β–α change is $\frac{1}{6}$ that at the γ–β change, or about 1 cal. per gm. The change, which must be truly polymorphic, also occurs in Ni and Co. As α– and β–Fe have the same space lattice, a polymorphic change does not necessarily involve a change in the space lattice, and the inverse must also be true.

2922. Ruff, O. [Equilibrium Diagram of Iron-Carbon Alloys.] Metallurgie, vol. 8, 1911, pp. 456–464, 497–508; Chem. Abs., vol. 5, 1911, p. 3793.

It is concluded from experiments that besides cementite, Fe_3C, which has been called triferrocarbide, a diferrocarbide exists, Fe_2C. The equilibrium concentrate of the triferrocarbide is always less than the saturation concentrate. Above 700° the carbides are endothermic compounds and at 2,220° the diferrocarbide is quite strongly dissociated into Fe and C. As the temperature is lowered, the diferrocarbide breaks down into Fe_3C and C, and eventually the Fe_3C breaks down into Fe and C. In the metastable system, the solidification takes place in 4 periods: (1) The time up to that point when the melt reaches the equilibrium concentrate; (2) the time during which the melt remains between the equilibrium concentrate and the saturated concentrate; (3) the time during which the carbide eutectic is solidifying; (4) the time during which the solid system is cooling. The amount of solid carbide formed from the liquid phase is determined chiefly by the decomposition velocity of the carbide and the difference between the equilibrium concentrate and the saturation concentrate and also is affected by the velocity of solidification. In the solid phase, the decomposition velocity of the carbide is always less than in the liquid phase. Thus, when the carbide is once formed as solids, it remains more stable in proportion as the temperature at which it is first deposited is low. Moreover, the more finely divided its condition, the more likely the carbide is to remain in metastable equilibrium with the surrounding solid solution. The reaction velocity of the carbide decomposition at 1,135° is such that about 50% of the carbide will decompose in 2 sec. Approximation formulas are developed for the results to be expected in the solidification of Fe–C alloys during the second and third periods.

2923. ———. [Phase-Rule Diagrams of Carbon With Nickel, Iron, Cobalt, and Manganese.] Ber. deut. chem. Gesell., vol. 45, 1912, pp. 3139–3148; Chem. Abs., vol. 7, 1913, p. 581.

In his electric vacuum furnace, Ruff has succeeded in maintaining temperatures up to above 2,700°. Thus the melting-point diagram of the V-C system has been followed to about 2,750°. In the Fe–C system, the probable existence of Fe_2C has been revealed, and in the Ni–C system, the compound Ni_3C was found. The melting point and vapor pressure diagrams of these systems are reproduced, together with those of Mn–C and Co–C, worked out with the help of Gersten and

Keilig. In the Mn–C system the compound Mn_3C appears to be more stable than any of the above mentioned compounds. Unlike the other carbides, Mn_3C forms a continuous series of mixed crystals with Mn. In the Co–C series, the formation of fumes at high temperatures caused so much trouble that the work is to be repeated. The melting-point diagram is very similar to that of Ni–C, although no transition point could be detected in the liquid before the boiling point was reached. (*See also* abs. **2924** and **2933**.)

RUFF, O., AND BORMANN, W. [Investigations at Higher Temperatures. VII. Iron and Carbon.] *See* abs. **2931**.

———. [Investigations at Higher Temperatures. V. Manganese and Carbon.] *See* abs **2929**.

———. [Investigations at Higher Temperatures. VI. Nickel and Carbon.] *See* abs. **2930**.

2924. RUFF, O., AND GERSTEN, E. [Triferrocarbide (Cementite) Fe_3C.] Ber. deut. chem. Gesell., vol. 45, 1912, pp. 63–72; Chem. Abs., vol. 6, 1912, p. 1409.

Campbell (Jour. Iron Steel Inst. (London), vol. 59, 1901, p. 217) and others hold that Fe_3C is an exothermic compound, 8,940 cal. being given off in its formation. Ruff (abs. **2922**) believes that it is endothermic and reports the following experimental work in confirmation of his theory. Pure Fe_3C, prepared by Werkmeister's method (Dissertation, Karlsruhe, 1910), is dark gray; its hardness is 3.2–33, sp. gr. 7.396 at 21°, mol. vol.=1/7=24.34. The molecular volume for 3 Fe and C is 27.84, giving a molecular contraction of 3.5. Burning Fe_3C with O_2 in a Berthelot bomb, under a pressure of 25 atm., gave 375.1 cal. for 1 mol. Fe_3C. In burning Fe to Fe_3O_4 and C to CO_2, 360 cal. are evolved, a difference of 15.1 cal. Therefore, the heat of formation of Fe_3C is 15.1 cal., and Fe_3C is endothermic. $3Fe+C \rightarrow Fe_3C+15.1$ cal.

2925. ———. [Carbides of Manganese and Nickel.] Ber. deut. chem. Gesell., vol. 46, 1913, pp. 400–413; Chem. Abs., vol. 7, 1913, p. 1848.

Molecular heats of formation of Mn_3C=—12.9±2.14, Fe_3C=—15.3±0.2 and Ni_3C=—394±10 cal. The Ni_3C is very unstable and is not obtained in a pure condition. Mn_3C is comparatively stable and is obtained by heating Mn in a C crucible with C at 1,600° in an electric vacuum furnace. Ni_3C is formed at 2,100°. The maximum amount of C found in the carbide is 6.42%.

2926. ———. [Iron Carbide.] Ber. deut. chem. Gesell., vol. 46, 1913, pp. 394–400; Chem. Abs., vol. 7, 1913, p. 1848.

Molecular heat of formation of Fe_3C was previously found to be —15.1 cal. Recalculation by Le Chatelier's method revealed the heat of oxidation of FeO to ⅓ Fe_3O_4 to be 28.6±1.8, while Le Chatelier obtained 25.7. Revised calculations gave the following results: Molecular heat of formation of Fe_3O_4 (Fe=55.8)=267.1± 0.2 cal.; of FeO=60.4±1.8 cal.; of Fe_3C from α-Fe and graphite= —15.3±0.2 cal. (*See* abs. **2924**.)

2927. RUFF, O., AND GOECKE, O. [Solubility of Carbon in Iron.] Metallurgie, vol. 8, 1911, pp. 417–421; Chem. Abs., vol. 5, 1911, p. 3221.

Solubility shows a maximum at 2,220° corresponding to the composition Fe_2C and a change in direction at 1,887° corresponding to the composition Fe_3C.

RUFF, O., AND KEILIG, F. [Investigations at Higher Temperatures. VIII. Cobalt and Carbon.] *See* abs. **2932**.

2928. RUFF, O., AND LAUSCHKE, G. [Investigations at Higher Temperatures. IV.] Ztschr. anorg. Chem., vol. 87, 1913, pp. 198–208; Chem. Abs., vol. 8, 1914, p. 2931.

2929. RUFF, O., AND BORMANN, W. [Investigations at Higher Temperatures. V. Manganese and Carbon.] Ztschr. anorg. Chem., vol. 88, 1914, pp. 365–385; Chem. Abs., vol. 9, 1915, p. 435.

The solubility of C in Mn is 6.82% at 1,312°, 6.93% at 1,427°, 7.05% at 1,492°, and 7.12% at 1,525°; the latter boils at 30 mm., and the vapor in equilibrium contains 1.94% C. Pure Mn boils at 1,510° at 30 mm. Since the vapor pressure of C up to 3,000° is small, the vapor in equilibrium with Mn melts probably contains its C as carbide; it is also probable that all of the C contained in the melt is combined as carbide.

2930. ———. [Investigations at Higher Temperatures. VI. Nickel and Carbon.] Ztschr. anorg. Chem., vol. 88, 1914, pp. 386–396; Chem. Abs., vol. 9, 1915, p. 435.

Addition of C to Ni lowers the melting point to a minimum at 1,311° and 2.20% C; the eutectic line could be followed to 0.3% C. With increasing temperature the solubility of C in the melt increases first slowly, then rapidly, to a flat maximum at 2,100° and 6.4% C; the melt is the almost pure Ni_3C. As the temperature is increased, the solubility of C first diminishes sharply then increases slowly to 6.3% C at 2,490°; the latter solution boils at 30 mm., and the vapor in equilibrium contains 0.28% C. Pure Ni boils at 30 mm. at about 2,400°.

2931. ———. [Investigations at Higher Temperatures. VII. Iron and Carbon.] Ztschr. anorg. Chem., vol. 88, 1914, pp. 397–409; Chem. Abs., vol 9, 1915, p. 435.

2932. RUFF, O., AND KEILIG, F. [Investigations at Higher Temperatures. VIII. Cobalt and Carbon.] Ztschr. anorg. Chem., vol. 88, 1914, pp. 410–423; Chem. Abs., vol. 9, 1915, p. 435.

Addition of C to Co lowers the melting point to 1,300° at 2.4% C; with increasing temperature the solubility of C in the melt increases, first slowly with increasing temperature, then more rapidly; at 2,100° and at 6.36% C and at about the composition of the compound Co_3C the solubility curve has an upward inflexion similar to, but not as marked as, that with Ni; the solubility of C then rises to 7.4% at 2,415°. The authors concluded that Co_3C had been formed, but on examination found only graphite, and, therefore, assumed that the Co_3C, if formed, had very quickly decomposed.

2933. RUFF, O., AND MARTIN, W. [Solubility of Carbon in Nickel.] Metallurgie, vol. 9, 1912, pp. 143–148; Chem. Abs., vol. 6, 1912, p. 1128.

At about 2,100°, Ni will dissolve 6.42% C, corresponding approximately to the formula Ni_3C. Under the microscope a new constituent, evidently the carbide, was distinguished from the ground mass of Ni. It was brown and resisted the etching solutions more than the Ni. The behavior of the Ni–C alloys when heated resembled that of the Fe–C alloys, indicating that Ni and Fe form similar carbides.

2934. RUFF, O., BORMANN, W., AND KEILIG, F. [Behavior of Carbon Toward Manganese, Nickel, Iron, and Cobalt.] Forschungsarbeiten Gebiete Ingenieurwesens, No. 209, 1918, pp. 5–46; Chem. Abs., vol. 16, 1922, p. 1713.

More extensive exposition of the data and phase rule diagrams reported in abs. **2923**.

2935. RUFF, O., JELLINEK, E., AND FOEHR, T. [Constitution and Thermal Stability of Carbides.] Ztschr. Elektrochem., vol. 24, 1918, pp. 157–162; Chem. Abs., vol. 13, 1919, p. 213.

Experiments on the formation of carbides lead to the conclusion that metal carbides in general are stable up to temperatures above 2,500°, and even at these elevated temperatures, C does not dissolve in the metals as such, but as a carbide of the metals. To date, the known metal carbides conform with the following hydrocarbons: CH_4, C_2H_6, C_2H_2, C_2H_4, and C_4H_{10}. In

the case of most metals the C concentration increases with increasing temperature. Within wide temperature limits carbides such as Mn_3C, Cr_3C_2, and W_2C are very stable; carbides such as Fe_3C, WC, and Cr_3C_2 decompose upon lowering the temperature to the melting point of the alloy into metal plus C. Fe_3C is difficult to obtain in the solid phase, and Ni_3C is altogether unstable as solid. All carbides dissociate more or less completely upon volatilization.

2936. RUHEMANN, M. Large-Scale Oxygen Production. Internat. Cong. Pure Appl. Chem, 11th Cong., 1947; British Abs., 1948, B, I, p. 300.

Economics of the production of O_2 so that it can compete with liquid air is reviewed. The development of new units, including expansion turbines, turbocompressors, packed regenerators and reversing heat exchangers with extended surfaces, have led to increased efficiency and reduction of losses.

2937. RUHL, O. [Liquid-Fuel Problems in Germany.] Jour. Fuel Soc. Japan, vol. 16, 1937, pp. 33–40.

Review of German developments in the I. G. coal-hydrogenation process and the Fischer process. By the latter process 1 m.^{3} $CO+2\ H_2$ (90%) produces in practice 100 gm. liquid products; about ½ of the H_2 in the gas mixture is converted to H_2O. The theoretical limit of production is 180 gm. of liquid products from 1 m.^{3} $CO+2\ H_2$. As 0.8 kg. of coal corresponding to 0.55 kg. coke is used in the production of 1 m.^{3} $CO+2\ H_2$, it follows that theoretically 35%, at most, of the heat value of the coal can be converted into liquid products, while in practice the figure is about 20%. Much steam also is produced, which is not included in the efficiency. The smallest economical size of Fischer plant is about 20,000 tons of gasoline per year. Plants at Ruhland, Rauxel, Holten, and Homberg have a capacity of 295,000 tons of gasoline per yr. Besides these plants, Kuhlmann in France is planning an installation of 30,000 tons capacity, and in Japan the Mitsui Co. is erecting a plant of 30,000 tons capacity. Two other plants are planned. Installation costs for the high pressure process and the Fischer process are about the same, and the cost of operation does not differ greatly. If gasoline is the main object, the high-pressure process operates most economically.

2938. RUHRCHEMIE A.-G. [Drawings of Medium-Pressure Reactors for the Fischer-Tropsch Process.] BIOS Microfilm FD 5422/47, frames 1–18; O. T. S. Bib. Tech. Rept., vol. 16, No. 3, 1951, p. 78, PB 104,126.

German report covering years 1942–44.

2939. ———. [Production of Soaps and Edible Fats From Fatty Acids.] BIOS Microfilm FD 5463/47, Frames 1–194; O. T. S. Bib. Tech. Rept., vol. 16, No. 3, 1951, p. 67; PB 104,187.

German report covering years 1939–43.

2940. ———. [Experiments for the Production of Aviation Spirit by Catalytic Cracking of Primary Products of the Fischer-Tropsch Synthesis.] BIOS Microfilm FD 5600/47, frames 1–387; O. T. S. Bib. Tech. Rept., vol. 16, No. 3, 1951, p. 78, PB 104,188.

German report covering years 1937–44.

2941. ———. [Technique of the Fischer-Tropsch Process.] BIOS Microfilm FD 5619/47, frames 1–43; O. T. S. Bib. Tech. Rept., vol. 16, No. 3, 1951, p. 79, PB 104,171.

German report covering years 1937–44.

2942. ———. [Course of the Pressure Synthesis When Using an Initial Gas Rich in Carbon Monoxide.] FIAT Reel K–20, no date, frames 11–17; PB 70,211; TOM Reel 287.

Gas used consisted of $CO:H_2=1:1$. Higher yields of liquid products were obtained than with normal synthesis gas. In order to obtain a good conversion of the CO, temperatures up to 215° were used. The total product consisted of about equal parts of gasoline, middle oil, and paraffin, the latter being about 8% less than in normal synthesis. The olefin content of the gasoline was 32–36 vol. % and that of the middle oil 24–27%. With a catalyst containing Co, 100; ThO_2, 15; kieselguhr, 600; and a gas rich in CO, considerably better results were obtained. The conversion of CO was 92% and the ratio of liquefaction 89%. The content of paraffin was 17% higher than with the normal catalyst.

2943. ———. [Kieselguhr.] FIAT Reel K–20, 1938, frames 18–23; PB 70,211; TOM Reel 287.

Microphotographs of 12 kieselguhr samples show great changes in structure after regeneration. It is believed that an examination of the microtexture of fresh and spent catalysts will provide valuable explanations on the evaluation of catalysts for the gasoline synthesis. The solubility of kieselguhr is determined by stirring at 80°–95° with various solutions occurring in the manufacture of catalysts, filtering and washing with hot water. In the filtrate, SiO_2, Fe_2O_3, Al_2O_3, and CaO are determined. Table and diagram.

2944. ———. [Thorium Regeneration.] FIAT Reel K–20, 1938, frames 24–31; PB 70,211; TOM Reel 287.

Auergesellschaft A.-G. has developed the following method: Fe–Th sludge is dissolved in HCl at a temperature of 80°. After cooling, the bulk of the solution is siphoned off, the residue is filtered, and the whole is mixed with H_2SO_4. The sulfate precipitates are centrifuged and covered with dilute H_2SO_4. The Th sulfate is then stirred with water and converted to Th hydrocarbonate. The yield of ThO_2 by this method is 94%. The method is compared with the Ruhrchemie method. The maximum content of SO_3 in the Th hydrocarbonate is given as 0.3%.

2945. ———. [Manufacture of a Catalyst With High Cobalt Content and High Activity.] FIAT Reel K–20, 1939, frames 40–43; PB 70,211; TOM Reel 299.

Following has been found to be the most favorable method for precipitating the catalyst consisting of 100 part Co, 15 ThO_2, and 12.5 purified kieselguhr. The boiling solution of 1 kg. Co and 150 gm. ThO_2, dissolved as nitrates in 20 l. of H_2O, is poured into the stirred boiling solution of 2.6 kg. soda in 40 l. H_2O. After addition of 125 gm. previously purified kieselguhr, the mixture is stirred for another 30–40 sec. The precipitate then is transferred to a suction filter, and the mother liquor is removed, after which the precipitate is covered 2 times with distilled H_2O and washed until less than 0.01 gm. soda per l. can be detected in the wash H_2O. After extensive dry suction the cake is placed in the drier and dried at 100° for 8 hr.

2946. ———. [Production of Cobalt Catalyst by Precipitation With Carbon Dioxide-Ammonia Gas Mixtures.] FIAT Reel K–20, frames 359–362; PB 70,211; TOM Reel, 287.

Communication from the Kaiser Wilhelm Institut für Kohlenforschung concerning the production of a very active catalyst. Co in the form of its nitrate, together with the corresponding amounts of Th or Mg nitrates, is dissolved in water. A NH_3–CO_2 gas mixture then is introduced cold. By test filtration the optimum precipitation is determined, and the stream of NH_3 is switched off. With the CO_2 still flowing, the solution is heated to the boiling point, kieselguhr is added, and the whole is mixed thoroughly. The catalyst then is dried and reduced with H_2.

2947. ———. [Fatty Acids and Soaps From the Hydrogenation of Carbon Monoxide.] FIAT Reel

K–20, various dates, 1936–43, frames 414–531; PB 70,211; TOM Reel 287.

Miscellaneous collection of papers, mostly by O. Roelen, on the development of the production of synthetic fats from Fischer-Tropsch paraffins and their transformation into soaps. The method of the Ruhrchemie and Brabag are compared. Analyses of products are given, and some rough drafts of patent specifications are presented.

2948. ———. [Recovery of Thorium.] FIAT Reel K–21, 1942, frames 806–892; PB 70,212; TOM Reel 288.

Paper reports all the experimental and practical work performed on the development of a method for recovering Th from the catalysts used in the hydrogenation of CO. The results of the entire work are contained in a patent application. The method consists in precipitating Th–K_2SO_4 from the Fe–Th sediments obtained by precipitation by adding K_2SO_4. After separation and washing, this is transformed into Th bicarbonate by boiling in concentrated soda solution.

2949. ———. [Paraffin Synthesis.] FIAT Reel K–21, 1939, frames 997–1008; PB 70,212; TOM Reel 288.

New catalysts of extraordinary efficiency are described, which differ from the previous Co catalysts by a very high $CoCO_3$ content, little kieselguhr, and a corresponding addition of Mn as activator. They bring about complete transformation of the CO–H_2 mixture at the lowest temperatures known, below 170°. This results in a high yield of paraffin.

2950. ———. [Properties of Kieselguhr.] FIAT Reel K–21, 1938, frames 1032–1075; PB 70,212; TOM Reel 288.

Average values of 3 types of reduction examined are found to lie very close together. It also was found by experiment that contrary to established theories the catalytic usefulness of kieselguhr in no way depends on its stability in alkali. It also was noticed in some samples from Kieselguhr Industrie, Hanover, that catalysts on kieselguhrs with high calcination loss did not react up to full activity. It is evident from studies made that there is a connection between the temperature treatment of a kieselguhr and its suitability as a carrier.

2951. ———. [Paraffin Synthesis on Iron Catalyst.] FIAT Reel K–21, March 3, 1941, frames 1123–1129. PB 70,212; TOM Reel 299.

Both in circulation and straight passage of gas, the Fe catalyst 100 Fe : 5 Cu : 10 : 150 kieselguhr consumes normal water gas at a pressure of 15–20 atm. and a temperature of 225°–250° in such a way as to permit operation in 2 or more stages. It is easily reproducible, has special grain solidity, and gives excellent yields of pure-white paraffin.

2952. ———. [Aromatizing Plant.] FIAT Reel K–24, July 3, 1940, frames 2,470–2,485; TOM Reel 291.

Report deals with the task of converting the gasoline boiling below 200° C., obtained from the Fischer synthesis, into a motor gasoline with an octane No. of 65. The costs and economy of a plant for catalytic cracking are compared with those of an aromatizing plant. Calculations and estimates in 8 enclosures.

2953. ———. [Manufacture of Higher Alcohols.] FIAT Reel K–24, April 9, 1940, frames 2,848–2,864; TOM Reel 291.

MeOH synthesis described, with references to literature and patents.

2954. ———. [Production of Ruhr-Gasoline Hard Paraffin in Connection With the Fuel Synthesis of Ruhrchemie.] FIAT Reel K–25, no date, frames 3, 572–3, 574; PB 70,216; TOM Reel 292.

Bergius process yields liquid fuels, while the Fischer-Tropsch method produces paraffins in small quantities. To obtain paraffin in larger quantities, this method was changed by Fischer and Pichler. They applied medium pressures of about 10 atm., and paraffin was produced in a liquid state. A solidly built-in catalyst containing Co is placed in a reactor with water pipes running vertically. In addition to light and heavy gasoline and gasol, a paraffin mixture is obtained, which can be processed into soft paraffin, through vacuum distillation, 3–6 mm. Hg., and about 300° C. and into Ruhr gasoline hard paraffin. This solid paraffin is oxidized with nitrous gases, produced by the combustion of NH_3. The long-chained molecules are less frequently cracked by this method than by O_2 oxidation.

2955. ———. [Calculation of a Plant for the Production of High-Molecular Fatty Acids With a Daily Output of 3 Tons Product.] FIAT Reel K–25, June 26, 1941, frames 3, 953–3, 956; PB 70,216; TOM Reel 292.

Method and calculations are described. (*See* abs. **3553**.)

2956. ———. [Monthly Reports of the Plant Laboratories, Ruhrchemie A.–G., Oberhausen-Holten.] FIAT Reel K–28, January 1938–March 1940, frames 5,734–6,080; PB 70,185; TOM Reel 295.

These monthly reports deal with the plant research on gasoline synthesis at the above laboratories. Aside from the general routine work for the supervision of the plants, special tasks have been carried out, the progress of which is reported. These special tasks consist of tests with gasolines, diesel oils, and paraffins; examination of the miscibility of several grades, emulsification and emulsifier properties, and oxidation of paraffins, acids, aldehydes, ketones, and alcohols.

2957. ———. [Recycle Benzine.] FIAT Reel K–28, Aug. 13, 1941, frames 6,081–6,098; PB 70,185; TOM Reel 295.

Examination was made of the suitability of recycle benzine (benzine obtained by recirculating residual gas mixed with fresh synthesis gas, obtained by synthesis over Co and Fe catalysts) for producing lubricating oil by polymerization. Recycling does not affect the polymerization properties or the value of the product. The lubricating oil prepared from benzine synthesized over the Fe catalyst possesses a more favorable viscosity pole height than that obtained with the Co catalyst. 15 tables, 4 diagrams.

2958. ———. [High-Temperature Refining and Storage Stability of Gasoline Produced Over Iron Catalyst.] FIAT Reel K–28, July 20, 1940, frames 6,268–6,271; PB 70,185; TOM Reel 295.

Gasoline produced over an Fe catalyst and refined by treatment with bleaching earth at 300° did not show the increase in octane number to be expected from the olefin content. Bomb-test results show that the storage stability of both refined and unrefined gasoline may be expected to be equally good.

2959. ———. [Carbon Dioxide in the Circulation Gas of Catalytic Reduction.] FIAT Reel K–28, July 7, 1938, frames 6,435–6,452B; PB 70,185; TOM Reel 295.

In a new catalytic reduction installation for the production of Fischer-Tropsch catalyst, the % of CO_2 in the reduction gas was examined during the reduction period. The CO_2, which originates mainly from the decomposition of the carbonates, attains its highest concentration after the first third of the reaction time. An apparatus for further formation of CH_4 converts only part of the liberated CO_2. A reaction on the already reduced catalyst thus results and leads to a loss of activity at reduction temperatures. 14 tables and graphs.

2960. ———. [Preparation of Iron Oxide for Iron Catalysts.] FIAT Reel K–29, 1939, frames 6,926–6,929; PB 70,218; TOM Reel 296.

Different electrical smelting processes for the preparation of nonconducting Fe oxide for catalysts are considered. Nothing different from the usual process is given. 1 drawing.

2961. ———. [Preparation of Catalysts With a High Cobalt Density.] FIAT Reel K–29, 1939, frames 6,968–6,972; PB 70,218; TOM Reel 296.

Directions are given for the preparation of new catalysts with a high Co density, which are supposed to give an especially good yield of paraffin.

2962. ———. [Cause of Cobalt Losses in Synthesis Installation.] FIAT Reel K–29, 1939, frames 6,981–6,986; PB 70,218; TOM Reel 296.

Sources of Co losses up to the present time in a synthesis installation are summarized. Their extent is determined in particular.

2963. ———. [Tests on the Precipitation of Cobalt Catalysts.] FIAT Reel K–29, no date, frames 6,991–6,994; PB 70,218; TOM Reel 296.

Description of tests on the precipitation of Co for the preparation of Co catalysts with kieselguhr as carrier material and with the use of a mixture of gaseous NH_3 and CO_2 for the precipitation instead of the usual Na_2CO_3. It is demonstrated that useful catalysts also can be prepared in this manner.

2964. ———. [Testing of Catalysts Under Pressure.] FIAT Reel K–29, 1940, frames 7,355–7,363; PB 70,218; TOM Reel 296.

In order to find the reaction of catalysts in the synthesis of gasoline under the conditions of operation on a large technical scale, a catalyst, which proved to be highly active in the laboratory test, has been examined in an assay furnace. The qualitative results of this test were confirmed. 2 diagrams.

2965. ———. [Synthesis of Light Hydrocarbons.] FIAT Reel K–30, Feb. 15, 1939, frames 7,593–7,595; PB 73,587; TOM Reel 297.

Brief report of an experiment to produce light hydrocarbons, particularly C_2H_4 and C_3H_6, from synthesis gas in a catalytic furnace having a small layer column. Up to 3.5% C_2H_4 could be detected in the end gas, which is nearly 20–25% of the amount of hydrocarbons produced.

2966. ———. [Gasoline Synthesis According to Fischer-Tropsch, Ruhrchemie, Oberhausen.] FIAT Reel L–2, no date, frames 1–559; FIAT Reel L–3, no date, frames 560–1,198; PB 70,156.

Film contains a collection of drawings of the entire Fischer-Tropsch plant.

2967. ———. [Drawings for Plant "F" of Ruhrchemie, Oberhausen-Holten.] FIAT Reel L–4, 1943–44, frames 1,199–1,397; PB 70,158.

Plant probably is used for production of synthetic gasoline. Drawings of several construction firms are presented.

2968. ———. [Synthetic Production of Wax Acids and Emulsifiers and Their Utilization.] FIAT Reel L–5, Feb. 16, 1943, frames 55–95; PB 70,159; TOM Reel, 299.

Report presents a survey on the wax acids and emulsifiers from products of the Fischer-Tropsch gasoline synthesis and on their utilization. The preparation of fully synthetic wax acids from synthetic paraffins has been achieved. Special consideration is given to the OP4, OP5, and OP32 acids produced by Ruhrchemie. From these wax acids the 3 emulsifiers FP 2035, 1025, and 1325 were developed. These serve to produce pastelike and liquid emulsions, respectively. The possibilities for the technical utilization of wax acids are commented on; they serve for instance for the production of high-melting lubricating greases and oils and as emulsifiers for shoe polish, etc. Wax acids and emulsifiers also can be utilized in the leather industries.

2969. ———. [Paraffin Synthesis on Iron Catalyst.] FIAT Reel L–5, Sept. 10, 1941, frames 96–108; PB 70,159; TOM Reel 299.

Paraffin synthesis was carried out with water gas ($CO:H_2=1.25$) in circulation on an Fe catalyst (100 Fe : 10 CaO : 5 Cu : 150 kieselguhr). This catalyst had been precipitated with KOH and had the highest kieselguhr content attained so far. The long duration test, 124 days at 247° and 20 atm., produced a yield of 134.6 gm. per $m.^3$ including gasoil and a $CO+H_2$ conversion of 75%. In contrast to previous tests a white crude paraffin, free of any catalyst particles was obtained. The long life of the catalyst is worthy of note.

2970. ———. [Wet Method for Paraffin Synthesis With Cobalt Catalyst.] FIAT Reel L–5, Sept. 6, 1941, frames 115–117; PB 70,159; TOM Reel 299.

Furnace was charged with a crushed Co catalyst mixture and oil condensate plus crude paraffin, m. p. 120°–320°. The temperature during the first few days of operation ranged 180°–190°. The yields obtained were not satisfactory. At 208°, the yield declined and was stabilized at about 60%. Compared with the normal dry synthesis, the wet synthesis does not offer any advantage.

2971. ———. [Olefin Synthesis by Water-Gas Circulation on Cobalt-Mixture Catalyst.] FIAT Reel L–5, Apr. 29, 1941, frames 118–135; PB 70,159; TOM Reel 299.

Synthesis operation was carried out in a double-tube furnace to obtain products with a high % of olefins. According to calculations, 1 $m.^3$ of water gas was needed to circulate for each 10 $m.^3$ of Co catalyst mixture; however, the quantity had to be increased to 1.2 $m.^3$ during the operation. The results of the synthesis, as obtained under normal conditions in a range of temperature 190°–225°, a gas pressure of 7 atm., and a catalyst life of 6 mo., are as follows: $CO+H_2$ conversion 63%; yield of liquid products 88–90 gm. per $m.^3$ of water gas; 52 wt. % benzine; 25, oil; 17, soft paraffin; 6, hard paraffin; olefins in benzine, 58–60 vol. % and in oil 42 vol. %.

2972. ———. [Paraffin Synthesis With Iron Catalyst.] FIAT Reel L–5, March 3, 1941, frames 136–143; PB 70,159; TOM Reel 299.

Summary of research development work performed in connection with the paraffin synthesis with Fe catalyst based on the general experience of all research laboratories. The following catalyst is recommended: 100 Fe : 5 Cu : 10CaO : 150 kieselguhr precipitated with KOH. The method for preparing the catalyst is given. The synthesis is performed at 15–20 atm. pressure and a temperature of 225°–250°, with circulation of water gas, a constant ratio of $CO:H_2$, and with operation in 2 or more steps. With this catalyst a 67% conversion is possible with yields of 129 gm. per $m.^3$ of synthesis gas and with 60–70% of the liquid product as pure-white paraffin.

2973. ———. [Recycle Method of Gasoline Synthesis.] FIAT Reel L–5, Feb. 19, 1941, frames 145–147; PB 70,159; TOM Reel 299.

End gas from the synthesis operation is mixed with fresh gas, and the mixture is charged into the converter. This recycle method insures the utilization of every particle of CO and H_2.

2974. ———. [Duration Test for the Olefin Synthesis in a Double Tube Furnace With a Cobalt Catalyst.] FIAT Reel L–5, Aug. 31, 1943, frames 157–172; PB 70,159; TOM Reel 299.

Test of 6 mo. duration with water gas recycle under 7 atm. pressure was carried out in a 4-m. double-tube

furnace with Co catalyst mixture. The average charge on the furnace during the test amounted to 1,190 m.³ of water gas. With the aging of the catalyst, its converting capacity was greatly reduced, in spite of a decrease of charge and an increase of temperature. The results of the tests are shown in several tables.

2975. ———. [Test With a Paraffin-Forming Iron Catalyst.] FIAT Reel L–5, Aug. 20, 1943, frames 173–183; PB 70,159; TOM Reel 299.

Paraffin-forming Fe catalyst (100 Fe, 5 Cu, 10 CaO, 150 kieselguhr), the reduction of which had been started at the factory, was examined. The test was carried out in a 4.5–m. double-tube furnace with water-gas recirculation. The yield, which was considered to be satisfactory, amounted to 120 gm. of liquid product per m.³ of useful gas, including gasol, and with a gas conversion of 70%. An intermediate extraction to attain the original high generation of paraffin did not have the desired result.

2976. ———. [Paraffin Synthesis With an Iron Catalyst.] FIAT Reel L–5, July 1943, frames 184–190; PB 70,159; TOM Reel 299.

Paraffin synthesis was carried out in a double-tube, 4.5–m. furnace with a filament grain (Fadenkorn) Fe catalyst; no details. This catalyst is very well suited for the paraffin synthesis with circulation of the useful gas. In order to maintain the desired conversion of $CO+H_2$ at about 70%, the temperature had to be raised from an initial 225° to about 245° after 45 days. The yield of liquid products plus gasol was then about 124 gm. per N m.³ of useful gas, of which 50–60% was paraffin. The average H_2: CO consumption ratio for this period was 1.26 corresponding virtually to the H_2: CO ratio in the water gas. A pressure of 20 atm. was maintained throughout.

2977. ———. [Water-Gas Circulation Test Over Iron Catalyst.] FIAT Reel L–5, July 25, 1942, frames 201–221; PB 70,159; TOM Reel 299.

Test was carried out with water-gas circulation in a Lamella furnace with a filament-grain Fe catalyst. The test was run for 140 operating days. From the values obtained it is plainly revealed that shortening the operating time of the Fe catalyst would produce the highest yields of hard paraffins. The test justifies the conclusion that the Fe catalyst can be effectively used for 3 months if a double-tube furnace is employed.

2978. ———. [Influence of a Variable H_2: CO Ratio in the Synthesis Gas on the Medium-Pressure Synthesis.] FIAT Reel L–5, Mar. 20, 1942, frames 222–232; PB 70,159; TOM Reel 299.

Object of this test was to determine whether, in the medium pressure synthesis, reactions different from those obtained under normal operating conditions would result from a constant change at regular intervals of the H_2: CO ratio in the synthesis gas. As a result of the tests, no disadvantages, which might have been caused by the constantly recurring change in the proportional share of H_2: CO from 1.75 to 2.25 in the synthesis gas at regular 6-hr. intervals, were observed. The conversion was slightly increased by this change and resulted in a corresponding increase in the yield. The constant change in the H_2: CO ratio does not allow a definite balance of reaction and thus prevents certain fatigue symptoms.

2979. ———. [Production of Aviation Gasoline.] FIAT Reel L–5, June 17, 1941, frames 242–268; PB 70,159; TOM Reel 299.

Properties required in an aviation gasoline are discussed, and the operating procedure for its production from the products of the Fischer-Tropsch synthesis is presented. There are 2 principal groups of substances to be used as base materials: The C_4 and C_5 hydrocarbons and those constitutents boiling above 200°. The latter are cracked in a plant especially developed by Ruhrchemie, while the primarily produced straight chain unsaturated C_4–C_5 hydrocarbons are isomerized into the corresponding branched hydrocarbons. These have the same qualities as the C_4–C_5 hydrocarbons obtained from the catalytic cracking. From these products a pure aliphatic aviation gasoline of high quality is obtained by polymerization and distillation.

2980. ———. [Properties of the Primary Products From Thorium and Magnesium–Thorium Catalysts.] FIAT Reel L–5, July 29, 1938, frames 423–451; June 17, 1938, frames 452–456; PB 70,159; TOM Reel 299.

Comparative survey of the results obtained from the examination of primary products from the above 2 catalysts when applied in single furnaces and in furnaces under ordinary working plant conditions, respectively. The gasolines produced in the single furnace from Mg–Th catalysts differ in no way from those obtained in actual plant operation. Any variations noted in the olefin content of the gasoline hydrocarbons are irrelevant. There is a definite relation between the boiling point and the octane number of the gasolines. A large amount of tabular data is presented.

2981. ———. [Hydrogenation of Carbon Monoxide at Normal Pressure With Addition of Acetylene or of Acetylene and Ethylene.] FIAT Reel L–5, 1942, frames 536–543; PB 70,159; TOM Reel 299.

Tests revealed that with the addition of C_2H_2 and C_2H_4 at normal pressure a highly olefinic product can be obtained in a comparatively simple manner. A further advantage is that the apparatus used in the normal pressure synthesis needs no alteration for this method.

2982. ———. [Hydrogenation of Carbon Monoxide by Addition of Acetylene in the Liquid Phase Under Pressure.] FIAT Reel L–5, Oct. 7, 1941, frames 565–567; PB 70,159; TOM Reel 299.

In the tests carried out under pressure in the liquid phase, heptane was used as the base material. It was ascertained that low-uressure hydrogenation of CO by addition of C_2H_2 in the liquid phase is not favorable for the production of unsaturated O–containing compounds. Comparative tests carried out under analogous conditions but with the addition of C_2H_2 in the gas phase show a considerable decline of the olefinic constituents in the gasolines thus produced.

2983. ———. [Fischer-Tropsch Plant.] FIAT Reel AA–77, Oct. 12, 1945, frames 1–135; PB 70,267; TOM Reel 281.

Report is a comprehensive description, in both German and English, of the Ruhrchemie Fischer–Tropsch plant and equipment, with flow sheets and plant diagrams. The following operations are described: Water-gas production, including feed-water purification and recooling; the synthesis plant, including desulfurizing of synthesis gas, H_2 production (CO conversion), and low-pressure and medium-pressure synthesis; condensation plant and operation; adsorption by active C; working up and stabilization of primary products; paraffin production; the alkazid process for production of CO_2 from residual gas; lubricating-oil production; and Oxo synthesis with flow sheet. Estimates are made of plant damage and time necessary to place the separate units in operation.

RUKA, R. *See* abs. **1284.**

2984. RUMFORD, F. Correlation of Adsorption and Catalytic Activity. I. Hydrogen Adsorption on Zinc-Chromium Catalysts. Jour. Roy. Tech. Coll. (Glasgow), vol. 4, 1939, pp. 427–440; Chem. Abs., 33, 1939, p. 5269.

Relation between catalytic activity and activated adsorption was investigated, but results are inconclusive. ZnO suspensions were mixed with chromic acid solution, dried at a temperature below 110°, and

screened to 10–40 mesh. Catalysts were reduced by CH_3OH vapor in the presence of airfree N_2. The method of operation was to introduce into the catalyst bulb a known weight of catalyst, approximately 5 cc in volume. The whole system then was closed, the apparatus evacuated, and the catalyst temperature raised to 500°. H_2 then was admitted to atmospheric pressure level and left for 15 min.; after this, the gas was removed again, and the catalyst was maintained at the lowest possible pressure for another 15 min. H_2 was then removed and the catalyst cooled to the desired temperature. H_2 gas for test then was admitted in 3 portions; this brought the pressure to levels of 250, 500, and 760 mm. of Hg, respectively. After each addition, the adsorption was continued for 20 min. The quantities of gas adsorbed varied 0.5–2.0 cc. By use of the method previously outlined, a series of adsorptions at 300°–500°, with 50° intervals was made. Plotting the results shows the catalysts fall into 2 classes—first, those in which a definite type of activated adsorption appears 300°–350°, and second, those in which a somewhat less definite change appears some 50° higher. Use of these measurements in calculating heats of adsorption or of activation are disappointing. The effect of CO on the mechanism of adsorption is not known.

2985. ———. Correlation of Adsorption and Catalytic Activity. II. Carbon Monoxide and Hydrogen Adsorption on Zinc–Chromium Catalysts. Jour. Roy. Tech. Coll. (Glasgow), vol. 4, 1940, pp. 643–649; Chem. Abs., vol. 34, 1940, pp. 4971–4972.

In 2 series of experiments, one at 300°, 360°, and 400° and the other at 360°, adsorption of CO on Zn–Cr catalyst decreased with increasing Zn content of the catalyst until the catalyst contained approximately 80 at. % Zn, then it passed through a maximum at approximately 85–88 at. % Zn. Adsorption of H_2 passed through a maximum at 60 at. % Zn in the first series, but, in the second series of experiments, the maximum was not determined, because values were obtained only with catalysts up to 78 at. % Zn content. In the decomposition of MeOH over Zn–Cr catalyst at 360°, each of 2 series of experiments showed a maximum decomposition with catalyst containing approximately 65 at. % Zn. Since approximately an equal number of molecules of H_2 and CO are adsorbed on catalysts, both series, containing 60–67 at. % Zn, which includes the catalyst composition corresponding to greatest MeOH decomposition, reaction is possibly greatest when the H_2 and CO are adsorbed in equal molecular quantities and less when one of the gases is adsorbed in excess. However, this does not explain why MeOH decomposition did not approach zero when adsorption of CO became zero in one series of results with a catalyst containing approximately 77 at. % Zn.

RUNTSO, A. P. *See* abs. **849.**

RUPING, H. *See* abs. **1402.**

RUPP, J. *See* abs. **1782.**

2986. RUPRECHT, P. [Japan Plant.] Oel u. Kohle, Erdoel Teer, vol. 14, 1938, pp. 83–85.

In an attempt to create independence from imported oil, a Fischer-Tropsch plant was completed in 1932 at Fushun with an output of 100,000,000 l. per year, and another will be completed in 1938 at Kyushu by the Mitsui Mining Co. with an output of 50,000,000 l. per year.

RUSCHENBURG, E. *See* abs. **1955.**

2987. RUSHTON, J. H. Liquid Fuels From Natural Gas. Am. Gas Jour., vol. 168, No. 3, 1948, p. 38.

Possibilities of producing liquid fuels from natural gas are outlined. There are enough reserves of natural gas in the southwest United States and southern California to support the operation of about 30 plants devoted to the synthetic production of fuels for approximately 140 years. Their daily production would be about 250,000 bbl.

———. *See* abs. **742.**

2988. RUSHTON, J. H., AND STEVENSON, E. P. Developments in Oxygen Production. Chem. Eng. Progress, vol. 1, No. 2, 1947; Trans. Am. Inst. Chem. Eng., vol. 43, 1947, pp. 61–69; Chem. Abs., vol. 41, 1947, p. 2213.

Rushton and Stevenson review process considerations, the low-pressure processes, the 1,000 cu. ft. per hr. unit, the low-pressure plants, the high-pressure processes including the Keyes unit, the Le Rouget process, and other high-pressure plants; equipment developments in terms of lightweight, high-speed reciprocating and rotary compressors, interchange and fractionating equipment, columns and packing, and the purification of the gases from H_2O and CO_2.

RUSOV, M. T. *See* abs. **2913.**

2989. RUSSELL, R. P. Costs of Fischer-Tropsch Gasoline. Oil Gas Jour., vol. 43, No. 27, 1944, p. 95; Am. Gas Assoc. Monthly, vol. 26, 1944, pp. 87–92; Chem. Abs., vol. 38, 1944, p. 1861.

Figures given before Senate subcommittee on war minerals. The cost of gasoline from coal by hydrogenation ranges from $0.155 in large (30,000 bbl. per day) plants to $0.226 in small (3,000–bbl.) units, using coal at $2.75 per ton. The Fischer process using coal gives gasoline for $0.192 per gal., with natural gas as the charging stock, $0.088. If suitable development is carried out, this synthesis will make gasoline for $0.048 per gal. or about equal that of petroleum gasoline.

2990. ———. Industrial Research and Its Importance to the South. Advisory Council, Southern Research Inst. Rept., 1946, 16 pp.

Paper presented at the annual meeting, Birmingham, Ala. In discussing the conversion of natural gas and coal into liquid fuels, it is remarked that the reason for placing so much emphasis on this field of research and development basically is not due to any fear of future oil shortage but to the cost of finding and producing oil. It has been stated that the oil industry expects to have as large proved reserves of crude oil in this country 20 yr. from now as it has today. In consequence of new developments demonstrated in large-scale pilot-plant operations, conversion of natural gas to gasoline already appears to be competitive with production of gasoline from petroleum. Largely because of the additional plant facilities required, the production cost of synthetic gasoline from coal is today slightly higher than the cost of gasoline from crude oil. For example, a plant to produce about 9,000 bbl. gasoline per day from coal, together with about 1,800 bbl. of diesel fuel or gas oil, would cost about $42,000,000. Sale of the nearly 40,000,000 cu. ft. per day of high-calorific-value gas at about $0.25 per 1,000 cu. ft. and allowance of suitable credit for the diesel oil and certain chemicals produced would give a final cost of gasoline from this plant, with coal at $2.50 per ton, of approximately $0.0725 per gal.; this figure does not include any return on the added investment cost of the plant. Even with a fair return on the greater investment, the average additional cost of synthetic gasoline to the American motorist should not exceed $0.10 per day. These new advances in the production of synthetic liquid fuels have been made possible by the development of fluid catalytic cracking. (*See* abs. **2344.**)

2991. ———. Petroleum Industry in 1946. Chem. Eng. News, vol. 25, 1947, pp. 86–87.

Survey of the trend in petroleum research and development. Considerable notice is given to the eco-

nomic possibilities of the new developments in this country in the Fischer-Tropsch process as exemplified by the Hydrocol process with some further intimations of the process characteristics.

2992. ———. Progress in Petroleum Research. Engineer, vol. 183, 1947, pp. 490–492, 508–509; Jour. Inst. Petrol., vol. 33, 1947, pp. 391–409; Petroleum, vol. 10, 1947, pp. 151–154, 186–189, 194; Petrol. Times, vol. 51, 1947, pp. 706–709, 749–751.

Abridgment of the second Cadman Memorial Lecture. It discusses the problem of the upward trend in the world demand for liquid fuels and the development of chemical methods for increasing the supply. Two chief processes are discussed: Fluid catalytic cracking and hydrocarbon synthesis. Comparative costs on the basis of a 420,000-ton-per-day synthesis plant utilizing natural gas as raw material at 3 d. per 100 cu. ft. are 3.9 d. per imperial gal. for synthetic gasoline and 5.7 d. for the same quality gasoline from a typical crude petroleum. Because of the added plant cost required, the production cost of synthetic gasoline from coal is slightly higher than the cost from crude oil. Taking the same size plant as above and allowing suitable credit for the gas and chemicals produced, with coal at 10 s. per ton, gasoline could be produced at 6.5 d. per imperial gal., a figure only slightly higher than that for gasoline from crude oil. The above estimates are all based on United States costs and prices.

RUSSELL, W. W. *See* abs. **2335a.**

2993. RUSSELL, W. W., AND MILLER, G. H. Catalytic Hydrogenation of Carbon Dioxide to Higher Hydrocarbons. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 2446–2454.

Study was made of several types of Cu–activated, Co catalysts for the synthesis of higher hydrocarbons from CO_2 and H_2 at atmospheric pressure and in temperature range 175°–300°. Catalysts containing no alkali produced no liquid hydrocarbons or only traces but yielded small amounts after suitable poisoning. Alkalizing with K carbonate or phosphate, was necessary in order to produce catalysts active for liquid hydrocarbon synthesis and it appears that the alkali can act as a selective poison for CH_4-forming catalyst centers. Small additions of Ce oxides to the alkalized catalysts were very effective in increasing synthesis life and catalyst stability. Although an alkalized, Ce-containing catalyst supported on a natural kieselguhr produced only CH_4, when a flux-calcined kieselguhr was substituted as a support, a catalyst was obtained that synthesized nearly as much liquid hydrocarbons as unsupported catalysts of about the same composition. The optimum synthesis temperature was near 225°, but it depended on catalyst composition and activity. Raising synthesis temperature some 25°–100° for several hours produced a selective poisoning of catalyst hydrogenation centers, which caused a marked increase in liquid hydrocarbon formation upon resumption of synthesis at the initial temperature. While the CO theoretically available from the water gas reaction is in all cases ample to account for all of the higher hydrocarbons formed, it is entirely inadequate to account also for the amounts of CH_4 formed. The maximum liquid hydrocarbon yield obtained was 95 ml. per $m.^3$ of CO_2 passed and was accompanied by 360 l. of gaseous hydrocarbons. The apparent activation energy for the overall synthesis was found to be 23.1 kcal.

2994. RUSSELL, W. W., AND TAYLOR, H. S. Promoter Action of Thoria on Nickel Catalysts. Jour. Phys. Chem., vol. 29, 1925, pp. 1325–1341; Chem. Abs., vol. 20, 1926, p. 325.

Reaction $CO_2+4H_2=CH_4+2H_2O$ is a surface reaction strongly affected by the adsorbing power of the catalyst surface for the reactant. The activity of Ni alone as catalyst, either supported or unsupported, is greater the lower the temperature at which the Ni was reduced, presumably because the number of highly unsaturated Ni atoms per vol. of catalyst is greater the lower the temperature of reduction. Heating a catalyst above the temperature at which it was reduced markedly reduces its activity, because the increase in the mobility of the atoms with temperatures brings about the coalescence of the unsaturated atoms with loss of effective adsorptive power. The primary function of ThO_2 as promoter with supported Ni catalysts is to make possible the existence of a greater number of Ni atoms of a highly unsaturated character per unit of catalyst, through the creation of ThO_2–Ni interfaces. With unsupported Ni catalysts, ThO_2 may function as promoter (*a*) by the creation of a more active surface through the above interface mechanism, (*b*) by an increase in the extent of surface, inasmuch as the promoter acts as a support, and (*c*) by a favorable alteration in the ratio in which the reacting substances, and possibly the products, are adsorbed. The activation of Ni by Th may be so extensive that the speed of reduction of CO_2 by H_2 to CH_4 is increased 10-fold. This may be due to the increase in surface area and the adsorption ability of this type of Ni catalyst. The conclusions are based on the results of both adsorption and reaction-velocity measurements on samples of promoted and unpromoted, supported and unsupported Ni catalysts.

2995. RUTHERFORD, R. W. Oil From Coal in Japan. Colliery Eng., vol. 21, 1944, pp. 40–42.

Brief review of industrial progress in hydrogenation of coal and Fischer synthesis for obtaining oils. Information is given on about 15 companies that are entering the coal-to-oil industry.

2996. RUTHRUFF, R. F. Petroleum: Basic Raw Material for Surface Coatings. Petrol. Processing, vol. 3, No. 1, 1948, pp. 21–24.

Various potentialities are presented for obtaining from both gaseous and liquid hydrocarbons the intermediates for representative polyhydric alcohol-polycarboxylic acid resins. The preparation of phthalic anhydride, intermediate for alkyd resins, from *o*–xylene secured by the aromatization of paraffinic naphthas is already relieving an acute shortage of naphthalene, formerly the principal charging stock for phthalic anhydride manufacture. Possibilities are seen and discussed for synthesizing drying or semidrying oil fatty acids from a synthetic petroleum oil produced by the Fischer-Tropsch synthesis.

2997. RYAN, P. Synthol Process. Oil Gas Jour., vol. 43, No. 47, 1945, pp. 264, 267, 268; Nat. Petrol. News, vol. 37, No. 14, 1945, pp. 36, 38; Gas Age, vol. 95, No. 10, 1945, pp. 18–19, 54, 56; Chem. Products, vol. 8, Nos. 11–12, 1945, pp. 86–88; Chem. Inds., vol. 56, 1945, p. 783; Petrol. Refiner, vol. 24, No. 4, 1945, pp. 130–136; Gas, vol. 21, No. 7, 1945, p. 30; Chem. Abs., vol. 39, 1945, p. 4218.

Process as developed by the M. W. Kellogg Co. is discussed from the point of view of its economic possibility when operated in conjunction with a petroleum refinery having available large reserves of natural gas and contiguous to low-cost transportation facilities. This process will produce motor gasoline, 75 clear octane CFR–M, for approximately $0.05 per gal., including 10% depreciation, from natural gas valued at $0.05 per 1,000 cu. ft. It is calculated that such a plant would pay out in about 8 yr., and in about 3 yr. if combined with a chemical plant for manufacture of hydrocarbons other than gasoline and of oxygenated chemical compounds. Approximately 11,000 cu. ft. of natural gas are required to produce 1 bbl. of liquid hydrocarbons.

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2998. SABALITSCHKA, T., AND HARNISCH, C. [Synthesis of Formaldehyde and Acetone From Oxides of Carbon and Hydrogen or Water Through Contact Substances.] Biochem. Ztschr., vol. 190, 1927, pp. 265–277; Chem. Abs., vol. 22, 1928, p. 1571.

Presence of demonstrable quantities of HCHO and Me_2CO in a mixture of CO and H_2, or CO_2 and H_2O at 300° in the presence of a great variety of contact substances (Ca_2C, SiO_2, kaolin, Fe, NaOH, wood charcoal, active C, etc.) is discussed. Data are presented in tabular form.

2999. SABATIER, P. Inversion of Reactions in Catalysis. Chem. and Ind., vol. 46, 1927, pp. 681–683, 702–705; Chem. Abs., vol. 22, 1928, p. 1085.

Ni catalysts generally are too active in the reduction of water gas to MeOH, the reduction going right to the CH_4 stage. Metallic oxides lead to the formation of primary and secondary alcohols. The use of high pressures stabilizes the MeOH and methyl aldehyde.

3000. SABATIER, P., AND MAILHE, A. [Catalytic Decomposition of Formic Acid.] Compt. rend., vol. 152, 1911, pp. 1212–1215; Chem. Abs., vol. 6, 1912, p. 619.

HCO_2H vapors were passed over 0.5 m. of the catalyzer at the rate of about 0.27 gm. per min. The following catalyzers decompose the acid almost exclusively into CO_2 and H_2: Pd sponge, action begins at 110° and at 245° decomposition is virtually complete; Pt sponge, begins 120°, complete 215°; reduced Cu produces 278 $cm.^3$ gas per min. at 190°; Ni, 290 $cm.^3$ at 280°; Cd, 325 $cm.^3$ at 280°; SnO begins above 150° and gives 172 $cm.^3$ gas at 285°; ZnO begins about 190° and gives 192 $cm.^3$ gas at 230°. TiO_2 and W_2O_5 (blue) decompose the acid exclusively into CO and H_2O above 170°. The same decomposition is produced by SiO_2, ZrO_2, Al_2O_3 and UO_2, but at the same time CO_2 is formed without H_2, indicating the decomposition of the acid into HCHO, CO_2, and H_2O; with Al_2O_3, the gas at 235° contains 6% CO_2; with UO_2 at 230°, 14% CO_2. Some catalyzers effect all 3 of the above decompositions. Thus, ThO_2 at 250° yields HCHO and a gas containing 75% (by vol.) of CO, 15% of CO_2, and 10% of H_2; at 320° the % of CO_2 increases to 45, and the condensed liquid contains $CH_2(OMe)_2$ (owing to the formation of MeOH from HCO_2H and HCHO); as the temperature is raised, the amount of MeOH formed increases; and, as the HCHO is then partly decomposed into CO and H_2, the % of the latter increases and that of CO_2 decreases. At 375°, the gas contains only 35% of CO_2. The blue Mo_2O_5, CaO, FeO, and Jena glass produce chiefly the decomposition into CO_2 and H_2; ordinary white glass brings about this decomposition and that into CO and H_2O to about the same extent; the latter is predominant, with pulverized pumice, MgO, light wood charcoal, CrO_3, V_2O_3, MnO, and BeO. These facts indicate that the action of the catalyzers cannot consist simply in lowering the temperature of reactions, which would take place without them; their chemical nature comes into play.

3001. SABATIER, P., AND SENDERENS, J. B. [Direct Hydrogenation of Oxides of Carbon in Presence of Various Finely Divided Metals.] Compt. rend., vol. 134, 1902, pp. 689–691; Bull. soc. chim., vol. 29, III, 1903, p. 294; Jour. Chem. Soc., vol. 82, II, 1902, p. 317.

Although CO is converted completely into CH_4 by H_2 in the presence of finely divided Ni at 250°, at 280° another reaction becomes obvious, the formation of CO_2 and finely divided C. Thus, at 280°, CO and H_2 (1:3) yield a gaseous mixture, which consists of CO_2, 10.5; CH_4, 67.9; H_2, 21.6%; whereas, when equal volumes of CO and H_2 (water gas) are used, 52.5% CO_2, 39.8 CH_4, 7.1 H_2, and 0.6 CO are formed. Co resembles Ni in its action on mixtures of CO_2 and H_2 and on CO and H_2 but is less energetic; the reduction of CO_2 begins at 300° and is rapid at 360°–400°; no formation of C or CO and no oxidation of the metal occur. CO begins to be reduced at 270°, but at 300° the formation of CO_2 and C also is noticeable; the latter reaction plays a more prominent part the higher the temperature and the greater the proportion of CO in the mixture of this gas and H_2, that is led over the Co. Pt sponge and Pt black, Pd sponge and reduced Fe do not bring about reduction of the oxides of C. Reduced Cu converts a mixture of H_2 and CO_2 into CO and H_2O at 430°.

3002. ———. [New Synthesis of Methane.] Compt. rend., vol. 134, 1902, pp. 514–516; Jour. Chem. Soc., vol. 82, I, 1902, p. 333.

When a mixture of CO and H_2 (1:3 vol.) is passed over reduced Ni at 250°, the 2 gases are converted completely into CH_4 and H_2O. CO_2 and H_2 react similarly in the presence of reduced Ni at a somewhat higher temperature yielding only CH_4 and H_2O.

3003. ———. [Synthesis of Varieties of Petroleum. Contribution to the Theory of Formation of Natural Petroleum.] Compt. rend., vol. 134, 1902, pp. 1185–1188; Jour. Soc. Chem. Ind. (Japan), vol. 21, 1902, p. 853.

When H_2 and C_2H_2 are passed over reduced Ni below 180° C., the liquid obtained consists almost entirely of paraffin hydrocarbons.

3004. ———. [Decarbonization of Carbon Monoxide.] Bull. soc. chim., vol. 29, No. 3, 1903, p. 294.

Decomposition of CO in presence of Ni begins at 230° and increases rapidly to 349°, at which point decomposition is complete.

3005. ———. [General Methods of Hydrogenation and of Molecular Reactions Based on the Use of Finely Divided Metals. I. II. Molecular Decomposition and Condensations.] Jour. Chem. Soc., vol. 88, 1905, I, pp. 333, 401; Ann. chim. phys., vol. 4, No. 8, 1905, pp. 319–432, 433–488.

General discussion of the mechanism of the action of metals in a finely divided condition on various classes of organic compounds. The catalytic action of Ni, Co, Pt, Pd, Cu, and Fe upon mixtures of CO and H_2 has been investigated at different temperatures and under a variety of conditions. The results show that, in the case of the hydrogenation of CO in the presence of finely divided Ni, the reaction $CO+3\ H_2 = CH_4+H_2O$ begins at 180°–200° and proceeds rapidly and without complications at 230°–250°. If care is taken that the temperature of 250° is not exceeded, the Ni is not impaired and retains its activity over long periods of time. By maintaining the volumetric relations of $CO : H_2 = 1 : 3$, the reaction is virtually complete and yields almost pure CH_4. The action of Co is similar to that of Ni but requires a higher temperature, whereas only negative results are obtained with Pt, Pd, Cu, and Fe. It is found that the passage of the vapors of primary and secondary alcohols over heated finely divided Cu is a convenient method of preparing the corresponding aldehydes and ketones.

3006. SABEL, —. [Ten Years of Oxygen Gasification at Leuna.] BIOS Final Rept. 199, 1945, 32 pp.; PB 67,541; TOM Reel 227.

Comprehensive coverage of experimental and operating data from 1929–43 on the production of water gas in Winkler generators by O_2 gasification of various type fuels. The development of the process is traced, and the reaction mechanism and the technical principles of O_2 gasification are discussed at length. Fuels for the process are analyzed and it is compared with the make-and-blow process.

3007. SABLATNÖG, A. [Purification of Synthesis Gases.] Österr. Chem.-Ztg., vol. 51, 1950, pp. 198–201, 220–223, 242–244; Chem. Abs., vol. 45, 1951, p. 4022.

In cleaning water gas for use in the Fischer-Tropsch synthesis, investigation was made of various purification masses to remove the so-called condensates that passed the usual purifiers and were present in the gas in a concentration of about 1 gm. per m.^{3} The mode of origin, the thermal stability, and the constituents of the condensates are discussed. The water-gas process of Koppers and Didier-Bubiag is described, and it is shown that the amount and composition of the condensates vary widely according to the process used, when the same brown coal was used for gasification. Four purification masses were investigated: (1) A mixture of Fe oxide and Na_2CO_3—this mixture does not remove all organic S compounds; thiophenes especially pass almost undecomposed, and gum-forming hydrocarbons always occur in the gas. (2) Active C—complete removal of gum formers and H_2S could be obtained and the organic S content was down to 0.01 gm. per m.^{3} synthesis gas. The method, however, was objectionable because the active C must be regenerated with a loss of absorption power after each regeneration. (3) Granular coke from brown coal—this cheap material almost equaled active C in purification power, but the service time was very short, so that replacements were often necessary. (4) Addition of finely powdered coke from brown coal to the synthesis gas—this method proved satisfactory and economical. With a gas flow of 50–100 m.^{3} per hr. the condensates with a concentration of 1 gm. per m.^{3} could be entirely removed by adding 30 gm. powdered brown coal coke per m.^{3} of gas, washed out after a contact time of 2–3 sec. The H_2S must be oxidized first by adding 1% air and then removed. The absorption temperature should not be higher than 30° if complete absorption is desired. Finally the method was tested in a large-capacity water-gas plant by using the Didier-Bubiag process. The conditions here were not so favorable as in the pilot plant. The gas had a powdered coke content of only 1–2 gm. per m.^{3}, the temp. was 50°–60°, and the contact time 1 sec. Even under these conditions the condensates concentration dropped from 1.0–1.5 gm. per m.^{3} to 0.2–0.3 gm. These residual condensates can only be removed with a higher coke-dust content, a longer contact time, and lower absorption temperature.

3008. SACHANEN, A. N. Conversion of Petroleum. Reinhold Publishing Corp., New York, 2d ed., chap. 2, 1948, pp. 172–181.

Fischer-Tropsch synthesis process and a modification of it, the Hydrocol process, are briefly summarized. The effect of certain operating variables upon the synthesis process, CO : H_2 ratio, catalysts, temperature, pressure, space velocity, and method of operation, are discussed.

———. *See* abs. **3154.**

3009. SACHS, A. P. Production of Synthetic Liquid Fuels. Combustion, vol. 13, 1925, pp. 358–360.

Brief discussion of the Badische MeOH process, the Fischer synthol process, and the Bergius process, with comments on the work of Fierz-David along the lines of the Bergius process.

SACHS, G. *See* abs. **2013, 2014.**

3010. SACHSSE, H. [Chemical Processing of Coking Gas.] Chemie-Ing. Tech., vol. 21, 1949, pp. 1–6; Chem. Abs., vol. 43, 1949, p. 3,595.

Conversion of coking gas to CO and H_2 by means of partial combustion of the main portion of CH_4 and C_2H_4 with O_2 (not air) and subsequent catalytic conversion of the remaining hydrocarbons with H_2O is discussed in detail with data and diagrams. A flow sheet for a N_2–H_2 synthesis gas is described, and a brief comparison of 4 methods for the production of synthesis gas is presented.

———. *See* abs. **149.**

3011. SACHSSE, H., AND KIENITZ, H. [Thermodynamics of Hydrocarbon Synthesis.] Ztschr. Elektrochem., vol. 53, 1949, pp. 254–257; Chem. Abs., vol. 44, 1950, p. 2358.

Summary and discussion of 15 yrs. of research on catalysts used in the synthesis of hydrocarbons from CO_2 and H_2.

SACHSZE, W. *See* abs. **1649.**

SADEK, H., AND TAYLOR, H. S. Heterogeneity of Catalyst Surfaces for Chemisorption. III. Metallic Nickel. *See* abs. **3339.**

3012. SAGE, B. H. Status of Thermodynamics in the Petroleum Industry. Ind. Eng. Chem., vol. 42, 1950, pp. 631–639; Chem. Abs., vol. 44, 1950, p. 5083.

Status of experimental and derived thermodynamic data for the pure light paraffin hydrocarbons from CH_4 through decane, and for binary mixtures of these hydrocarbons, as well as for some binary mixtures of normal C_1 to C_5 hydrocarbons with the nonhydrocarbon components, CO_2, H_2S, N_2, and H_2O is reviewed. 274 refs.

———. *See* abs. **626.**

3013. SAHASRABUDHEY, R. H., AND KALYANASUNDARAM, A. Interaction of Carbon Monoxide and Hydrogen in Silent Discharge: Production of Formaldehyde. Proc. Indian Acad. Sci., vol. 27A, No. 5, 1948, pp. 366–374; Chem. Abs., vol. 43, 1949, p. 1272.

Report of work dealing with the production of formadehyde by interaction of CO and H_2 in silent discharge at 500 cycles per sec. The absolute yield of formaldehyde was highest with an approximately equimolecular mixture of the constituent gases. An excess of either CO or H_2 appeared to affect the yield adversely. A decrease in yield was obtained at higher rates of circulation of the gases.

3014. SAITÔ, S. Saturation Value of Magnetization of Cementite. Sci. Repts. Tôhoku Imp. Univ., vol. 9, 1920, pp. 319–322; Proc. Phys. Math. Soc. Japan, vol. 2, No. 3, 1920, p. 91; Chem. Abs., vol. 15, 1921, p. 1650.

Cementite was electrolytically isolated from a steel containing 1.58% C and pressed into the form of a cylindrical rod. The density ρ was 4.35. The intensity of magnetization was measured in the field of a Du Bois electromagnet. The magnetization reached saturation in a field of over 10,000 gausses, the value found being $\sigma=I/\rho=135$ C. G. S. units. Measurements also were made on white cast Fe containing 3.75% C. From the known proportion of ferrite and cementite and from the measured saturation value of the specimen, the saturation value of cementite was calculated to be $I=955$ or $\sigma=I/\rho=135$, which is the same value as was found directly. The same measurements were made for the double carbides of Fe and W and Fe and Cr and for a number of different steels; the results are given graphically.

———. *See* abs. **1897, 1898, 1899.**

3015. SAKATA, T. [Effect of Pressure on the Catalytic Reaction Between Hydrogen and Carbon Monoxide.] Rev. Phys. Chem. Japan, vol. 19, 1945, pp. 50–66; Chem. Abs., vol. 45, 1951, p. 3681.

Synthesis of MeOH with a catalyst prepared from CrO_3 and ZnO was studied at 330°–400° in the pressure range 100–300 atm. The content of MeOH in the crude liquid product increased with pressure. A catalyst prepared from $K_2Cr_2O_7$, ZnO, and KOH was used for the synthesis of isobutanol from H_2 and CO. The

crude liquid product obtained at 300 atm. was richer in isobutanol than that at 100 atm., but the ratio isobutanol: MeOH was not affected by the pressure.

3016. SAKMIN, P. K. [Obtaining Crude Nitrogen–Hydrogen Mixtures for the Synthesis of Methanol and Ammonia.] Jour. Chem. Ind. (U. S. S. R.), vol. 13, 1936, pp. 1459–1462; Chem. Abs., vol. 31, 1937, p. 2783.

To separate coke gas at —160°, the optimum pressure is 100 atm. The gas phase then contains 94% H_2 and N_2, 2% CH_4, and 4% CO and O_2. 90% of the H_2 can be obtained for synthesis.

3017. ———. [Recovery of a Crude Nitrogen–Hydrogen Mixture for Methanol and Ammonia Synthesis by Condensation of Charkow Coke-Oven Gas at Low Temperature and High Pressure.] Brennstoff-Chem., vol. 18, 1937, pp. 69–71; Chem. Abs., vol. 31, 1937, p. 4794.

Resulting mixture, suitable for synthesis use above 1,000 atm., contains 18.4% N_2 and 74.5% H_2.

SAKON, K. *See* abs. **2413, 2425.**

3018. SALVI, G. [Synthetic Fatty Acids From Paraffin.] Riv. combustibili, vol. 2, 1948, pp. 221–230; Fuel Abs., 1949, abs. 2932.

Oxidation with air or air–O_2, generally in the presence of $KMnO_4$, was applied on a large scale in Germany for the purpose of working up the gatsch residue from the Fischer-Tropsch synthesis and low-temperature carbonization and producing useful products and artificial fatty acids. The methods are described briefly. The lower fractions, C_4–C_9, were used as plasticizers, the medium fractions, C_{10}–C_{15}, for soaps, and the higher range, C_{18}–C_{20}, for lubricants. A portion of the C_{10}–C_{18} fraction was used for manufacturing triglycerides to make up the shortage of natural fats. These artificial triglycerides with odd number of C atoms were regarded as very suitable ingredients for the diet of diabetics as they are converted to propionic acid and, finally, to CO_2 and H_2O and do not raise the acetone content of the blood above the limit of tolerance as the natural triglycerides do.

———. *See* abs. **2560.**

SALZER, F. *See* abs. **938.**

3019. SANBOUGI, K. Reduction Equilibria of Iron Oxides. I. Measurements of the Equilibria of Reaction. Sci. Repts. Tohôku Imp. Univ., ser. A, vol. 1, 1949, pp. 213–222; Chem. Abs., vol. 45, 1951, p. 6020.

Equilibria equations were derived for the following reactions: Fe_3O_4 (in wüstite) + CO = 3 FeO (in wüstite) + CO_2; Fe_3O_4 (in wüstite) + H_2 = 3 FeO (in wüstite) + H_2O; Fe_3O_4 (in wüstite) = 3 FeO (in wüstite) + ½ O_2. Calculations were given of the activities of FeO and Fe_3O_4 in wüstite at several O_2 concentrations and temperatures. Other thermodynamic calculations were made for the various equilibria in wüstite.

3020. SANDER, A. [Chemical Transformation of Methane.] Glückauf, vol. 66, 1930, pp. 89–93; Chem. Abs., vol. 24, 1930, p. 2575.

Technical and economic outlook for the transformation of CH_4 into liquid fuel by several new methods developed at the Kaiser Wilhelm Institut für Kohlenforschung, is discussed. In addition to the production of CO–H_2 mixtures for catalytic syntheses, 3 other processes are of economic importance to the welfare of Germany: 1. The thermal conversion of CH_4 into benzol and its homologs 1,000°–1,100°. 2. Conversion of CH_4 into C_2H_2 by means of electric discharges at low pressure and polymerization of the C_2H_2 to benzol over active C or silica gel at 650°–700°. 3. The first step as in 2, then the hydrogenation and condensation of the C_2H_2 in gasoline and homologs over Fe, Cu, Ni, and alkali-mixed catalysts at about 250°.

SANDFORD, F. *See* abs. **1386.**

3021. SANDONNINI, C. [Action of Acetylene on Carbon Oxides.] Gazz. chim. ital., vol. 57, 1927, pp. 781–792; Brennstoff-Chem., vol. 9, 1928, pp. 162–163; Chem. Abs., vol. 22, 1928, pp. 758–759.

Following a review of the literature, experiments are described that deal with the reactions of CO and of CO_2 and C_2H_2 in the presence of catalysts, the object of which is to aid in explaining the origin of higher hydrocarbons in the reduction of CO and of CO_2 by H_2. The gaseous mixture was passed over the catalyst at constant temperature and the compositions of the entering and issuing gases were compared.

SANDS, A. E. *See* abs. **144a.**

3022. SANDS, A. E., AND SCHMIDT, L. D. Recovery of Sulfur From Synthesis Gas. Ind. Eng. Chem., vol. 42, No. 11, 1950, pp. 2277–2287.

Review of the more important commercial processes for removing H_2S from synthesis gas made from coal. Factors that differentiate synthesis gas-purification from other gas-purification problems are discussed. The relation between S content of the coal used for synthesis-gas production and the cost of synthesis-gas purification is explored by cost estimates for gas purification and S recovery. These estimates are not to be considered precise or final but have been prepared as a basis for discussion and future revised cost estimates of a more accurate nature.

3023. SANDS, A. E., WAINWRIGHT, H. W., AND EGLESON, G. C. Organic Sulfur in Synthesis Gas—Occurrence, Determination, and Removal. Proc. Am. Gas Assoc., 1950, pp. 564–602; Bureau of Mines Rept. of Investigations 4699, 1950, 51 pp.

Progress report on the determination and removal of organic S from synthesis gas with some calculations as to the cost of S removal on a commercial basis. Laboratory studies were made of several known methods for the determination of organic S and details and modifications of the methods are presented. Among the methods investigated were the following: Referee method, Institute of Gas Technology burner method, Rogers and Baldaste method, Betz-Hellige turbidimetric method, Lusby's Pt spiral method, Huffs catalytic method, and the activated C method. In general, purification was found effective down to less than 0.1 grain of total S per 100 cu. ft. of purified gas. Tentative cost estimates of total S removal in a hypothetical plant indicate that costs would decrease from a figure of about $0.01 per 1,000 cu. ft., when the coal S content is 1%, to a cost of about $0.006 per 1,000 cu. ft., when the S content of the coal is 5%. These costs are predicated on the conditions that recovered S is credited at $18.00 per ton, less costs for conversion of H_2S to elemental S and at a plant capacity of 336,000,000 cu. ft. per day.

3024. SANDS, A. E., WAINWRIGHT, H. W., AND SCHMIDT, L. D. Purification of Synthesis Gas Produced From Pulverized Coal. Ind. Eng. Chem., vol. 40, 1948, pp. 607–620; Chem. Abs., vol. 42, 1948, p. 4330.

Production of synthesis gas directly from coal, instead of using coke as generator fuel, presents new and greater difficulties in connection with purification of the gas to render it suitable for synthesis purposes. With special reference to gas made directly from pulverized coal, this paper outlines the purification specifications for Fischer-Tropsch synthesis gas, some of the established purification processes that may be used to meet these specifications, and the analytical methods that may be used to deal with the extremely low concentrations of impurities that may be tolerated in the purified gas. Bibliography of 92 refs.

3025. SANDS, A. E., GRAFINS, M. A., WAINWRIGHT, H. W., AND WILSON, M. W. Determination of Low Concentrations of Hydrogen Sulfide in Gas by the

Methylene-Blue Method. Bureau of Mines Rept. of Investigations 4547, 1949, 19 pp.

Colorimetric method has been developed for determining traces of H_2S in synthesis gas used in the Fischer-Tropsch process. The maximum concentration of S that can be tolerated to avoid poisoning of the catalyst is 0.1 grain per 100 cu. ft. The method is applicable not only to synthetic mixtures of CO–H_2 but to coke-oven gas, carburetted water gas, and blue water gas. Mercaptans, CS_2, and thiophene do not interfere with H_2S determination. The preferred absorbent for H_2S is 2% zinc acetate solution. H_2S is determined by the photoelectric or spectrophotometric measurement of the quantity of light absorbed by solutions of methylene blue produced by the reaction of H_2S with p-aminodimethylaniline sulfate. Absorption measurements are made with a Klett-Summerson photoelectric colorimeter, employing a No. 66 filter, and with a Beckman spectrophotometer at a wavelength of 745 mμ. As little as 0.001 grain of S per 100 cu. ft. can be detected by means of this test, when the volume of gas sample is 1 cu. ft. When the gas contains 0.05 grain of S as H_2S, only 1 per 10 cu. ft. of gas is required, and the result is obtained in less than 30 min.

3025a. SAPPER, W. Polymerization of Gaseous Olefins to Gasoline Hydrocarbons on Phosphoric Acid Catalysts. Erdöl u. Kohle, vol. 4, 1951, pp. 550–557; Jour. Inst. Petrol., vol. 38, 1952, p. 34 A; Chem. Abs., vol. 46, 1952, p. 1238.

Gaseous olefins and corresponding paraffins are found in cracked gases, in primary and cracked products of the Fischer-Tropsch synthesis, and in primary products of the Hydrocol process, the C_3–C_4 fraction of which consists almost completely of olefins. Polymerization processes embodying phosphoric and sulfuric acid catalysts with low temperature and pressure are used to convert such olefins to gasoline hydrocarbons. Catalytic polymerization of olefinic gases combined with procedures such as thermal cracking, Fischer-Tropsch, and the Carburol Kogasin-cracking process, give marked improvement in gasoline yields, since about 80% of the charge is convertible to high octane number product. Mechanism of reactions, effects of pressure and temperature, influence of molecular size of feed gases, and operating techniques are discussed. The following average yields were obtained on polymerization plant at 30–300 atm. with Fischer-Tropsch olefins as feed: 29% polymer gasoline, 62% propane butane, 5% polymers b. >200° and 4% gases. Polymer gasoline was blended with Fischer-Tropsch primary gasoline; propane-butane fraction was used partly as motor fuel and partly fractionated, propane being sold for domestic use, while butane was used as running-in fuel for aircraft engines. High-boiling polymers were added to Kogasin Diesel fuel, while the gases were used for heating. Differences are noted between the polymerization of naturally occurring iso–C_4 olefins and that of straight-chain synthetic Fischer-Tropsch olefins.

SARKER, J. M. *See* abs. **466.**

3026. SARTORI, G. [Adsorption of Hydrogen, Carbon Monoxide, and Carbon Dioxide on Zinc Oxide at the Temperature of Synthesis of Methyl Alcohol.] Gazz. chim. ital., vol. 67, 1937, pp. 98–104; Chem. Zentralb., 1937, II, p. 944; Chem Abs., vol. 31, 1937, p. 6077.

Adsorption of H_2 and CO on ZnO is greater at 430° than at 0°–120°. This fact is attributable in part to an activated adsorption and in part to diffusion within the catalyst. CO_2 is adsorbed to a smaller extent at 430° than at room temperature, because at 430° chemical sorption is no longer possible and because diffusion is less than for the lighter gases. Mathematical assumptions made in analyzing the phenomena were verified by the fact that the experimental results could be recalculated in a satisfactory manner with the formulas derived from them. A further confirmation perhaps is to be found in the fact that the velocity constants of adsorption are related in the same way as are the dipolar moments and diffusion constants, that is, inversely to the square roots of the molecular weights of the individual gases. The conclusions that may be drawn from these facts with respect to the catalytic synthesis of MeOH and comparisons of various catalysts will be published in a forthcoming paper.

3027. SARTORI, G., AND FANO, U. [Adsorption of Hydrogen, Carbon Dioxide, and Methanol on Zinc Oxide.] Gazz. chim. ital., vol. 67, 1937, pp. 69–85; Chem. Zentralb., 1937, II, p. 944; Chem. Abs., vol. 31, 1937, p. 6077.

Work is an extension, with an improved apparatus, of the experiments of Natta and Casazza (abs. **2386**). The adsorption isotherms of H_2, CO, CO_2, and MeOH on ZnO at 0°, 36°, 76°, 106°, and 120° were measured. The ZnO was prepared by thermal dissociation of smithsonite. Adsorption of H_2 and CO followed closely the Langmuir law, but that of CO_2 and MeOH showed deviations from this law, as a result of chemical sorption of CO_2 and capillary condensation of MeOH. The periods of permanence of the adsorbed molecules were determined. The periods for CO_2 and MeOH were much longer than for H_2 and CO, and this fact is shown to be related to the character of their adsorption isotherms. The thermal coefficients were not linear functions; this indicates that the centers of adsorption activity at different temperatures have different potentials. The calculated heats of adsorption agree with the experimental values of Taylor and Sickman (abs. **3342**). The heat of adsorption of MeOH equals the heat of condensation; this confirms the concept of capillary condensation. The kinetics of adsorption of H_2 can be derived from the equation of Langmuir. CO and CO_2 show deviations proportional to the square roots of their molecular weights, and related to the rates of diffusion in the pores of the catalyst. The kinetics of adsorption of MeOH can be derived by dividing the phenomenon into 2 phases, an instantaneous phase and an exponential phase.

3028. SARTORI, G., AND NEWITT, D. M. Influence of Pressure Upon the Water-Gas and Other Equilibria. Inst. Gas Eng., Copyright Pub. 222–92, 21 pp.; Gas World, vol. 111, 1939, pp. 414–415; Gas Jour., vol. 229, 1940, pp. 32, 81; Chem. Abs., vol. 34, 1940, p. 5337.

Effect of pressure upon the equilibrium constants of reversible gas reactions is discussed. At high pressures, the partial pressure of a reactant gas is not a true measure of its active mass, hence, even in gaseous systems in which reaction takes place with no change in density, the value of equilibrium constant K_p shows a drift with progressive changes in the total pressure. Experimental data for the water-gas reaction over a pressure range of 100 atm. are given. By replacing partial pressures by equilibrium pressures, a true constant independent of total pressure is obtained. Compressibility and other derived physical properties of reversible gaseous systems are discussed and illustrated by references to the variation of heat capacity with pressure.

3029. SASTRI, M. V. C. Theory of the Fischer-Tropsch Synthesis. Current Sci., vol. 16, 1947, pp. 4–5; British Abs., 1948, B, I, p. 95.

Review of the theory of the formation of a carbide surface and its limited reduction to long CH_2 chains, stressing the importance of the chemisorbed H_2 in the disruptive reduction of these chains to molecules of appropriate length.

———. *See* abs. **1192, 1193, 1193a, 1194.**

3029a. SASTRI, M. V. C., AND SRIKANT, H. Adsorption of Hydrogen at Elevated Pressures on a Promoted

Iron-Synthetic Ammonia Catalyst. Current Sci., vol. 19, 1950, p. 313; Chem. Abs., vol. 45, 1951, p. 9,993.

Static volumetric method for measuring adsorption of gases by solids at elevated pressures was developed, and the adsorption of H_2 on a $Fe–K_2O–Al_2O_3–TiO_2$ catalyst at temp. 50°–350° and pressures 15–50 atm. was studied. 2 distinct types of activated adsorption of H_2 were found, 1 with a maximum at about 150°, the other with a maximum at about 300°. The results indicate the superposition of adsorption on the chemisorption of the H_2.

3030. ———. Adsorption of Nitrogen at Elevated Pressures on a Promoted Iron Synthetic-Ammonia Catalyst. Current Sci., vol. 19, 1950, p. 343; Chem. Abs., vol. 45, 1951, p. 7406.

Adsorption isotherms were determined for N_2 on an $Fe–K_2O–Al_2O_3–TiO_2$ catalyst at 7 temperatures 50°–350°, and 15–50 atm. Adsorption at lower pressures (20 and 30 atm.) exhibits only 2 maxima at 150° and 300°, respectively; however, at 50 atm., 3 maxima are observed, 100°, 200°, and 300°. For an adsorption of 0.05–0.15 cc. per gm. at 20 atm., a value of 23 kcal. is obtained for the isobaric heat of adsorption.

3030a. ———. Mixed Adsorption of Hydrogen and Nitrogen at Elevated Pressures on a Promoted-Iron Synthetic-Ammonio Catalyst. Current Sci., vol. 20, 1951, pp. 15–16; Chem. Abs., vol. 45, 1951, p. 10018.

An $Fe–K_2O–Al_2O_3–TiO_2$ catalyst was used. The individual adsorption of H_2 and N_2 from a 3 : 1 mixture were determined on the same catalyst at 50°–350° and at a total gas pressure up to 50 atm. Adsorption of H_2 from the mixture increased regularly with its partial pressure at all the temperatures studied, whereas that of N_2 exhibited this regularity only at the highest temperature. In practically every case the adsorption of H_2 at a given partial pressure from the mixture was considerably higher than that from the pure gas at an equivalent pressure. Similarly, except at 203° and 300°, N_2 adsorption was increased in the presence of H_2. At 350° when the partial pressure of N_2 exceeded 7 atm., the ratio of the respective increments of N_2 and H_2 adsorption varied successively from 1 N : 1 H, through 1 N : 2 H, to finally 1 N : 3 H. These observations suggested the successive formation of –NH–, $–NH_2$, and NH_3 complexes on the active surface of the catalyst.

SASTRY, S. L. *See* abs. **1185.**

SATO, K. *See* abs. **12.**

3031. SAUERLAND, W. [Iron Carbide.] Neue Giesserei, Tech.-Wiss. Beihefte 1, 1949, pp. 43–44; Chem. Abs., vol. 44, 1950, p. 5242.

Relations among heat of reaction, reaction entropy, reaction work, and equilibrium constant are indicated for the reaction $3Fe+C=Fe_3C$. Up to 627°, the reaction does not proceed spontaneously. Although the driving force of the reaction increases with increasing temperature, the equilibrium in this range remains on the side 3Fe+C. Numerical values for the reaction heat, entropy, work, and equilibrium constant are given at 100° intervals for the temperature range 300°–900° K.

3032. SAUVAGEOT, —. [Delayed Solution and the Premature Precipitation of Cementite in Eutectoid and Hypereutectoid Carbon Steel.] Compt. rend., vol. 173, 1921, pp. 297–300; Chem. Abs., vol. 15, 1921, p. 3813.

Temperature necessary for complete solution of cementite is not always proportional to the C content but depends to a considerable extent on the initial condition of the Fe_3C.

SAWADA, Y. *See* abs. **1893, 1894, 3314.**

3033. SAWAMURA, H. [Dissociation of Carbon Monoxide in Contact With Various Kinds of Iron Ore.] Tetsu-to-Hagane, vol. 22, 1936, pp. 121–126; Japan. Jour. Eng., vol. 16, p. 122; Chem. Abs., vol. 33, 1939, p. 4500.

Sawamura made experiments on 2 important behaviors of CO in contact with various kinds of Fe ore in a more rigid manner than was done in the experiments hitherto published, namely: (1) The dissociation velocity of CO at 450°; (2) effect of C deposited in Fe ore owing to the dissociation of CO upon the disintegration of Fe ore. For this purpose, 13 kinds of original ore, besides 5 agglomerated and 1 roasted ore, were taken as samples. For measuring the dissociation velocity of CO, Honda's thermobalance was used. Disintegration of Fe ore heated in CO takes place when it expands, owing to the C deposited in it. This expansion was measured by a special dilatometer, the so-called gas-dilatometer devised by Sawamura. No definite relation could be found between the experimental results and the porosity and the content of Fe having 2 valences in Fe ore. It was found, however, that the dissociation velocity of CO is greater when in contact with hematite or limonite than when in contact with magnetite, and that hematite or limonite in CO is liable to disintegrate more easily than magnetite.

3034. SAYERS, R. R. Natural-Gas Research; Its Importance and Possibilities. Am. Gas Assoc. Monthly, vol. 26, 1944, p. 247.

After the recovery of liquid hydrocarbons from condensate wells, these gas wells become a reservoir of dry gas, and research is now in progress for the utilization of this gas as a source of liquid hydrocarbons by the Fischer-Tropsch process.

3035. SCARLOTT, C. A. Bright New Future of Coal. Westinghouse Eng., vol. 7, 1947, pp. 143–149.

Review of information taken from many sources on the processing of coal to produce liquid fuel. The article discusses our fuel reserves, gas synthesis by Fischer-Tropsch process, coal hydrogenation, high- and low-temperature coke making, underground gasification of coal, and the factors affecting coal conversion, including costs and economic possibilities.

3036. ———. [Future for Coal.] Rev. quim. ind., vol. 18, No. 212, 1949, pp. 16–19; British Abs., 1950, B, I, p. 827.

Account of the Fischer-Tropsch process for making synthetic fuels and of the Bergius hydrogenation process, the steps of the processes being shown in diagrams. Brief note on the possibilities of the underground gasification of coal.

3037. SCHAARSCHMIDT, A., AND MARDER, M. [Synthetic Benzine From Water Gas.] Brennstoff-Chem., vol. 13, 1932, pp. 412–413; Chem. Abs., vol. 27, 1933, P. 2017.

Heptane fraction of the aliphatic portion of synthetic benzine by the Fischer-Tropsch process has been found, with 20 mol. % $SbCl_5$ at 0°, to consist of ⅛ R_3CH-type hydrocarbons and ⅞ *N* or quaternary hydrocarbons.

3038. SCHADE, H. A., FORAN, E., AND ALDRICH, R. C. Fischer-Tropsch Process. Nat. Petrol. News, vol. 37, No. 45, 1945, p. R924; CIOS Rept. VI–22, X–18, X–22, XV–5, 1944, 25 pp., PB 373; TOM Reel 199; Chem. Abs., vol. 40, 1946, p. 7565.

Further extract from a study of the Harnes plant in France. The plant capacity was 20,000 ton of liquid products per yr. One-third of the water gas (CO, 40; H_2, 50; CO_2, 5; N_2 and CH_4, 5%) produced from high-temperature coke in water-gas generators of conventional design was passed over a catalyst of FeO at 500° with steam, giving a product rich in H_2 and CO_2.

This gas was blended with the rest of the original water gas to give a synthesis gas (CO, 27; H_2, 54; CO_2, 14; N_2 and CH_4, 5%). S was removed in 3 stages: A countercurrent tower wash with NH_3 water to remove H_2S; passage through purifying boxes containing Fe oxide and sawdust; and removal of organic S by passing over a catalyst of FeO and Na_2CO_3 at 200°–300°. The gas ready for synthesis is compressed to 3 p. s. i. before entering the 24 reactors, all cooled by a hot water-steam system so arranged that each pair of reactors shares a common header and control valve. A cooling system capable of removing approximately 7,000 B. t. u. of heat per lb.-mol. of liquid product is important for 2 reasons: The reaction must occur at a definite temperature range (in this case 200°+or−3°), enough to promote the reaction but not so high as to decompose the products into CH_4, and the catalyst itself is a very poor conductor of heat. Therefore, to prevent a hot spot in the catalyst bed, the mean path of heat travel from any catalyst particle to the cooling surface is kept below 2 mm. The reactors are square boxes consisting of 600 thin baffles pierced by 600 tubes filled with hot water. Each reactor has a total surface of 5,000 m.^{2} and weighs 50 metric tons. The catalyst fills the voids between baffles and tubes. The density of the reactor thus filled is approximately 60% of that of solid steel. Of the 24 reactors, 16 are normally used for the 1st pass. The effluent from these is cooled and condensed, and the resulting heavy product is removed. The gases are sent next to the remaining 8 reactors for the 2d pass, which produces a lighter product than the 1st pass.

3039. SCHAUB, —. [Removal of the Heat of Reaction in the Synthesis of Hydrocarbons.] Erdöl u. Kohle, vol. 3, No. 1, 1950, p. 9.

Paper presented at the 1949 meeting of the Deutsche Gesellschaft Mineralölwissenschaft u. Kohlechemie. Discusses derivation of equations for the conductivity of heat in catalytic reactions, such as those of the Fischer-Tropsch synthesis.

3039a. SCHAUB, F. [Applications and Limitations of the Fluidization Technique.] Chem. Ing.-Tech., vol. 24, 1952, pp. 98–103; Chem. Abs., vol. 46, 1952, p. 3810.

Discussion of factors which influence the fluidized state, of dust removal, solids transport, heat transfer, and pressure drop. Some of the applications mentioned are catalytic cracking of hydrocarbons, Fischer-Tropsch synthesis, coal hydrogenation, gas generation.

3040. SCHEEPERS, L. [Catalytic Dissociation of Carbon Monoxide.] Rev. univ. mines, vol. 19, 1943, pp. 121–131; Chem. Zentralb., 1943, II, pp. 1782–1783; Chem. Abs., vol. 38, 1944, p. 5720.

Experiments on the dissociation of CO with catalysts of the Fe group, according to $2\,CO=CO_2+C+36.4$ kcal., are described in which the dissociation of CO was investigated with natural magnetite and, at the same time, the reduction of the Fe_3O_4 contained therein in a semiautomatic apparatus under a current of gas. The crushed magnetite was separated into 3 fractions of which the 1st (largest) was strongly magnetic, the 2d (smaller) weakly magnetic, and the 3d (about 3%) nonmagnetic with no dissociating action. The strongly magnetic material had, in a constant gas current, at first a small and then increasing reaction; the formation of CO_2 tended to assume a constant value, even though the reduction was not yet complete. With increasing temperature the dissociation increased up to a maximum at 550° and then decreased again. The less magnetic material had a much stronger and almost immediate action. Although the 1st fraction gave, at 515°, at the start, only 2 cc. CO_2 per hr., an addition of 0.2 gm. of the 2d fraction increased CO_2 formation suddenly to 760 cc. per hr. Natural magnetite, crushed but not separated magnetically, showed an increase of CO_2 formation with decreasing flow velocity of the gas and with decreasing grain size. The catalytic effect of a mixture of Fe_2O_3–Al_2O_3 was investigated also with regard to the effect of CO, in which it seems that the Fe produced by the reduction leads to the dissociation of the CO. Two types of such mixed catalyst are prepared (*A*) by precipitating the Fe hydroxide from a suspension of Al and calcining of the product at 750° and (*B*) by simultaneous precipitation of both substances and calcining as before. Results show at first a period of rapid CO_2 formation, which gradually slows down and becomes stationary. The catalyst mixture with 15% Al had an effect superior to all others and to Fe_2O_3. The destruction of ceramic materials (lining of blast furnaces) by CO is probably due to C precipitations in the vicinity of Fe-containing impurities, whereby even minute amounts of C are enough to disintegrate the brick.

3041. SCHEER, W. [Synthesis of Aliphatic Benzines From Low-Molecular Hydrocarbons.] Oel u. Kohle, vol. 38, 1942, pp. 691–696; Chem. Abs., vol. 36, 1942, p. 5974.

Use of the low-molecular hydrocarbons produced as byproducts in the hydrogenation or synthesis of higher hydrocarbons from pit coal and lignite, the polymerization of the olefins they contain, and the condensation of the saturated and unsaturated hydrocarbons present by known processes is discussed.

3042. ———. [Franz Fischer and the Chemistry of Coal.] Glückauf, vol. 80, 1944, pp. 76–78.

Chronological survey of Fischer's work as director of the Kaiser Wilhelm Institut für Kohlenforschung. The first results of the research by Fischer and Tropsch on oil synthesis from water gas were attained in 1922 when Synthol, a mixture of hydrocarbons, acid-containing compounds, and lower alcohols, was produced by conducting the $CO+H_2$ mixture over alkalized Fe catalyst at 100–150 atm. pressure and 400°–450°. It was later discovered that by using a Zn–Cr oxide catalyst, MeOH could be produced. Further tests, largely by varying the catalyst, led in 1926 to the Kogasin synthesis, by which the same synthesis gas, under normal pressure and temperature around 200°, was converted into saturated hydrocarbons of the paraffin series ranging from CH_4 to high molecular paraffins. In conjunction with Koch, Meyer, and Roelen, this process was so far perfected that in 1934 the Ruhrchemie A.-G. established it on a commercial scale. Experiments were continued to raise the yield of solid paraffins, and, in 1936, Fischer and Pichler developed the medium-pressure synthesis with the Co catalyst at 10 atm. pressure. A year later the use of an Fe catalyst was established. The next development was the use of the Ru catalyst and the production of still higher paraffins. The high versatility of the Fischer synthesis was next revealed by the discovery that, under specific conditions, the formation of unbranched paraffins could be curtailed and the production of branched hydrocarbons promoted. These hydrocarbons as produced by the so-called isosynthesis are distinguished by their high antiknock value. Thus, the final development by Fischer before his retirement in October 1943, went far to correct a serious disadvantage positively connected with the original benzine synthesis process, that of a low-octane fuel.

———. *See* abs. **2044.**

SCHEFFER, F. E. C. *See* abs. **2243, 2244, 2245, 2246, 2247.**

3043. SCHEFFER, F. E. C., DOKKUM, T., AND AL, J. [Dissociation of Methane.] Rec. trav. chim., vol. 45, 1926, pp. 803–816; Chem. Abs., vol. 21, 1927, p. 690.

Continuous current method has been replaced by one of circulation of the gas. Both C_2H_4 and CH_4 were used as a source of activated C obtained in the presence

of Ni as a catalyst. An account of the preparation of the gas and manner of carrying on experiments is outlined carefully. The reaction was studied 480°–680°, since below these temperatures, C reacts with the Ni catalyst. The substance formed is stable at 340°–420° and has an exothermic formation. Mathematical deductions of the 2 equilibrium curves are given from data obtained at atmospheric pressure and different temperatures.

3044. SCHEIL, E. [Stability of Iron Carbide at High Pressure.] Ztschr. anorg. Chem., vol. 158, 1926, pp. 175–180; Chem. Abs., vol. 21, 1927, p. 848.

By means of temperature-concentration diagrams and from theoretical considerations, a p, t, x, diagram has been built up, showing that Fe_3C is stable at high pressure.

3045. SCHELLENBERG, A. [Decomposition of Methanol by Metals and Metallic Oxides.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 9–12; Chem. Zentralb., 1926, I, p. 3298; Chem. Abs., vol. 21, 1927, p. 3531.

Compilation of literature on thermal decomposition of MeOH by various contact substances.

———. *See* abs. **1045, 1046, 3460, 3461, 3464.**

3046. SCHENCK, H. Einführung in die physikalische Chemie der Eisenhüttenprozesse. Die Grundstoffe und Grundreaktionen der Eisenhüttenprozesse. J. Springer, Berlin, 1932, vol. I, pp. 137–170; Chem. Abs., Vol. 26, 1932, p. 4293.

Literature review and critical discussion of the reactions $2\ CO \rightleftharpoons CO_2+C$; the equilibrium constants of Fe_3O_4 with CO–CO_2 mixtures, $3\ Fe+2\ CO \rightleftharpoons Fe_3C+CO_2$; Fe carbonyl; and the water gas reaction, $CO+H_2O \rightleftharpoons CO_2+H_2$, and H_2-H_2O with Fe_3O_4.

3047. SCHENCK, R. [Decomposition of Carbon Monoxide. Correction.] Ber. deut. chem. Gesell., vol. 36, 1903, pp. 3663–3664; Jour. Chem. Soc., 1904, II, p. 28.

There are a few corrections of the numbers in the previous paper (abs. **3068**). These do not affect the main deductions already given.

3048. ———. [Chemical Equilibrium in the Reduction and Cementation of Iron.] Ztschr. Elektrochem., vol. 24, 1918, pp. 248–255; Jour. Soc. Chem. Ind., 1918, A, p. 624; Chem. Abs., vol. 14, 1920, p. 396.

In the interaction between Fe and CO, the Fe is carburized by C resulting from the decomposition of the CO. This is concluded from a comparison of the temperature and pressure equilibrium involved in this reaction and those involved in the reaction $C+CO_2 \rightleftharpoons 2\ CO$. The unpublished work of Juschkewitsch on the equilibrium between 618°–718° in the reaction $C+CO_2 \rightleftharpoons 2\ CO$ in which metallic Co was used as a catalyzer furnishes the missing data for the temperature-pressure curve and makes possible the comparison. The presence of the C resulting from the action $Fe+CO$ is not shown by the usual treatment with HCl, since, having interacted with the ferrite, it is present as carbide. The equilibrium between ferrite, carbide, and the oxides of Fe and C exist at low pressures. The CO content of the gaseous phase is somewhat larger than that in the equilibrium $C+CO_2 \rightleftharpoons 2\ CO$. The carbide obtained in this manner is different from cementite Fe_3C in that it does not decompose into $Fe+C$ on being heated to 400° and, according to theoretical consideration, contains less C. This new carbide is likened to a manganese carbide, which is different from Mn_3C and contains enough C to correspond to Mn_7C or Mn_5C. The new Fe carbide is named bunsenite after Robert Bunsen.

3049. ———. [Equilibrium Relations Between Iron, Oxygen, and Carbon.] Stahl u. Eisen, vol. 46, 1926, pp. 665–682; Chem. Abs., vol. 21, 1927, p. 1743.

It is established from data on indirect reduction of Fe oxides by CO, that, in addition to magnetic Fe oxide and FeO, solid solutions of these in one another and in Fe take part in the equilibria as O-containing phases. The probable presence of an Fe suboxide, stable only below 720°, is deduced from these equilibria. The equilibria for the system Fe, Fe carbide, CO, CO_2 cannot be determined experimentally because of simultaneous oxidation, but data for the system Fe, Fe carbide, CH_4, H_2 are given, and from these the constants for the first named system are calculated. The results are used to deduce the conditions for indirect cementation of Fe by CO and CH_4 as well as for direct cementation processes. From the equilibrium between Fe and CO below 600°, the existence of a percarbide of Fe, with a considerably higher C vapor pressure than cementite or elementary C, is rendered probable. The equilibrium isotherms for CO–CO_2 in the presence of Fe are determined and from them a space model showing the relation between temperature, pressure, and concentration in the gaseous phase is constructed; from this a curve is derived for the relation of gas composition to temperature, which is very similar to curves experimentally obtained from observations on blast furnaces. Information on the equilibria in ore-roasting processes is derived from these isotherms.

3050. ———. [Equilibrium Relations in the Reduction, Oxidation and Carburization of Iron. I.] Ztschr. anorg. Chem., vol. 164, 1927, pp. 145–185; Chem. Abs., vol. 21, 1927, p. 3334.

Thorough study of the systems represented by the following 2 reactions is undertaken: (I) $Ch_4=C+2H_2$, (II) $CH_4+3Fe=Fe_3C+2H_2$. CH_4 was prepared either by treating Al_4C_3 with water or by fractionating liquefied natural gas. H_2 was prepared electrolytically and by the action of Al on alkali. To facilitate reaction the Fe used was deposited on porous pieces of pumice. The pumice was soaked in $Fe(NO_3)_3$ solution, heated to redness, and the Fe was obtained by reduction in H_2. Pure Fe_3C was prepared by the action of CH_4 on Fe at 700°. The reactions 300°–500° were carried out in a Jena glass tube heated to constant temperatures by contact with liquids at their boiling points. Reactions 500°–900° were carried out in porcelain tubes heated in an electric tube furnace, the temperature being kept constant to within 2°. The progress of reactions (I) and (II) at the various temperatures was followed by reading the pressure developed in the reaction tubes. No CH_4 is decomposed by Fe at 300°. At 350°, about 1% by vol. is decomposed, and the presence of Fe_3C can be detected. At 445°, about 4.4% is decomposed. The proportions are the same if H_2 is passed over heated Fe_3C, thus proving the existence of a true equilibrium in reaction (II). The decomposition of CH_4, according to reactions (I) and (II), is plotted against the temperature. Above 695°, the curve for (II) has 2 branches. One along which CH_4 and H_2 are in equilibrium with ferrite and dilute carbide-ferrite mixed crystals, the other along which the gases are in equilibrium with Fe_3C and concentrated carbide-ferrite mixed crystals. The points of similarity between the systems studied and the Fe–C system are pointed out. Using his experimental results, Schenck calculates that the heat of formation of Fe_3C is −15,405 cal., in close agreement with the values obtained calorimetrically. This is taken as a proof that the observations made really pertain to the equilibrium represented by reaction (II). Schenck outlines the application of the findings to problems arising in the carburization of Fe by hydrocarbons. From the data obtained for systems (I) and (II) and the previously determined equilibrium relations in the system $2\ CO=C+CO_2$, are calculated and plotted the equilibrium relations, which, theoretically, should exist in the system $3\ Fe+2\ CO=Fe_3C+CO_2$.

3051. SCHENCK, R., KRÄGELOH, F., AND EISENSTECKEN, F. [Equilibria in the Reduction, Oxidation, and Carburization of Iron. II. Methane-Hydrogen Equilibria in the Presence of Cobalt.] Ztschr. anorg. Chem., vol. 164, 1927, pp. 313–325; Chem. Abs., vol. 21, 1927, p. 3799.

Authors wish to show whether the equilibrium conditions resulting from the action of Co upon CO are solely those due to the reaction (1) $2\ CO \rightleftharpoons C + CO_2$, or whether other equilibria involving a Co carbide also must be considered. The results of an incomplete series of experiments performed in 1914 are given. At that time, Co was considered to act solely as a catalyst in the recation mentioned above and no carbide equilibria were thought to be involved. Doubt in the matter has led the authors to determine the equilibrium conditions in the closely related system $CH_4 \rightleftharpoons C + 2\ H_2$ catalyzed by Co. The procedure is the same as that used in the system Fe–CH_4 (abs. **3050**). The primary reaction is a catalytic decomposition of the CO according to (I). Co is a better catalyst for this reaction than Fe. Superimposed upon this equilibrium is another involving Co carbide. This equilibrium is reached more slowly than the former. Both equilibria are studied quantitatively over the range 310°–740°. Above 680°, the reaction involving the carbide is no longer encountered. Although Co carbide was not isolated, its properties are predicted. The parallelism between the effects of Fe_3C and Co carbide on the decomposition of CH_4 leads the authors to believe that, as with Fe, it is likely that Co carbide forms mixed crystals with Co. The heat of formation of Co carbide is found by calculation to be —11,300 cal. The authors draw the following conclusions with regard to the influence of Co upon equilibrium (I): Above 668° the influence is purely catalytic; below this temperature it is difficult to explain the equilibrium relations unless the existence of dilute mixed crystals of Co carbide in Co is postulated.

3052. SCHENCK, R., DINGMANN, T., BÖKMANN, J., EBERT, W., KESTING, W., LEPETIT, G., MÜLLER, J., AND PRATJE, W. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. III. (4). Systematic Investigations of the Oxidation-Reduction Relations Existing in the Systems of the Iron Oxides With Iron, Carbon Monoxide, and Carbon Dioxide.] Ztschr. anorg. Chem., vol. 166, 1927, pp. 113–154; Chem. Abs., vol. 22, 1928, p. 566.

Continuation of the work that will finally lead to knowledge of the equilibrium relations in the system Fe–C–O_2. A precision method is used to determine the equilibrium relations in the systems $Fe_3O_4 + CO \rightleftharpoons 3\ FeO + CO_2$ and $FeO + CO \rightleftharpoons Fe + CO_2$, the vapor phase in each case being a mixture of CO and CO_2. Simultaneously the regions of stability of solid solutions of FeO and Fe_3O_4 and of FeO and Fe were established. The method used allowed the oxides of Fe to interact at a definite temperature with a small quantity of CO until equilibrium was established. The gaseous phase consisting of CO and CO_2 then was withdrawn and analyzed. These small additions of CO were continued until the oxides were deoxidized almost completely. The material composing the boat containing the oxides had a pronounced influence upon the equilibria resulting. The presence of MgO or SiO_2 produced noticeable changes in the equilibrium curves. Similar changes in the curves would result from the addition of any foreign substances likely to form solid solutions with the Fe oxides or to combine with them. Al_2O_3 produces little effect. By plotting the % of CO or CO_2 in the gas phase against the temperature, the equilibrium diagram is obtained. It discloses an invariant point, 560°, at which Fe, FeO, Fe_3O_4, CO, and CO_2 can coexist. The existence of 2 solid solutions is shown: (1) A solution of small quantities of Fe_3O_4 in FeO for which the name "wüstite" is coined, and (2) a solution of small quantities of FeO in pure Fe for which the name "oxoferrite" is coined. Wüstite exists only above the nonvariant point, 560°, and 76% Fe, 24% O_2. Below this it separates in Fe_3O_4 and oxoferrite. FeO was not encountered as an independent solid phase, and it is, concluded, therefore, that this oxide cannot be made in a stable condition at temperatures up to 1,100°. Below 560° Fe_3O_4 can be deoxidized to oxoferrite directly. Adding MgO to the system lowers the invariant point markedly and broadens out the area of existence of wüstite. The authors intend to study in detail the influence of CaO, Al_2O_3, MnO, and SiO_2. The practical value of these researches is discussed.

3053. ———. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. IV. (5). Iron Carbide, Iron Oxides, and Iron Under an Atmosphere of Carbon Monoxide and Carbon Dioxide.] Ztschr. anorg. Chem., vol. 167, 1927, pp. 254–314; Chem. Abs., vol. 22, 1928, p. 937.

FeO is prepared by heating FeC_2O_4 in vacuo. It is mixed with powdered Fe and finely divided C, and the mixture is subjected to a CO_2 atmosphere at definite temperatures. The concentrations of CO and CO_2 are determined after equilibrium has been established. Wüstite and oxoferrite are formed as has been reported. The addition of small quantities of Hg to the system reduced the solubility of FeO in Fe and, thus, produced an oxoferrite (solid solution of FeO in Fe) of relatively low O_2 content. Likewise the wüstite formed was poorer in O_2 and, hence, was nearer FeO in composition. The CO–CO_2 atmosphere above the mixture also was poorer in the O_2-rich CO_2 than was the case when Hg was absent from the mixture. This is another illustration of the marked influence that foreign substances have upon the equilibrium in the Fe–C–O_2 system. Quantitative studies of the influence of additions of other substances are in progress. Pure Fe was partly changed to Fe_3C by cementation, CH_4 being used. This carburized mixture then was allowed to come to equilibrium at various temperatures under an atmosphere of CO and CO_2. Both C and O_2 are absorbed by the solid phases. The results indicate a bivariant equilibrium with the following 3 phases: (1) Gaseous (CO and CO_2); (2) Fe_3C; (3) ternary solid solution of Fe_3C, FeO, and Fe. For the ternary solid solution the name "oxoaustenite" is suggested. This solution also is undoubtedly present in the univariant equilibrium mixtures of wüstite, oxoferrite, CO, and CO_2, since the solid phases always yield either free C or hydrocarbons upon treatment with diluted acids. The reaction between Fe_3C and Fe_2O_3 and Fe_3O_4 was studied by heating known mixtures to 600°, 650°, and 700°. When equilibrium has been attained, the pressure and composition of the evolved gases are determined. The following concurrent reactions occur: (1) $4\ Fe_3C + Fe_3O_4 \rightleftharpoons 15\ Fe + 4\ CO$, (2) $2\ Fe_3C + Fe_3O_4 \rightleftharpoons 9\ Fe + 2\ CO_2$. An isotherm at 650° shows the equilibrium existing at definite total pressures and definite concentrations of CO. The phases appearing are Fe_3O_4, wüstite, Fe_3C, oxoaustenite, and gas. The equilibrium diagram is given for the system wüstite–oxoferrite–oxoaustenite from 600°–1,000° at 1 atm. pressure and under varying concentrations of CO.

3054. SCHENCK, R. [Equilibrium in the Reduction, Oxidation, and Carburization of Iron. V.] Ztschr. anorg. Chem., vol. 167, 1927, pp. 315–328; Chem Abs., vol. 22, 1928, p. 2132.

Summary of the previous papers in this series. The 3-dimensional equilibrium model of the system Fe–C–O_2 is discussed, the system being under an atmosphere of CO and CO_2 and at various temperatures 500°–1,000°. An isobar at 1 atm. shows the concentrations of CO and CO_2 and the temperatures at which

the following will be stable: Fe_3C, Fe_3O_4, wüstite, oxoferrite, and oxoaustenite. Isotherms at 50° intervals 542°–1,000° show the range of stability of the above-mentioned substances when under pressures ranging from 0–1,200 mm. The remarkable influence that impurities have upon the equilibrium is stressed again. The effect of MgO is given in detail. Problems for future solution are: (1) The systematic investigations of the influence of impurities; and (2) the determination of the composition of the solid solutions oxoferrite and oxoaustenite as they exist under various gas pressures and compositions.

3055. SCHENCK, R., AND DINGMANN, T. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of iron. VI.)7). Solubility of Oxygen in Iron.] Ztschr. anorg. Chem., vol. 171, 1928, pp. 239–257; Chem. Abs., vol. 22, 1928, p. 3612.

Polemical. 16 refs. (*See* abs. **193.**)

3056. SCHENCK, R., AND KLAS, H. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. VII. (8). Cobalt in a Methane–Hydrogen Atmosphere.] Ztschr. anorg. Chem., vol. 178, 1929, pp. 146–156; Chem. Abs., vol. 23, 1929, p. 2116.

Two reactions are possible, 1 in which Co acts purely as a contact substance, expressed by the equation $CH_4 \rightleftharpoons C + 2\ H_2$, and 1 in which the formation of carbide occurs; $nCo + CH_4 \rightleftharpoons Co_nC + 2\ H_2$. The system is investigated in the range 680°–900°, and the composition of the gas phase is varied between 0 and 100% for both H_2 and CH_4, with small additions of CO and N_2. The presence of Co–Co carbide mixed crystals follows from the gradual increase in % CH_4. At first more diluted mixed crystals are formed, which are in equilibrium with low CH_4 concentrations. With carbide increase in the solid solution, CH_4 concentration increases, reaching its maximum when saturation with carbide is attained, and the occurrence of the pure carbide phase begins. This saturation concentration of CH_4 is about 18% at 680°, 15% at 700°, 14% at 720°, 10% at 760°, 7.5% at 800°, and 3.7% at 900°. Co carbide is found to be more stable than Fe carbide. Complete decarburization is not obtained with less than 97% H_2 in the gas phase. Phase diagrams are given that show the limits of the mixed crystal field.

3057. SCHENCK, R., DINGMANN, T., KIRSCHT, P. H., AND WESSELKOCK, H. [Equilibrium Studies of the Reduction, Oxidation, and Carburization Processes of Iron. VIII. (9). System Iron–Oxygen.] Ztschr. anorg. Chem., vol. 182, 1929, pp. 97–117; Chem. Abs., vol. 24, 1930, p. 44.

Object was to study the minima attained in the oxidation of Fe with small quantities of CO_2 and their dependence upon the O_2 content of the basic material. The O_2 saturation of the homogeneous *oxyferrite* phase at different temperatures likewise was determined. The metal used in the experiments was carefully freed of H_2 by many days heating in a high vacuum, while the gas used was pure CO_2 gas under diminished pressure or, in a few cases, mixtures of CO_2 and CO. At 700°, the reaction velocity was very slow, while at 1,000° the stable zone was reached in the course of the 1st day. The stable *wüstite-oxyferrite* equilibrium corresponds at 700° to a gas phase composition of 40.3% CO_2 and 59.7% CO, at 800° to 35.1% CO_2 and 63.9% CO, and at 1,000° to 28.5% CO_2 and 71.5% CO. At 800° and 1,000° the O_2 taken up in homogeneous solid solution is about 0.4%, the higher values previously obtained being due to the occurrence of a metastable wüstite poor in Fe_3O_4. With mixtures of CO_2–CO, the relation between CO and CO_2 in the gas phase was determined along the stable wüstite-oxyferrite boundary. The new values for maximum O_2 content require a diminution in the extent of the oxyferrite zone in the Fe–O equilibrium diagram. The possibility of preparing FeO in the pure state is discussed, and it is suggested that small additions of MgO or MnO would increase the stability of FeO. Addition of 0.5%, 1.0%, and 4.0% Cu as well as 4% Ni was studied and resulted in a slight displacement of the wüstite-oxyferrite border toward higher CO_2 concentration, as well as a more rapid attainment of the stable wüstite-metal boundary. The solubility of O_2 is reduced more than 50%.

3058. SCHENCK, R., FRANZ, H., AND WILLEKE, H. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. IX. (10). Influence of Foreign Oxides Upon the Equilbria.] Ztschr. anorg. Chem., vol. 184, 1929, pp. 1–38; Chem. Abs., vol. 24, 1930, p. 1788.

By means of an apparatus and a method previously described, the effect of MnO, ZnO, BeO, CaO, and Al_2O_3 on the equilibrium obtained during the reduction of Fe oxides by CO was studied. The mixed oxides usually were obtained by the ignition of a mixture of the corresponding nitrates, which had been formed by evaporation of a solution. In the case of the lime mixtures, mixed hydroxide and carbonates were ignited; the MnO mixtures were obtained by ignition of a mixture of oxalates. The molecule mixtures used were Fe_2O_3: MnO 1 : 8, 1 : 1, 2 : 1 at 800°; Fe_2O_3: ZnO 1 : 1, 2 : 1, 1 : 10 at 700°, Fe_2O_3: Al_2O_3 1 : 10, 1 : 3, 1.5 : 1 at 800°, 900°; Fe_2O_3: CaO 1 : 10, 1 : 1, 1.5 : 1, 3 : 1 at 900°, 1,050° Fe_2O_3: BeO 2 : 1, 1 : 1, 1 : 18 at 800°. Even when the foreign oxide is not reduced by CO it affects the equilibrium of the Fe_2O_3 reduction if it (1) forms mixed crystals with the oxides of Fe, for example, Al_2O_3 with Fe_2O_3 or MnO with FeO; (2) forms compounds with the oxides of Fe as spinels or ferrites. This is the case with Al_2O_3, MnO, ZnO, and particularly with CaO. The mixed crystals become more difficult to reduce than the wüstite phase, the greater the content of foreign oxide. Oxides that form neither mixed crystals nor compounds do not affect the equilibrium in any way, for example, BeO. ZnO does not affect the wüstite-metal equilibrium. The reduction of ZnO by CO is hampered by the presence of any oxide phase of Fe.

3059. SCHENCK, R., DINGMANN, T., KIRSCHT, P. H., AND KORTENGRABER, A. [Equilibrium Investigations of the Reduction, Oxidation, and Carburization Process of iron. X. (11). The System: Iron–Oxygen; Abnormal Oxidation; Activation of Iron Without Additions.] Ztschr. anorg. Chem., vol. 206, 1932, pp. 73–96; Chem. Abs., vol. 26, 1932, p. 4571.

Constancy of weight of Fe foil in a stream of CO_2–CO (19.15% CO_2) at high temperatures is due to the compensation of 2 effects, oxidation and the loss of small quantities of volatile Fe carbonyl. In a CO-rich atmosphere Fe powder gives up Fe carbonyl, but its formation is suppressed if the CO_2 content of the atmosphere is above that corresponding to the stable metal-wüstite limit. The high absorption of O_2 observed with finely powdered Fe is attributed to the presence of active particles, which are oxidized in a CO_2–CO mixture, the composition of which is below the normal metal-wüstite range.

3060. SCHENCK, R., FRANZ, H., AND LAYMANN, A. [Equilibrium Investigations in the Reduction, Oxidation, and Carburization Processes of Iron. XI.] Ztschr. anorg. Chem., vol. 206, 1932, pp. 129–151; Chem. Abs., vol. 26, 1932, p. 5521.

Influence of the oxides of Si, Ti, and P upon reduction equilibrium was studied. Reduction to metal is most favorable with wüstite free from added oxides, and, in practice, the goal is to add suitable materials, which will favor the greatest possible wüstite formation.

3061. SCHENK, R., AND DINGMANN, T. [*Equilibrium* Studies in the Reduction, Oxidation, and Carburization Processes of Iron. XII.] Ztschr. anorg. Chem.,

vol. 209, 1932, pp. 1–10; Chem. Abs., vol. 27, 1933, p. 1302.

Micro methods of gas analysis used in this series of investigations are described. Apparatus is shown for the accurate collection and analysis of small quantities of CO_2 and CO, depending on CO_2 absorption and measurement of the residual volume of CO. Where the gas mixture contains other constituents, a type of micro Orsat apparatus is used, containing, however, no rubber connections. CO is not determined by absorption but is burned to CO_2 and then absorbed. Unsaturated hydrocarbons are absorbed in fuming H_2SO_4, but the time of contact must be limited to 3–5 min. to prevent absorption of some CH_4 and H_2. If CH_4 content is high, it is better to keep it below 40% by adding H_2, otherwise some of it will be converted into CH_3OH or CH_2O in the combustion pipet. Details of the apparatus are shown in sketches.

3062. SCHENCK, R., LAYMANN, A., AND JENCKEL, E. [Equilibrium Investigations in the Reduction, Oxidation, and Carburization Processes of Iron. XIII.] Ztschr. anorg. Chem., vol. 235, 1937, pp. 65–76; Chem. Abs., vol. 32, 1938, p. 2418.

System Fe–O–Ca was studied by determining the decomposition diagrams of Fe_2O_3–CaO mixtures at 900° and with a range of 23–79% CO_2 in the atmosphere. The following phases are found to exist: Fe_3O_4, wüstite, $CaO.Fe_3O_4$, and $(CaO)_2.Fe_2O_3$. In the presence of even small concentrations of CO in the atmosphere, the phase $CaO.Fe_2O_3$ cannot exist. The results are plotted with triangular coordinates.

3063. SCHENCK, R. [First Stages in the Development of Our Views Concerning the Equilibrium System Iron–Carbon–Oxygen.] Ztschr. Elektrochem., vol. 34, 1928, pp. 399–403; Chem. Abs., vol. 23, 1929, p. 2086.

Reply to Falcke's criticisms (abs. **867**).

———. Equilibrium in the Reduction, Oxidation, and Carburization of Iron. V. *See* abs. **3054**.

SCHENCK, R., AND DINGMANN, T. Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. VI. (7). Solubility of Oxygen in Iron. *See* abs. **3055**.

———. Equilibrium Studies in the Reduction, Oxidation, and Carburization Processes of Iron. XII. *See* abs. **3061**.

3064. SCHENCK, R., AND HELLER, W. [Reactions in the Reduction of Iron.] Ber. deut. chem. Gesell., vol. 38, 1905, pp. 2132–2139; Jour. Chem. Soc., 1905, II, p. 526.

When CO is heated with metallic Fe, the pressure observed after equilibrium is attained is extremely small, and it appears that virtually all the gas is removed. This is due to the oxidation of the Fe and the deposition of the C in the solid form. As pure CO cannot oxidize Fe, it is assumed that the Fe reacts in 2 ways: (1) Catalytically decomposing the CO into C and CO_2, and (2) as a reducing agent on the CO_2, producing ferrous oxide and CO. These 2 reactions proceed until equilibrium is established between Fe, ferrous oxide, C, CO, and CO_2. The partial pressures of CO and CO_2 and also the sum of these are dependent on the temperature only. For each temperature there is a definite partial pressure for each oxide and a definite total pressure. It thus follows that in the blast furnace ferrous oxide will only be reduced by CO in the presence of C if the total pressure of the CO and CO_2 is less than the pressure of the total equilibrium. If, on the other hand, the pressure of the gas mixture at the given temperature is greater, then the reoxidation of the Fe occurs and deposition of C. The pressures for the total equilibrium for temperatures 400°–800° have been determined by 2 methods: (1) Heating CO with finely divided Fe and measuring the pressure when equilibrium is attained; and (2) heating ferrous oxide and C in a vacuum and determining the pressure at fixed temperatures. The 2 methods give concordant results. Some of the numbers are: 468°, 10.3 mm.; 620°, 81.5 mm.; 728°, 438 mm.; and 780°, 780 mm. Similar experiments were performed with Mn, and, as this is much more readily oxidized than Fe, the pressures are smaller: At 1,200°, 10 mm.; 1,229°, 15.3 mm.

SCHENCK, R., AND KLAS, H. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. VII. (8). Cobalt in a Methane–Hydrogen Atmosphere.] *See* abs. **3056**.

SCHENCK, R., AND MEYER. [Carbide Studies in the Methane Synthesis. IV. Chemistry of Double Carbide.] *See* abs. **3072**.

———. [Studies of Carbides by the Methane Synthesis Method.] II. *See* abs. **3070**.

3065. SCHENCK, R., AND STENKHOFF, R. [Decomposition of Iron Carbide by Acids.] Ztschr. anorg. Chem., vol. 161, 1927, pp. 287–303; Chem. Abs., vol. 21, 1927, p. 2091.

Cementite (C, 6.69; Fe, 98.25; Si, 0.04; SO_4, 0.08%) prepared in the usual way and freed from ferrite and pearlite was treated separately with 600 cc. H_2SO_4 (I) (1/30, 1/3, 5 *N*) benzenesulfonic acid (II) (0.5, 1 *N*) and AcOH (III) (1, 3 *N*) in the presence of 0–220 gm. of the corresponding ferrous salts. Determinations using 0.2 gm. cementite were conducted for 3 weeks at 60°. The amount of free C precipitated increases with the increase in concentration of ferrous ion and the decrease in strength of acid. The decrease or even failure in the formation of hydrocarbon is the result of the impossibility to attain the thermodynamically possible maximum yield owing to low reaction velocity; the depression of the H-ion concentration by anions and the simultaneous ennobling of the Fe owing to ferrous ions. According to the mass law these phenomena should supplement each other. The results for the strong acid (II) are not in accord, but this probably is due to absorption of the acid by the C, thus indicating in the analysis an erroneously high value for C. The results are given in tables and graphs.

3066. SCHENCK, R., AND WESSELKOCK, H. [Activation of Metals by Addition of Foreign Substances. I.] Ztschr. anorg. Chem., vol. 184, 1929, pp. 39–57; Chem. Abs., vol. 24, 1930, p. 2035.

Effect of CaO, MgO, MnO, and Al_2O_3 separately and Al_2O_3 and MgO jointly on the oxidation of Ni and Co at 900° in an atmosphere of CO_2 was studied. The mixtures M : MO (1 : 10); M : Al_2O_3 (1 : 3); M : Al_2O_3 : MgO (1 : 10 : 2) were usually prepared by reduction in H_2 of mixtures of nitrates or oxalates that had been precipitated together. (*See* abs. **3055**, **3057**, and **3058**). The equilibria appearing after the addition of CO_2 at 900° were determined as previously described. The activities of both Ni and Co were increased by the presence of the oxides in the order CaO, MgO, MnO. These oxides have the same crystal lattice as NiO and CoO. The activity does not seem to be closely related to the similarity of crystal lattice constants of these oxides with those of Ni and Co. The irregularities in the progress of the oxidation are attributed to the heterogeneous distribution of the reduced metal in the oxide. This heterogeneity, which is most evident in the Co–MnO mixtures, is due to the fact that the mixed oxalates are not homogeneous. Determination of the gaseous equilibrium by fractional oxidation (successive addition of small quantities of CO_2) offers a method for measuring the uniformity of distribution of the metal in the oxide as well as determining the areas containing metal of similar degree of dispersion. This lack of uniformity may explain the centers of activity often met in mixed catalysts. The mixtures Co–3 Al_2O_3 and Ni–3 Al_2O_3 exceed finely re-

duced Fe in activity. The addition of MgO to these mixtures enhanced their activity. The activation seems to be specific for O. The general problem of the activity of metals toward specific elements is indicated by the observations reported. When the O is transferred from the CO_2 to the metal, which is dispersed in the isomorphous oxide, it takes a position in the lattice occupied before reduction by O_2. If it is desired to activate a metal toward N_2 the nitride of the metal should be dispersed throughout a stable isomorphous nitride and then reduced to metal. The reasoning is carried over to activation toward S.

3067. SCHENCK, R., KURZEN, F., AND WESSELKOCK, H. [Activation of Metals by Foreign Substances. II.] Ztschr. anorg. Chem., vol. 206, 1932, pp. 273–288; Chem. Abs., vol. 26, 1932, p. 4549.

Fe and W in MgO make it difficult to form carbide by action of CH_4, if in the carbides of these metals 1 C atom is attached to several metallic atoms, as in Fe_3C or W_5C_2. Carbide formation is not hindered by the addition of inert oxides if the carbide consists of an equal number of metal and C atoms, as WC. These experiments show that linkage of metal atoms with a C atom can only occur with a favorable spatial distribution of the metal atoms.

3068. SCHENCK, R., AND ZIMMERMANN, F. [Decomposition of Carbon Monoxide and Chemical Equilibrium in the Blast Furnace.] Ber. deut. chem. Gesell., vol. 36, 1903, pp. 1231–1251; Jour. Chem. Soc., 1903, II, pp. 423–425.

Reversible reaction $2\,CO \rightleftharpoons CO_2 + C$ has been studied as a true reaction in the presence of metals and metallic oxides. The metals employed, Fe, Co, and Ni and their oxides, were deposited on pumice, which had been reduced in a stream of pure H_2 and then extracted with diluted HCl. By this means, the whole of the original Fe compounds in the pumice were removed. The oxides were obtained by saturating the pumice with solutions of the metallic nitrates and then strongly heating. The oxides of Co and Ni completely oxidize CO to CO_2 at 445° and they are reduced to the metallic state. With Fe oxide only part of the CO is oxidized. With a gaseous mixture containing 1 CO : 4 CO_2 no reduction of the Fe oxide occurs, and the pressure remains constant. The CO_2 obtained by Boudouard must have been due to the oxidation of the CO by the Fe oxide and not to the catalytic decomposition of the CO. Finely divided metals accelerate the decomposition of CO into C and CO_2 in a remarkable manner. With Ni at 445° the reaction has been shown to be bimolecular and should be represented as $2\,CO = C + CO_2$; at 310° and 360°, however, the reaction appears to be unimolecular and probably occurs in 2 stages: $CO = C + O$ and then $CO + O = CO_2$, the 2d reaction proceeding much more rapidly than the first. The reaction does not appear to be complete but is reversible, and a state of equilibrium is established even at temperatures of 445°. When Co is used, the numbers agreed with neither a unimolecular nor a bimolecular reaction. This probably is due to Fe contained as an impurity in the Co. When Fe is used, the pressure never becomes absolutely constant so long as any gas is present, and ultimately the whole of the C present is deposited in the free state and Fe oxide is formed. It would appear that the Fe first reacts as a catalyzer, decomposing the CO into C and CO_2. When the concentration of the CO_2 has increased and that of CO decreased to a certain limit, the metal begins to reduce the CO_2, and the 2 reactions then proceed simultaneously so that the composition of the gas remains the same. Experiments made at 360° and 445° indicate that the reaction is unimolecular but that at 508° it becomes bimolecular. The compositions of the gaseous mixtures are as follows:

360°	10.5% CO	and 89.5% CO_2,
445°	52.8% CO	and 47.2% CO_2,
508°	47.1% CO	and 52.9% CO_2.

The numbers obtained at 260° probably indicate the presence of some oxide other than ferric oxide.

SCHENCK, R., FRANZ, H., AND LAYMANN, A. [Equilibrium Investigations in the Reduction, Oxidation, and Carburization Processes of Iron. XI.] *See* abs. **3060.**

SCHENCK, R., FRANZ, H., AND WILLEKE, H. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. IX. (10). Influence of Foreign Oxides Upon the Equilibria.] *See* abs. **3058.**

SCHENCK, R., KRÄGELOH, F., AND EISENSTECKEN, F. [Equilibria in the Reduction, Oxidation, and Carburization of Iron. II. Methane-Hydrogen Equilibria in the Presence of Cobalt.] *See* Abs. **3051.**

3069. SCHENCK, R., KURZEN, F., AND WESSELKOCK, H. [Studies of Carbides Prepared With Methane. I.] Ztschr. anorg. Chem., vol. 203, 1931, pp. 159–187. Chem. Abs., vol. 26, 1932, p. 1536.

Formation and composition of the carbides of Fe, Cr, W, Mo, and Re are followed by analysis of the CH_4 and H_2 gases in equilibrium over the carbide. Results with Fe justify the method Cr at 600°, 700° and 800° forms a carbide, Cr_5C_2, and a mixed crystal phase containing 11.5% C (probably containing Cr_3C_2). W forms the stable WC at 800°. At 700°, the unstable W_5C_2 is observed as well as a mixed crystal phase, the composition of the higher carbide being uncertain. Mo forms the single stable Mo_2C at 800° and the metastable phase MoC at 700°. The reaction of CH_4 with Re is too slight for definite observation.

3070. SCHENCK, R., AND MEYER, K. [Studies of Carbides by the Methane Synthesis Method. II.] Ztschr. anorg. Chem. vol. 239, 1938, pp. 161–179; Chem. Abs., vol. 32, 1938, p. 8900.

Carbonization of Mn and CH_4 is studied in the temperature range 700°–970°. $CH_4 : H_2$ equilibrium measurements indicate a change of state at 740° and 955°. Below 740°, Mn_3C is not present as a pure compound, though solid solutions of this compound appear. Mn_4C exists in a metastable state between 700° and 750°. Above 750° and up to 950° Mn_3C exists independently. It can take up more C to form a solid solution phase whose saturation limit at 970° is about 9% C. In the range 750°–950°, the saturation limits of a solid solution phase poorer in C could be determined. Appreciable differences from the conclusions of Vogel and Döring (abs. **3570**) in the number and limits of the phase fields are indicated.

3071. SCHENCK, R., MEYER, K., AND MAYER, K. [Carbide Studies in the Methane Synthesis. III.] Ztschr. anorg. Chem., vol. 243, 1939, pp. 17–31; Chem. Abs., vol. 34, 1940, p. 4974.

Space isotherm for the Mn–Fe–C system at 800° was constructed by measuring displacements in the equilibrium, $Mn + CH_4 \rightleftharpoons MnC + 2\,H_2$, at 760 mm. The space model shows 4 zones of the compositions indicated: *A*, containing (1) a field of β–Mn and a weak MnC phase, (2) a field of mixed crystals of γ–Fe, (3) a field of mixed crystals of β–Mn and γ–Fe; *B*, containing as its fundamental phases a univariant equilibrium γ–Fe and carbides of Mn; *C*, a univariant equilibrium containing Mn carbides; *D*, in which $(Mn, Fe)_3C$ and a C-rich phase (7.4% C) prevail. An alloy, 95% Mn+5% Fe, shows a maximum solubility of C (8.4%). In the steel region, the isotherms of C show several small fields corresponding to various groups of Mn steels.

3072. SCKENCK, R., AND MEYER, K. [Carbide Studies in the Methane Synthesis. IV. The Chemistry of

Double Carbide.] Ztschr. anorg. Chem., vol. 243, 1940, pp. 259–268; Chem. Abs., vol. 34, 1940, p. 4974.

From the carbonization isotherms at 800° for 7 mixtures of Fe and W, a space model for the overall isotherms was prepared. By projection on the base, 6 fields were obtained, having the following compositions: *A*, consisting of the double carbide $Fe_6W_6C_6$ and γ–Fe; *B*, α–Fe, W, and $Fe_6W_6C_6$; *C*, η–W, $Fe_6W_6C_6$, and $FeW_{23}C_7$; *D*, mixed crystals of W (containing C and Fe) and $FeW_{23}C_7$; *E*, α–FE (containing W); *F*, α– and β–Fe (stable). $Fe_6W_6C_6$ is considered a compound of Fe_3C and W_2C; it decomposes above 800° into graphite and mixed crystals. Other carbides are indicated by vapor-pressure measurements on the CH_4 phase.

SCHENCK, R., KURZEN, F., AND WESSELKOCK, H. [Activation of Metals by Foreign Substances. II.] *See* abs. **3067.**

SCHENCK, R., LAYMANN, A., AND JENCKEL, E. [Equilibrium Investigations in the Reduction, Oxidation, and Carburization Processes of Iron. XIII.] *See* abs. **3062.**

SCHENCK, R., MEYER, K., AND MAYER, K. [Carbide Studies in the Methane Synthesis. III.] *See* abs. **3071.**

3073. SCHENCK, R., SEMILLER, H., AND FALCKE, V. [Experimental Studies on the Reduction and Carbide Formation of Iron.] Ber. deut. chem. Gesell., vol. 40, 1907, pp. 1704–1725; Jour. Soc. Chem. Ind., 1907, p. 692; Chem. Abs., vol. 1, 1907, p. 2772.

Gas pressures at temperatures 550°–700° were measured in the following systems: (1) Fe, FeO, C (amorphous), CO, CO_2; (2) Fe, FeO, graphite, CO, CO_2; (3) Fe_3C, FeO, C (amorphous), CO, CO_2; (4) Fe_3O_4; FeO, C (amorphous), CO, CO_2. Moreover, in order to define the state of these systems completely, the composition of the gas phase was determined. The data enabled prediction of the proper conditions for the formation of Fe carbide, at any temperature, or for the formation of any of the other phases. The authors conclude that the equilibrium $C+CO_2 \rightleftarrows 2\ CO$ varies with the form of C employed. Unfortunately the observations could not be carried above 700° on account of complications owing to the formation of mixed crystals between Fe and cementite. Mn lowers the pressure of the C oxides to a striking degree.

SCHENCK, R., DINGMANN, T., KIRSCHT, P. H., AND KORTENGRABER, A. [Equilibrium Investigations of the Reduction, Oxidation, and Carburization Processes of Iron. X. (11). The System: Iron-Oxygen; Abnormal Oxidation; Activation of Iron Without Additions.] *See* abs. **3059.**

SCHENCK, R., DINGMANN, T., KIRSCHT, P. H., AND WESSELKOCK, H. [Equilibrium Studies of the Reduction, Oxidation, and Carburization Processes of Iron. VIII. (9). System Iron–Oxygen.] *See* abs. **3057.**

SCHENCK, R., DINGMANN, T., BÖKMANN, J., EBERT, W., KESTING, W., LEPETIT, G., MÜLLER, J., AND PRATJE, W. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. IV. (5). Iron Carbide, Iron Oxides, and Iron Under an Atmosphere of Carbon Monoxide and Carbon Dioxide.] *See* abs. **3053.**

———. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. III. (4). Systematic Investigations of the Oxidation-Reduction Relations Existing in the Systems of the Iron Oxides With Iron, Carbon Monoxide and Carbon Dioxide.] *See* abs. **3052.**

3074. SCHENK, —. [Carbon Dioxide Content of Thorium and Magnesium Catalysts.] FIAT Reel K29, frame 7,184, 1938; PB 70,218; TOM Reel 296.

It is established that the CO_2 content of catalysts is subject to variations according to the degree of dryness, but that within these variations no difference exists in the CO_2 content between Th and Mg catalysts.

3075. ———. [Influence of the Reduction and the Granular Form of Cobalt Catalysts on the Cobalt Density.] FIAT Reel K–29, frames 7,164–7,165, 1938; PB 70,218; TOM Reel 296.

It is established by tests that, by reduction, an increase of the Co density of 25% (Co–kieselguhr ratio 1: 1) and 5% (Co–kiselguhr ratio 1: 2) is obtained. Besides that, the Co density depends on the method of grinding the kieselguhr. 1 table.

3076. ———. [Manufacture of a Cobalt–Magnesium Catalyst.] FIAT Reel K–20, frames 47–49, January 31, 1938, PB 70,211; TOM Reel 287.

Catalyst substance consists of 100 parts of Co, 15% of MgO, 200 kieselguhr. It is prepared as follows: 3.2 kg. soda are heated with 30 l. of distilled H_2O until boiling; then the boiling Mg solution is slowly added while stirring. The boiling Co solution now is added, and the mixture is stirred for a further 30 sec. After 2 kg. of kieselguhr has been added, the whole is thoroughly stirred again and then suction filtered, and the cake is washed with hot distilled H_2O for ½ hr. Care must be taken that the cake always is covered with a H_2O layer of 1 cm. thickness. After washing, the cake is mashed with 50 l. of distilled H_2O in a precipitating vessel, the dust from the shaping process being added. After discharge into the suction filter, the H_2O is exhausted, and the cake is pressed. The small pieces are dried in the drying oven.

3077. ———. [Manufacture of Thorium–Magnesium Thread Grain Catalyst.] FIAT Reel K–20, frames 44–46, Feb. 1, 1938, PB 70,211; TOM Reel 287.

Solution of Th and Mg nitrates is added to the Co solution before precipitation. Then all 3 parts are precipitated at once. After the thread grain has been formed, dried, and sieved, the continuous reduction takes place. The reduced grain falls directly into an impregnation container filled with oil. After drying, the grain is emptied into tight Fe barrels.

3078. ———. [Reducibility of Cobalt Catalysts.] FIAT Reel K29, frames 7, 134–7, 135, 1938; PB 70,218; TOM Reel 295.

It is established by experiments that the reducibility of a constant volume of 3 types of catalysts (Co–Th–, Co–Th–Mg–, and Co–Mg–) decreases with an increasing proportion of kieselguhr, and that, with a kieselguhr proportion of 200, about 3 times the quantity of H_2 is necessary to reduce Th–Mg and Mg catalysts, compared with pure Th catalyst under otherwise equal conditions. 1 diagram.

3079. ———. [Regeneration of Cobalt Solutions From Catalyst Production.] FIAT Reel K–29, frames 7,124–7,128, 1938; PB 70,218; TOM Reel 296.

Description of tests on the regeneration of Co solutions by evaporation by which up to 90% of the Co has been recovered in form of lime-free Co nitrate salt. 2 tables.

3080. ———. [Cobalt–Nickel Catalysts.] FIAT Reel K–21, frames 1119–1121, July 22, 1941, PB 70,212; TOM Reel 288.

When ThO_2 was used as activator and under normal precipitating conditions, 35–50% of the Co was replaced successfully by Ni. The catalysts thus obtained showed fairly normal activity and satisfactory yields but a considerably lowered durability. In medium-pressure synthesis, the same catalysts, because of low activity, showed diminished Co output and correspondingly lower yields. The abundant formation of CH_4 in case of synthesis gas can be avoided by operating with water gas. Paraffin is formed only in insignificant amounts.

Increased addition of Mn has no considerable influence on this. The boiling point is virtually the same with synthesis gas and with water gas.

3081. ———. [Wet Synthesis.] FIAT Reel K–22, frames 1242–1249. FIAT Reel K–31, Jan. 20, 1942, pp. 1108–1115; Bureau of Mines Transl. T–459, July 8, 1948; TOM Reel 274, frames 1620–1631.

Wet synthesis experimental test was performed in 2 reactors: The 1st containing 55 l. of catalyst-oil mixture, the 2d, 85 l. Ten l. of catalyst (100 Fe : 5 Cu : 10 Mn : 100 kieselguhr) per reactor were found to give the highest conversion yield (73–75% in a single stage and 93–94% in 2 stages). The theoretical yield of 170 gm. has been reached in a 2-stage test with a total conversion of $CO+H_2$=90–93%. The average operating temperature varied 230°–250°. The synthesis pressure was 15 atm. The formation of CH_4 was lower throughout than in the corresponding dry synthesis test. When catalysts are used that produce paraffin preferentially and have a low tendency for producing CH_4, and average gasification of 3–4% may be counted on with a total conversion of 70–90%. The consumption ratio $CO : H_2$ was shifted towards the H_2 side in comparison with the dry synthesis. In the 1st stage, the ratio was mostly greater than 1 : 1.30. In the 2d stage, however, the reverse is true, and the consumption ratio is equal to about $CO : H_2$=1.0 : 0.90. The total consumption rato in the 1st and 2d stages corresponds to the proportion in the water gas and varies between 1 : 1.24 and 1 : 1.26. As in the dry synthesis, the composition of the products depends primarily on the nature of the catalysts and secondarily on experimental conditions such as temperature, pressure, circulation, etc. The products are always somewhat more saturated than in the dry synthesis. The tests have been run for 7.5 weeks without much reduction in activity. The gas throughput consisted of 1 synthesis gas to 2.5–3.0 recycle gas.

———. *See* abs. **2880.**

SCHENK, P. *See* abs. **408.**

SCHESSLER, D. O. *See* abs. **3501.**

3082. SCHEUMANN, W. W., AND RESCORLA, A. R. Aromatic Adsorption Index as Rapid Method for Approximating Catalyst Activity. Oil Gas Jour., vol. 46, No. 28, 1947, pp. 231–232, 234; Petrol. Refiner, vol. 26, No. 12, 1947, pp. 815–817; Petrol. Processing, vol. 2, No. 12, 1947, pp. 946–947; Chem. Abs., vol. 42, 1948, p. 1726.

This paper was presented at the 27th annual American Petroleum Institute meeting in Chicago. Of the various test methods for evaluating the activity of a catalyst, 2 have been used in the authors' laboratory: The Kellogg fluidized fixed-bed activity test based on a standardized laboratory cracking and the aromatic adsorption index based on surface area reactions. This paper presents data showing the degree of correlation between the 2 methods on both natural and synthetic fluid catalysts. A modified procedure, based upon the ability of a cracking catalyst selectively to adsorb aromatic hydrocarbons from a hydrocarbon mixture, is described in detail as better meeting personnel requirements and time limits for performing the tests. The test, in brief, is carried out by first heat treating the catalyst sample at a temperature of 850° F. A 3.5-gm. sample is then weighed into an adsorption vessel to which is added 5 ml. of a hydrocarbon mixture consisting of 30% toluene and 70% isooctane. The adsorption vessel is shkaen for 2 hr., after which the refractive index is determined on the supernatant liquid. The aromatic adsorption index is the difference between the refractive index of the original hydrocarbon mixture and that of the hydrocarbon mixture, after contact with the catalyst multiplied by 10^4.

SCHIBSTED, H. *See* abs. **1454.**

3083. SCHICK, F. [Developments in Coal Processing.] Braunkohle, vol. 24, 1926, pp. 1065–1070; Chem. Abs., vol. 20, 1926, p. 2240.

Discussion of cracking and hydrogenation processes and of the Synthol and synthetic MeOH processes.

3084. SCHILLER, G. [Synthetic Fats as Basis of Saturated Fatty Acids.] Ztschr. Lebensm. Untersuch. Forsch., vol. 88, 1948, pp. 174–190.

Review of the synthesis of fatty acids and fats by the Fischer-Tropsch method.

———. *See* abs. **1711, 1713, 1715, 1717.**

3085. SCHILLER, P. Oil Synthesis in Relation to Electricity and Gas Supply. Engineering, vol. 167, 1949, pp. 17–18; Fuel Abs., vol. 5, 1949, abs. 4976.

Relative overall thermal efficiencies of coal carbonization and electricity generation are discussed and the coal-economy efficiencies of gas and electricity are compared. There is every reason to expect the gradual replacement of natural petroleum products by synthetic products in the more distant future. The manufacture of synthetic hydrocarbons from coal is considered in some detail, particularly from the economic standpoint. A decline in the use of gas for domestic and industrial purposes is anticipated, but a far wider field for the carbonizing industry is expected in the combined carbonization and synthesis plants of the future.

SCHINDLER, H. *See* abs. **873, 874, 875, 876, 877, 878, 1477.**

3086. SCHLAPFER, P. [Manufacture of Replacement Fuels in Switzerland.] Schweiz. Ver. Gas- u. Wasserfach., Monats-Bull., vol. 18, 1938, pp. 49–60; Chem. Abs., vol. 32, 1938, p. 7241.

Review of the nature and extent of the national fuel requirements, and a discussion of the processes available for manufacture of motor fuels in Switzerland from domestic materials. In the absence of any quantity of suitable coal, peat and wood are suggested as raw materials for the synthesis of gasoline. High-pressure hydrogenation hardly can be considered for Swiss conditions. Synthesis by the Fischer-Tropsch process is practicable in small units and can be arranged to utilize wood, lignin, or mixtures of these with coke; there is also the possibility of using electrical energy in place of coke and in the preparation of H_2 by electrolysis. Cost estimates are presented, and the energy balance of various methods for producing fuel are shown. Each of these processes is discussed, and reference is made to the possibility of supplementary industries associated with the hydrolysis of wood and to the desirability of maximum recovery of motor fuel from gas works.

3087. ———. [Gas Research and Gas Evaluation.] Schweiz. Ver. Gas- u. Wasserfach., Monats-Bull., vol. 25, 1945, pp. 3–7, 61–68, 77–82; Chem. Abs., vol. 40, 1946, p. 7565.

Lecture reviewing recent developments in gas technology, especially various types of Fischer-Tropsch reactions, with their economic significance for Switzerland.

3088. SCHLATTMANN, O., AND KOPPENBERG, H. Motor Fuel Produced From Coal by 3 Processes in Germany. Trans. World Power Conf., 3d Conf., II, 4–5, September 1936, 20 pp.; Nat. Petrol. News, vol. 28, No. 37, 1936, pp. 24E–24H, 26, 28, 30, 32, 34; Chem. Abs., vol. 30, 1936, p. 8569.

Motor fuel is produced by high-pressure hydrogenation of coal and the products recovered therefrom; by low-temperature carbonization and extraction by synthesis; and by low-temperature carbonization, distillation, cracking, and extraction. The properties of gasoline produced from each method are compared. It is seen that the types of gasoline obtained by hydro-

genation and synthesis are fully equal to the refined gasolines obtained from crude oil. The raw material consumption per kg. of gasoline and the smallest economical operating unit for the various raw materials are as follows: By high-pressure hydrogenation of brown coal, 2.5 kg. and 40,000 tons; of bituminous coal, 1.66 kg. and 40,000 tons; of low-temperature brown coal tar, 1.25 kg. and 35,000 tons; by synthesis from brown-coal briquets, 10 kg. and 25,000 tons; from bituminous-coal coke, 5.4 kg. and 20,000 tons. Taking into account all the sources of energy, the thermodynamic efficiency (energy of finished products/energy of raw material) of the synthetic process lies 0.2–0.3, compared with 0.3–0.4 for the hydrogenation process.

3089. SCHLEEDE, A., RICHTER, M., AND SCHMIDT, W. [Zinc Oxide as a Catalyst.] Ztschr. anorg. Chem., vol. 223, 1935, pp. 49–83; Chem. Abs., vol. 29, 1935, p. 6827.

ZnO prepared by the thermal decomposition of Zn $(NO_3)_2$ at 360° luminesces oranged-red when excited by ultraviolet light or X-rays; and it does not catalyze the decomposition of MeOH at 360°. The luminescence is caused by the presence of twinning planes or boundary surfaces formed by the crystallizing together from the nitrate melt of crystallites into compact particles of ZnO. The lack of catalytic action is due to the compact nature of the product. On the other hand, ZnO prepared by the thermal decomposition of hydrated $Zn(OH)_2$ or $ZnCO_3$ at 360° does not luminesce, but it is a very active catalyst for the MeOH decomposition. Inasmuch as this ZnO was not crystallized from a melt, it lacks the twinning planes that cause fluorescence, whereas its noncompact, porous character favors catalytic action. Extreme purity of the initial substances used in preparing the ZnO is not a factor involved in these differences in behavior. The properties of ZnO prepared by other methods may lie between these 2 extreme cases. The luminescence of ZnO may be used analytically as an indication of the method of its preparation. The crystalline structure, size of the crystallites, and surface development of several differently prepared samples of ZnO were studied by means of Debye and Scherrer structure diagrams, by weighing and microcounting, by the determination of the degree of packing when jolted, by precipitation velocities, and by the adsorption of CO_2 and N_2.

3090. SCHLESINGER, M. D., CROWELL, J. H., LEVA, M., AND STORCH, H. H. Fischer-Tropsch Synthesis in the Slurry Phase. Ind. Eng. Chem., vol. 43, No. 6, 1951, pp. 1474–1479.

Study has been made of the slurry process as a means of developing an improved method for synthesizing liquid hydrocarbons from coal. A finely divided Fe catalyst suspended in oil is circulated by natural convection through a reactor in the presence of CO and H_2. A pilot-plant operation is described, and the effect of operating conditions on the synthesis is discussed. An increase in CO conversion with increasing temperature was noted, as was the formation of light hydrocarbons. The effect of operating pressure on light hydrocarbon production was found to be small; an increase in pressure at constant space velocity is accompanied by increased synthesis gas conversion. On a basis of the CO reacted, 5% appeared as C_1+C_2 hydrocarbons, 43% as heavier hydrocarbons (58% of which boiled in the gasoline range), and 42% as CO_2. Large amounts of oxygenated compounds were obtained in the light-oil and H_2O fractions. Potentially important advantages for the slurry process are indicated by the improved temperature control, mass transfer, and flexibility of operation.

3091. SCHMAHL, N. G. [Hydrolysis of Carbides.] Ztschr. Elektrochem., vol. 40, 1934, pp. 68–70; Brennstoff-Chem., vol. 15, 1934, p. 154; Chem. Abs., vol. 28, 1934, p. 2288.

It is known that in the hydrolysis of various carbides, hydrocarbons are produced. Thus, in the decomposition of (Ca, Sr, Ba, Mg, Be) C_2, of (Li, Na, K, Rb, Cs)$_2$ C_2 and of $Al_2(C_2)_3$ with H_2O, C_2H_2 is formed, while with Al_4C_3 and Be_2C, CH_4 and with Mg_2C_3 propyne is obtained. The reason for the formation of specific hydrocarbons is that in the decomposition at every point of the carbide lattice through oxide formation and the splitting of the lattice, determined amounts of H_2 and energy are available, which are divided among the hydrocarbon atoms present. Thus, in the decomposition of BeC_2, only C_2H_2, and in that of Be_2C only CH_4 can be produced according to the equations: $BeC_2+H_2O=BeO+C_2H_2$ and $Be_2C+2H_2O=2BeO+CH_4$. The relations are not quite so clear when mixtures of various hydrocarbons are produced. With the carbides of the rare earths besides other hydrocarbons, C_2H_2 and CH_4 are formed, in the ratio of 3:1, according to the equation: $4XC_2+6H_2O=2X_2O_3$ (hydrate) $+3C_2H_2+CH_4+CH_2$. The CH_2 radical may form various hydrocarbons depending on the energy relations. If the heat effect of oxide formation is strictly positive, then hydrocarbons with great energy demands (for example C_2H_4) are formed, if the opposite is true, liquid hydrocarbons are formed. With acid decomposition of Fe carbides, not only gaseous and liquid hydrocarbons are produced but also solid hydrocarbons and carbon. This makes the clarification of the reaction mechanism difficult. One must assume the presence of a carbide richer in C (for example FeC_2). There is considerable known of its existence, although there is yet no sure proof of it. The operating technique of catalysts appears to agree with the points discussed.

SCHMERLING, L. *See* abs. **1579a.**

3091a. SCHMERLING, L., AND IPATIEFF, V. N. Mechanism of the Polymerization of Alkenes. Advances in Catalysis, Academic Press, Inc., New York, 1950, vol. 2, pp. 21–80.

The discussion deals chiefly with polymerizations catalyzed by acid-acting catalysts. 89 refs. are listed.

3092. SCHMIDT, A. W. [Problem of Diesel Fuels.] Brennstoff-u. Wärmewirt., vol. 20, 1938, pp. 20–26; Brennstoff-Chem., vol. 19, 1938, p. 346; British Chem. Abs., 1938, p. 1007.

Developments in the production of diesel fuel from German raw material are reviewed. Cetene numbers, varying from 40 for brown-coal, low-temperature tar oils to 120 for fuels prepared by the Fischer-Tropsch process, are now available.

3093. SCHMIDT, A. W., AND KNEULE, F. [Motor Evaluation of Diesel Fuels.] Oel u. Kohle Erdoel Teer, vol. 14, 1938, pp. 1034–1041; Brennstoff-Chem., vol. 20, 1939, p. 272; British Chem. Abs., 1939, **B**, p. 234; Chem. Abs., vol. 33, 1939, p. 7989.

Tests for ignition characteristics are discussed and test results for several motors are tabulated. The effects of supplementary agents and various constituents, such as Kogasin, paraffins, phenol, etc., are set forth in detail with curves. Carbonization tendencies are discussed.

3094. SCHMIDT, J. [Catalytic Reductions of Carbon Monoxide.] Schweiz. Apoth. Ztg., vol. 64, 1926, pp. 237–240; Chem. Abs., vol. 21, 1927, p. 1699.

Review of the work of Fischer and Tropsch on Synthol produced at high pressures and on the synthesis at ordinary pressure of CH_4 and higher petroleum hydrocarbons.

3095. ———. [Nonexistence of a Higher Nickel Carbide.] Ztschr. anorg. Chem., vol. 216, 1933, pp. 85–98; Chem. Abs., vol. 28, 1934, p. 1618.

Since Fe forms a higher carbide and since H. Tutiya had reported detecting a higher Ni carbide, (abs.

3505) Schmidt attempted to prepare it by X-ray analysis. CO was passed over Ni (reduced by H_2) for 240–465 hr. at 240°–250°. All samples of carbide thus obtained contained 0.4–1.3% free C and 6.8–7.8% combined C. Although the latter was higher than the theoretical (6.37%) for Ni_3C, this was the only compound detected by X-ray studies. As all the possible places for C in the space lattice of Ni_3C are not filled, Schmidt assumes that the excess C takes some of these places without distorting the crystal. The density of Ni_3C computed from crystal data is 7.880 gm. per cc.; the experimental value (d^{25}_4) was found to be 7.957 gm. per cc. The excess C in the crystal may help account for the difference. The products of decomposition with acids were CH_4, C_2H_6, C_2H_4, and H_2, all being evolved in varying proportions. The results of decomposition were not reproducible. When CH_4 was passed over Ni, C was formed but no carbide. C_2H_2 gave Ni_3C and much C. Bibliography.

3096. ———. [Decomposition of Carbides by Water or Dilute Acids.] Ztscher. Elektrochem., vol. 40, 1934, pp. 170–174; Chem. Abs., vol. 28, 1934, p. 4675.

Carbides that are decomposed by H_2O or dilute acids may be divided into 3 groups: (1) Carbides of Fe, Co, Ni, and Mn having the formula M_3C. Al_4C_3 probably is to be included in this group. These carbides have a lattice in which the C atoms are separated, so that the products formed on treatment with H_2O or dilute acid result from the action of the H_2 set free by the decomposition upon each C atom separately. The reaction proceeds in several steps; $=CH_2$ radicals are formed 1st, and these are either converted to CH_4 by hydrogenation or polymerized to C_2H_4. From C_2H_4, by hydrogenation, polymerization, and further addition of $=CH_2$, hydrocarbons are formed with a larger number of C atoms. C_2H_2 is not formed by the decomposition of these carbides. (2) Carbides that give C_2H_2 on decomposition with H_2O or dilute acid. To this group belong the carbides of the elements of groups I and II of the periodic table; also Al_2C_3 and $Ce_2(C_2)_3$. The formation of C_2H_2 is due to the presence of C–C linkages in the crystal lattices of these carbides. UC_2 and the carbides of the rare earths give not only C_2H_2 but other unsaturated as well as saturated hydrocarbons, the composition of the gaseous product varying with the conditions of the decomposition. These carbides have the lattice of CaC_2 or one very similar. Their irregular behavior is due to the conversion of the metal, upon decomposition of the carbide, from the bivalent to the trivalent or quadrivalent form. (3) Carbides that give allylene upon decomposition. Only Mg_2C_3 is known here. Since the structure of its crystal lattice has not been investigated, no definite statement can be made in regard to the mechanism of the decomposition, but the production of pure allylene would indicate the presence of C–C–C linkages in the lattice.

3097. ———. Das Kohlenoxyd, seine Bedeutung und Verwendung in der technischen Chemie. Akad. Verlagsgesell., Leipzig, 1935, 235 pp.; Brennstoff-Chem., vol. 16, 1935, p. 220.

Chapter IV discusses the technical synthesis of MeOH, the higher alcohols, the CH_4 and benzine synthesis, and some others such as CH_2O, fatty acids, etc. The MeOH synthesis is treated very fully, but the benzine synthesis is covered in only 5 pages without a very comprehensive description.

3098. Schmidt, J., and Neumann, B. [Equilibrium: Methane–Carbon Dioxide and Carbon Monoxide–Hydrogen.] Ztschr. Elektrochem., vol. 38, 1932, pp. 925–934; Chem. Abs., vol. 27, 1933, p. 1260.

Equilibrium $CH_4+CO_2 \rightleftarrows 2\ CO+H_2$ was investigated experimentally, 500°–800°, and the equilibrium constants are compared with those calculated from the free energy data. Above 600° there is agreement, but below 600° the observed CH_4 transformation is larger than that calculated. This is due to 2 by reactions: $H_2+CO_2=CO+H_2O$ followed by $H_2O+CH_4=CO+3\ H_2$. The equilibrium was approached from the CH_4, CO_2 side, and the reaction proceeded without separation of C. The catalyst used was reduced Ni supported on SiO_2 gel. As an intermediate step in the primary reaction, NiO apparently is formed.

3099. Schmidt, L. D. Synthesis Gas From Pulverized Coal, Oxygen, and Highly Superheated Steam Is Produced in Pilot Plant. Am. Gas Jour., vol. 175, July 1951, pp. 10–14, 42.

Work described in this paper is given in full detail in Bureau of Mines Rept. of Investigations 4733 (abs. **3306**).

———. *See* abs. **144, 768, 2455, 3022, 3024, 3150, 3151, 3152 3305a, 3306.**

3100. Schmidt, L. D., McGee, J. P., and Slone, M. C. Pilot Plant for Gasifying Powdered Coal Entrained in Oxygen and Steam. Chem. Eng. Progress, vol. 44, No. 10, 1948, pp. 737–744; Chem. Abs., vol. 43, 1949, p. 378.

Pilot plant for producing low-cast synthesis gas from powdered coal, superheated steam, and O_2 is described, and some of the factors involved in its design are considered. Only a preliminary-progress report is made as the plant is not completed and no experimental operating data are yet available. Some potential thermodynamic approximations are presented for the purpose of discussion. O_2 production is to be studied in 2 plants—1 producing 1,000 cu. ft. per hr. and the other, a German Linde-Fränkl installation, 23,000 cu. ft. per hr. The latter has operated for the production of 98% O_2 at a consumption of only 13.1 kw.-hr. per 1,000 cu. ft. O_2.

3101. Schmidt, R., and Groh, E. [New Process for the Continuous Production of Water Gas and Synthesis Gas. I.] Braunkohlenarch., No. 44, 1936, pp. 50–53; Chem. Abs., vol. 30, 1936, p. 5757.

Experimental apparatus and process are described using brown-coal coke and depending upon supplying endothermic heat for the water-gas reaction by means of heated, highly conductive steel tubes.

3102. ———. [New Process for the Continuous Production of Water Gas and Synthesis Gas. II.] Oel u. Kohle Erdöl Teer, vol. 12, 1936, pp. 41–51; Chem. Abs., vol. 30, 1936, p. 5757.

Theoretical aspects and previous laboratory findings are discussed. Technical scale apparatus of 2,000 $m.^3$ per day capacity and its operation are described. Tests of 90 and 69 hr. using low-temperature coke to produce synthesis gas ($CO:H_2$ ratio 1:2) were made; slight changes in design reduced CH_4 content of gas from 3.6% to 2.2%. Technical and domestic possibilities are discussed.

Schmidt, W. *See* abs. **3089.**

Schmitt, K. *See* abs. **3168.**

Schmitt, P. *See* abs. **1604.**

3102a. Schmitz, D. [Synthetic Gasoline, Its Past and Its Prospects for the Future.] Ind. chim. belge, vol. 16, 1951, pp. 335–347.

Summary, 44 refs.

3103. Schmitz, E. [Germany and Liquid Fuels.] Chaleur et ind., vol. 16, 1935, pp. 69–70.

Brief account of the Fischer-Tropsch process with some remarks as to the nature of the products.

3104. Schneider, A. [Synthetic Mineral Oils.] Leben u. Umwelt, vol. 6, 1950, pp. 81–87; Chem. Abs., vol. 44, 1950, p. 2731.

Illustrated discussion of the Bergius and Fischer-Tropsch processes.

SCHNEIDER, H. J. *See* abs. **7**.

SCHÖNFELDER, R. *See* abs. **1205**.

SCHOON, T. *See* abs. **1368, 1369**.

SCHRADER, A. *See* abs. **1170, 1356**.

3105. SCHRADER, H. [Production of Formic Acid From Carbon Monoxide and Steam, and From Carbon Dioxide and Hydrogen, at High Temperatures and Pressures.] Ges. Abhandl. Kenntnis Kohle, vol. 6, 1921, pp. 65–78; Chem. Abs., vol. 19, 1925, p. 36.

By heating 20 cc. of water with Co under 135 atm. pressure in Fe autoclaves, 14.2 and 7.2 cc. of 0.1 *N* HCO_2H were obtained at 350° and 400°, respectively, while the residual gases contained, respectively, 14.0% and 28.0% of CO_2. Considerable quantities of Fe carbonyl were in the solution. On using a Cu-lined autoclave, the quantity of HCO_2H produced increased successively from 5.55 cc. to 14.4 cc. of 0.1 *N* solution in 5 experiments, and the CO_2 content of the residual gases fell 34.1–4.2%. Apparently some impurity with a harmful catalytic action was removed gradually from the apparatus or was rendered inactive; these results, however, could not always be repeated. Only small quantities of formic acid could be obtained in autoclaves lined with Ag, and, moreover, the residual gases contained but little CO_2. The action of Fe and Cu agrees with observations by Armstrong and Hilditch (abs. **76**). The hydrogenating action of CO and steam upon coal (see abs. **749** and **750**, Part I, of Bibliography of Pressure Hydrogenation, Bureau of Mines Bull. 485), apparently depends upon the intermediate formation of HCO_2H. In the thermal decomposition of HCO_2H at 400° under 120 atm. pressure in Cu autoclaves, the proportion remaining undecomposed was approximately the same as that produced from CO and steam, but, at 300°, the proportion undecomposed was somewhat greater than that formed at the same temperature. The formation of HCO_2H from a mixture of CO_2 under 30 atm. and H_2 under 50 atm. pressure was much greater in Fe than in Cu autoclaves. In the presence of Na_2CO_3, the yield of 0.1 *N* HCO_2H was 78.3 cc. at 350°. H_2 and Na_2CO_3 solution, on heating in Fe autoclaves, yielded 15.7 cc. of 0.1 *N* HCO_2H, but none was obtained in Cu autoclaves.

3106. SCHRAUTH, W. [Fatty Acids From Coal.] Chem.-Ztg., vol. 63, 1939, pp. 274–278, 303–306; Allgem. Oel- u. Fett-Ztg., vol. 36, 1939, pp. 413–419; Chem. Abs., vol. 34, 1940, p. 8315.

C_{20}–C_{35} fraction (b. above 350°) is considered most suitable for oxidation. For the mechanism of oxidation, a CH_2-group near the center is oxidized preferentially.

3107. SCHREIBER, —. [Dehydrogenation of Long-Chain Paraffin Hydrocarbons.] FIAT Reel K–28, frames 6426–6434, Feb. 12, 1944; PB 70,185; TOM Reel 295.

Th, Zn, and Cu chromites are suitable catalysts for the dehydrogenation of long-chain hydrocarbons. Increasing the olefin yields over 23% is not recommended, as above that a considerable aromatization begins. The olefins are well-suited for lubricating-oil synthesis, but generation of aromatics in the dehydrogenation process makes the method unfavorable from an economic point of view.

3108. SCHREINER, E., AND GRIMNES, F. B. [Reversible Reaction Between Iron and Steam.] Ztschr. anorg. Chem., vol. 110, 1920, pp. 311–334; Chem. Abs., vol. 14, 1920, p. 3346.

Measurements of the equilibrium pressures of H_2O vapor and H_2 in the reaction $Fe+H_2O \rightleftharpoons FeO+H_2$ were made 595°–920°, using an apparatus similar to that 1st used by Denville (Compt. rend., vol. 70, 1870, pp. 1105, 1205.) It was shown that refinements in the apparatus introduced by other workers with the object of accelerating the diffusion of the gases in the reaction tube were unnecessary. The values obtained for $K=pH_2O/pH$ were in good agreement, starting from either side of the equilibrium position. There are considerable discrepancies between the results obtained by different workers, particularly at high temperatures, where, in all cases, the value of K is much lower than that calculated from thermodynamic principles. The discrepancies probably are due to reactions in the solid phase, for example, the formation of solid solutions between Fe and FeO, or to the different behavior of different modifications of Fe. Further experiments are suggested to test this hypothesis.

3109. SCHROEDER, W. C. Investigation of the German Synthetic Liquid Fuel Industry. PB 283–S, 13 pp.

This report supplements PB 283 (abs. **96**) and deals primarily with synthetic fuels. A list of the major plants and laboratories investigated, their location, and products is shown in table 1. The Winkler and Lurgi processes for gasification of solid fuels are mentioned, as well as the Fischer-Tropsch process for liquid fuels, the hydrogen process, 3 methods for producing lubricating oil, and a like number of shale extractions.

3110. ———. Fuels and Fuel Research in Great Britain During the War. Mech. Eng., vol. 65, 1943, pp. 881–884, 892.

Among other things are discussed the production of liquid fuels from coal by the Imperial Chemical Industry, Ltd., at Billingham and by the Fuel Research Station on a laboratory scale by the hydrogenation and Fischer-Tropsch processes, respectively.

3111. ———. Conversion of Coal to Oil. United States Senate, 78th Cong., 1st sess., on S. 1243, 1944, pp. 221–224.

Taken from Synthetic Liquid Fuels Hearings before a subcommittee of the Committee on Public Lands and Surveys, and touches on the status of coal hydrogenation development in Great Britain and the relation of the United States to it.

3112. ———. German Synthetic Liquid Fuels Industry. United States Senate, 79th Cong., 1st sess., on S. Res. 36, June 19–25, 1945, pp. 349–360.

Account at the hearings before a special committee investigating petroleum resources of the visit of American technologists to, and their investigations of, the German synthetic oil industry in 1945. It was found that German technology with respect to synthetic fuel was in advance of American technology, and research development had progressed so far and so rapidly that, even in the German plants, commercial application had not kept pace. However, the opinion was confirmed that, on the basis of large operating units, American engineering practice could improve materially the process development and the operating status over German standards with a considerable reduction in costs. It was thought that aviation-grade gasoline was being produced for about $0.16–0.25/gal.

3113. ———. Technical Oil Mission Studies German Petroleum-Research Activities. Oil Gas Jour., vol. 44, No. 29, 1945, pp. 112, 115, 116; Chem. and Met. Eng., vol. 53, No. 1, 1946, pp. 220, 222, 224.

Paper presented at the November meeting of the American petroleum Institute. No special progress is reported in Fischer-Tropsch technology; no plant has been built since 1938. Synthesis gas was made almost universally by the water-gas reaction, using coke; brown coal was just being tested. Both atmospheric and medium pressure (10 atm.) were being applied, the latter being preferred. All commercial operations were carried out with the Co–Th–Mg–kieselguhr catalyst; only pilot plants were using the Fe catalyst. In general, 2-stage conversion was practiced; 1 plant used a 3-stage process. Gas was not recycled except in pilot plants; this and the Fe catalyst increased the

olefin content and, thus, the octane rating of the product. Synthesis of alcohols was a live problem; the Oxo process was particularly interesting (abs. **2531**). At a pressure up to 200 atm. and temperatures below 300°, it was reported that C_2H_4 and C_3H_6 and probably other unsaturates could be converted to alcohols by reaction with H_2O in the presence of W oxide on silica gel. The synthesis of isoparaffins is an important laboratory development. By using catalysts of Al_2O_3, ThO_2, ZnO, or mixtures of these at pressures of 300 atm. and 400° with a synthesis gas containing 20% more CO than H_2, a product can be obtained whose C_4 and C_5 fractions contain over 90% of isocompounds. The yield is about 100 gm./per. m.^{3} of synthesis gas. Research, not considered promising in Germany, has been carried out on the synthesis of aromatics in the range 475°–500° at elevated pressures using catalysts of Cr, Mo, and Th oxides. The yield of product was low but did contain about 50% aromatics and the same amount of naphthenes. Research on lubricating oil was very successful: 4 methods were in commercial use: Cracking of Fischer-Tropsch wax or oil and subsequent polymerization; chlorination of Fischer-Tropsch middle oil and subsequent reaction with naphthalene in the presence of $AlCl_3$ catalyst; synthesis from C_2H_4 in the presence of a specially prepared $AlCl_3$ catalyst; and a modification of the first-named process (no details).

3114. ———. Production of Synthetic Liquid Fuels From Coal, Lignite, and Oil Shale. Report to Federal Power Commission, June 1946, 7 pp.

Brief review of Bureau of Mines synthetic liquid fuels program, including investigation of German plants and processes.

3115. ———. Synthetic Liquid Fuels in the United States. Mech. Eng., vol. 69, 1947, pp. 989–995; vol. 70, 1948, pp. 555–556; Oil Gas Jour., vol. 46, No. 31, 1947, p. 128; Chem. Abs., vol. 42, 1948, p. 733.

Synthetic fuels industry capable of producing 1–2,000,000 bbl./day should be established as soon possible so as not to cause too great a drain of national resources during a possible future emergency. Depending upon the raw materials available, the H_2O supply, the predominant type of products wanted, the location of the market, and the transportation expense, such a fuel will range in cost from \$0.03–\$0.05 per gal. above present petroleum fuel prices. Raw materials will be natural gas, coal, and oil shale. From an available 50 trillion cu. ft. of natural gas, 4–5 billion bbl. of liquid products should be obtained. Coal hydrogenation is well adapted to the production of aviation fuel and is the only synthetic process at present that will give a base stock for 100-octane gasoline with good rich-mixture performance. It does not produce good Diesel fuel and will not produce motor gasoline as cheaply as the Fischer-Tropsch process. Oil shale is simple to process, takes less initial investment, and can be refined to yield fuel oil and Diesel fuel with a cetane rating 34–45. Gasoline from oil shale is, at present, unsuitable for motor fuel as it has an octane number of only 50–60. Two new catalytic oil-processing methods have been developed and give promise of satisfactory commercial application: The fluidized technique of the oil industry and the oil-cooled catalyst method of the Bureau of Mines.

3116. ———. Comparison of Major Processes for Synthetic Liquid Fuels. Chem. Inds., vol. 62, No. 4, 1948, pp. 575–577, 682.

Three processes for the production of synthetic liquid fuels—oil shale retorting, Fischer-Tropsch gas synthesis process using coal, and coal hydrogenation—are compared with respect to the types of fuels produced, the state of development of the process technology, the amounts and location of raw materials required, and the indicated investment and operating costs. Oil shale is now best adapted to the production of fuel and heavy Diesel oil. The Fischer-Tropsch process yields good motor gasoline and excellent Diesel fuel. Coal hydrogenation gives aviation gasoline or a range of fuel oils. Considerable variation in estimates of the cost of the finished products is to be expected. For crude shale oil under large-scale operations, the capital cost is placed at \$2,000 per bbl. per day, whereas production costs are estimated at from \$1.75–\$2.75 per bbl. Like estimates for the gas synthesis process using coal are \$9,000–\$10,000 per bbl. per day for plant and \$3.50–\$4.50 per bbl. for the gasoline product. Any reduction in the latter figure will have to result from lower synthesis gas costs. For coal hydrogenation, the respective figures are \$10,700 per bbl. per day and \$0.14–\$0.19 per gal. of aviation gasoline. Approximately 50% of the cost of fuel production is in the H_2. The use of natural gas at \$0.05 per 1,000 cu. ft. instead of coal at \$3.00 per ton would reduce this cost about ⅔. How technical improvements in the equipment and the operations are leading to lower costs also is pointed out.

3117. ———. Fischer-Tropsch Alcohol. Chem. Eng. Progress, vol. 44, No. 1, 1948, pp. 15–17.

Raw materials and the processes for making synthetic alcohols are discussed. Two processes have been developed: The Synol and the Oxo processes. The chemistry of each of these processes is explained, the former gives straight-chain, the latter branched-chain alcohols.

3118. ———. Synthetic Fuel Production. Petrol. Eng., Refining Gas Processing Sec., vol. 21, October 1949, p. A–53.

Paper presented at United Nations Resources conference. Estimates are shown on the cost of producing petroleum substitutes from coal, either by hydrogenation or by synthesis, and from oil shale by retorting: From oil shale, \$0.055 per gal.; from natural gas, \$0.072 per gal.; from gas derived from coal, \$0.121 per gal.; from coal hydrogenation, \$0.126 per gal. These figures are based on a hypothetical industry with a productive capacity of 2,000,000 bbl. per day. Such an industry would require a capital investment of about 12 billion dollars. Capital investment per bbl. per day is estimated at \$3,100 for shale oil, \$5,300 for synthetic oil from natural gas, \$8,600 for synthetic oil from coal by gas synthesis, and \$9,000 for oil from coal by hydrogenation. A comparative estimate of the capital investment necessary to find, develop, produce, transport, and refine crude petroleum is \$5,000–\$6,000 per bbl. per day.

3119. ———. Synthetic Fuel Production. Petrol. Eng., Refining Gas Processing Sec., vol. 22, No. 5, 1950, pp. A53, A56, A60, A64, A66, A68.

Recent progress in the production of synthetic liquid fuel by pressure coal hydrogenation, Fischer-Tropsch process and retorting of oil shale is reported. Active study of the Fischer-Tropsch synthesis process centers around the production of synthesis gas and development of reaction chambers with high production capacity. 3 types are under investigation: The 1st uses a fluidized catalyst with removal of heat by circulation of cooling water; the 2d uses a fixed-bed catalyst, either pelleted or granulated, immersed in oil to control the temperature; the 3d uses a finely powdered catalyst suspended in an oil bath and cooled by heat exchange. Intensive studies are being made of the coal-hydrogenation process to raise the thermal efficiency above the possible present practical range of 45–50%. The dry hydrogenation of coal also is receiving considerable developmental study. In the oil shale demonstration plant, mining methods and equipment have been developed to assure low-cost production. 3 retorting methods are being studied: The gas flow retort of the

Bureau of Mines, the fluid-flow unit of the Standard Oil Development Co. and the internally fired underfeed retort of the Union Oil Co. of California. It is expected that 1 or more of these methods will be found suitable for economical retorting of American oil shales.

3120. ———. Synthesis of Chemicals From Coal and Oil Shale. Chem. and Eng. News, vol. 29, 1951, p. 1830.

Paper presented at the National Capital Section meeting of the American Institute of Chemical Engineers. Motor fuels from oil shale are now capable of competing successfully with fuels from petroleum. It is predicted that an oil-shale plant designed to produce gasoline, motor oil, and Diesel fuel will pay for itself in 8–10 yr. If operated to manufacture chemicals it could pay for itself in 2–3 yr. There should be no delay in establishing a synthetic fuels industry; a satisfactory supply of petroleum is to be expected until about 1954, and then increasing shortages will develop. Nor can the country depend upon imports, particularly during wartime, to make up severe shortages of petroleum. Furthermore, the cost of producing petroleum will inevitably rise because of the added costs for exploration and for drilling deeper wells. At the same time, the cost of obtaining synthetic fuels from coal and oil shale is bound to decline.

———. *See* abs. **96, 97, 926, 2437, 2530b.**

3121. SCHROEDER, W. C., AND FIELDNER, A. C. American Advances in the Manufacture of Synthetic Liquid Fuels. Internat. Chem. Eng., vol. 31, 1950, pp. 503–506.

Paper read at the 4th World Power Conference, London, 1950. A review of developments in coal hydrogenation, the Fischer-Tropsch process, and oil-shale processing in the United States is presented. The improved relative cost position between the products of synthesis and of petroleum is discussed; the trend is growing in favor of the synthetic product, and it is probable that a large synthetic fuel industry based on coal and oil shale will develop. An estimate has been made of the initial and the operating costs of a 30,000-bbl.-per-day coal-hydrogenation plant using Wyoming bituminous coal. From a consumption of 11,830 short tons of coal per day, 21,660 bbl. gasoline, 7,100 bbl. L. P. G. and 1,240 bbl. phenols would be produced. The cost of the gasoline, with L. P. G. and phenols credited at $0.08 per gal. and $0.10 per lb., respectively, would be $0.101 per gal. The total plant cost would be 243 million dollars or $8,100 per bbl. per day. At present, cost estimates for commercial Fischer-Tropsch plants operating on coal are in a preliminary stage; estimates are awaited from the demonstration plant being erected at Louisiana, Mo. It appears at present that the initial cost of a 10,000-bbl.-per-day plant will be about $7,500 per bbl. per day. The cost of producing gasoline and other products appears to be about the same as for coal hydrogenation. Estimates have been made for an oil-shale plant to produce about 100,000 bbl. of oil per day. The initial investment for the entire plant from mining to refining would approximate 409 million dollars or $4,090 per bbl. of oil per day. Operating costs for shale-oil production are about $1.43 per metric ton of shale or $2.00 per bbl. of crude shale oil. Assuming a 75% recovery in the refinery, the final products will cost about $3.50 per bbl., or $0.084 per United States gal. A breakdown of mining costs totaling $0.65 per metric ton is given.

3122. SCHROEDER, W. C., AND ORCHIN, M. Oxo Reaction. Chem. Eng., vol. 58, No. 3, 1951, pp. 135–136.

Oxo process for production of aldehydes and alcohols from olefins by reaction with CO and H_2 has stimulated considerable interest and process development. The status of the reaction is at present highly competitive and process developments have not been revealed. It has been quite firmly established that either dicobalt octacarbonyl or cobalt hydrocarbonyl is the active catalyst and that these compounds are readily formed from any salt of Co or from the activated metal. There are some advantages (such as lower reaction temperature) to using preformed dicobalt octacarbonyl as the catalyst. Basic research on the chemistry of the Oxo process being conducted at the Bureau of Mines has led to some valuable developments: (1) 1-stage production of alcohols by using fairly large Co concentrations and higher-than-usual temperatures; (2) hydrogenation of aliphatic aldehydes and ketones to alcohols and of aromatic ketones and alcohols by hydrocarbons under Oxo conditions; (3) evidence that the hydrogenation is homogeneous and, therefore, applicable to S-containing compounds; (4) the homologation reaction by which MeOH can be converted to EtOH, benzyl alcohol to 2-phenyl ethanol, and tertiary butyl alcohol to isoamyl alcohol. The process has not been in operation long enough to permit evaluation of its impact on the chemical industry. It is likely that the reaction will receive consideration wherever large quantities of any kind of olefins are available. Those of interest not only include those in cracked gases, alkylation byproducts, and Fischer-Tropsch oils but other materials, such as the terpenes and unsaturated fats and oils.

SCHROETER, K. *See* abs. **3251.**

3123. SCHROETER, R. [New Methods in Organic Synthesis. XIII. Hydrogenation With Raney Catalysts.] Angew. Chem., vol. 54, 1941, pp. 229–234, 252–260; Chem. Abs., vol. 35, 1941, p. 6241.

Comprehensive review of the preparation and properties of Raney metals, hydrogenation with catalysts of Fe, Cu, Co, and Ni, hydrogenation of C_2H_4 and C_2H_2 bonds and of the CO group, introduction of the NH_2 group by catalytic reduction, reduction of the COOH group and of halogen-containing compounds, and hydrogenation of aromatic and heterocyclic compounds.

3124. SCHUESSL, F. [Conversion of Carbon Monoxide Under Increased Pressure With Steam.] Gas- u. Wasserfach, vol. 82, 1939, pp. 359–362; British Chem. Abs., 1939, B, p. 685; Chem. Abs., vol. 33, 1939, p. 6562.

Catalyst composed of active C and MgO promotes the conversion of $CO+H_2O=CO_2+H_2$ at 350°–420° and 12–14 atm. with little tendency to CH_4 formation or other side reactions. It is insensitive to S, converting organic S compounds into H_2S and destroying NO. The process is well adapted for producing gases for synthesis of NH_3, MeOH, etc. and for detoxifying town gas. Working results of 2 installations are summarized.

3125. SCHUFF, —. [Thorium–Magnesium Catalysts for Gasoline Synthesis.] FIAT Reel K–30, frames 7448–7453, no date, PB 73,587; TOM Reel 297.

Report of the experiences gained with the Th–Mg catalysts in the gasoline synthesis. The catalysts were supplied by the Kator-Fabrik at Holten. These catalysts were definitely superior to the Th catalysts.

3126. ———. [Experiences With Thorium and Magnesium Catalysts in the Plants of the Ruhrchemie A.-G.] FIAT Reel K29, frames 7,109–7,115, 1938; PB 70,218; TOM Reel 296.

Survey of experiences with catalysts prepared by licensees of the Ruhrchemie. No results of general importance were obtained.

3127. ———. [Influence of the Reduction Conditions on the Activity of Thorium and Thorium–Magnesium Catalysts.] FIAT Reel K–29, frames 7,136–7,138, 1938; PB 70,128; TOM Reel 296.

Description of some tests on the experimental confirmation of old conceptions concerning the nature of

the catalytic process, especially of the action of catalyst additions. Some practical conclusions are drawn from the results.

———. *See* abs. **1171.**

3128. SCHUFTAN, P. M. Modern Gaseous Oxygen Production Methods. Gas Times, vol. 54, 1948, pp. 274–281; British Abs., 1948, B, I, p. 299.

Paper read to the Institute of Chemical Engineers, February 1948. Methods for the production of medium-purity O_2 are discussed in detail. The development of regenerators and reversing exchangers as efficient heat exchangers and purifiers and of highly efficient machines for cold production by isentropic expansion, assisted by the possibility of using more efficient rectification processes, led to an increase of the thermodynamic efficiency of medium-purity O_2 plants to 19%, compared with 13% achieved in the best classical plants. Prospects of further improvements are discussed. A further approach to more reversible rectification methods appears to offer most promise. In this connection the Rescol process, a development of the British Oxygen Co. is described; detailed estimates of power consumption of this and 3 other medium-purity O_2 processes, the Linde-Fränkl expansion-engine type, the Linde-Fränkl turbine type, and the Kellogg plant, are given. The problem of producing enriched air is discussed; large-scale developments are imminent.

SCHULTE, F. *See* abs. **167.**

3129. SCHULTES, W. [Manufacture of Water Gas and Gas for Synthesis From Bituminous Coal.] Glückauf, vol. 72, 1936, pp. 273–285; Chem. Abs., vol. 30, 1936, p. 6168.

Development of the water-gas generator is traced, and its application in producing synthesis gas ($CO+2H_2$) for making synthol of Fischer–Tropsch is discussed. Both coke and bituminous coal are considered as fuels. The Didier chamber-oven process involving production of low-temperature gas, which is cracked in the process to supplement the water gas H_2, is one of the most economical. Low-grade noncoking coal is used. Graphs are given showing costs per kg. oil, using various water-gas methods, with varying costs per ton of fuel.

SCHULTZ, P. R. *See* abs. **2836, 2837.**

3130. SCHULTZE, G. R. [Thermodynamic Equilibria of Hydrocarbon Reactions Applied to Destructive Hydrogenation. III.] Angew. Chem., vol. 49, 1936, pp. 284–288; Chem. Abs., vol. 30, 1936, p. 6176.

Fischer process is workable at ordinary pressures because the hydrogenated products are stable at the low temperatures used. However, the Bergius process requires high pressures owing to the unfavorable position of the equilibria of certain cyclic reaction types at the high temperatures necessary for the destructive hydrogenation. Lowering the required high pressures should be possible if highly active catalysts can be developed. This does not hold if aromatic gasolines of high knock rating are to be produced.

3131. SCHULZ, B. [Progress in the Production and Utilization of Liquid Fuels.] Brennstoff-u. Wärmewirt., vol. 9, 1927, pp. 9–16; Chem. Abs., vol. 21, 1927, p. 1532.

Discussion, with bibliography.

3131a. SCHULZ, G. [Drilling Oil.] Erdöl u. Kohle, vol. 4, 1951, pp. 288–290; Chem. Zentralb., 1951, II, p. 3,537.

Bohrmittel Hö is obtained through the action of SO_2 and Cl_2 on Mepasin (hydrogenated Kogasin), subsequent conversion of the sulfochlorinated mixture by NH_3 and chloroacetic acid. The active ingredient of the final mixture is the Na salt of Mepasinsulfamidoacetic acid. H_2O emulsions containing from 0.5–5% are effective coolants and lubricants for many types of metal working and will prevent corrosion. It is an effective emulsifier for mineral oils.

3132. SCHUMAN, S. C. Role of the Carbides of Iron in the Fischer–Tropsch Synthesis. Jour. Chem. Phys., vol. 16, 1948, p. 1175; Chem. Abs., vol. 43, 1949, p. 1636.

Equilibrium constants have been calculated for the formation of hydrocarbons from Fe_2C, CO, and H_2 in accordance with the reactions:

$$(1)\ Fe_2C+(2n-1)H_2+(n-1)CO=C_nH_{2n}+2Fe+(n-1)H_2O$$

$$(2)\ Fe_2C+2nH_2+(n-1)CO=C_nH_{2n+2}+2Fe+(n-1)H_2O$$

by which hydrocarbons are produced with each hydrocarbon molecule containing 1 C atom derived from an Fe_2C intermediate, using the free energy data for Fe_2C given by Kummer, Browning, and Emmett, and the data for CO, H_2O, and hydrocarbons of Rossini. The equilibrium constants for both reactions are shown at 227° and 327° for $n=2$ and $n=8$. These data indicate that the formation of hydrocarbons from Fe_2C is thermodynamically possible under the conditions employed in the Fischer-Tropsch synthesis. While no claim is made that reactions (1) and (2) represent the chemical process responsible for the formation of Fischer-Tropsch hydrocarbons, they are at least as compatible with the experimental synthesis data as the reactions considered by Kummer, Browning, and Emmett.

3133. SCHUSTER, —. [Adsorption of Gases on Catalyst Carriers and Hydrogenation Catalysts.] I. G. Farbenindustrie-Zetko Rept., FIAT Reel C–29, frames 1415–1425, April 1939, 11 pp.; PB 76,463; Bib. Sci. Ind. Repts., vol. 7, 1947, p. 570.

Measurements on catalyst carriers have been made in order to determine the conditions upon which the adsorption depends. The selective effect of adsorption for a number of gases, such as C_2H_2, C_2H_4, C_2H_6, H_2, or A, has been studied on several catalysts, such as pumice, bauxite, silica gel, charcoal, activated aluminum gel, Zn oxide, and catalyst 5058 consisting of heavy metal sulfides. Tables and graphs comparing adsorption isotherms and tables of reaction and of adsorption on the catalyst.

3133a. SCHUSTER, C. [Oxo Synthesis.] Fortschr. chem. Forsch., vol. 2, 1951, pp. 311–374; Chem. Abs., vol. 46, 1952, p. 886.

Comprehensive summary of the literature concerning the Oxo synthesis, discussing the reaction conditions (pressure, temperature, catalysts), reaction mechanisms, and the application of the synthesis to aliphatic olefins and dienes, C_2H_2, aromatics, cyclic olefins, arylolefins, halogens, N, and O compounds. 86 references.

3134. SCHUSTER, F. [Technical] Practicability of the Production of Liquid Fuels in Gasworks and Coke-Oven Plants.] Chem.-Ztg., vol. 57, 1933, pp. 661–662; Chem. Abs., vol. 28, 1934, p. 2878.

Various methods for converting coal into liquid products by way of gasification and hydrogenation are brought together into a single flow sheet. The table shows the temperature, pressure, and catalysts necessary, and the suitability of the different methods for use in gasworks and coke ovens is discussed.

3135. ———. [Water-Gas Equilibrium and Nonpoisonous Gas.] Gas- u. Wasserfach, vol. 80, 1937, pp. 304–307; Chem. Abs., vol. 31, 1937, p. 5133.

New values for the water-gas equilibrium constant were calculated with the latest values and new equations for the specific heat of CO_2, CO, H_2, and H_2O. These values for the water gas equilibrium (given from 300°–600°) are about 12% lower than those used earlier

and are in agreement with the experimental results at 400°. Experiments were made as to the effect of use on the catalyst employed. This catalyst consisted of colloidal Fe oxide activated with KOH and formed into balls with cement. Initially, absorption of CO_2 by the catalyst increased its temperature, although this was lowered somewhat by desorption. The conversion of the higher Fe oxides into lower ones by the reducing gases required less heat than was supplied by the combination of CO and H_2. When equilibrium is reached with the catalyst, heat is continually evolved owing to the exothermic nature of the reaction of CO and H_2, and this heat is enough to cover process requirements. These laboratory observations were confirmed by observations at the Hameln plant.

3136. ———. [Production of Standard Public-Utility Gases From Combustible Industrial Gases.] Gas- u. Wasserfach, vol. 85, 1942, pp. 174–177; Chem. Abs., vol. 37, 1943, p. 3907.

Discussion of the possibility of changing the composition of typical combustible gases, for example, gas from the low-temperature carbonization of coal, residual gas from the Fischer-Tropsch process, and sewage gas, to that of town gas or coke-oven gas by addition of water gas having a suitable CO : H_2 ratio. Theoretical examples are worked out.

3137. SCHUSTER, F., PANNING, G., AND BUELOW, H. [Methane Formation in Carbon Monoxide- and Dioxide-Containing Gas Mixtures With Various Nickel Catalysts.] Brennstoff-Chem., vol. 16, 1935, pp. 368–369; Coal Carbonisation, vol. 1, 1935, p. 127; Chem. Abs., vol. 30, 1936, p. 3967.

After referring to Fischer and Pichler's observations on the effects of Ni–Al catalyst in the formation of CH_4 from mixtures of CO_2, CO, H_2, the authors present the results of their own investigations with town gas subjected to water-gas catalysis (activated Fe oxide contact at 450° C. with steam) and then passed over electrically heated Ni contacts. The results confirm Fischer and Pichler's observations. The effects of different catalysts vary, and the following cases have been found: (1) Selective hydrogenation of CO, the CO_2 being attacked after complete conversion of CO; (2) simultaneous hydrogenation of both oxides without preferential complete conversion of either; (3) simultaneous hydrogenation of both oxides with preferential complete conversion of CO to CH_4. In (2) and (3), the formation of CH_4 depends upon the ratio of CO to CO_2 and excess H_2. With Ni catalysts the reaction continues to water-gas equilibrium after CH_4 catalysis has been poisoned.

3138. SCHUSTER, L. [Status of Coal Liquefaction.] Dingl. poly. Jour., vol. 345, No. 10, 1929, pp. 184–187.

MeOH synthesis of I. G. Farbenindustrie A.-G. and lignite high-pressure hydrogenation are discussed, and a brief general description of Bergius, Fischer-Tropsch methods.

3139. SCHÜTZA, H. [Behavior of Active Cobalt Toward Water in the Fischer-Tropsch Catalyst.] Chemie-Ing. Tech., vol. 21, 1949, pp. 177–179; Ind. Chemist, vol. 25, 1949, pp. 450–451; Chem. Abs., vol. 43, 1949, p. 6497.

Metallic Co in active form is contained in the catalyst of very small particle size. The equilibrium $CoO+H_2 \rightleftharpoons Co+H_2O$ is calculated on the basis of increased active surface and resulting higher surface energy. The calculations and some of the experimental data indicate that in commercial practice oxidation of the catalyst may occur with corresponding inactivation of the metallic Co.

3140. SCHWAB, G. M., AND DRIKAS, G. [Inhibiting Action of Methane on the Reaction of Oxygen and Hydrogen on a Copper Oxide Catalyst.] Ztschr. Elektrochem., vol. 50, 1944, pp. 97–103; Chem. Abs., vol. 39, 1945, p. 858.

At pressures of 1–9 mm., CH_4 in a mixture with O_2 is not oxidized below 600° but is oxidized when present in H_2–O_2 mixtures at 400°. This inhibiting action is not due to displacement of the reactants from the catalyst by the CH_4, since this hypothesis is invalidated by the conditions of concentration and temperature. Nor can it be understood that, as a result of thermal diffusion, the CH_4, whose molecular weight lies between that of H_2 and O_2, drives the O_2 away from the H_2 and the wire; on the one hand, the reaction is much slower than the expected velocity of diffusion to the wire, and, on the other hand, the calculated speed of thermal diffusion is so low that the stationary thermal stratification of the gases appears to be virtually nonexistent because of the diffusion in concentration. It can be explained best by picturing the oxy-hydrogen reaction as a branched-chain reaction set up by a chain carrier formed on the catalyst; CH_4 inhibition takes place then through a further chain rupture with consumption of CH_4. The suggested chain of reactions is: (1) $Cu+O_2 \rightarrow CuO+O$, (2) $O+H_2 \rightarrow OH+H$, (3) $OH+H_2 \rightarrow H+H_2O$, (4) $H+O_2 \rightarrow OH+O_2$.

3141. SCHWAB, G. M., AND NAICKER, K. [Water-Gas Reaction on a Platinum Surface at Low Pressures.] Ztschr. Elektrochem., vol. 42, 1936, pp. 670–673; Chem. Abs., vol. 30, 1936, p. 7979.

Kinetics of the reaction $H_2+CO_2=CO+H_2O$ have been studied on a Pt filament 700°–1,200° and at pressures up to 0.3 mm. By use of H_2SO_4 for removing the H_2O formed, the authors found the rate was independent of the partial pressure of CO_2 and was a complicated function of the partial pressure of H_2 and CO. The reaction was autocatalytic in the absence, but not in the presence, of an initial partial pressure of CO. If P_2O_5 was used to remove the H_2O formed, the time of half conversion was proportional to the pressure; the rate was independent of the H_2 pressure. No autocatalysis but marked inhibition by CO was observed. If a cold bath (−90°) was placed around the reaction vessel to remove the H_2O formed, the character of the reaction changed completely. No reaction occurred below 730°; above 800° the rate was very high and independent of temperature. The observed rate was 10^{-4}, which would be calculated by assuming the surface to be covered with adsorbed H and that a reaction occurred every time a CO_2 molecule struck the surface. The results are interpreted as indicating the existence of enough active points to cover 10^{-4} of the surface and points active enough to permit the reaction to occur with no energy of activation.

3142. SCHWAB, G. M., AND SCHWAB-AGALLIDIS, E. [Alloys as Catalysts.] Naturwissenschaften, vol. 31, 1943, pp. 322–323; Chem. Abs., vol. 38, 1944, p. 1679.

Effect of separation of phases in alloys on their catalytic effect was studied. An alloy of Al with 9.7 at. % Ag has the homogenous δ phase above 490°; below this temperature it has the hexagonal γ phase. This change of phases, however, does not affect the catalytic effect of the alloy on decomposition of EtOH above and below 490°. The heat of activation of the reaction with the alloy was 25–26 kcal.; that on the separately prepared pure γ phase, 28 kcal. The same holds for MeOH decomposition. Any effect of C on the surface is considered improbable. With the decomposition of HCO_2H over Cu–Ag catalysts, it appeared that the heat of activation changed from 18 kcal. for pure Ag to 24 for Cu; it was 24 for 5 at. % Ag, and 20.2 for 7.5 at. % Cu. The method used was direct determination of gas flow (H_2 and CO_2) resulting from the vapor-phase reaction. Results by a static method agreed with the above. A simple mixing rule seems to hold.

3143. SCHWAB, G M., AND ZORN, H. [Kinetics of the Hydrogenation of Ethylene on Skeleton Contacts.] Ztschr. physik. Chem., vol. 32, B, 1936, pp. 169–201; Chem. Abs., vol. 30, 1936, p. 4745.

Activated centers are in the interior of the catalysts. According to the activity and the temperature, the rate-determining process depends on these activated centers or diffusion through the pores of the material. For highly dispersed substances, the configuration of the inner surfaces is extremely significant, since their active centers are accessible to gases only by diffusion.

SCHWAB-AGALLIDIS, E. *See* abs. **3142.**

SCHWARTZ, F. G. *See* abs. **3595.**

3144. SCHWARTZ, H. A. Metastability of Cementite. Trans. Am. Soc. Metals, vol. 23, 1935, pp. 126–150; Chem. Abs., vol. 29, 1935, p. 3959.

In an Fe–C alloy containing also 0.03% Si and not over 0.04% of other elements, the reaction $Fe_3C \rightleftharpoons 3Fe+C$ proceeds to the right at all temperatures from 630° to above the eutectic melting point. The A_1 stable critical point is found 15° above A_1 metastable in this alloy.

3145. ———. Conversion of Solid Cementite Into Iron and Graphite. Jour. Iron Steel Inst., vol. 138, 1938, pp. 205P–240P; Chem. Abs., vol. 32, 1938, p. 9012.

Our knowledge of the heat, entropy, and free energy changes accompanying the reaction $Fe_3C=3Fe+C$ are still unsatisfactory owing to the imperfections in the best existing work on the underlying data. Evidence is offered regarding the possibility of the existence of 2 types of solid solutions and the relationship of this possibility to the constitutional diagram, especially the A_3, or $G'S'$, line of the double diagram. The graphitizing reaction involves the formation of graphite nuclei, the solution of cementite in Fe, the dissociation of cementite into Fe and C, the migration of C either before or after dissociation, and the crystallization of graphite. The reaction rate is shown to be controlled by the migratory rate, this being the slowest step except at the very beginning and end of the process. The graphitizing rate is thus, in fact, mainly a function of the nodule (nucleus) number and migratory rate. The nodule number is determined largely by the prevalence of interfaces in the metal at the graphitizing temperature. The number of interfaces depends on the fineness of the original white-Fe structure, which in turn is a function of the cooling rate. Supercooled white cast Fe, the matrix of which is hypereutectoid in composition, may carry additional interfaces into the graphitizing temperature range. For a given set of interfaces the nucleus number is a function of the graphitizing temperature, the O content of the metal, and other variables of the melting operation. The migratory rate of C is influenced mainly by the presence of other alloying elements. Certain elements present in atomic solution or as chemical compounds appear to retard the migratory rate, whereas a few accelerate graphitization, probably by increasing the migratory rate. The effectiveness of the elements of group VI of the periodic table on the migratory rate and the fact that the effectiveness of elements in a given group often decreases with increase of the atomic weight may be of interest from the electronic viewpoint. 64 refs.

3146. SCHWARTZ, H. A., JOHNSON, H. H., AND JUNGE, C. H. Graphitization of Prequenched White Cast Iron. Trans. Am. Soc. Steel Treating, vol. 17, 1930, pp. 383–399; Chem. Abs., vol. 24, 1930, p. 5272.

Study of the acceleration of graphitization produced by prequenching hard Fe before annealing. The reactions involved are interfacial in character and represent the rate of solution of Fe_3C in the metallic matrix. Prequenching accelerates migration of C rather than diffusion, because of a greatly increased number of graphite nuclei with the accompanying decrease in migratory distance.

3147. SCHWARZ, C., AND ULICH, H. [Specific Heat, Entropy, and Energy of Formation of the Iron Carbide Fe_3C.] Arch. Eisenhüttenw., vol. 10, 1936, pp. 11–12; Chem. Abs., vol. 30, 1936, p. 7021.

Specific heat of Fe_3C can be expressed by 2 equations, 1 below and 1 above the magnetic transformation point; for the range 273.2°–407.1° K. $C=16.8-0.028\ T$ cal. per mol., and from 407.1° K. upward $C=28.2$. The energy of formation is represented by 3 $Fe_\alpha+C_\beta$—graphite$\rightarrow Fe_3C$; energy=2,600 cal. per mol. Heat content I and entropy S for temperatures above 407.1° K. (134°) and for 298.2° K. (25°) as base are expressed by 298.2 $I^T=28.2\ T-8575.4$; 298.2 $I^{407.1}=2906$ cal. per mol., ${}_0S^T=28.2\ ln\ T-137.8$; ${}_0S^{407.1}=32.176$ cal. per degree per mol. 5 refs.

SCHWARZ VON BERGKAMPF, E. *See* abs. **340.**

3148. SCIENCE MUSEUM—LONDON. Science Library Bibliographical Series No. 304; Chem. Abs., vol. 31, 1937, p. 5137.

Production of benzine from water gas, 1932–36 is reviewed. 58 refs.

SCOTT, H. *See* abs. **2330.**

3149. SEBASTIAN, J. J. S. Catalytic Reduction of Carbon Monoxide to Methane at Atmospheric Pressure. Carnegie Inst. Technol., Coal Research Lab. Contrib., vol. 35, 1936, 8 pp.; Cong. chim. ind., 15th Cong., Brussels, 1936, pp. 875–885; Brennstoff-Chem., vol. 17, p. 393; British Chem. Abs., 1936, B, p. 531; Chem. Abs., vol. 30, 1936, p. 3968.

Rate of reduction of CO at normal pressures over various catalysts maintained at temperatures in the range 200°–550° was studied. Mixtures (1:3) of CO and H_2, both pure and with the addition of 0.003% H_2S, were tried. Ni gave good conversion but was rapidly poisoned. Mo was active and not so sensitive to poison, but 2 Mo oxide preparations proved inactive. MoS_2, alone or mixed with silica gel, showed activity and was resistant to poisoning. The nature as well as the amount of hydrocarbons was affected by the catalyst and by the temperatures and rate of flow. Over Ni and over MoS_2, CH_4 predominated in the product, but up to 8% C_2H_6 and C_3H_8 might be present.

3149a. ———. Powdered-Coal Gasification. Effect of Variables. Ind. Eng. Chem., vol. 44, 1952, pp. 1,175–1,184.

Very large quantities of low-cost synthesis gas required for the production of synthetic gasoline and other liquid fuels necessitate the large-scale gasification of powdered coals with O_2 and superheated steam. Investigation was undertaken to determine how the considerable differences among various types of coals influence their relative value for synthesis gas production. It seemed also that investigation of the effects of other process variables should determine the conditions under which a given coal can be gasified with maximum process efficiency, lowest O_2 requirement, and lowest cost. Sufficient evidence has been obtained to conclude that young high-volatile coals of high O_2 content yield better results than high-rank, low-volatile coals of low O_2 content. Yet, high-ash or high-S coals can be gasified as easily as high-grade coals, nor does it make any difference whether the coal is strongly coking or noncoking. For a given coal of predetermined particle size, gasified in a given generator, at its maximum capacity, a proper combination of the O_2: coal ratio, steam: coal ratio, and steam temperature will result in the maximum completion of gasification and lowest O_2 requirement per unit volume of synthesis gas made. The beneficial effect of the addition of lime to the powdered coal under certain conditions (slagging

generators) has been established in special experiments made.

———. *See* abs. **144.**

3150. SEBASTIAN, J. J. S., EDEBURN, P. W., BONAR, F., AND SCHMIDT, L. D. Development of Synthesis Gas Process in Experimental Unit Operating on Entrained Powdered Coal. Am. Chem. Soc., 114th Meeting Abs., September 1948.

Laboratory-size pilot unit has been designed, and a method has been developed for the gasification of 10–30 lb. of pulverized coal per hr. by entrainment in O_2 and steam at generator temperatures ranging 1,800°–2,400°. The purpose was to obtain the necessary engineering design data for the construction of large-scale units producing synthesis gas from powdered coal and to test various types of fuels for their relative value in synthesis gas production. A brief discussion is given of the principles of aerodynamics applied in the process utilizing a turbulent downward flow of O_2, steam, and product gases, which carry the powdered coal and residual dust along in a thorough entrainment inside an 82-in. long, vertical, refractory tube, 6-in. inside diameter. Typical data obtained in 37 runs under widely different operating conditions are given. Graphical analysis and study of the operating results led to several conclusions, which appear to be useful in controlling the quality of the synthesis gas produced and in predicting yields and efficiency under various combinations of operating conditions.

3151. SEBASTIAN, J. J. S., EDEBURN, P. W., BONAR, F., BONIFIELD, L. W., AND SCHMIDT, L. D. Laboratory-Scale Work on Synthesis-Gas Production. I. Development of Process in Laboratory Unit Operating on Entrained Powdered Coal. Bureau of Mines Rept. of Investigations 4742, 1951, 33 pp.

Investigations have shown that a synthesis gas of high quality can be continuously produced from powdered coals by entrainment in O_2 and steam. The quality of the gas depends upon controllable operating variables, such as type and size of coal charged, coal feed rate, oxygen : coal and steam : coal ratios, and steam temperature. 2 different types of bituminous coal were used : A noncoking, low-ash, low–S coal from Wyoming No. 9 seam and a strongly coking, high-ash, high-S from the Sewickley seam in West Virginia. A synthesis gas of low CO_2 content (7%) can be made from both types of coal, pulverized either 70 or 90% minus-200-mesh, if the ratios of O_2 : steam and C : O_2+steam are high enough. The dry, ash-free coal gasified in a single pass ranged 60–70%, with yields of CO+H_2 ranging 15–22 standard cu. ft. per lb. of dry, ash-free coal charged, depending on the choice of values for the operating variables. The combined CO+H_2 in the synthesis gas produced ranged 76–91%. With coal feed rates up to 45 lb. per hr., corresponding to hourly fuel throughput rates up to 33 lb. per cu. ft. of generator volume, gas output rates as high as 600 standard cu. ft. CO+H_2 per cu. ft. generator space per hour have been obtained. Indications are that even this unusually high gasification rate would be considerably exceeded when younger coals are gasified. Synthesis-gas production rates as high as these per unit volume of generator space are important factors in reducing capital and production costs for the manufacture of gas on a commercial scale. (*See also* abs. **3150.**)

3152. ———. Laboratory-Scale Work on Synthesis-Gas Production. II. Experimental Pilot Unit for Underground Gasification Studies With Highly Superheated Steam and Oxygen. Bureau of Mines Rept. of Investigations 4742, 1951, pp. 33–41.

As underground gasification is essentially gasification of coke walls resulting from the carbonization of coal seams by intense heat, it was decided to study the gasification of run-of-oven, high-temperature coke cemented together into a strong, circular wall about 2 ft. thick. A preliminary run of 31 hr. duration in a pilot unit was performed with O_2 and highly superheated steam. Although operating results were incomplete, it was proved that the production of synthesis gas is possible even from such unreactive substances as high-temperature coke containing 23% inert material. Although the run was discontinued because of the failure of the cemented circular coke wall, the feasibility of gasification was demonstrated.

SEELIG, H. S. *See* abs. **2754a, 3618, 3642b.**

3153. SEELIG, H. S., AND MARSCHNER, R. F. Production of Synthesis Gas by Catalytic Decomposition of Methanol. Ind. Eng. Chem., vol. 40, No. 4, 1948, pp. 583–586; Chem. Abs., vol. 42, 1948, p. 4328.

Moderate amounts of a synthesis gas (CO : H_2=1 : 2) has been obtained by decomposing MeOH over a Filtros-supported catalyst of Cu and Ni oxides, U. S. Patent 2,010,427. The decomposition temperature is 350°–400° and 100–200 vol. of MeOH vapor pass over 1 vol. of catalyst per hr. The life of the catalyst is about 200 hr. and can be regenerated several times by periodically burning off the deposited C. The only byproducts of the operation are traces of CO_2, gaseous hydrocarbons, and C. A service unit to produce 250–300 cu. ft. per hr. of synthesis gas and its operation is described. Diagrams included.

3153a. SEELIG, H. S., WECK, H. I., VOSS, D. J., AND ZISSON, J. Hydrocarbon Synthesis Studies. Effects of Addition of Alkali to an Iron Catalyst. Am. Chem. Soc., 122d Meeting abs., September 1952, p. 4–0.

Experiments in both fixed-bed and fluidized-bed hydrocarbon synthesis reactors have shown that addition of K_2CO_3 promoter as a dry solid to Fe will produce a catalyst giving CO conversions and product yields comparable to those obtained with a catalyst prepared by a conventional aqueous impregnation method. Addition of alkali increases CO conversion, the yields of high molecular weight products and oxygenated compounds, the % of olefins in the low-molecular weight hydrocarbons, and frequently the carbide content of the catalyst. Fe_3C is a likely choice as the catalytically active Fe component. The effects produced by addition of K_2CO_3 can be explained by assuming that the catalyst has a defect or *p*-type character which is modified by the promoter.

3154. SEGER, F. M., DOHERTY, H. G., AND SACHANEN, A. N. Noncatalytic Polymerization of Olefins to Lubricating Oils. Ind. Eng. Chem., vol. 42, 1951, pp. 2446–2452; Chem. Abs., vol. 45, 1951, p. 1757.

Thermal, noncatalytic polymerization of 1–olefins produces excellent lubricating oils. Reaction conditions are 600°–650° F., reaction time about 10 hr., and pressures of 250–500 p. s. i. The preferred range of 1–olefins is from hexene to dodecene. Such olefins from any source, as cracked paraffin wax or Fischer-Tropsch products, can be used for the synthesis.

3154a. SEITZ, F. Fundamental Principles of Catalytic Activity. Advances in Catalysis, Academic Press, Inc., New York, 1950, vol. 2, pp. 1–19.

Activity of heterogeneous solid catalysts is discussed. Energy surface, isomeric and more complex reactions and characteristics of solid catalysts are described. Solids are classified into 4 types: Valence crystals, metals, ionic crystals, and molecular crystals.

3155. SEKITO, S. [X-Ray Analysis of the Cementite Obtained by Tempering Quenched Steels.] Sci. Repts. Tôhoku Imp. Univ., vol. 20, 1931, pp. 313–322; Chem. Abs., vol. 25, 1931, p. 4833.

Method and technique are described for obtaining the quantitative measurement of cementite by X-ray analysis.

3156. SELASINSKY. A. V. [Soap From Coal.] Rundschau deut. Tech., vol. 18, No. 1, 1938, p. 9; Chem. Abs., vol. 32, 1938, p. 3179.

Historical review, especially describing the Imhausen-Troschke process and its importance for Germany's economical situation.

SELIGMAN, B. *See* abs. **44, 45, 46, 48, 50, 52, 53, 53a, 53b, 2228.**

3157. SELIGMAN, H. Application of Isotopes in Chemical Industry. Chem. and Ind., 1951, pp. 724–727.

Uses of isotopes in chemical research and in the inspection and chemical-process control.

3158. SELTZ, H., MCDONALD, H. J., AND WELLS, C. Heat Capacity of Iron Carbide 68°–298° K. and the Thermodynamic Properties of Iron Carbide. Am. Inst. Min. and Met. Eng., Tech. Pub. 1137, 1939, 11 pp.; Chem. Abs., vol. 34, 1940, p. 1904.

Heat capacities of Fe_3C were determined experimentally 68°–298.1° K. The entropy was calculated $S_{298.1}=25.7$ (± 1) e. u. From the solubility curves of Wells for C and Fe_3C (β) in austenite, the free energy and heat of formation of carbide are evaluated. At 298.1° K., $\Delta H=5{,}800$ cal., $\Delta F°=4{,}700$ cal. for the formation of Fe_3C (α) and $S_{298.1}=24.7$ e. u. The temperature at which $\Delta F°=0$ for 3 Fe (γ)+C (graph.)=Fe_3C (β) is 1,082° K.

3159. SELVIG, W. A., ODE, W. H., AND DAVIS, J. D. Low-Temperature Carbonization of Alaskan Coals. Bureau of Mines Tech. Paper 668, 1944, 16 pp.

Assays of 14 Alaskan coals are reported as part of a general plan to test the coals of this region for their suitability as a source of liquid fuel by way of hydrogenating the tar and using the low-temperature coke for the Fischer-Tropsch synthesis.

3160. SELWOOD, P. W. Magnetism and Catalysis. Chem. Rev., vol. 38, 1946, pp. 41–82.

Possibility of relationships between catalytic activity on the one hand and magnetic fields and magnetic properties on the other, has interested many workers. It cannot be denied that those chemical elements that show the most pronounced catalytic activity, namely, the transition group elements, are also the elements that show the most interesting magnetic properties. In at least 1 case, the ortho-para-H_2 conversion, there is a clean-cut relationship between magnetic moment and catalytic activity. This is not to say that all catalytic activity is due to magnetism. It may yet appear that catalysis and magnetism are different manifestations of some more fundamental atomic property. But for the present, the chief applications of magnetism to catalysis are in structural studies of catalytic solids. A review of such applications and of certain related effects is the purpose of this article. Susceptibility data are included for some substances of major catalytic interest. 222 literature refs.

3160a. ———. Magnetism and the Structure of Catalytically Active Solids. Advances in Catalysis, Academic Press, Inc., New York, vol. 3, 1951, pp. 27–106.

Status of magnetic studies on catalyst structure is given. The following conclusions are drawn: The magnetic methods often give evidence for the oxidation state of catalytically active solids which contain elements of the transition series. This is especially true for V, Cr, Mn, Fe, Co, Ni, and Cu. Sometimes the magnetic method reveals the existence of valence bonds between adjacent positive ions, such as between Fe and Fe in hydrous or supported Fe sesquioxide. Almost always the magnetic method gives some information concerning the atomic environment of positive ions in hydrous or supported oxides. This information is related to the number of positive ions surrounding a given positive ion, for example, to the number of nearest Fe neighbors to a given Fe ion in Fe sesquioxide. The magnetic method, together with other methods, has revealed that the oxidation state of a supported oxide may, under certain circumstances, be influenced by the crystal structure of the support. In some cases there has been established a definite relation between the information obtainable from magnetic measurements and the actual catalytic activity. The methods described are not yet applicable to diamagnetic substances such as alumina or silica, but have definite applications to some systems in which these substances are used as supports. The thermomagnetic method of analysis is a tool of major use in detecting and estimating certain components in catalysts. These components are the ferromagnetic substances Fe, Co, Ni, Fe_3O_4, γ–Fe_2O_3, Fe_3C, and Fe_2C. In certain cases of a ferromagnetic metal supported or alloyed with a nonferromagnetic metal the thermomagnetic method can reveal alloy structure in a manner inaccessible by other tools. 62 refs. given.

———. *See* abs. **2327, 3500.**

SEMILLER, H. *See* abs. **3073.**

SEN, R. *See* abs. **467.**

SEN, S. *See* abs. **1186.**

SENDERENS, J. B. *See abs.* **3001. 3002, 3003, 3004, 3005.**

SENGLET, R. *See* abs. **356.**

SENOO, H. *See* abs. **2502, 2503.**

SEON, M. *See* abs. **2194.**

3161. SEPULCHRE, —. [Gasification in Relation to the Synthesis of Fuels.] Petroleum et remplacement, April 1944, pp. 21–22; Chaleur et ind., vol. 26, 1945, p. 45D.

Theoretical study of gasification leading to the production of a mixture of $CO+H_2$ in the desired proportions and the necessity of eliminating the inerts CO_2 and CH_4. The idea is set forth of a total gasification by cracking, making use of the reaction $CH_4+CO_2=2\ CO+2\ H_2$—61 cal. and then removing the inerts.

3162. SERGIENKO, S. R. [Mechanism and Relative Rapidity of the Aromatization of Paraffinic Hydrocarbons. I.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1941, pp. 177–190; Chem. Zentralb., 1942, I, p. 2219; Chem. Abs., vol. 37, 1943, p. 3064.

Octane and 1 : 1 mixtures of octane and heptane have been aromatized in the presence of Cr_2O_3–CoO and Al_2O_3–Cr_2O_3–CoO catalysts at 475°–500° and a throughput of 0.15–0.3 vol. % of the starting material per vol. of catalyst. By periodic regeneration (after every 2–12 hr.) of the catalyst, it will retain its original activity after 700 working hr. Under these conditions, octane is aromatized 1.5 times more rapidly than heptane. Depending on the reaction temperature, the throughput and the nature of the starting material, about 25–60% is converted to aromatics. The proposed reaction scheme agrees with the multiple theory of Balandin. By the use of oxide catalysts, the course of aromatization is through olefin intermediate products. With Pt catalysts, no olefin intermediates are formed. Along with aromatization, a partial cracking takes place, and the latter increases with increasing molecular weight of the aliphatic hydrocarbons.

3163. ———. [Catalytic Cyclization of Paraffinic Hydrocarbons. II. Investigation of the Reaction Products.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1941, pp. 191–200; U. O. P. Co. Survey Foreign Petroleum Literature, Transl. 373, 1943; Chem. Zentralb., 1942, I, p. 2219; Chem. Abs., vol. 37, 1943, p. 3065.

Cyclization experiments were conducted at 475° with the catalysts Al_2O_3–Cr_2O_3–CoO and Cr_2O_3–CoO, the charge was the C_7, C_8, and C_9 fractions of synthin. The

products were at least 50% aromatic. Cracked materials did not exceed 5–10% and unsaturates varied from 4–12%, depending on the catalyst used.

———. *See* abs. **1704.**

SERPEK, H. O. *See* abs. **2785.**

3164. SERRUYS, M. [Use of Motor-Fuel Substitutes.] Jour. soc. ing. automobile, vol. 14, 1941, pp. 153–180; Chem. Abs., vol. 41, 1947, p. 3598.

Yield of motor fuels obtainable by different industrial processes in terms of horsepower per kg. of coal is estimated to be 0.73 in the Fischer or Bergius processes, 1.91 in the carbonization of coal, 1.98 in gas producers, 0.97 in making MeOH from coke, 1.39 in making C_2H_2 via calcium carbide, 0.240–0.577 in making alcohol from agricultural products, and 0.545 in making gas from wood.

3165. SEVASTYANOV, Y. [Synthesis of Ammonia and Methanol.] Khimstroi, vol. 6, 1934, pp. 112–120; Chem. Abs., vol. 28, 1934, p. 4843.

Discussion and mathematical analysis of the process.

SEVER'YANOVA, M. G. *See* abs. **1673.**

SEYFRIED, W. D. *See* abs. **38, 3391.**

SEYMOUR, W. *See* abs. **625.**

SHAPIRO, M. I. *See* abs. **1107, 1584, 3769.**

SHARKEY, A. G. *See* abs. **1091, 1091a.**

SHARKOV, V. I. *See* abs. **2470.**

3166. SHATWELL, H. G. Production of Synthetic Motor Spirit With Special Reference to the Fischer-Tropsch Process. Colliery Guard., vol. 155, 1937, pp. 1125–1126; Iron and Coal Trades Rev., vol. 135, 1937, pp. 965–966; Jour. Inst. Fuel, vol. 11, 1938, pp. 209–213; Fuel, vol. 17, 1938, pp. 1–2; Brennstoff-Chem., vol. 19, 1938, p. 345; Chem. Abs., vol. 32, 1938, p. 8105.

Most of the subsequent work on the process since the advent of Synthol has been directed toward deciding the effect of various factors, such as composition of the initial gas mixture, nature of the catalyst, temperature and pressure in the reaction vessel, and the nature and amount of the product obtained. It now is proposed to produce the synthesis gas of proper $CO:H_2$ ratio by mixing blue water gas with the essential quantity of reformed coke-oven gas. As to catalysts, it appears that Fe, Co, and Ni, promoted by other metals and oxides, give the best results. It generally is agreed that Fe is the most sluggish but can be used over a longer temperature range, that Co yields a product containing a substantial proportion of olefins, and that Ni is extremely active but tends to produce CH_4 and liquid and solid hydrocarbons, which are almost entirely paraffinoid in nature. It has been found necessary to reduce the S content of the reaction gas to a maximum of 1 gm. per 1,000 cu. ft.; search should be made for a S-tolerant catalyst. Pressure must not be much in excess of atmospheric or alcohols and other oxygenated compounds will appear in the products. The temperature must be controlled carefully, from 190°–200° C for Ni, 200°–210° for Co, and not above 250° for Fe-base catalysts; CH_4 is produced if these temperatures are exceeded. As the reaction is strongly exothermic, this need for careful temperature control is difficult, and special types of reaction chambers with restricted depths of catalyst are required in order to effect easy cooling and prevent local overheating. The products are essentially paraffinoid in nature and straight-chain for the most part. The yield of motor fuel is relatively high but of low fuel value, whereas the diesel-oil fraction has a cetene number of 100 and is useful for blending with inferior diesel fuels, such as tar oils. In the author's opinion, the main disadvantage of the process, apart from the disappointing nature of the motor fuel, is the fact that it is conducted at atmospheric pressure, thus necessitating large reaction chambers and large quantities of catalyst with increased tendency to poisoning and probably a heavy capital expenditure on catalysts.

———. *See* abs. **757.**

SHAW, L. See abs. **53a.**

3167. SHEELY, M. L. Production of Synthetic Fatty Acids. BIOS Misc. Rept. 26, 1945, 31 pp.; PB 93,709. Chem. Abs., vol. 38, 1944, p. 5200.

An investigation of the 2 major synthetic fatty acid producing units in Germany: I. G. Farbenindustrie A.-G. at Oppau and the Deutsche Fettsäurewerke at Witten. Describes processes of oxidation of paraffins to fatty acids and the uses made of the resulting products. The report contains a translation of abs. **2170.**

3168. SHERWOOD, P. W. Oxidation of Methane to Formaldehyde; Interrogation of Dr. Karl Schmitt of Bergwerks Gesellschaft, Hibernia A.-G., at Herne. FIAT Final Rept. 608, June 1946, 6 pp.; PB 44,656.

Process is described for the partial oxidation of CH_4 by ozonized O_2. The reaction is said to take place at atmospheric pressure, with an $O_2:CH_4$ ratio of 40:60 and at a temperature of 110°–120° C. The catalyst is not very active <110° C, and >120° C. oxidation tends to go beyond the formaldehyde stage. The raw materials for the process consisted of CH_4, approximately 70% from the separation of coke-oven gas, and Linde-Frankl O_2, about 98%, which was ozonized to an ozone content of 0.5–2.0 vol. %. The preparation of the barium peroxide catalyst is also briefly described. A drawing of Dr. Schmitt's 2-pass ozonizer is shown.

3169. SHERWOOD, P. W. Aldehydes From Hydrocarbons. Petrol. Processing, vol. 4, No. 7, 1949, pp. 794–800.

Describes 2 processes for the manufacture of aldehydes directly from hydrocarbons. Partial oxidation of hydrocarbons can be made on the basis of formaldehyde and acetaldehyde production. The more recent Oxo process for the synthesis of aldehydes by the catalytic reaction of olefins with water gas, shows interesting potentialities for the manufacture of propionaldehyde, butyraldehyde, and valeraldehyde. At present, however, it is used only as a 1st step in the production of isooctyl and nonyl alcohols and other derivatives. By indirection, it can be used for the synthesis of an unlimited variety of aldehydes. Technical details of the oxidation and Oxo processes are described, and their possibilities and limitations are discussed briefly. German experience on the oxoation of olefins is summarized in describing the Italian Bambrini plant, which was designed by the I. G. Farbenindustrie but not constructed as planned. The economic prospects of the manufacture of aldehydes by the Oxo process are, at the present time, wholly a matter of speculation.

3170. ———. From Synthetic Fuels, What Chemicals! Chem. Eng., vol. 56, No. 9, 1949, pp. 99–101.

The chemicals obtainable from the Fischer-Tropsch reaction, from high-pressure hydrogenation, and from shale oil are enumerated. Estimates are given of the probable amounts recoverable. Their occurrence and yields vary widely. Reviews of the literature.

3171. ———. Primary Long-Chain Alcohols. New Petrochemical. Oil Gas Jour., vol. 48, No. 5, 1949, pp. 71–72, 74–76, 82.

Two processes, the Synol and the Oxo processes, are available for the synthesis of primary long-chain alcohols. The latter has achieved commercial realization, and further development is in progress. The former has not reached industrial utilization because the alcohol production is nonselective; the product ranges from EtCH to its homologs of high molecular weight as well as a large output of hydrocarbons. The reaction mechanism involving the Synol synthesis is not clearly

understood but is thought to be similar to the Fischer-Tropsch mechanism. The most striking characteristic of the product is the almost complete absence of secondary or branched-chain alcohols. Separation of the alcohols from the hydrocarbons is accomplished most efficiently by forming the boric acid esters. The Oxo reaction, on the other hand, is remarkably versatile and takes place readily with a number of olefinic and acetylenic compounds. Olefins ranging from ethylene to diisobutylene from cyclohexene to pinene have been successfully processed, usually with yields in excess of 90%. Thus, it is ideally suited for the manufacture of a wide range of primary monoalcohols and a more limited range of aldehydes. Where the alcohol is the desired final product, the reaction is carried in 2 successive stages: Oxoation followed by hydrogenation of the aldehydic product. Where the desired product is 1 particular product rather than a mixture, it is necessary to employ a highly purified olefin as starting material. A limitation of the process is that it is not possible to effect the reaction with aromatic compounds.

3172. ———. Byproduct Hydrocarbon Gases. Gas, vol. 26, No. 5, 1950, pp. 54, 59–61.

Quantity and composition of byproduct gases from petroleum processing are given as a source of comparison with byproduct gases from Fischer-Tropsch, coal-hydrogenation gases, and shale-oil gases. Byproduct gases formed during the Fischer-Tropsch synthesis depend to a great extent on the catalyst employed, as well as on the interrelation of operating temperature and $CO : H_2$ ratio in the synthesis gas, operating pressure, and converter design. A striking characteristic is the high olefin content (25–60% for the Co catalyst and 20–80% for the Fe catalyst) and the comparatively small amount of C_2 hydrocarbons. Wide variations in the amount of permanent byproduct gases may be expected. An average expectancy would be about 1,000 cu. ft. per bbl. of total oil yield. In addition there may be 150 cu. ft. per bbl. of liquid petroleum gases and another 150 cu. ft. per bbl. of propylene and butene for chemical processing. Gases from coal hydrogenation differ markedly from the Fischer-Tropsch gases in the complete absence of olefins. The 2 phases of the hydrogenation process yield unequal amounts of byproduct gases; the larger portion being derived from the primary liquefaction. The composition of the gas is surprisingly independent of the feedstock employed and of operating conditions. Typical byproduct gas from coal liquefaction is about 90% C–C_3 and from the vapor phase about 90% C_3 and C_4. Unlike the dilute Fischer-Tropsch tail gases with an average heating value of only 650 B. t. u. per cu. ft., the permanent gases from coal hydrogenation are rich enough (1,065 B. t. u. per cu. ft.) to justify cross-country transmission. Byproduct gases from oil-shale retorting depend on the type of process used, but are normally of low heat value. Those gases from the hydrogenation of shale oil are quite similar to those from coal hydrogenation.

3172a. ———. Water Gas From Methane. Petrol. Processing, vol. 5, 1950, pp. 1,308–1,311; Chem. Abs., vol. 45, 1951, p. 2,650.

Survey of various methods for producing water gas from CH_4 and steam is given.

SHEVYAKOVA, L. *See* abs. **2774.**

3173. SHIBATA, Z., AND MORI, I. [Reduction Equilibrium Between Metallic Oxide and Hydrogen. I. Measurement of $CoO+H_2 \rightleftarrows Co+H_2O$ by New Methods.] Ztschr. anorg. Chem., vol. 212, 1933, pp. 305–316; Chem. Abs., vol. 27, 1933, p. 4468.

Equilibrium $CoO+H_2 \rightleftarrows Co+H_2O$ was studied at 921°, 821°, 721°, 622°, 522°, and 422°. The relation between the equilibrium constant K and temperature is: $\log K = (494.191/T) + 1.08690$. The dissociation pressure of CoO and the equilibrium of H_2O gas at 400°–1,000° are calculated.

3174. SHIBATA, Z., AND TERASAKI, Y. [Promoting Carburization of Iron by Barium Carbonate.] Nippon Kinzoku Gakukai-Shi, vol. 2, 1938, pp. 187–192; Chem. Abs., vol. 32, 1938, p. 7382.

Electrolytic Fe specimen was carburized by CO at 900° for 2 hr. When $BaCO_3$ was placed in the carburizing chamber, it accelerated the carburization. Conclusion: CO gas is adsorbed on the surface of $BaCO_3$ and then decomposed by the reaction: $4\ CO = C_3O_2 + CO_2$. C_3O_2 is desorbed and partly polymerized and decomposed by the reaction: $C_3O_2 = C_2 + CO$. This C_2 gas will diffuse into the Fe, and solid solution is formed.

SHIFFLER, W. H. *See* abs. **2771.**

SHILLING, W. G. *See* abs. **2578, 2579.**

SHIMAMURA, K. *See* abs. **1344, 1345, 1346, 1349, 1350.**

3175. SHIMURA, S. [Study of the Structure of Cementite.] Proc. Imper. Acad. (Tokyo), vol. 6, 1930, pp. 269–271; Proc. World Eng. Cong., Tokyo, 1929, vol. 34, 1931, pp. 223–225; Chem. Abs., vol. 24, 1930, p. 5271.

Preliminary report on the X-ray structure of cementite and spiegeleisen, both of which have the same dimensions for the unit cell. Both belong to the simple orthorhombic lattice Γ_0 and the space group V^{16}_h. It is concluded that C is contained as neutral atoms in austenite but comes to take the configuration of the cementite molecule with neighboring Fe atoms as austenite changes to martensite, and it always segregates out as cementite at the A_1 transformation point. C metastably contained in α–Fe (this is less than 0.03%) also takes the cementitic arrangement.

SHIRAI, S. *See* abs. **1754a, 3178.**

3176. SHIRAI, S., KIMUMAKI, J., AND OGAWA, T. [Iron Catalyst for Synthesis of Gasoline.] Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 329–331; Chem. Abs., vol. 42, 1948, p. 6082.

Catalyst for the hydrogenation of CO should not be heated to a temperature above that at which it is used in the synthesis. The alkali promoter should be evenly distributed; this is effected by using KNO_3 instead of K_2CO_3 to activate the catalyst.

3177. OGAWA, T., KIMUMAKI, J., AND FUJISAKI, T. [Iron Catalyst for Synthetic Petroleum. II. Some Characteristic Properties of Iron Catalyst for Synthetic Petroleum.] Jour. Soc. Chem. Ind. (Japan), vol. 47, 1944, pp. 242–243; Chem. Abs., vol. 42, 1948, p. 7011.

Activity of the ordinary Fe catalyst, which does not contain excess alkali, increases with time, passes through a maximum, and then decreases. The maximum is affected strongly by the reaction temperature. The higher the reaction temperature or activation temperature, the earlier the appearance of the maximum. Thus, it is possible to decrease the time of activation and increase the yield.

3178. KIMUMAKI, J., SHIRAI, S., AND FUJISAKI, T. [Iron Catalyst for Synthetic Petroleum. III. Influence of Barium Nitrate on Iron Catalyst.] Jour. Soc. Chem. Ind. (Japan), vol. 47, 1944, pp. 244–247; Chem. Abs., vol. 42, 1948, p. 7011.

$Ba(NO_3)_2$ was found to be an excellent accelerator for Fe catalyst, especially for low-alkali catalyst. The optimum amount of K_2CO_3 for the catalyst was 2%. The order of immersion in K_2CO_3 and $Ba(NO_3)_2$ did not affect the activity.

SHOKAL, E. C. *See* abs. **2441, 2442.**

SHOKOL, A. A. *See* abs. **2730.**

SHPULENKO, K. B. *See* abs. **3366.**

SHUĬKIN, N. I. *See* abs. **3761.**

3179. SHUĬKIN, N. I., MINACHEV, K. M., AND ROZHDESTVENSKAYA, I. D. [Hydrogenation and Dehydrogenation of Hydrocarbons With Low-Percent Nickel Catalysts.] Doklady Akad. Nauk S. S. S. R., vol. 72, 1950, pp. 911–913; Chem. Abs., vol. 44, 1950, p. 8332.

Catalysts with Ni contents of 0.125–4% were prepared by 40–45 min. impregnation at 30°–35° of 1 gm. activated charcoal with 2 ml. solution of $Ni(NO_3)_2$, drying at 125°, and reduction in H_2 at 330°. Hydrogenation (I) of C_6H_6 was carried out in a stream of excess H_2 at 115°–176°, space velocity 0.025–0.2 l. per l. catalyst per hr.; dehydrogenation (II) of cyclohexane at 300°–302°, space velocity 0.2. (I) proceeds to a significant extent with catalysts containing 1% Ni or more; the reaction is just barely noticeable with 0.5% Ni. In (II), the initial activity of the catalyst varies very little with the Ni content, varying from 0.5–4%; with the progress of the reaction, the activity of the catalysts falls rapidly, by a factor of 3–4 after 2,000 min. In reaction (I), the degree of hydrogenation is virtually independent of the temperature at 120°–176° and is not affected by a variation of the space velocity by a factor of 4; under these conditions, it attains 100%. Further increase of the space velocity, by a factor of 8, lowers the degree of hydrogenation 68–70%. At constant space velocity of 0.06, the activity of the 4% Ni catalyst maintains itself at a near 100% level for more than 25 hr., and that of the 2% catalyst falls off only slowly.

3180. SHULER, K. E., AND LAIDLER, K. J. Kinetics of Heterogeneous Atom and Radical Reactions. I. Recombination of Hydrogen Atoms on Surfaces. Jour. Chem. Phys., vol. 17, 1949, pp. 1212–1217; Chem. Abs., vol. 44, 1950, p. 4760.

Data on the kinetics of the recombination of H atoms on various types of surfaces are analyzed in the light of the theory of absolute reaction rates. Expressions are derived for the recombination coefficient and the 1st-order-rate constant, enabling these quantities to be calculated on the basis of postulated mechanisms. The experimental activation energies are consistent with estimates using either Hirschfelder's rule or an expression utilizing the experimental desorption temperature. For the reaction on dry oxides and dry glass, good agreement is found, assuming that reaction occurs between a gas-phase H atom and an adsorbed H atom, the adsorption being of the van der Waals type at low temperatures and chemisorption at higher ones. The mechanism of surface poisoning by water vapor is not due to the necessity for desorbing the water molecule: In the high-temperature region it is due to an increase in activation energy, the mechanism being $S—OH+H \rightarrow S—O+H_2$; in the low-temperature region it is due to a decrease in the number of active centers, the reaction being between a gaseous atom and a van der Waals adsorbed H atom above the water layer.

3181. SHULL, C. G. Production of Highly Polarized Neutron Beams by Bragg Reflection From Ferromagnetic Crystals. Phys. Rev., vol. 81, 1951, p. 626; Chem. Abs., vol. 45, 1951, p. 4,517.

Monochromatic beam of neutrons (λ=1.204 A) was reflected from the (220) planes of a magnetized slice of crystalline Fe_3O_4 with the slice set in transmission orientation and with the magnetization vector perpendicular to the plane of scattering. The reflected beam was polarized 100 ±5%.

3182. SHULL, C. G., WOLLAN, E. O., AND STRAUSER, W. A. Magnetic Structure of Magnetite and Its Use in Studying the Neutron Magnetic Interaction. Phys. Rev., vol. 81, 1951, pp. 483–484; Chem. Abs., vol. 45, 1951, p. 4502.

Effect of the magnetization in different directions on the (111) Fe_3O_4 neutron-diffraction peak is shown. The pronounced dependence of neutron scattering intensity on magnetization direction suggests that the reflection might have interesting application as a fast-neutron shutter. In a single-crystal reflection large neutron currents are attainable and rapid field variations with the small fields required for saturation of single crystals can be achieved in this or other members of the ferrite series. 9 refs. given.

SHULTZ, J. F. *See* abs. **50, 53, 833, 834, 835, 3679.**

SCHULTZ, J. F., SELIGMAN, B., LECKY, J., AND ANDERSON, R. B. Studies of the Fischer-Tropsch Synthesis. XII. Composition Changes of Nitrided Iron Catalysts During the Synthesis. *See* abs. **53b.**

SCHULTZ, J. F., SELIGMAN, B., SHAW, L., AND ANDERSON, R. B. Fischer–Tropsch Synthesis. XI. Effect of Nitriding on 3 Types of Iron Catalysts. *See* abs. **53a.**

SHURMOVSKAYA, N. *See* abs. **332.**

3183. SHVAĬTZER, I. [Use of the Byproducts of the Groznenskiĭ Acetone-Butyl Alcohol Factory.] Jour. Chem. Ind. (U. S. S. R.), vol. 12, 1935, pp. 345–349; Chem. Abs., vol. 29, 1935, p. 7571.
Production of MeOH and dry ice.

SICKMAN, D. V. *See* abs. **3342.**

3184. SIDGWICK, N. V., AND BAILEY, R. W. Structures of the Metallic Carbonyl and Nitrosyl Compounds. Proc. Roy. Soc. (London), vol. 144, A, 1934, pp. 521–537; Chem. Abs., vol. 28, 1934, p. 4676.

For the compounds $M_x(CO)_y(NO)_z$, $G-[(xm+2y+3z)/x]=x-1$; (m=atomic number of M, G=atomic number of the next inert gas). For carbonyls (z=O) the binding must be $M^-—C^+\equiv O^+—M^-$; if x=1, the link is linear; x=3, triangular, x=4, tetrahedral; a CO is on each edge. The crystal structures of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ are compatible with this. For ntrosyis, the binding is $M^{--}—N^+\equiv O^+$. Nlearly all the carbonyls and a great many nitrosyls obey these rules.

SIDOROV, N. V. *See* abs. **2757, 3364, 3365, 3366.**

3185. SIEVERTS, A., AND HAGEN, H. [Ability of Cobalt to Absorb Hydrogen and Nitrogen.] Jour. Phys. Chem. (U. S. S. R.), vol. 169, A, 1934, pp. 237–240; Brennstoff-Chem., vol. 15, 1934, p. 414; Chem. Abs., vol. 28, 1934, p. 6606.

Pure Co powder was first reduced with H_2 at 800° and then at the same temperature in a quartz absorption flask stirring for 10 days. Fresh H_2 was used continuously to measure the absorption at various temperatures. The volume of the free gas was determined with argon. The solubility of the H_2 increased with rising temperature, at atmospheric pressure and 600°, 0.08 mg. H_2 and 1,200° 0.5 mg. H_2 per 100 gm. Co were absorbed. At varied pressures, the amount absorbed was proportional to the sq. root of the pressure. The absorbability of technical Co turnings containing 2.5% Fe was the same as with pure Co. N_2 is virtually insoluble in Co up to 1,200°. A comparison of H_2 absorption for Fe, Co, and Ni showed that absorbability of Co up to 900° is only a little less than that of α Fe; above 900°, the difference becomes greater because here the γ Fe with its higher solubility appears. The absorbability of Ni for H_2 is considerably greater than that of Fe. The magnetic transformations with any of the 3 metals have no noteworthy effect on the H_2 absorption. The differences in the properties of Fe, Co, and Ni, with regard to the absorbability, are correlated with the various crystal structures.

SILINA, N. P. *See* abs. **729.**

3186. SIMCOX, A. K. Future of Synthetic Detergents in Relation to the Petroleum-Chemical Industry. Chem. and Ind., 1950, pp. 178–182.

Review of development of synthetic detergents by way of fatty acids from natural fat to synthetic fatty acids from nonfat materials such as petroleum paraffins and Fischer–Tropsch paraffins. Shows growing trend in the consumption of synthetic detergents from nonfat sources and its effect on the increasing satisfaction of the demand for edible fats.

3187. ŠIMEK, B. G., AND KASSLER, R. [Conversion of Carbon Monoxide by Water Vapor on Iron Catalysts.] Chim. et ind. Special No., April 1934, pp. 330–337; Chem. Abs., vol. 28, 1934, p. 5626.

In order to ascertain the part played by secondary reactions in the catalytic conversion of mixtures of water gas and water vapor over Fe catalysts, comparative tests were carried out with reduced aluminoferric and with pig Fe, both activated with K_2CO_3, with the following results: (1) at 500°, the reduction of the catalyst to oxide by CO alone stops before liberation of metallic Fe. (2) The metallic Fe formed by reduction at 500° with H_2 alone is oxidized by H_2O, so that the catalyst is in equilibrium with the gaseous phase. (3) The C liberated by known decomposition of CO on Fe catalysts, starting at 500°, can be gasified by H_2O, so that the homogeneous conversion of water gas over an Fe catalyst can be considered as the resultant of several reactions taking place successively in heterogeneous medium. (4) The importance of the conversion reaction proper, as compared to the decomposition of CO, was determined under varying conditions of flow, with reduced Fe and pig Fe as catalysts. (5) The catalyst prepared from pig Fe has a lower efficiency than the precipitated catalyst, but the secondary reactions are more intense in the former case than in the latter; their importance, however, decreases when the rate of flow is increased above a certain value. (6) H_2S exerts a poisoning action on the reduced precipitated Fe catalyst. (7) The degree of conversion over precipitated catalyst varies with the flow and exhibits a maximum for a definite flow, which itself depends on the temperature; the degree of conversion over activated pig Fe also exhibits a maximum, which does not correspond to a minimum of the secondary reactions.

3188. ———. [Conversion of Carbon Monoxide by Water Vapor on Iron Catalysts.] Zprávy Ústavu Vědecký Výzkum Uhli v Praze, vol. 2, 1935, pp. 113–128; Chem. Abs., vol. 30, 1936, p. 6168.

To determine the role of secondary reactions in the process of conversion of water gas on Fe catalysts, comparative experiments were conducted on often used precipitated ferric aluminum catalyst and on the crude Fe, both activated with K_2CO_3. The oxide catalyst, after being reduced to metallic iron by the H_2, is oxidized again by water gas. C obtained by the decomposition of CO on oxide contact can be changed into gas again by water gas, beginning around 500°. The influence of H_2S poisoning on the activity of precipitated oxide catalyst was observed also.

3189. ŠIMEK, B. G., COUFALIK, F., AND ZAMRZLA, E. [Conversion of Methane in a Water-Gas Generator.] Mitt. Kohlenforsch.-Inst. Prag, vol. 3, 1937, pp. 236–255; Hornicky Vestnik, vol. 19, 1937, p. 414; British Chem. Abs., 1938, B, p. 1004; Chem. Abs., vol. 32, 1938, p. 7701.

Mixture of CH_4 (I) and steam (II) was passed over coke in a water-gas generator, starting at 1,200° and continuing to not lower than 1,000°. By varying conditions and proportions of (II), products having H_2: CO ratios of 1.02–11.76 were obtained. The most important factor in practicable water gas production from (I) was the temperature, which should be more than 1,100°. Increasing the rate of introducing (I) did not hinder its utilization as long as the temperature was maintained but was a hindering factor at lower temperatures. It is advantageous to use (I) and (II) in proportions required for making a product of H_2: CO=2. Use of too much (II) hinders utilization of (I); smaller amounts of (II) increased decomposition of (I), giving finely divided C and a gas of higher H_2 content. The use of (I) and (II) in a water-gas generator is more desirable than the usual process from both thermodynamic and heat economy viewpoints. Tabulated data and methods of calculation.

SIMIZU, J. *See* abs. **3313.**

3190. SIMONET, R. [Synthesis of Methanol.] Peintures, pigments, vernis, vol. 8, 1931, pp. 1450–1452, 1475–1478; Chem. Abs., vol. 25, 1931, p. 3617.

General discussion.

3191. SIMONOVITCH, M. Problem of Synthetic Liquid Fuels Under Present Conditions in Europe. Fuel, vol. 18, 1939, pp. 130–131; Rev. univ. mines, vol. 15, 1939, pp. 109–127.

General consideration followed by discussion of problems confronting different countries. It is concluded that Britain and the United States dominate the situation.

———. *See* abs. **2083.**

SIMONS, H. P. *See* abs. **144.**

3192. SINGER, L. [Latest Literature on Motor Fuels.] Petrol. Ztschr., vol. 25, 1929, pp. 513–524; Chem. Abs., vol. 23, 1929, p. 4043.

Complete review with 227 refs.

3193. ———. [Recent Work on Motor Fuels.] Petrol. Ztschr., vol. 25, 1929, pp. 152–153; Chem. Abs., vol. 23, 1929, p. 1734.

Comprehensive review with 31 refs. to original papers.

3194. SINGH, A. D. Fluidized-Coal Devolatilization. Power Plant Eng., vol. 51, No. 10, 1947, pp. 112–115.

Term "fluid devolatilization" is applied to the distillation of gas from coal fluidized by passage of gas or steam through a bed of the finely divided material. Pulverized coal is screw-fed from a hopper into pipes through which steam or recycled gas produced in the process flows fast enough to prevent settling of the largest particles. The coal is carried thus into a vertical, electrically heated retort. Tar vapor and gas are quickly evolved, and agglomeration of the char occurs only to a slight extent owing to preliminary oxidation of the coal and recirculation of about the same weight of char as that of the coal fed to the retort. The char is recovered by cyclone separators, and the tar vapor and gas pass to a cooling and condensing system for byproduct recovery. Heat transfer in the fluidized material may be nearly 6 times that of conventional coking, probably owing to the scrubbing action on the gas films surrounding the particles. Char leaving the fluidizer system at temperatures in the range 700°–800° should be an ideal fuel for cyclone burners, making possible very high rates of heat release. From 4–6% can be added to the overall heat recovery by the elimination of stack losses associated with the combustion of H_2. Char of 12,180 B. t. u. per lb. can be obtained from 11,460 B. t. u. coal, in addition to 9,300–16,600 cu. ft. of fuel gas and 14 gal. of tar per ton of coal. S is removed from the coal by the process.

3195. SINGH, A. D., AND KRASE, N. W. Synthesis of Acetic Acid From Methanol and Carbon Monoxide. Ind. Eng. Chem., vol. 27, 1935, pp. 909–914; Chem. Abs., vol. 29, 1935, p. 6571.

Catalytic, vapor-phase synthesis of AcOH (I) from MeOH and CO under pressure was studied. The reaction goes at 300°–500° and 2,000–4,000 p. s. i. pressure.

Under the same conditions, recirculation of the exit products gave about 2 times the yield of (I) as that obtained by a once-through operation. Me_2O is 1 of the main byproducts, but since it is formed by a reversible reaction, recirculation of noncondensable gases builds its concentration to a constant value at about 2.4%. Use of 85% MeOH is best. The maximum catalyst temperature is 400°. Active C impregnated with H_3PO_4 was used as a catalyst. Its life is limited, owing, presumably, to volatilization.

3196. SINNATT, F. S. Oils From Coal—Potentialities of a New Industry. Iron and Coal Trades Rev., vol. 128, 1934, pp. 139–140; Chem. Abs., vol. 28, 1934, p. 3873.

Various methods (high- and low-temperature carbonization, synthesis from water gas and H_2, hydrogenation of tar and coal) are compared briefly as to yields of motor and fuel oils.

3197. ———. Coal's New Industry—the Production of Oil. Gas Jour., vol. 212, 1935, pp. 711–712; Chem. Abs., vol. 30, 1936, p. 1205.

Review. The yield of liquid products is 100–120 gm. per $m.^3$ of gas containing 29% CO and 58% H_2. They consist almost exclusively of straight-chain paraffins and olefins; their antiknock value therefore is low, but, on the other hand, the synthesis can be worked to give excellent Diesel fuel. In addition, the products can be converted by further treatment into lubricating oils of good quality. A small experimental unit has been set up at the Fuel Research Station with the object of developing the process in this direction.

3198. SINNATT, F. S., AND KING, J. G. [Tars and Oils From Coal.] Jour. Soc. Chem. Ind. [Japan], vol. 44, 1925, pp. 413–424T; Colliery Guard., vol. 130, 1925, p. 320; Chem. Age, vol. 13, 1925, pp. 95–96; Chem. Abs., vol. 19, 1925, p. 3156.

General discussion and compilation of relevant data; the Bergius and Synthol processes are discussed briefly.

3199. SIOMI, K., AND IWAMOTE, T. [Hydrogenation of Acetylene.] Jour. Soc. Chem. Ind. (Japan), vol. 41, 1938, p. 401B.

Best catalyst for obtaining liquid hydrocarbons and C_2H_4 from C_2H_2 and H_2 at ordinary pressure is a mixture of Ni, Co, and Cr.

3200. SIPS, R. Structure of a Catalyst Surface. Jour. Chem. Phys., vol. 16, No. 5, 1948, pp. 490–495.

Mathematical method is described that makes it possible to calculate rigorously the distribution of the adsorption energies of the sites of a catalyst surface when the adsorption isotherms are known, if the adsorption is localized and there are no interactions. This method is applied to a Freundlich isotherm, and to a new theoretical isotherm, which reduces to the Freundlich type for small pressures but exhibits saturation for large pressures. It is shown that this isotherm corresponds to a distribution function that differs very little from a Gaussian one. The case of atomic adsorption of gases is considered also.

3201. SIROVICH, G. [Polymorphic Transformation of Iron at 370° and the Possibility of Solution of Cementite in α_1–Iron.] Gazz. chim. ital., vol. 53, 1923, pp. 674–688; Chem. Abs., vol. 18, 1924, p. 960.

In a previous paper, Metall. italiana, vol. 14, 1922, pp. 3–17, Sirovich and Ariano demonstrated that α-Fe exists in 2 forms. One of these, called α_1, is stable and magnetically resistant and in it C is soluble in the solid state; the other, the α_2–form, is formed at 370°, is relatively soft, is magnetic, but does not dissolve C in the solid state. The above and other conclusions are confirmed in this paper by further results (1) on the existence of an A_0 point at 370° indicating polymorphic transformation of Fe and (2) on the possibility of causing solution of cementite in α_1–Fe without having recourse to tempering. Earlier work on (1) is reviewed. It has been considered generally that there is a complete continuity in the dilatometric behavior of Fe from ordinary temperatures up to 700°. The results given here were obtained with the photographically registering dilatometer of Montemartini and Bosana. A parallelpiped (4.7 cc. in vol.) of electrolytic Fe was placed in fused Sn for the determinations. Other details are given. The volume as registered showed a distinct break at 370°. The same results were obtained with a fused Fe (C 0.04, Mn 0.048, S 0.052, P 0.034%), showing that the effect is not due to any H_2 present in the other specimen of Fe used. The Sn was then replaced with melted paraffin in order to eliminate any possible effect of the Sn, but without changing the results. The same determination when carried out with a specimen of Mn-containing Fe (C 0.07 Mn 0.49, Si trace, S 0.035, P 0.04%) showed only a slight change in direction at 370°–380° but no discontinuity. Sirovich suggests that previous failures by other workers to obtain a transformation at 370° are due to the effects of impurities as in the case of Mn here reported. In the experiments on the solution of cementite in α_1–Fe steels containing cementite and ferrite in extreme dispersion, a hypoeutectoid steel with C 0.53, Mn 0.51, Si 0.11, S 0.039, P 0.06 was used. It was heated at 850° for 0.5 hr. The external decarbonized part was ground off and Brinell hardness test was made (182). The piece then was introduced into a fused Sn bath kept at 300°±5° (heated in an electric coil). The Brinell test and the micrographic structure were determined after 288, 528, and 3,501 hr., at which times the hardness was 216, 241, and 241, respectively. The micrographs showed a progressively increasing homogeneity, but completion of the process is prevented by retarded diffusion. The possibility of obtaining some solution of cementite in α_1–Fe in the field of stability of the latter with pearlitic steels was established.

3202. SITTENFIELD, M. Economic Outlook for Synthetic Detergents. Chem. Inds., vol. 62, No. 4, 1948, pp. 584–585, 650, 652, 658.

An appraisal of the outlook for the various types of detergents from a raw materials and cost standpoint. It is expected that within a period of 2 yr. the long-chain alcohols obtained from the Fischer-Tropsch synthesis using the Oxo process will be offering competition with sulfated alcohols from other sources. It is estimated that long-chain mixed alcohols can be produced at a cost of $0.10–0.15 per lb., at which price the sulfated alcohol type of surface active compounds will become highly competitive with soap and with other classes of synthetic detergents.

3203. SITTIG, M. Exothermic Reaction Techniques. Petrol. Processing, vol. 5, 1950, pp. 1080–1082.

Exothermic reaction techniques are classified, and their application to heat removal and control in commercial chemical processes is reviewed. Use of fluidized solids reactors in the Fischer-Tropsch process has served greatly to reduce the total volume of cooling surface required. Since a rocket motor is essentially an exothermic reactor, application of the same principle in chemical process reactor design is considered a possibility.

SKAPERDAS, G. T. *See* abs. **2128.**

SKINNER, L. C. *See* abs. **155, 156, 3311.**

3204. SLATER, W. E. Influence of Different Surfaces on the Decomposition of Methane. Jour. Chem. Soc., vol. 109, 1916, pp. 160–164; Chem. Abs., vol. 10, 1916, p. 1589.

To determine whether the amount of decomposition of CH_4 in contact with heated surfaces depends upon the kind of substance exposed, or whether it is a function of the surface area only, the gas was heated to

910° at constant pressure and time with various refractory materials, the degree of decomposition being determined by measuring the amounts of H_2 in the residual gases. The results showed that the rate of decomposition depends upon the nature of the heated surface. It was found that Si, MgO, Al_2O_3, and BaO did not accelerate the reaction and that Cu, carborundum, graphite, charcoal, and Fe did.

SLIN'KO, M. G. *See* abs. **305.**

SLONE, M. C. *See* abs. **3100.**

3205. SLOSSE, —, AND SOLVAY, —. [Electrical Discharge.] Bull. Acad. roy. Belg., vol. 35, No. 3, 1898, pp. 547–551; Chem. Zentralb., 1898, II, p. 421.

Further evidence is presented that CH_2O is produced when a mixture of CO_2 and H_2 and when one of CO and H_2 are submitted to the influence of the silent electric discharge.

SMART, J. S. *See* abs. **2216.**

SMIRNOVA, Z. M. *See* abs. **1671.**

SMITH, A. E. *See* abs. **181.**

SMITH, C. C. *See* abs. **437.**

3206. SMITH, D. F. Equilibrium Condition in the Formation of Hydrocarbons and Alcohols From Water Gas. Ind. Eng. Chem., vol. 19, 1927, pp. 801–803; Chem. Abs., vol. 21, 1927, p. 2783.

Study of equilibrium conditions in the reactions between CO and H_2 to produce CH_4, C_2H_6, C_3H_8, C_6H_6, MeOH, EtOH, and BuOH. Conclusions: (1) It is easier to form the higher paraffin hydrocarbons than the lower ones from water gas at all temperatures, and there is a much greater tendency for the O_2 to go to CO_2 than to H_2O; (2) the tendency to form aromatic and probably branched-chain and cyclic hydrocarbons is generally greater than to form straight-chain compounds; (3) the lower alcohols cannot be formed from water gas at atmospheric pressure and temperatures of 300° and above, while the higher alcohols can be formed in considerable amounts with water gas under these conditions; (4) the tendency to form all these compounds falls rather rapidly with increasing temperature; (5) maximum possible yields can be calculated from the values of K (given in a table); and (6) the acuracy of the free-energy values given should be satisfactory on the alcohols, and reasonably so on the hydrocarbons.

3207. ———. Note Concerning Thermodynamic Calculations. Ind. Eng. Chem., vol. 20, 1928, pp. 859–860; Chem. Abs., vol. 22, 1928, p. 4339.

Synthesis of hydrocarbons especially C_6H_6, from water gas is considered. The rate of reaction is stressed as an important factor, for free-energy values alone will not tell what species predominates. Comments are made on Francis' calculations of the free energies of various hydrocarbons and alcohols (abs. **1079**), and it is pointed out that the use of thermal data often leads to erroneous results. Values from equilibrium constants, where all substances involved are at the standard fugacity of 1 atm., are more reliable.

3208. ———. [Reply to the Criticism of Hans Tropsch of My Paper on the Equilibrium Conditions for Formation of Hydrocarbons and Alcohols From Water Gas.] Brennstoff-Chem., vol. 9, 1928, pp. 248–249; Chem. Abs., vol. 22, 1928, p. 4773.

Polemical, dealing with equilibrium constants calculated by Smith and Tropsch (abs. **3206** and **3449**). Smith's conclusion "at all temperatures in increasing measure it is easier to obtain the higher hydrocarbons from water gas" is attacked by Tropsch. Smith further explains his data, and Tropsch adds further comment.

293793°—54——28

3209. SMITH, D. F. AND BRANTING, B. F. Equilibrium Between Methanol, Carbon Monoxide, and Hydrogen. Jour. Am. Chem. Soc., vol. 51, 1929, pp. 129–139; Chem. Abs., vol. 23, 1929, p. 1337.

Equilibrium $CH_3OH/(CO)(H_2)^2$ at 1 atm. over ZnO and the 4 Zn : 1 Cr catalyst of Smith and Hawk (abs. **3210**) was studied by a direct method giving $K=5.57\times 10^{-4}$ at 303.8°, error=5%. From this equilibrium value and the heat data of Smith (abs. **3206**), the free-energy change is $\Delta F=-20{,}857+41.17\ T\log T-0.01423\ T^2-54.42\ T$, giving 16,070 cal. at 700° K.

3210. SMITH, D. F., AND HAWK, C. O. Catalytic Decomposition of Methanol. Jour. Phys. Chem., vol. 32, 1928, pp. 415–424; Chem. Abs., vol. 22, 1928, p. 1520.

Rate of decomposition of CH_3OH by 36 different metallic and oxide catalysts, at atmospheric pressure was measured, mainly at 300°, by the dynamic method. The methods of preparation and the composition of the various catalysts are given. ZnO, made by igniting $ZnCO_3$, mixtures of ZnO and Cr_2O_3 in the atomic proportions 4 Zn : 1 Cr, mixtures of ZnO and UO_2, and perhaps also mixtures of ZnO and V_2O_3 and of CdO and Cr_2O_3, would be considered very good catalysts for the decomposition of CH_3OH into CO and H_2. These substances also should be good catalysts for the formation of CH_3OH from water gas. The activity of pure ZnO and also of ZnO–Cr_2O_3 catalysts is to a considerable degree dependent on the heat and other treatment to which they are subjected. The specific catalytic effect of pure Cr_2O_3 is absent in the ZnO–Cr_2O_3 catalysts. X-ray powder photographs indicated that in these catalysts the Cr_2O_3 does not exist in the ordinary form but is either amorphous or has combined with ZnO. Small amounts of CO_2 were present as a byproduct of the decomposition in virtually all cases.

3211. SMITH, D. F., AND HIRST, L. L. Reactions That Occur on a Methanol Catalyst. Ind. Eng. Chem., vol. 22, 1930, pp. 1037–1040; Chem. Abs., vol. 24, 1930, p. 5586.

CO_2 and H_2 react on a ZnO–Cr_2O_3 catalyst at 304° to form MeOH, CO, and H_2O. CO and H_2O also react to give CO_2 and H_2, and equilibrium may be closely approached in the water gas reaction. It was found impossible to determine which of the reactions comes nearest equilibrium when this catalyst acts on H_2CO_2–H_2O mixtures. It is suggested that the formation of MeOH from CO and H_2 may not be direct, especially as a steady state is approached.

3212. ———. Reliability of the Heat Data as a Factor in Calculating Equilibria Involving Methanol. Ind. Eng. Chem., vol. 22, 1930, pp. 634–635; Chem. Abs., vol. 24, 1930, p. 3408.

Reply to B. F. Dodge (abs. **704**).

3213. SMITH, D. F., DAVIS, J. D., AND REYNOLDS, D. A. Synthesis of Higher Hydrocarbons From Water Gas. I. Ind. Eng. Chem., vol. 20, 1928, pp. 462–464; Chem. Abs., vol. 22, 1928, p. 1948.

Study was made of the efficiency of different catalysts in producing liquid hydrocarbons from water gas at atmospheric pressure. Under the best conditions, with Co–Cu–Mn catalyst, 66 gm. of oil were produced per $m.^3$ water gas.

3214. SMITH, D. F., HAWK, C. O., AND REYNOLDS, D. A. Synthesis of Higher Hydrocarbons From Water Gas. II. Ind. Eng. Chem., vol. 20, 1928, pp. 1341–1348; British Chem. Abs., 1929, B, p. 82; Chem. Abs., vol. 23, 1929, p. 814.

Catalyst made from coprecipitated hydroxides of Co, Mn, and Cu was used to synthesize hydrocarbons from purified water gas at atmospheric pressure and at temperatures about 250°. Space velocities 120–360 were used. Extensive tabulation is made of the nature and quantities of hydrocarbons formed, the quantities

of water gas converted, and their relation to the temperature and space velocity. The quantities of oxygenated products formed were comparatively small. The percent of CH_4 in the hydrocarbon product was higher the higher the temperature and the more active the catalyst. The proportion of very heavy hydrocarbons was greater at the lower space velocities and the higher temperatures. At the higher space velocities and higher temperatures, relatively more unsaturated hydrocarbons were formed. At 260° and 260 space velocity, the hydrocarbon product was 21% by weight CH_4, 45% enriching hydrocarbons (German Gasol), 34% motor fuel. The yields of hydrocarbons, exclusive of CH_4, vary 92–156 gm. per m.^{3} of H_2+CO converted. At 203° and 230 space velocity, about 18% of the water gas was converted in a single pass.

3215. SMITH, D. F., HAWK, C. O., AND GOLDEN, P. L. Mechanism of the Formation of Higher Hydrocarbons From Water Gas. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 3221–3232; Chem. Abs., vol. 24, 1930, p. 4755.

Experiments are reported that show that cracking of the heavier hydrocarbons does not play any considerable part in the formation of the mixture of hydrocarbons higher than CH_4 when the synthesis is carried out on a Co–Cu–Mn oxide catalyst under the conditions described. The experiments in which Me_2CO was passed over the catalyst with H_2, N_2, or CO indicate that Me_2CO likewise is not a predominating intermediate. Me_2CO is almost never present in the products from water gas alone. Polymerization of C_2H_4 or of higher olefins does not occur. C_2H_4, at least in concentrations over 10%, enters into reaction upon the Co–Cu–Mn oxide catalyst in the presence of water gas, forming higher hydrocarbons and large quantities of O-containing compounds. The O-containing compounds dehydrate to a greater or less extent, producing hydrocarbons. The dehydration is accompanied by some polymerization. The extent to which C_2H_4 enters into these reactions does not change largely with the C_2H_4 concentration when this is above about 10%, but formation of these intermediate products depends quite markedly upon the concentration of water gas. The mechanism forming hydrocarbons may be regarded as follows: There is some association of H_2 and CO on the catalyst surface. This complex may either decompose, giving an olefin and H_2O, or C_2H_4 or other olefin may combine with it to form an O-containing compound, which may either pass into the products or eliminate H_2O to form a higher olefin hydrocarbon. The olefins are to be regarded as the primary hydrocarbon products. They may later be hydrogenated to form paraffin hydrocarbons or pass on into the products, depending upon the experimental conditions of H_2 concentration, space velocity, catalyst, and temperature. The mechanism of H_2 formation on an Fe–Cu catalyst is essentially different from that on a Co–Cu–Mn oxide catalyst, aside from the relative amounts of CO_2 and H_2O formed, since in this case C_2H_4 does not enter into reaction.

SMITH, D. F., HAWK, C. O., AND REYNOLDS, D. A. Synthesis of Higher Hydrocarbons From Water Gas. II. *See* abs. **3214.**

3216. SMITH, E. W. Economic Utilization of Coke-Oven Gas. Gas World, vol. 121, 1944, pp. 130–133; Gas Jour., vol. 244, 1944, pp. 208–209; Jour. Inst. Fuel, vol. 17, 1944, pp. 188–189, 191; Chem. Abs., vol. 38, 1944, p. 5661.

Address in which the coordination of a coke plant with an undertaking distributing gas to consumers is discussed as a means for disposing of the plant's surplus gas. The use of coke-oven gas as a raw material in the synthesis of oil by the Fischer–Tropsch process also is considered.

3217. SMITH, F. Chemicals From Petroleum. Jour. Inst. Petrol., vol. 32, A, p. 262; Jour Roy. Soc. Arts, vol. 45, 1945, pp. 566–598.

Three lectures are recorded. Among the many products mentioned in (I) are those from H_2 and CO by the Fischer–Tropsch synthesis. (III) gives an outline from the use of synthetic hydrocarbons as fuels. The relation between their structures and efficiency in internal combustion engines is discussed. A graph shows the approximate relation between octane numbers and the number of methyl groups in the paraffin chains.

3218. SMITH, G. E. P., AND PALMER, H. F. The Coming Petrochemical Industry. Nat. Petrol. News, vol. 36, 1944, pp. 571–575R; Chem. Abs., vol. 38, 1944, p. 6080.

Review showing the importance of petroleum and natural gas as raw materials in the synthesis of commercial organic chemicals.

SMITH, G. H. *See* abs. **422.**

3219. SMITH, H. M. Possible Utilization of Natural Gas for the Production of Chemical Products. Bureau of Mines Inf. Circ. 6388, 1930, 5 pp.; Chem. Abs., vol. 25, 1931, p. 397.

Chart shows the products obtainable from natural gas by oxidation, pyrolysis and chlorination, and the uses of each. These products and the compounds derived from them are: Oxidation—water gas, H_2, MeOH acetone, formaldehyde (bakelite); pyrolysis—$H_2(NH_3)$, $C_2H_4(C_2H_5OH$, $C_2H_2Cl_2$, $C_2H_2(OH)_2)$, C_3H_8 (isopropyl alcohol), C_4H_8 (secondary Bu alcohol), anthracene (alizarin), naphthalene (indigo), C_2H_2 (CH_3CHO), butadiene (rubber), C_6H_6 (resorcinol), C_7H_8 (saccharin), xylene and C black; chlorination—CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4.

3220. SMITH, H. M., AND HOLLIMAN, W. C. Utilization of Natural Gas for Chemical Products. Bureau of Mines Inf. Circ. 7347, 1947, 24 pp.; Petrol, vol. 26, No. 4, 1947, p. 365; Rept. to Federal Power Commission, June 1946, 11 pp.

Revision of Bureau of Mines Inf. Circ. 7108, 1940. It shows in graphic form the general reactions used and the chemical products that can be obtained from natural gas as the raw material.

SMITH, L. B. *See* abs. **1743, 1744, 2484.**

SMITH, L. G. *See* abs. **2824.**

3220a. SMITH, P. I. Soap From Synthetic Fatty Acids. Am. Perfumer Essent. Oil Rev., vol. 58, July 1951, pp. 53–55; Chem. Abs., vol. 45, 1951, p. 10,621.

Use for soap manufacture of the wax fraction obtained during the Fischer-Tropsch hydrocarbon synthesis is discussed. The unpleasant odor associated with the synthetic fatty acids must be removed by suitable treatment before and not after saponification.

SMITH, P. V. *See* abs. **2325a.**

SMITH, R. N. *See* abs. **2700.**

SMITH, S. L. *See* abs. **1331, 1332, 1335a, 1336.**

SMITH, W. R. *See* abs. **1771.**

3221. SMITHELLS, C. J. Permeability of Metals to Hydrogen. Nature, vol. 139, 1937, p. 1113; Chem. Abs., vol. 31, 1937, p. 6088.

Rate of diffusion of H_2 was determined in cc. per cm.^{2} per sec. at 760 mm. pressure for metal 1 mm. thick at 1,000°, 500°, and 0°. Calculations were made for the following: Fe, Ni, Mo, Pt, Cu, Al. Apparatus for work at high pressures is made of steel to provide the necessary strength. The diffusion of H_2 cannot be reduced greatly by increasing the thickness. At room temperature, 1 mm. Cu would be as effective as 5 miles of steel, and 1 mm. Al would be better than 10^{13} miles of Pd in retarding this diffusion.

3222. SMITS, A., AND WOLFF, L. K. [Velocity of Transformation of Carbon Monoxide. I.] Proc. "Koninkl. Akad. Wetenschappen Amsterdam", vol. 5, 1903, pp. 417–424; Jour. Chem. Soc., vol. 83, II, 1903, p. 276; Jour. physik. Chem., vol. 35, 1903, pp. 199–215.

From a study of the catalytic action of Fe, Ni, and Co on the system $2CO \rightleftharpoons CO_2+C$, Boudouard found that at 1,000°, CO_2 in contact with C is almost wholly converted into CO, while, at 445°, the reverse is true. The authors examine the conditions of the action below 445° when CO is in a metastable condition. The catalyst was finely divided Ni reduced at 445°. Observations made at 256°, 310°, and 340° indicated that the action was unimolecular. The reaction constants, calculated from $K=1/t \log P_o/2P_t-P_o$, were determined at the above temperatures, the values being 0.000279, 0.00186, and 0.00527, respectively. During these measurements the activity of the catalyst had not decreased. The 2 following hypotheses are adduced for the mechanism of the reaction: First (1) $CO_2=CO+O$ (with measurable velocity), (2) $CO+O=CO_2$ (with immeasurable velocity); secondly, (1) $CO+Ni=C+NiO$, (2) $CO+NiO=CO_2+Ni$. In the latter case, the 2d stage takes place more quickly than the 1st, but it need not be assumed that the velocity of one of the stages is immeasurable. The catalyst was actually Ni and not the C with which it was mixed.

3223. ———. [Velocity of Transformation of Carbon Monoxide. II.] Proc. "Koninkl. Akad. Wetenschappen Amsterdam," vol. 6, 1903, pp. 66–72; Jour. Chem. Soc., vol. 83, II, 1903, p. 628.

By the method previously used, it was proved, with pumice Ni–C as catalyst, that at 445° the conversion of CO into CO_2 and C is an unimolecular reaction, contrary to Schenck and Zimmerman's statement. No satisfactory reaction constant could be obtained at 445° owing to the fact that at this temperature the reaction is reversible, although Boudouard has stated that at 445° CO can be completely decomposed into C and CO_2. Starting with CO_2 in the reaction vessel at 445° it was found that after prolonged heating CO was formed, but the same equilibrium could not be obtained as when the experiment was carried out with CO. Even on using a catalyst obtained by reducing Ni oxide with H_2, it has not been found possible to verify Schenck and Zimmerman's results, and no explanation can be offered of why they obtained results leading to the conclusion that the reaction is bimolecular.

3224. SMITTENBERG, J. [Influence of Temperature and of Pressure on the Adsorption of Hydrogen by Nickel.] Rec. trav. chim., vol. 52, 1933, pp. 112–122; Chem. Abs., vol. 27, 1933, p. 2362.

Isotherms for the adsorption of H_2 gas on Ni at 300°, 210°, 123°, and 15° and the isobar at 760 mm. for this temperature range were obtained. Adsorption is of 2 types: Between 10 and 760 mm. it is rapid and and reversible; below 10 mm. it is slow, and equilibrium is reached only after some days.

3225. ———. [Absorption and Adsorption of Hydrogen by Nickel.] Rec. trav. chim., vol. 53, 1934, pp. 1065–1083; Chem. Abs., vol. 29, 1935, p. 977.

Adsorption of H_2 by Ni in the form of wire 0.022 mm. diameter gives data in good agreement with those found by Sieverts. Adsorption is very small even at 90° abs. The heat of absorption is calculated to be −2.62 ky-cal. Certain hysteresis effects are ascribed to impurities in the Ni. A test on adsorption also was made with A as the gas. Sorption of H_2 and He with temperature was also found from 90° to 800° abs.

3226. SMOLENSKI, K. [Synthetic Raw Materials.] Gaz. Cukrownicza, vol. 83, 1938, pp. 115–123, 149–161; Chem. Abs., vol. 33, 1939, p. 1409.

Review of developments and methods used to produce several synthetic raw materials as gasoline, rubber, fats, etc.

3227. SMOLEY, E. R., TORREY, R. M., AND KNIEL, L. Chemicals From Petroleum. Petrol. Refiner, vol. 26, No. 11, 1947, pp. 768–772; World Petrol., vol. 18, No. 12, 1947, pp. 78–81; Chem. Abs., vol. 42, 1948, p. 1043.

Production of synthetic chemicals from petroleum has expanded from an output of 150,000 lb. in 1925 to almost 4 billion lb. in 1946. The trend still is upwards with addition of several new chemicals. The Fischer-Tropsch process also is adding many chemicals to the list, as is evidenced by the expected production from the 2 plants under construction for processing natural gas. The estimated production of chemicals from one Hydrocol plant alone amounts to 152,450,000 lb. per yr. The manufacture of C_2H_4 from petroleum and natural gas constituents is discussed at length, and a list of plants with approximate production is given.

3228. SMOLUCHOWSKI, R. Diffusion Rate of Carbon in Iron–Cobalt Alloys. Phys. Rev., vol. 62, 1942, pp. 539–544; Chem. Abs., vol. 37, 1943, p. 819.

Studies of rates of various transformations and reactions in Fe alloys seem to indicate that certain elements have a definite effect on the rate of diffusion of C in γ–Fe. In particular, Co shows a pronounced accelerating effect. By direct measurement of the rate of diffusion of C in Fe–Co alloys, this conclusion is confirmed, and an increase in the diffusion coefficient is established. An addition of 4% Co decreases the activation energy from 32,500–30,000 cal., corresponding to an almost twofold increase of the diffusion rate at 1 at. % C concentration. At higher C contents, the accelerating effect of Co is smaller. This property of Co is unusual, especially in view of the fact that both Mn and Ni are known to have virtually no effect on the diffusion of C.

SNIGUROVSKA, Y. O. *See* abs. **3758.**

3229. SNODGRASS, C. S., AND PERRIN, M. Production of Fischer-Tropsch Coal Alcohol and Its Improvement by Cracking. Jour. Inst. Petrol. Technol., vol. 24, No. 175, 1938, pp. 289–301; Petrol. Times, vol. 39, No. 1002, 1938, pp. 395–397; Engineering, vol. 145, 1938, pp. 236–238; Gas Jour., vol. 221, 1938, p. 665; Colliery Guard., vol. 156, 1938, pp. 483–484; British Chem. Abs., 1938, B, p. 876; Chem. Abs., vol. 32, 1938, pp. 6447, 9441.

Description of the Fischer-Tropsch process pointing out the paraffin-wax formation and the desirability of cracking this to improve the yield of motor fuel. Fischer-Tropsch fuels are generally of poor octane number and difficult to crack. Operation of a successful vapor phase process using a cycle gas system is described; flow sheets are presented and properties of the products are tabulated. Motor fuels of octane Nos. 62–75 are produced. It is impracticable to crack the Fischer-Tropsch gaseous product directly; separation from lean gas and steam must first be made by condensation.

SNOWDEN, F. F. *See* abs. **1214.**

3230. SOAP AND SANITARY CHEMICALS. German Soap Substitutes. Vol. 22, October 1946, pp. 75, 77.

Brief account of the development and operation of the Oxo process for the manufacture, from Fischer-Tropsch olefins, of fatty alcohols, which are sulfonated to give detergents.

3230a. SOBCOV, H. Analysis of Liquid Hydrocarbon Mixture by Mass Spectrometry. Anal. Chem., vol. 24, 1952, pp. 1386–1388; Chem. Abs., vol. 47, 1953, p. 298.

Application of matrices and IBM techniques is discussed in the analysis of hydrocarbon mixtures b. 82°–231° F. (isopentane to toluene). Problems of mass

spectrometer reproducibility and close spectral similarities require fractionation of the sample by distillation. The smallest number of fractions required seems to be 4 and the largest useful matrix is of the 15th order. Many of the observations from this study are general enough to be applicable to other problems in mass spectrometry.

3231. SOETERS, C. J. [Synthesis of Fatty Acids.] Olien, Vetten Oliezaden, vol. 26, 1942, pp. 245–247, 275–279; Chem. Zentralb., 1943, I, p. 1431; Chem. Abs., vol. 38, 1944, p. 1731.

Technical report on the manufacture and properties of fatty acids obtained by oxidation of paraffins in Germany.

SOFER, M. A. *See* abs. **1590.**

3232. SOLLIDAY, A. L. Significance of Hydrocarbon Synthesis in Western Kansas. Oil Gas Jour., vol. 46, No. 48, 1948, pp. 110–111.

In the belief that the process of synthesizing liquid hydrocarbon fuels from gas and coal will be the future cornerstone of our oil supply, the Stanolind Oil & Gas Co. has undertaken over a period of several years a vast program of research and development to improve and perfect the process. A plant to process 100 million cu. ft. of natural gas per day is being built in the Hugoton gas field. Some general details of the plant and its operation are presented, and criticism is made of the Government's entry into the production field in competition with private industry.

3233. ———. Synthetic Fuels. Oil Gas Jour., vol. 48, No. 24, 1949, pp. 86–88, 125; Petrol. Refiner, vol. 28, No. 11, 1949, pp. 81, 83, 85, 238; Jour. Inst. Petrol. Technol., vol. 1, sec. 1, October 1949, pp. 4–8.

Paper presented to the Petroleum Branch of the American Institute of Mining and Metallurgical Engineers. It is estimated that the United States has enough reserves of petroleum to supply the domestic demand until 1961 before it will need to turn to coal and oil shale. By 1965 the Nation's petroleum deficit may amount to about 420,000 bbl. per day and increase to around 1,260,000 bbl. by 1975. There is nothing to indicate that construction of synthetic fuel plants should begin immediately. By the time they are needed, technical developments in the design of plants and methods of operation should lower the construction expenditures and bring lower investment costs, enabling synthetic fuels to compete with natural petroleum. Using present designs, the motorist would have to pay \$0.15–0.20 more per gal. for synthetic gasoline. An economic study is presented.

3234. ———. Public Being Misled by Bureau of Mines Synthetic Fuels Figures. Nat. Petrol. News, vol. 42, No. 12, 1950, pp. 16, 23; Oil Gas Jour., vol. 48, No. 46, 1950, p. 160.

Criticism of the 1949 annual report of the Secretary of the Interior. In arriving at cost estimates of synthetic fuels, the Bureau's figures are inadequate, it is stated, to show a basis for arriving at its published estimates. The Bureau figures of \$0.09 and \$0.145 per gal. for liquid fuel from oil shale and coal hydrogenation, respectively, are greatly out of line with the comparative industrial estimates of \$0.225 for the same fuels. It is charged that the Bureau is confusing the public by basing its costs on calculations that are "no more than wishful thinking." This report illustrates the need for the Bureau of Mines to publish detailed breakdowns of all economic calculations including investment costs so as to allow the public to compare Government and private industry estimates and to show clearly whether synthetic fuels represent a sound or an unsound investment.

SOLVAY, —. *See* abs. **3205.**

SOUTHWICK, C. A. *See* abs. **1099.**

3235. SPAGHT, M. E. German Wartime Aviation Fuels by Hydrogenation of Coal. Ruhrchemie Catalytic Cracking Process. U. S. Naval Tech. Mission in Europe, Rept. 145–45, 1945, 45 pp., PB 1,657; Oil Gas Jour., vol. 44, No. 41, 1946, p. 124; BIOS Misc. Rept. 72, 1948, 45 pp., PB 1,657.

Describes process for cracking the highly paraffinic Fischer-Tropsch products to form a maximum of olefins for chemical synthesis intermediates. A synthetic silica-alumina catalyst was used, 0.7 apparent specific density, with a space velocity of 0.1. yielding a 40% conversion per pass on a 340°–660° F. Fischer-Tropsch fraction, of which nearly 70% was olefins up to C_5 and only 15% gasoline. The process was intermittent and catalyst was regenerated after 20–25 min. cycles, showing about 1.5% coke deposition. Product distribution was as follows in % wt. of feed: Gasoline C_6 to about 320° F. 6–8; C_5 7.6–9.6; C_4 10–12; C_3 8–10; C_2 2–2.8; CH_4 and H_2 0.4–0.8; coke 1.2–1.6.

3236. ———. Manufacture of Synthetic Butter. CIOS Rept. XXXI–79, 1945, 5 pp., PB 23,753. TOM Reel 199; U. S. Naval Technical Mission in Europe Rept. 144–145.

During the war, a synthetic butter was manufactured by the Deutsche Fettsäure Werke in Witten, Germany. The output of finished product was 11,000 lb. per day. The process involved the oxidation of Fischer-Tropsch wax paraffins at 230° F., with a $KMnO_4$ catalyst to produce straight-chain fatty acids of C_{11} and C_{12} and their esterification with glycerine to yield edible esters. The esterification was catalyzed with 0.2% of finely divided Sn or Zn. The resulting ester mixture was refined and purified, giving a product with all the outward appearance of natural butter; the same consistency and softening characteristics. Its taste was pleasant but slightly waxy. It was sold largely to hospitals where it was favored for certain diets, and the remainder was purchased by the Army. The product was competitive with margarine in price and could have been sold with profit at 60% of the price of natural butter. The prevailing prices in the same market for natural butter and margarine were RM 1.6 and 0.9 per lb., respectively. (*See* abs. **2176.**)

3237. ———. Future Research in Hydrocarbons. Chem. and Ind., 1947, pp. 241–242.

Abridgement of a paper presented before the American Section of the Society of Chemical Industry. It is believed that the cheapest way of producing liquid hydrocarbons from coal will be via a water gas reaction and subsequent synthesis by the Fischer-Tropsch reaction. Direct hydrogenation of solids is not yet to be counted out of competition but, at this time, the Fischer-Tropsch route is the brightest hope for the conversion of coal. Recovery of oil from shale represents another possibility, but, at the moment, it is farther from commercial reality than those utilizing either CH_4 or coal.

3238. SPARKS, W. J., AND YOUNG, D. W. Plasticizers From Oxo Alcohols. Ind. Eng. Chem., vol. 41, 1949, pp. 665–670; Chem. Abs., vol. 43, 1949, p. 5627.

Information on the chemical and physical properties of new octyl and nonyl alcohols, manufactured by the Oxo reaction. Olefins are converted with H_2 and CO under high pressures in the presence of a Co catalyst to aldehydes, which are then hydrogenated to alcohols. In this study Oxo alcohols were reacted with phthalic anhydride as well as phosphorus oxychloride to form plasticizers.

3239. SPAUSTA, F. [Motor Fuels.] Österr. Chem.-Ztg., vol. 41, 1938, pp. 65–75; British Chem. Abs., 1938, B, p. 477.

Production and properties of a wide range of motor fuels (benzine from petroleum, benzol, motor fuels pro-

duced by hydrogenation or synthesis, EtOH, C_3H_8+ C_4H_{10} and other compressed fuels, etc.) are summarized.

3240. SPENCER, H. M., AND JUSTICE, J. L. Reaction of Carbon Monoxide on Molybdenum Oxides. Jour. Am. Chem. Soc., vol. 56, 1934, pp. 2301–2306; Chem. Abs., vol. 29, 1935, p. 700.

MoO_2 reversibly is reduced by CO at 560°, but the reaction is masked by the catalytic decomposition of CO. At about 810°, the reaction proceeds smoothly, with no separation of C: $2\ MoO_2+6\ CO \rightleftharpoons Mo_2C+5\ CO_2$. For 810°, K_p is calculated as 1.46 for 750 mm. pressure.

SPENCER, W. B. *See* abs. **2010.**

3241. SPENCER, W. D. Oil and Smokeless Fuel From Coal. Plan for the Development of the Carbonization Industry. Petroleum (London), vol. 6, No. 11, November 1943, pp. 163–167.

Process which consists of a combination of low-temperature and high-temperature carbonization together with a Fischer-Tropsch oil synthesis based on the utilization of intermediate products. From 1 ton of coal 7.5 cwt. of smokeless fuel, 50 gal. of liquid fuel, 3 gal. of refined tar acids, 20 lb. paraffin wax, and 65 lb. of pitch are produced. The overall thermal efficiency of the combined process is 70% (67% if it is found impossible to dispose of the pitch for plant fuel). A flow chart is shown. The coal is carbonized in retorts heated by producer gas; the low-temperature coke is sold as smokeless fuel, and the high-temperature coke is used for the production of producer gas to heat the retorts and to make the water gas required in the process. The gases from the retorts are cooled to separate the tar, mixed, purified, and the composition is adjusted by adding water gas and steam conversion to the requirements of the Fischer-Tropsch plant. The tar from the retorts is distilled to remove the pitch, fractionated, the fractions are refined together with the Fischer-Tropsch oil, and the final cuts are obtained. From ¼ ton of coke 16,000 cu. ft. of water gas could be obtained, this mixed with 21,500 cu. ft. (11,000 cu. ft. per ton of coal+360 lb. steam) of converted gas gives a total of 37,500 cu. ft. of synthesis gas of composition $1\ CO+2\ H_2$. A conservative estimate of oil yield per cu. ft. of synthesis gas is 4 gm., representing an efficiency of 74% of the theoretical yield, so that 42 gal. of oil (4.5 liquefied gas, 22.5 motor fuel, 15.0 diesel oil) and 19.8 lb. of paraffin wax would be obtained.

3242. ———. Science of Coal-to-Oil Conversion. IV. Fischer-Tropsch Synthesis. Petroleum (London), vol. 7, 1944, pp. 90–94; Chem. Abs., vol. 39, 1945, p. 2391.

Other articles in this series deal with: General Considerations, pp. 25–28; Low-Temperature Carbonization, pp. 34–36, 39; Hydrogenation of Coal, pp. 76–79; High-Temperature Carbonization, pp. 135–139; Summary and General Conclusions, pp. 184–186. The development of the synthesis process began in 1902 with Sabatier and Senderens, who investigated the reactions $CO+3\ H_2=CH_4+H_2O$ and $CO_2+4\ H_2=CH_4+2\ H_2O$ at 200°–250° over a reduced Ni catalyst. In 1913, the Badische Anilin und Sodafabrik, by employing catalysts consisting of the oxides of Co, Os, or Zn at 400° and 100 atm., obtained a complex mixture of hydrocarbons and their O derivatives. By increasing the pressure, the I. G. Farbenindustrie A.–G. later developed the process for synthesizing MeOH from water gas. Fischer and Tropsch in 1922, using an Fe catalyst impregnated with K_2CO_3 and passing over it a mixture of CO and H_2 at 400°–450° and 100–150 atm., obtained a product, which they called Synthol, consisting of a mixture of alcohols, aldehydes, ketones, and fatty acids. By reducing the pressure and the temperature, a less highly oxygenated product was obtained, but the rate of reaction likewise fell off, making it necessary to find a more active catalyst. It was not until 1928 that Fischer, with Koch and Meyer, succeeded in producing catalysts that were active at atmospheric pressure and temperatures below 200° and capable of retaining their activity for several months. To preserve the catalyst activity, it was found that S present in the synthesis gas, which consisted preferably of a water gas containing H_2 and CO in the ratio 2:1, must not exceed 0.1%. The product obtained by this latest process was called Kogasin; it consisted of gaseous liquid and solid hydrocarbons composed mainly of straight-chain paraffins and olefins and could be broken down into a series of fractions consisting of low-boiling hydrocarbons (up to 30° C), gasoline (30°–200°), diesel oil (200°–350°), and solid paraffin wax. The exact composition of the fractions is a function of the catalyst and of the operating conditions. By 1934, the process had reached such a stage of development that it was taken over by the Ruhrchemie A.–G., and a plant was constructed and put into operation in 1936 at Oberhausen. By 1940 German output of oil from the Fischer-Tropsch process was estimated at 1,000,000 tons per yr. The theory of the process may be represented empirically by the equation:

$$CO+2H_2=(CH_2)+H_2O+48{,}000\ \text{cal.}$$

It appears that the 1st stage in the process is adsorption of CO on the catalyst, followed by reduction to carbide, which reacts with the H_2 to form CH_2 groups, which either combine with H_2 to form CH_4 or polymerize with formation of higher hydrocarbons. The catalyst usually used industrially consists of $Co:ThO_2$: kieselguhr in the proportions 100:18:100. Fe or Ni can be used. The latter cannot be used at medium or high pressure, since Ni carbonyl is formed and removed from the system because of its volatility. Under low pressure, it increases the degree of saturation of the product. Fe gives good results. At low pressures, the yield of hydrocarbons is small but increases with increase in pressure. The operating temperature should be higher than with Co, and the ratio H_2: CO should be lower. The products are more unsaturated and contain less wax. A new catalyst is reported, but not named, with which a C_4 fraction is obtained containing 90% of isobutane. The temperature is above 200° and the pressure above 100 atm. With another catalyst, naphthenes and aromatics can be obtained. With Ru as a catalyst, a temperature of 200°, and pressures of 100–200 atm., a mixture of solid waxes is obtained with a m. p. up to 134° C. The Fischer-Tropsch synthesis was originally operated at atmospheric pressure to cut down the formation of alcohols and other oxygenated compounds, but it has been found that certain advantages exist in using pressures of 7–8 atm., among which is the reduction in size of the plant. The theoretical yield of hydrocarbons from 1 cu. m. of ideal synthesis gas (66.7% H_2, 33.3% CO) is 208 gm., but, in practice, the yield does not normally exceed 140 gm. per $m.^3$ for a 1-stage medium-pressure process or 160 gm. for a 2-stage process. Several steps occur in the manufacture of oils: (*a*) Manufacture of synthesis gas; (*b*) purification of gas; (*c*) hydrocarbon synthesis; (*d*) manufacture of catalyst; (*e*) distillation and refining of primary products; (*f*) further treatment of products, for example, cracking or isomerization of gasoline, conversion of wax to lubricants. Each of these steps is discussed with a variety of data and a flow sheet. The capital cost of a plant (100,000 tons per yr. of finished products) should not exceed £3,300,000 (based on 1938 prices) or £7 3s. per ton per yr. of coal consumed, calculating 4.5 tons per ton of finished products. Such a plant, allowing for certain improvements in operation and design and 10% for depreciation and overhead, should produce gasoline and diesel oil at a cost not to exceed 9 d. per gal. Whether the Fischer-Tropsch process is assessed on its own merits or regarded as an adjunct

to carbonization, it has the advantage that all products are valuable materials. Although emphasis is usually placed on the production of motor fuels, it is possible that in the future the real value will be considered to be its use in the manufacture of synthetic chemicals giving hydrocarbons, alcohols, acids, esters, organic solvents, plastics, and many other aliphatic compounds containing C, H, and O. Coal tar would remain the chief source of aromatic compounds, and petroleum refinery byproducts would provide a source of aliphatic hydrocarbons and chemicals based on them. This would provide a basis for a coordinated group of processes feeding the organic chemical industries.

3243. SPENGLER, H. [Physicochemical Behavior of Fischer-Tropsch Catalysts.] Erdöl u. Kohle, vol. 3, No. 1, 1950, p. 10.

Paper presented at the 1949 meeting of the Deutsche Gesellschaft Mineralölwissenschaft u. Kohlechemie. Aside from the purely chemically limited properties, the physical or physical-chemical data for the behavior of a catalyst is important. Of special significance for the movements occurring within are the geometric structure of the catalyst grains, the inner surface area as the seat of the catalytic reactions, and the adsorption behavior in the presence of the reaction gases. Measurements of the geometric structure give numerical values for the porosity of the catalyst grains and the dimensions of the pores. Tests of the permeability of the catalyst grains with different gases show that greater amounts of H_2 and CO pass through the grain than must be the case with experimentally determined pore radii. This additional flow is called surface diffusion. It explains the otherwise difficultly explicable fact that the whole catalyst grain is utilized by the reaction, although the pores are filled with the products of the reaction. The inner surface area of a Co catalyst lies in the magnitude of 100 $m.^2$ per gm. In the range of adsorption measurements for determination of the inner surface area, the adsorption of CO and H_2 was measured also. From the measurements, it was seen that the CO molecule is more strongly bound than is the H_2 molecule, and the temperature range applied in the Fischer-Tropsch synthesis lies within the transition range of physical and chemical adsorption.

———. *See* abs. **370.**

3244. SPILKER, A. [Refining of Coal and Its Liquefaction.] Braunkohle, vol. 26, 1927, pp. 545–553; Chem. Abs., vol. 21, 1927, p. 4047.

General discussion of coal liquefaction, the MeOH process of the I. G. Farbenindustrie A.-G., the benzine synthesis of Fischer-Tropsch, the Synthol process, and the direct hydrogenation of coal by the Bergius process.

3245. SPINGLER, H., AND REINHARD, O. ["Magnetocatalytic Effect" in the Hydrogenation of Carbon Dioxide or Carbon Monoxide on Nickel.] Ztschr. physik. Chem., vol. 190, A, 1942, pp. 331–340; Chem. Abs., vol. 37, 1943, p. 4958.

Mixture of CO or CO_2 and H_2 was passed over powdered Ni heated to temperatures near the Curie point (350°–360°) in an apparatus similar to that of Fischbeck and Salzer (abs. **938**). The amount of reaction was determined by collecting and weighing the H_2O formed and the residual CO_2. The percent of CO_2 hydrogenated in 15 min. increased with increase in temperature, but there was no discontinuity in the curve at the Curie point. Analogous results were obtained for decreasing temperatures. In the hydrogenation of CO there is a decided increase in activity beginning at approximately 350° and ending at approximately 370° in a sudden decrease (abs. **1387**). The sudden decrease at 370° apparently is independent of the proximity of the Curie point; it may result from the deposition of C on the catalyst as a result of disproportionation of CO (abs. **130**). No change could be detected in the catalyst in this temperature region. Above 370°, the curve of % hydrogenation of CO versus temperature was very irregular; this is attributed to the antagonistic effects of the activating and poisoning mechanisms. The change in the catalytic activity of Ni in the region of the Curie point probably is not related to the Curie transformation but depends on the specific catalytic properties of the stable phase in that temperature region; hence, the existence of the magnetocatalytic or Hedvall effect is doubtful.

3246. SPIRK, L. [Soap Production From Mixtures of Natural and Synthetic Olefinic Hydrocarbons.] Časopsis Mydlář Voňavkář, vol. 20, 1942, pp. 97–98; Chem. Zentralb., 1943, I, p. 1120; Chem. Abs., vol. 38, 1944, p. 3864.

Various raw materials are: Lignite coking oil (b. 200°–350°), definite fractions of cracked gas oil (b. 200°–325°) with 70–75% olefins of natural origin or synthesized by hydrogenation of CO. Production of these synthetic raw materials and oxidation of the products are discussed. The fatty acids produced are neutralized at 250°–300° with amines or alkaline earths. The soaps are odorless and contain no unsaponifiable matter. 4 practical methods of producing these soaps are described.

3247. SPISKE, —. [Aftertreatment of a Catalytic Cracking Benzine With Borylphosphate or Bleaching Earth.] FIAT Reel L–5, frames 549–553, Dec. 22, 1941, PB 70,159; TOM Reel 299.

Tests were carried out with the object of determining whether or not an aftertreatment with borylphosphate or bleaching earth would raise the octane number of a catalytic cracking benzine. The results did not show any improvement of the aftertreated benzine over the unprocessed benzine.

SPIVEY, E. *See* abs. **1467a, 1468.**

SRIKANT, H. *See* abs. **3029a, 3030, 3030a.**

3248. SRIKANTAN, B. S. Reactions at the Surface of Hot Metallic Filaments. I. The Reaction $CO_2+H_2 \rightarrow H_2O+CO$ on Platinum. Jour. Indian Chem. Soc., vol. 6, 1929, pp. 931–947; Chem. Abs., vol. 24, 1930, p. 2036.

Reaction between CO_2 and H_2 on a Pt wire at about 1,000° is unimolecular except for the initial fall in reaction velocity, which is due to poisoning of the more active centers by the CO formed. Poisoning was eliminated by prior heating *in vacuo*. The rate of reaction was not influenced by dilution of the gases with N_2. The nature and treatment of the surface of the wire are important; thus, a rough surface is more active than a smooth one. The energy of activation is 38,000 cal.

3249. ———. Reactions at the Surface of Hot Metallic Filaments. II. The Reaction $CO_2+H_2 \rightarrow CO+H_2O$ on Platinum–Iridium Alloys. Jour. Indian Chem. Soc., vol. 6, 1929, pp. 949–958; Chem. Abs., vol. 24, 1930, p. 2036.

Pt wire containing 5–30% Ir is more active than pure Pt. The 30% Ir alloy is most active. The energy of activation is less with a powerful catalyst than with a poor catalyst. Temperature coefficients are calculated.

3250. ———. Reactions at the Surface of Hot Metallic Filaments. III. The Reaction $CO_2+H_2 \rightarrow H_2O+CO$ on Platinum Coated With Barium Oxide. Jour. Indian Chem. Soc., vol. 6, 1929, pp. 959–967; Chem. Abs., vol. 24, 1930, p. 2036.

Layer of BaO, formed on a Pt wire by thermal decomposition of $Ba(NO_3)_2$, adsorbs 1 of the reactants, CO_2, and gives reproducible results in studying the formation of CO and H_2O at 612°–826°. The reaction velocity rises slowly at the beginning of the reaction until a steady state is reached. The rate increases

with increasing pressures of CO_2 up to 300 mm. and is depressed by excess H_2. The temperature coefficient and energy of activation fall with rise of temperature.

3251. STÄBLEIN, F., AND SCHROETER, K. [Determination of the Magnetic Saturation of Iron Carbide.] Ztschr. anorg. Chem., vol. 174, 1928, pp. 193–215; Chem. Abs., vol. 22, 1928, p. 4349.

Ballistic method for finding the saturation value of the intensity of magnetization is described in detail, including the calibration of the apparatus and the experimental determination of the various corrections necessary. The results indicated that the method could be relied upon for powders. Fe_3C was prepared from pig Fe by solution in 0.1 *N* cold H_2SO_4. Tests on this gave 12,400 gausses as the saturation value for $4\pi J$, where J is the intensity of magnetization. By extrapolation from 2 specimens of C steel containing 0.46% and 0.95% of C, respectively, an average value of 12,300 gausses was obtained. The authors, therefore, conclude that the most probable value for saturation is $4\pi J$=12,350 gausses.

3252. STADLINGER, H. [Raw Materials for Paraffin Oxidation in Germany.] Deutsche Chem.-Ztg., vol. 1, 1949, pp. 55–60; Chem. Zentralb., 1950, I, p. 2049.

Comprehensive survey is made of the production and utilization of technical paraffin for catalytic oxidation and the recovery of fatty acids for soaps and synthetic fats. Discussion is made of lignite paraffin, high-temperature hydrogenation paraffin, and Fischer gatsch. Some instructions are included concerning the quality of the paraffin to be oxidized.

3253. STADTHERR, J. J. Basic Petroleum Chemistry for Refinery Employees. IX. Potential Sources of Liquid Fuel. Petrol. Refiner, vol. 26, No. 3, 1947, pp. 137–140.

Brief review of methods of producing substitute fuels.

3254. STAMMER, K. [Phenomena Connected With Reduction, Especially of Iron by Carbon Monoxide.] Ann. Chim., vol. 82, 1851, pp. 136–141.

It is assumed that the decomposition of CO on Fe results in carbide formation.

3255. STANBURG, W. A. Making Oil From Coal. Coal Age, vol. 54, No. 7, 1949, pp. 70–77.

Comprehensive survey of plant and process development in making oil from coal in accordance with the Government program as it is being carried out at the various plants operated by the Bureau of Mines. The various steps in the coal-to-oil development are briefly described: Coal preparation, cleaning, drying and storage; complete gasification, the vortex method, underground gasification, continuous high-temperature pebble-stove gasifier, O_2–steam gasification, O_2 production; Fischer–Tropsch gas conversion and internally cooled and slurry-type converters; 2-stage hydrogenation, liquid- and vapor-phase processes, and economics.

3256. STANLEY, H. M. Recent Advances in Our Knowledge of Natural Gas and Cracking Gas and Their Industrial Utilization. Jour. Inst. Petrol. Technol., vol. 15, 1929, pp. 516–552; Chem. Abs., vol. 24, 1930, p. 1496.

Comprehensive review of the subject, particularly with reference to recent work upon fractionation, analysis, utilization and synthesis. Bibliography of 74 refs.

3257. ———. Production of Water Gas From Methane and Other Hydrocarbons. Sci. Petrol., vol. 3, 1938, pp. 2164–2173.

Survey of the literature and discussion of methods for CH_4 conversion by partial oxidation, CH_4–steam reaction, CH_4–CO_2 reaction, and reaction of higher hydrocarbons with steam.

———. *See* abs. **2369**.

3258. STANLEY, H. M., AND NASH, A. W. Higher Hydrocarbons From Methane. Nature, vol. 122, 1928, p. 725; Chem. Abs., vol. 23, 1929, p. 3212.

Fischer's work on thermal decomposition of CH_4 with formation of higher hydrocarbons (abs. **954**) is confirmed.

3259. ———. Production of Gaseous, Liquid, and Solid Hydrocarbons From Methane. I. Thermal Decomposition of Methane. Jour. Soc. Chem. Ind., vol. 48, 1929, pp. 1–8T; Chem. Abs., vol. 23, 1929, p. 1866.

Under suitable conditions, CH_4 forms higher liquid and solid hydrocarbons when heated. These conditions have been found to be short times of contact on the order of less than 1 sec. and at temperatures of 1,000°–1,200°. The products may consist of C_2H_2, C_2H_4, C_2H_6, higher olefins, benzene, and higher aromatic hydrocarbons, C, and H_2. The % conversion of CH_4 into higher hydrocarbons increases rapidly with increasing gas rate and rapidly reaches a maximum at a given temperature.

3260. ———. Production of Gaseous, Liquid, and Solid Hydrocarbons From Methane. II. Action of Spark Discharge on Methane. Jour. Soc. Chem. Ind., vol. 48, 1929, pp. 238–242T; Chem. Abs., vol. 24, 1930, p. 1076.

Main primary product of the reaction is C_2H_2, the higher hydrocarbons probably being formed by the further action of the discharge on the C_2H_2–H_2 mixture produced.

3261. STANLEY, J. K. Diffusion and Solubility of Carbon in α–Iron. Jour. Metals, vol. 1, No. 10, Trans., 1949, pp. 752–761; Chem. Abs., vol. 43, 1949, p. 9004.

Diffusion of C in α–Fe was determined by 2 methods. 1, the Van Orstrand-Dewey method, consisted of diffusing the C from a high-C Fe containing 0.68% C, corresponding to fine pearlite, into an essentially C-free Fe. The diffusion of C does not appear to be affected by grain size, deoxidation, or small additions of Se and Co. The present methods did not lend themselves toward determining if D varied with concentration. At 725° the diffusion of C is over 100 times as fast as it is in α–Fe.

3262. STANLEY, J. K., HOENE, J. V., AND HUNTOON, R. T. Oxidation of Pure Iron. Trans. Am. Soc. Metals, No. 5, 1950, 21 pp.; Chem. Abs., vol. 44, 1950, p. 9886.

Oxidation of high purity electrolytic Fe (Puron) in air 500°–900° proceeds by the common parabolic rate law, $W^2=Kt+C$. The oxidation process as a function of temperature follows the usual exponential law. The rate constant, K, shows the temperature dependence $K=0.37e^{-33,000/RT}$. A Geiger counter X-ray spectrometer showed only 1 oxide, Fe_3O_4, at 500°, but 3 oxides, α–Fe_2O_3, Fe_3O_4, and FeO, at the higher temperatures; metallographic examination resolved the various oxide strata. FeO could be cooled to room temperature without decomposition to Fe and Fe_3O_4. Photomicrographs show typical structures.

STARKWEATHER, H. W. *See* abs. **3331**.

3263. STAVELEY, L. A. K., AND HINSHELWOOD, C. N. Reaction Chains in the Decomposition of Organic Compounds. Jour. Chem. Soc., 1937, pp. 1568–1573; Chem. Abs., vol. 31, 1937, p. 8329.

Decomposition of an organic molecule involves either an internal rearrangement to stable products or the production of free radicals and chain reactions. The addition of NO inhibits the latter. With this reagent, it has been found that the decomposition of ethers, aldehydes, from $MeCH_2CHO$ up the series, and C_2H_6 involve chain reactions, whereas the decomposition of AcH, ketones, MeOH, and HCO_2Me do not. A discussion of the theoretical aspects of the chain length in the chain reactions indicates that even when these occur, it is unnecessary to change any fundamental

views on the mechanism of activation in unimolecular reactions.

3264. STEACIE, E. W. R., AND ELKIN, E. M. Comparison of the Catalytic Activities of Liquid and Solid Surfaces—Decomposition of Methanol on Solid and Liquid Zinc. Proc. Roy. Soc. (London), vol. 142, A, 1933, pp. 457–465; Chem. Abs., vol. 28, 1934, p. 960.

Temperature effect on the decomposition rate of gaseous MeOH over solid and liquid Zn was investigated 300°–440°. The catalytic activity of the Zn depends directly on the temperature. There is no discontinuity at the melting point of the catalyst. Catalytic activity is attributed to the entire uniformly active surface of the metal rather than to some limited part.

3265. ———. Further Investigations of Catalysis by Liquid Metals. Canadian Jour. Research, vol. 11, 1934, pp. 47–52; Chem. Abs., vol. 28, 1934, p. 7132.

Kinetics of MeOH decomposition on solid and liquid Zn were examined in greater detail. The order of the reaction lies between zero and ½ on both solid and liquid. The heat of activation is approximately 30,000 cal. per gm.-mol. The reaction is mainly dehydrogenation. Unsuccessful attempts to investigate certain other reactions on liquid metals are described.

3266. ———. Catalysis by Fusions: A Reply to the Paper by Adadurow and Didenko. Jour. Am. Chem. Soc., vol. 58, 1936, pp. 691–692; Chem. Abs., vol. 30, 1936, p. 3306.

Reply to the criticisms of Steacie and Elkin's work (abs. **3264**) by I. E. Adadurow and P. D. Didenko (abs. **2**). They are based partly on an incorrect interpretation of their own data and partly on an incorrect mechanism for the decomposition of MeOH.

3267. STEFANOVSKIĬ, A. M., TATARSKIĬ, E. S., AND ZELYAKOV, N. V. Dependence of the Structure of an Ammonia Catalyzer Upon the Conditions During Its Reduction. Compt. rend. acad. sci. U. R. S. S., vol. 3, 1935, pp. 21–24 (in English); Chem. Abs., vol. 29, 1935, p. 8244.

Catalyzer prepared by oxy-acetylene fusion consisting mainly of 72% Fe_2O_3 and 27% FeO was reduced at temperatures 450°–800°. Its efficiency dropped abruptly from 61% for that prepared at 500° to 2% for that prepared at 600°. X-ray studies of changes involved show that the fall in activity cannot be accounted for by a change in size of the crystals but to a qualitative change of the surface. At higher temperatures, the defects, which are the active centers in NH_3 synthesis, disappear. This illustrates the use of X-ray photographs in the study of active centers.

STEFFENS, L. R. *See* abs. **1460.**

STEIN, K. *See* abs. **1449a.**

3268. STEINBERGER, K. F. [Raw Materials for the Production of Acetylene and Ethylene.] Angew. Chem., vol. 19, B, No. 8, 1947, pp. 211–214.

Important prewar source for the raw materials of C_2H_2 and C_2H_4 was the hydrogenation gases from the Fischer-Tropsch and the I. G. Farbenindustrie A.–G. hydrogenation processes. The total amount was 650,000–660,000 tons per yr., of which the Fischer-Tropsch process contributed 80,000–90,000 tons. The Fischer-Tropsch gases contained 35–40% olefins, mostly C_3 and C_4, while those from the I. G. Farbenindustrie A.–G. process were mostly saturated hydrocarbons. In general, they contained about 18% CH_4, 11–12% C_2H_6, 12% C_3H_8, 5% C_4H_{10} and 1% C_5H_{12}, 32–33% H_2, with small amounts of N_2, CO, CO_2 and H_2S. These gases were processed by cracking in the electric arc, whereby, mainly C_2H_2 and some C_2H_4 were obtained, and by pyrolytic cracking of the saturated hydrocarbons, whereby, mainly, C_2H_4 was produced. Cracking plants erected in Leuna, Holten, Heydebreck, and Moosburg had a capacity of 4,000 tons per yr. of C_2H_4.

3269. STEINBRECHER, —. [Influence of Synthesis Gas and Its Impurities Upon the Efficiency and Life of the Catalysts in Gasoline Synthesis.] FIAT Reel K–25, frames 3,782–3,796, Jan. 5, 1938; PB 70,216; TOM Reel 292.

Research report on the influence of synthesis gas and its impurities on the efficiency and life of the catalysts in gasoline synthesis of Braunkohle-Benzin A.–G. plant, Ruhland. The life of the catalysts (Co-kieselguhr) is shorter if synthetic gas, purified by regular routine of plant operation, is applied than if ideal gas (33.3% CO+66.7% H_2) is applied. This is caused by impurities like inert gas, O_2, S–compounds, resins, and resin-forming products. By adding inert gases, the speed of reaction is decreased rapidly. Adding O_2 of more than 0.6% has a strong influence in decreasing the output. S–compounds affect the Co catalyst. The presence of over 0.2 gm. per 100 N $m.^3$ causes disturbances. It appears that thiophene and other S–compounds substituted in the nucleus cause the strongest reactions, followed by mercaptan and finally CS_2 and COS. Tests to establish results on resin-forming substances were not successful. Further tests were conducted on reducing the contact period of the gas with the catalyst by increased gas flow with lower height of layer. The absolute yield was increased thereby.

3270. STEINBRECHER, —., AND WEINGÄRTNER, —. [Efficiency and Life of the Gasoline Synthesis Catalyst.] FIAT Reel K–30, frames 7,468–7,492, January 1938, PB 73,587; TOM Reel 297.

Laboratory and plant tests on the influence of the synthesis gas and its impurities on the efficiency and life of the catalyst. Included among the impurities of the synthesis gas are inert gases (N_2, CO_2, CH_4, C_2H_6, etc.), O_2, S compounds, resins, and resin-forming substances. All these impurities diminish the efficiency of the catalyst and shorten its life. Tests aiming at the reduction of this deterioration by increasing the gas throughout and diminishing the height of the charge still are underway.

3271. STEINBRECHER, H. [Petroleum Substitutes in Germany.] Hamburger Tech. Nachrichten, Jan. 28, 1936; Coal Carbonisation, vol. 2, 1936, p. 81.

Production of oil from brown coal by low-temperature carbonization, hydrogenation, and gasification will supply about 35% of the domestic demand for motor and fuel oil; present construction of low-temperature plants will increase the national output considerably. The high-pressure hydrogenation process, mainly applied to the production of gasoline, can be adapted to the production of gas oil, fuel oil, and lubricating oil as required. The gasification of brown coal or its semicoke is very attractive, the water gas being synthesized by the Fischer-Tropsch process with a good yield of liquid hydrocarbons. It is considered that all German motor fuel requirements could be met by processing brown coal, leaving the small domestic supply of natural petroleum for use in preparing lubricants.

STEINBRINK, H. *See* abs. **1834, 1835.**

3272. STEINKAMP, J. H. [Synthesis of Oils From the Gasification Products of Coal by the Fischer-Tropsch Process.] Het Gas, vol. 48, 1928, pp. 507–513; Chem. Zentralb., 1929, I, p. 819.

Brief review of the Bergius and Synthol processes at high pressures and a description of the newer method for producing liquid hydrocarbons from gases at atmospheric pressure and by the use of suitable catalysts.

3273. STEINKOHLENBERGWERK. [Fuels, Lubricants, Textile Auxiliaries, and Other Organic Products.] FIAT Reel X117, frames 2,561–3,422; PB 82,011.

In addition to brief single reports and monthly and activity reports, the film contains detailed summarizing reports on lubricating oil synthesis, Oxo synthesis,

paraffin oxidation, paraffin chlorination, etc. In particular, the reports deal with synthesis lubricating oil from kogasin and tar distillation products, condensation of cracked Fischer gatsch and naphthalene, chlorinated Fischer hydrocarbons and naphthalene, testing various oils, consistent greases from synthetic fatty acids with the use of the acids of the 1st and last runnings from the paraffin oxidation, production of solid soaps from liquid fatty acids and the application of dicarboxylic acids for fully synthetic fibers.

STEINMANN, A. *See* abs. **1611.**

3273a. STEITZ, A., AND BARNES, D. K. Products of the Hydrogenation of Carbon Monoxide Over an Iron Catalyst. Water-Soluble Oxygenated Compounds. Am. Chem. Soc., 121st Meeting abs., March–April, 1952, p. 10–M.

Seven acids and 27 nonacid chemical compounds have been identified in the H_2O stream produced by hydrogenation of CO over an Fe catalyst. These compounds are principally straight-chain alcohols, acids, aldehydes, and ketones. Esters, cyclic ketones, and branched-chain alcohols, aldehydes and acids are present in minor amounts. The nonacid chemicals were separated from the H_2O stream by fractional distillation to 96°, and the acids were separated from the aqueous residue by solvent extraction. After removal of the solvent, the acids were recovered in high purity by fractionation. Upon fractionation of the concentrated nonacid chemicals, a distinctive distillation curve exhibiting 6 plateaus was obtained. Most of these plateaus represented complex mixtures of binary and ternary azeotropes. Quantitative analysis of the nonacid chemicals was obtained by a combination of fractional distillation and analysis for functional groups.

STENKHOFF, R. *See* abs. **3065.**

STERLIGOV, O. D. *See* abs. **1706.**

3274. STERN, D. J. Production of Oil From Coal. South African Min. and Eng. Jour., vol. 61, II, 1951, pp. 851–855; Chem. Abs., vol. 45, 1951, p. 4910.

Principles of the Bergius and Fischer-Tropsch processes, the mechanical engineering problems involved, underground gasification, Russian developments, and American practices are surveyed.

3274a. ———. Production of Synthetic Gas. South African Min. and Eng. Jour., vol. 62, I, 1951, pp. 143–145, 181–193; Chem. Abs., vol. 45, 1951, p. 10545.

Exposition of basic factors and industrial processes by which coal or hydrocarbon gases can be transformed into fuels and lubricants. More detailed description devoted to the Koppers and Lurgi processes.

3275. STERN, G. [Isolation and Identification of Hydrocarbons From Mixtures by New Methods.] Reichsamt Wirtschaftsausbau, 1940, Prüf-Nr. 43, pp. 15–56, PB 52,003; Chem. Abs., vol. 41, 1947, p. 6490.

Procedures are described for the analysis of the products of the cracking of oils and the products of the $CO–H_2$ synthesis of hydrocarbons. Extensive tables are included, which describe the alcohols, acids, and esters isolated and identified in certain fractions of oil produced through the $CO–H_2$ synthesis process.

STERNBERG, H. W. *See* abs. **3656a.**

3275a. STERNBERG, H. W., WENDER, I., AND ORCHIN, M. Analysis of Mixtures of Dicobalt Octacarbonyl and Cobalt Carbonyl Anion. Anal. Chem., vol. 24, 1952, pp. 174–176.

Study of the hydroformylation (Oxo) process in the laboratory required the analysis of mixtures containing both dicobalt octacarbonyl, $[Co)(CO_4]_2$, and Co carbonyl anion, $[Co(CO)_4]^-$, the latter being present either as Co hydrocarbonyl, $HCo(CO)_4$, or as a Co salt. Because no method was available for this purpose, the authors devised the present procedure. The 2-step method depends on the decomposition of all corbonyls, by treatment with I, to yield CO; and the selective precipitation of the anion by Ni o–phenanthroline chloride, followed by decomposition of the precipitate with liberation of CO. As the determination is based on a gasometric procedure, it is suited for the analysis of mixtures, such as those from the hydroformylation reaction, which may contain Co salts and metallic Co.

STERNBERG, H. W., WENDER, I., FRIEDEL, R. A., AND ORCHIN, M. Chemistry of the Metal Carbonyls. II. Preparation and Properties of Cobalt Hydrocarbonyls. *See* abs. **3656b.**

———. Chemistry of the Metal Carbonyls. III. Reaction Between Dicobalt Octacarbonyl and Dimethylamine. *See* abs. **3656c.**

STERNBERG, J. C. *See* abs. **154.**

STERNINA, D. G. *See* abs. **2757.**

STEVENS, N. P. *See* abs. **175.**

STEVENSON, E. P. *See* abs. **2988.**

STEWART, L. *See* abs. **2601.**

3276. STIEF, F. [Pintsch-Hillebrand Continuous Blue-Gas Generator at the Hamburg Gas Works. I.] Gas-u. Wasserfach, vol. 75, 1932, pp. 581–586; Chem. Abs. vol. 26, 1932, p. 5402.

Continuous blue-gas generator has been devised to overcome the known faults of the intermittent process, involving the distillation of brown-coal briquets by hot blue gas and the gasification of the resulting semicoke in an annular generator in a stream of blue gas at about 1,300° carrying the required amount of steam. A portion of the blue gas is burned in 1 of the 2 regenerators, while the other regenerator, previously heated, is used to heat the blue gas saturated with water at 60°–74° to the above temperature. The distillation gas is passed through an electric tar precipitator and mixed with blue gas passing to the regenerators. A portion of the gas from the generator is withdrawn for use and contains about 4.2–8.6% CO_2, 35.4–39.4% CO, 50.4–51.0% H_2, 1.0% CH_4, and 4.8–5.0% N_2. The gas yield was 27,000–29,000 cu. ft. of approximately 300 B. t. u. gas per net ton with a thermal efficiency of 52%. A plant having a capacity of about 1,500,000 cu. ft. per day was operated for some time. Difficulties were found in keeping refractory walls tight, etc., but it is believed that these difficulties have been solved.

3277. MÜLLER, H. [Generation of Water Gas From Brown Coal in the Pintsch-Hillebrand Generator of the Hamburg Gas Works. II.] Gas- u. Wasserfach, vol. 78, 1935, pp. 431–436; Chem. Abs., vol. 29, 1935, pp. 6397–6398.

Further operation of this generator has been carried out successfully on a continuous basis with only a few minor difficulties. The generator proper is an annular ring 4.7 m. in internal diameter with a minimum thickness of 55 cm. Coal is fed to distillation chambers above this generator, where it is preheated to 700° by hot water gas. The water-gas generator is heated internally by recirculated gas from the generator, freed from dust and tar, saturated with water, and preheated in one of two regenerators to 1,300°; the other regenerator is heated to 1,350° by burning the generator gas, and then is used in turn to heat the recirculated gas. Part of the heated recirculated gas and water gas passes through the coal-distillation chambers. The gas yield is approximately 35,000 cu. ft. per net ton of brown coal briquets, with a heating value of approximately 290 B. t. u. per cu. ft. The thermal efficiency of the generator is given as 58.3%, and a complete thermal balance and a thermal diagram are given. Only a small amount of the S used to cement the brown-coal briquets appears in the gas, the larger part being

fixed as CaS in the ash. Cost data are given for German conditions. Improvements suggested are use of dry producer gas for heating the regenerators, use of waste-heat boilers, and proper gas velocity to avoid combustible matter in the fly ash. This process is especially adapted for the manufacture of gas for synthetic purposes as it is readily possible to secure a H_2 : CO ratio of 2 : 1.

3278. STIEF, F. [Generation of Water Gas and Synthesis Gas From Brown Coal, Peat, and Bituminous Coal in the Pintsch-Hillebrand Plant at the Hamburg Gas Works.] Gas- u. Wasserfach, vol. 83, 1940, pp. 1–6; Chem. Abs., vol. 34, 1940, p. 2569.

Present German endeavors are to increase the quantity of gas by diluting coal gas with water gas. The cheapest source of this gas is the Pintsch-Hillebrand continuous water-gas generator using brown coal. Improvements were made in this generator so that it has been possible to operate continuously and shut down the regular (coke) water-gas plant. One advantage of this process is the reduced content of organic S and H_2S in the gas, owing to the reforming of the carbonization products by passage through the generator fuel bed. The most important change has been to use producer gas for heating the regenerators, with the burners at the top of the regenerators. The length of time that the regenerators are used for heating the circulating gas also has been increased. Tar yields are about ⅔ of that indicated by the Fischer retort test. The best fuel is brown coal, preferably in briquet form. This coal should not have too high an ash content or too low an ash melting point, and the ash should not react with the refractories. Good results also were secured with peat. Bituminous coal (high volatile) also was tested, but its low reactivity did not permit complete gasification. If certain changes in construction were made, it should be possible to use this coal but it would be necessary to use the resultant high-ash coke in gas producers.

3279. ———. [Gasification of Fuels in Gas Works With Special Consideration of the Continuous Production of Water Gas.] Gas- u. Wasserfach, vol. 85, 1942, pp. 367–374; Chem. Abs., vol. 37, 1943, p. 4551.

Review of gas production from coke (generator gas with a heat of combustion of 1,200 kcal. per $m.^3$ (under standard conditions) and a heating value of 1,150 kcal. per $m.^3$, water gas of a heating value of 2,700 kcal. per $m.^3$), coal (generator and water gas, heating value 3,000 kcal. per $m.^3$) and by the continuous Pintsch-Hillebrand water-gas process. A flow sheet of the latter process, together with drawings of generators of various designs for this and the older process, is given. A plant operating by the continuous process was in operation for 300 days per yr. for 6 yr. Brown coal of reasonable low ash content and fairly high melting point of the ash is a suitable raw material for the process, but the use of bituminous coal is limited to a few special grades. The temperature of the gas-steam mixture in the gas collection cupola is about 1,300°; the temperature in the regenerator chambers, which are used alternately in a 16-min. cycle, is 1,500°–1,600°. The heating value of the water gas remains virtually constant and changes only by about 40 kcal. per $m.^3$ during the periodic change from one regenerator to the other. The heat of the combustion of the gas can be kept easily at 2,750–2,800 kcal. per $m.^3$ The ratio CO : H_2 can be brought to 1 : 2 by increasing the amount of steam added so that the gas becomes suited for use in synthetic processes. The economy of the process is determined by the quality of the refractories used in the generator because they must be able to withstand the continuously high working temperature. 15 refs.

3280. STILES, H. A. Synthetic Liquid Fuels. Petrol. Refiner, vol. 29, No. 10, 1950, pp. 99–102; Brennstoff-Chem., vol. 31, 1950, pp. 93–95.

Summary of the development of a synthetic fuels industry by the Bureau of Mines. The status of work at each of the Government plants—coal hydrogenation, gas synthesis, and shale-oil production—is described.

3281. STINZENDÖRFER, H. [Determination of the Constitution of the Fatty Acids Produced in the Fischer-Tropsch Synthesis.] Tech. Mitt. Krupp. Forschungsber., vol. 5, 1942, pp. 34–36; Chem. Zentralb., 1942, I, p. 2955; Chem. Abs., vol. 37, 1943, p. 3623.

Fatty acids contained in the remaining gases of a large-scale plant operating according to the Fischer-Tropsch process were isolated and separated by vacuum distillation into individual fractions. The mixture of fatty acids consisted essentially of saturated monobasic fatty acids, about the series of valeric to capric acids. Only very small amounts of unsaturated fat acids occurred.

3282. STORCH, H. H. Behavior of Zinc Oxide and Zinc Oxide–Chromium Oxide Catalysts in the Decomposition and Synthesis of Methanol. Jour. Phys. Chem., vol. 32, 1928, pp. 1743–1747; Chem. Abs., vol. 23, 1929, p. 816.

Details of preparation of several precipitated and supported ZnO and ZnO–Cr_2O_3 catalysts are reported. Their activities for the synthesis of MeOH from 4 H. : 1 CO gas mixtures at 3,000 l. per sq. in. and about 350° are compared. The addition of Cr_2O_3 to a ZnO catalyst in proportions of 200 gm. ZnO to 22 gm. Cr_2O_3 showed more activity than pure ZnO or pure Cr_2O_3. There was, however, no appreciable difference in activity between the catalysts when used to decompose MeOH at atmospheric pressure. The mixed oxide catalyst was virtually inactive for the synthesis of MeOH below 300°, and at 350° the yield was less than at 330°.

3283. ———. Activity and Activation Energy in Heterogeneous Catalysis of Gas Reactions. Jour. Am. Chem. Soc., vol. 57, 1935, pp. 1395–1398; Chem. Abs., vol. 29, 1935, p. 6495.

Relation $A = C_o e^{cE}$ between the activity A and the energy of activation E for contact catalytic reactions cannot be due entirely to a probability distribution of active centers. 2 other factors enter: (1) the frequency of energy exchange in the adsorbed phase may be reduced by adsorption, so that it becomes a function of the spacing of the catalyst atoms; (2) in reactions of low activation, energies involving H quantum leakage through the energy barrier may be considerable. The 1st hypothesis is supported by evidence, but there is none either for or against the 2d. Further experiments are suggested.

3284. ———. Synthetic Fuel Processes. Coal Age, vol. 48, January 1944, p. 117.

Estimates of the price of gasoline per gal. are given as $0.075 for an improved indirect Fischer-Tropsch method and from $0.055–$0.13 by hydrogenation. Figures are quoted regarding the position of synthetic fuel manufacture in the United States, Germany, Japan, and Great Britain.

3285. ———. Synthetic Liquid-Fuel Processes—Their Development in Germany and Great Britain and a Suggested Program for the United States. Synthetic Liquid Fuels Hearings Before a Subcommittee of the Committee on Public Lands and Surveys, U. S. Senate, 78th Cong., 1st sess., on S 1243, 1944, pp. 268–273.

Nontechnical discussion of the development of the Bergius and Fischer-Tropsch methods of liquid-fuel production with descriptions of the processes. Recommendations for the establishment of a national synthetic liquid-fuel industry from our vast resources of coal, lignite, natural gas, and oil shale are ably set forth.

3286. ———. Catalysis in Synthetic Liquid-Fuel Processes. Ind. Eng. Chem., vol. 37, 1945, pp. 340–351.

Fischer-Tropsch catalysts that are active in the synthesis of normally liquid hydrocarbons from CO and H_2—namely, Fe, Co, Ni, and Ru—form relatively unstable carbides on exposure to CO in the temperature range of the synthesis (185°–215° for Co and 240°–320° for Fe catalysts). Since the reaction $2\,Co+2\,CO \rightarrow Co_2C+CO_2$ is much too slow to account for the rate of hydrocarbon formation, it is conceivable that H_2 acts as catalyst for metal carbide formation by way of an unstable metal hydride according to the equation $2\,Co+CO+H_2 \rightarrow Co_2C+H_2O$. The mechanism of carbide formation on the Co catalyst, where the main oxygenated product is H_2O rather than CO_2, is difficult to apply to Fe catalysts, and it is, probable therefore, that, although metal carbides are formed on both Co and Fe, the mechanism of the synthesis differs for the 2 substances. The hydrocarbons produced on sintered Fe catalysts, reduced with H_2 at 650°–850°, are largely branched-chain paraffins, whereas those formed on Fe catalysts reduced at 400° or less contain very little isoparaffins. An essential condition for the production of isoparaffins, therefore, is apparently the absence of ferrous oxide in the Fe catalyst and a critical spacing of the Fe atoms in the Fe carbide lattice to permit cross linkages to form. Previous investigations are reviewed on the effect of pressure, diluents, and contact time on the Fischer-Tropsch synthesis and the poisoning of catalysts by S compounds.

3287. ———. Synthesis of Hydrocarbons From Water Gas. Chemistry of Coal Utilization (H. H. Lowry, ed.). John Wiley & Sons, Inc., New York City, 1945, vol. II, chap. 39, pp. 1797–1845.

Industrial developments, methods of production of synthesis gas and of H_2, mechanism of the reactions, factors involved that affect the composition and yield, properties of Fischer-Tropsch products, and the economics of coal and CO hydrogenation are thoroughly reviewed. Bibliography of 178 refs.

3288. ———. Fischer-Tropsch and Related Syntheses. Crucible, vol. 31, 1946, pp. 52, 54, 56, 58, 60.

Paper given before the Physical Chemistry Division of the Pittsburgh Section of the American Chemical Society, which reviews German process development, followed by an analysis of kinetic data pertaining to the mechanism of the synthesis. The prevailing operating process in Germany was that with a Co–Th–Mg–kieselguhr catalyst at 200°, 1–10 atm. pressure, and in 2–3 stages with yields of 150 gm. of product per cu. m. of $2\,H_2+1$ CO. This method was improved by recycling 3 vol. of endgas from the lst stage, with condensation of product after each cycle and increase in yield of 30%. By using H_2+1 CO insead of $2\,H_2+1$ CO, olefins were increased 20–55%. A hot-gas recycle process was developed using a sintered Fe catalyst at 320°, 20 atm., and ¾ sec. contact time. The space-time yield was 1 kg. per l. of catalyst per day. A liquid phase operation with suspended Fe catalyst also was under development which yielded a better grade of gasoline of 90 octane number and more diesel fuel. Two outstanding developments were the Synol and Oxo processes. The former produces liquid hydrocarbons (50–65%) and alcohols (50–35%), boiling at 50°–350°, operates at 18–25 atm. and 200°–235°, with gas of $1\,CO+0.8\,H_2$ composition, using as catalyst granules of fused Fe_3O_4: Al_2O_3: K_2O=97 : 2.5 : 0.4. The hydrocarbons are partly branched, the alcohols are normal. The Oxo process consists in reacting a slurry of olefins with 3–5% of Co : ThO_2 : MgO : kieselguhr=30 : 2 : 2 : 66 catalyst with $1\,CO+1\,H_2$ gas at 200 atm. and 150°–170°. The product (80% aldehydes and 20% alcohols) is hydrogenated at the same pressure and 180°–200° to produce the alcohol corresponding to the treated olefin with the addition of a C atom. Important factors in the probable mechanism of the Fischer-Tropsch process are discussed. The order of the reaction on Co, Ni, Fe, and Ru catalyst appears to be 0–1. The life of the catalysts is increased markedly by operation at 7–20 atm. Maximum conversion is obtained with Co catalysts at 5 atm. and space velocity of 150 vol. of gas per vol. of catalyst per hr.; with Ru more than 200 atm. is necessary. The temperature coefficient on Co and Fe catalyst is about 1.6 per 10° in the range 190°–235°, corresponding to an activation energy of 20 kcal. per mol. of $2\,H_2$: 1 CO. The above catalysts form relatively unstable carbides with CO, which react with H_2 at temperatures below 350° to yield, quantitatively, CH_4 plus C_2H_6. Above 350°, considerable decomposition to C occurs. For maximum activity and life, Co catalysts should be inducted and reduced with H_2, and the initial synthesis should be prolonged at atmospheric pressure for several days before increasing the pressure to 10 atm. Fe catalysts are preferably pretreated with CO at 0.1 atm. at the rate of 100 l. per 10 gm. of Fe, space velocity 4–25 l. of CO per hr., 325° before operation with synthesis gas at 10 atm. Treatment with H_2 after the carbiding does not affect the activity of Fe catalysts, although the Fe carbide is converted to elemental Fe. It is believed that the initial carbiding distorts the lattice structure enough that subsequent exposure to synthesis gas reforms the carbide. Bureau of Mines tests show that the carbiding rate on Co catalysts is of the same order of magnitude as that of the synthesis. The ratio of CH_4 : C_2 hydrocarbons in the products from a Co catalyst is about 10, while that from an Fe–Cu catalyst is 0.5. C_2H_4 plays an important role in the synthesis on Co but not on Fe-Cu catalysts. The proportion of oxygenated organic compounds (chiefly alcohols) in the liquid products from Fe catalysts is greater than that from Co catalysts. The chief oxygenated product from Co catalysts is H_2O and from Fe catalysts is CO_2, the ratio of H_2O : CO_2 in the products from the latter increasing with the pressure. The reaction in the Fischer-Tropsch synthesis is relatively slow, 30 sec. of contact for a 60–70% conversion, as compared with 0.2 sec. for the reaction CO and steam over a Co–Cu catalyst at 325°. This probably is due to the critical spacing of the metal atoms in the catalysts lattice. A possible mechanism for the synthesis on Co and Fe catalysts is outlined in a series of equations depicting the reactions involved in the formation of normal α olefins, branched paraffins and oxygenated compounds.

3289. ———. Motor-Fuel Synthesis. Oil Gas Jour., vol. 46, No. 26, 1947, p. 96.

Paper presented at the meeting of the Philadelphia section of the American Chemical Society. The fluidized catalyst technique is described, pilot-plant tests of which have shown that such a plant may operate continuously for as long as 1,600 hr. and will produce chiefly gasoline with minor amounts of diesel fuel and chemicals. The method developed by the Bureau of Mines for removing the exothermic heat of reaction from the synthesis converter by injecting oil into the converter with the gas mixture also is described. The efficiency of the method is high but still has 2 disadvantages over the fluidized catalyst method in that the latter is about 50% faster in operation and requires about 25% less steel for installation. Further experiments are under way which may improve the efficiency of the oil-cooled converter.

3290. ———. Development of Processes for Producing Synthetic Liquid Fuels From Coal. Chem. and Eng. News, vol. 26, 1948, pp. 3821–3822.

The fifteenth annual Pittsburgh award address of the Pittsburgh Section of the American Chemical Society. The work undertaken by the Bureau of Mines during the past several years on the production of syn-

thetic fuels from coal is reviewed, and the present program is outlined. The greater progress made in the hydrogenation of CO, as compared with that in hydrogenation of coal, is due to the inherently greater simplicity of the chemistry involved in the mechanisms concerning CO. In addition to the dearth of laboratory and experimental-plant research on coal hydrogenation, the meager knowledge of the chemical constitution of coal and of the mechanism of its pyrolysis and hydrogenolysis has greatly retarded the development of new processes. For this reason, emphasis must be placed on the acquisition of basic information on the chemistry and physics of coal. In synthesizing liquid fuels from coal by way of synthesis gas, about 60–70% of the cost of the liquid fuel product lies in the synthesis gas itself. Therefore, a very efficient conversion of this mixture of H_2 and CO is necessary if the process is to be industrially successful. 2 methods to accomplish this are being studied: The internally cooled, fixed-catalyst-bed process, in which the exothermic heat is removed efficiently and rapidly by the circulation of a relatively nonvolatile oil through the bed of graular catalyst; and the oil-catalyst-slurry process, in which a powdered catalyst is suspended in an oil that is nonvolatile under operating conditions and the synthesis gas is bubbled through this suspension. The 2d method is less efficient than the 1st in that the conversion of CO is only about 25–50% of that obtained in the 1st method. It does, however, have the advantage of the possible continuous removal of partly spent catalyst and the continuous introduction of regenerated or fresh catalyst. As regards the direct hydrogenation of coal, a basically new approach and a radical departure from the conventional Bergius process is under investigation. It is based on the rapid conversion of coal to distillable oil, gas, and coke at moderate pressure and relatively high temperatures. 2 times as much coal as is required for hydrogenation is passed through the reactor; about ½ of this is converted to oil and gas and the remainder to coke which is burned for steam and power production. This makes possible the appearance in the oil and gas of the H_2 from that half of the coal feed converted to coke. It has been found possible to replace the H_2 by water gas under proper operating conditions. Since H_2 constitutes about 50% of the total cost of the liquid fuels, this is an important consideration. Use of byproduct hydrocarbon gases, which, when reacted with steam, yield a mixture of CO_2 and H_2, also save in the cost of H_2.

3291. ———. Fischer-Tropsch and Related Processes for Synthesis of Hydrocarbons by Hydrogenation of Carbon Monoxide. Advances in Catalysis, Academic Press, Inc., New York, 1948, vol. I, pp. 115–156.

Review. The following points are discussed: Development of the Ruhrchemie process and modifications thereof, such as Lurgi, I. G., Farbenindustrie, A.-G., fluidized catalyst; related processes, such as Synol, Oxo, and isosynthesis; carbide and elemental C formation; kinetics and reaction mechanisms. 91 refs.

3292. ———. Review of Development of Processes for Synthesis of Liquid Fuels by Hydrogenation of Carbon Monoxide. Chem. Eng. Progress, vol. 44, No. 6, 1948, pp. 469–480; Chem. Abs., vol. 42, 1948, p. 5200.

Brief review of the early work of Fischer and his associates is followed by a more detailed discussion of process development work in Germany and the United States since about 1938. The salient features of all processes are collected in a single table, so as to facilitate comparisons of operating temperatures, pressures, space-time yields, product distribution, and steel requirements. Also describes related processes, such as the Synol, Oxo, and isoparaffin syntheses. Some discussion of the mechanism of the synthesis process and of the problem of C deposition on Fe catalysts.

3293. ———. Liquid Fuels From Coal and Oil Shales. Advances Chem. Ser. No. 5, 1951, pp. 138–150; Chem. Abs., vol. 45, 1951, p. 10,558.

Desirability of long-range development work on synthetic liquid fuel processes is discussed. The basic chemical and engineering problems involved in coal gasification, coal hydrogenation, hydrogenation of CO, retorting of oil shale, and refining of shale oil are presented. Brief mention is made of recent laboratory experiments in hydrocarbonization of coal in a fluidized bed at H_2 pressures of 1,000 p. s. i. or less. 37 refs.

3293a. ———. [Liquid Fuels From Coal and Oil Shale.] Riv. combustibili, vol. 6, 1952, pp. 139–163; Jour. Inst. Petrol., vol. 38, 1952, p. 397 A.

———. *See* abs. **42a, 43, 50, 98, 647, 648, 1232, 1370, 2035, 2102, 2103a, 3090, 3654, 3656.**

3294. STORCH, H. H., AND GOLDEN, P. L. Preparation of Pure Methane From Natural Gas. Jour. Am. Chem. Soc., vol. 54, 1932, p. 4662; Chem. Abs., vol. 27, 1933, p. 589.

Higher hydrocarbons are removed from natural gas by passing it through a layer of active coconut charcoal.

3295. STORCH, H. H., AND PINKEL, I. I. Preparation of an Active Cobalt–Copper Catalyst for the Water-Gas Shift Reaction. Ind. Eng. Chem., vol. 29, 1937, p. 715; Chem. Abs., vol. 31, 1937, p. 5977.

If a mixture of $CoCO_3$ and 5–25% of CuO is heated rapidly (in about 3 min.) from room temperature to 900°–1,100° C., a sintered, pumicelike mass of granules is obtained, which has excellent mechanical properties and is a very active catalyst when properly reduced and subsequently protected from S poisoning. Slower heating of the mixture results in a powder of inferior quality. A mixture of water gas with 4 vol. of steam was passed through this catalyst at 310° C. for more than 100 hr. without impairing the activity. The original water gas contained about 68% H_2, 23% CO, and small amounts of CO_2, N_2, CH_4, and O_2. The average analysis of the gas after the catalytic treatment was 73.8% H_2, 0.3% CO, 18.7% CO_2, with the remainder N_2 and CH_4. The activity of the catalyst is destroyed rapidly by contact with S compounds but easily can be regenerated to its original properties by heating to 900° C. in a stream of air.

3296. STORCH, H. H., GOLUMBIC, N., AND ANDERSON, R. B. The Fischer-Tropsch and Related Syntheses. John Wiley & Sons, New York, 1951, 610 pp.

Much current interest has been aroused by the Fischer-Tropsch process—a process that will undoubtedly benefit our fuel economy when its technology becomes better known and more profitable. Its possibilities are being explored in several directions at the present time; ultimately this versatile and flexible process may play a major role in the utilization of our fuel resources. Written primarily for chemists and chemical engineers engaged in the Fischer–Tropsch or similar process development, this book, in the main, is concerned with a critical review of the development of this and related syntheses. The Fischer–Tropsch process—one of the most-recent advances in the scientific and industrial development of CO reactions—synthesizes liquid aliphatic hydrocarbons, alcohols, fatty acids, ketones and aldehydes by hydrogenation of CO. The basic chemistry, industrial operations, and the result of catalyst testing and pilot plant developments by industrial laboratories and by the Bureau of Mines are presented together with a discussion of theoretical and applied contact catalysis, synthesis mechanism, kinetics, and thermodynamics.

3297. STORCH, H. H., ANDERSON, R. B., HOFER, L. J. E., HAWK, C. O., ANDERSON, H. C., AND GOLUMBIC, N. Synthetic Liquid Fuels From Hydrogenation of

Carbon Monoxide. Bureau of Mines Tech. Paper 709, 1948, 213 pp.

This paper contains a review of the literature up to October 1946, a report of Bureau of Mines research on the effect of preparation, reduction, and induction procedures on the activity of the catalysts and a correlation of the physical properties of the catalysts with their activity. The paper also includes data on the X-ray diffraction patterns, the magnetic susceptibility, the surface area, and the porosity of the catalysts.

3298. STOSSEL, E. Oxidation of Paraffins. Oil Gas Jour., vol. 44, 1945, No. 11, pp. 130, 132, 134, 137, 139; No. 15, pp. 145, 147, 148, 151; No. 17, pp. 69, 70, 73, 74, 77.

Major steps in the oxidation of paraffin waxes to form fatty acids and other oxygenated products are presented together with the various theories of the sequence of steps in the oxidation process. Also discussed are the possibilities of synthetic fatty acids produced by oxidation of paraffin in the light of the cheap raw materials made available in the slack wax from the Fischer–Tropsch synthesis. Consideration also is given to the closely related products and intermediates of the paraffin oxidation reaction, for example, alcohols, aldehydes, ketones, and wax esters. The mechanism of the oxidation is still a matter of discussion, the simplest reaction being as follows:

(1) $R\cdot CH_2\cdot CH_2\cdot CH_3+O_2\rightarrow R\cdot CH_2\cdot CH_2\cdot CH_2OH+\rightarrow$

$$R\cdot CH_2\cdot CH_2\cdot \overset{\overset{H}{|}}{C}=O \quad +O_2\rightarrow R\cdot CH_2\cdot CH_2\cdot COOH;$$

(2) $R\cdot CH_2\cdot CH_2\cdot CH_3+O_2\rightarrow R\cdot CH_2\cdot CHOH\cdot CH_3+O_2\rightarrow$
$R\cdot CH_2\cdot CO\cdot CH_3+O_2\rightarrow R\cdot CH_2\cdot CO\cdot COOH.$

It is not as simple as this, however, since H_2O, formic acid, and peroxides are always formed. One theory postulates that our C–H bond is split and unsaturated compounds are formed, which subsequently oxidize; another proposes the free radical mechanism whereby the attack takes place through rupture of a C–C bond; by the peroxidation mechanism, peroxides are always formed at the start and reach a maximum after 2–3 hr., after which they decrease rapidly and acid formation takes place; by the hydroxylation theory, alcohols are formed as the 1st step in the sequence: Hydrocarbon–alcohol–glycol–aldehyde–acid–carbon dioxide, the process repeating itself until the final degradation products are CO_2 and H_2O. Below 100° C., oxidation proceeds slowly, but, by preheating the hydrocarbons with alkali manganates to 100°–200° for several hr., oxidation proceeds well at 80°–100°. The longer the straight chain of C atoms contained in organic molecules, the less difficulty is encountered in their oxidation. Oxidation also is preceded by an induction period, after which the reaction is more rapid. The use of catalysts shortens the oxidation period by eliminating the induction period, destroying anti-oxygens or inhibitors present in the original material, and producing prooxidants, which direct the course of the oxidation. Catalytic material from a few thousandths up to 3% by weight of the initial material is generally used. Suitable catalysts are carboxylic acid salts, especially those of higher fatty acids, and oxides of the metals of groups 5 and 6. There is an optimum temperature range, which varies with the materials used and the results desired. For maximum yields of alcohols or high-molecular weight fatty acids the oxidation temperature is kept 110°–140° at a pressure of 60–150 p. s. i. A typical analysis of a Fischer–Tropsch slack wax used for oxidation is:

$C_{16}H_{34}$ to $C_{19}H_{40}$ 27.4%; $C_{23}H_{48}$ to $C_{25}H_{52}$ 23.6%;
$C_{20}H_{42}$ to $C_{22}H_{46}$ 31%; $C_{26}H_{54}$ to $C_{28}H_{58}$ 13.3%.

Bibliography of 145 refs.

3299. STRADA, M. [Catalysts in the Synthesis of Aliphatic Alcohols: Their Behavior and the Relation Between Their Composition and Activity.] Giorn. chim. ind. applicata, vol. 14, 1932, pp. 601–607; British Chem. Abs., 1933, B, p. 259; Chem. Abs., vol. 27, 1933, p. 2131.

It has already been shown in the previous papers that K salts of aliphatic acids catalyze the synthesis of alcohols from CO_2 and H_2. The results make it seem probable that the presence of the K salt of the particular alcohol desired would accelerate the formation of this alcohol. As catalysts, HCO_2K, AcOK, $EtCO_2K$, $PrCO_2K$, and $BuCO_2K$ were used. HCO_2K and AcOK have the highest catalytic powers. Analysis of the catalyst after it has been in use for some time shows a composition tending to become the same regardless of which salt was used to start. The catalytic action is determined by the % of K_2O present rather than its form.

3300. ———. [Influence of the Catalyst Used on the Purity of the Methyl Alcohol Produced Synthetically From Water Gas.] Giorn. chim. ind. applicata, vol. 15, 1933, pp. 168–176; Chem. Zentralb., 1933, II, p. 278; Chem. Abs., vol. 27, 1933, p. 4632.

Systematic study of the action of various catalysts, which have been suggested or patented for the preparation of MeOH, including ZnO obtained by various chemical means, ZnO and Cr_2O_3 in various proportions, $ZnO–Al_2O_3$, ZnO–MgO, ZnO–MnO, $ZnO–Cr_2O_3–Fe_2O_3$, and smithsonite from various sources. The smithsonites give the best results, the MeOH being more nearly pure; higher acids, aldehydes, and ketones are present in minute amounts, no higher alcohols are present, and the amount of hydrocarbon formed is low. Smithsonites also retain their activity much better than the artificially prepared catalysts examined.

3301. ———. [Fatty Acids Formed Along With the Aliphatic Alcohols in Syntheses Under Pressure From Carbon Monoxide and Hydrogen.] Giorn. chim. ind. applicata, vol. 16, 1934, pp. 62–70; British Chem. Abs., 1934, B, p. 616; Chem. Abs., vol. 28, 1934, p. 5042.

In the acid portion of the product formed during the synthesis of alcohols from CO and H_2 under pressure, the following were identified: Normal acids, from formic to heptylic; isobutyric, isovaleric, isocaproic and isoheptylic; several acids with a side chain at the α–C (methylethylacetic, methylpropylacetic, and methylbutylacetic acids). The molecular weight of the high-boiling fraction indicates that acids containing 14–16 C atoms are present. The fact that most of the acids formed correspond to the alcohol also formed in this reaction tends to confirm the theory that the higher alcohols are derived by the reduction of the corresponding acid, that is, $EtCO_2H+2H_2\rightarrow EtCH_2OH+H_2O$.

———. *See* abs. **2398, 2399, 2400.**

STRAUSER, W. A. *See* abs. **3182.**

3302. STRAUSS, R. [Fatty Acids by Oxidation of Hydrocarbons.] Fette u. Seifen, No. 10, 1936, p. 200; Petrol. Refiner, vol. 24, No. 2, 1945, pp. 73–76, 117–120.

Review of processes that lend themselves to commercial operation for the production of synthetic fatty acids derived from liquid or solid hydrocarbon material. 30 refs.

3303. STREVENS, J. L., AND CROSS, A. C. Motor Spirit From Coal. Nature, vol. 141, 1938, pp. 812–814, 1058–1059; Chem. Abs., vol. 33, 1939, p. 3110.

Reviews hydrogenation, coal-oil distillation, and synthesis methods of production.

3304. STRICKLAND-CONSTABLE, R. F. Synthesis of Methane From Carbon Monoxide and Hydrogen on a Nickel Catalyst. Study of the Mechanism of Reaction. Gas Research Board Commun. 46; Gas

World, vol. 130, 1949, pp. 629–631; Chem. Abs., vol. 43, 1949, p. 7666.

It has been shown that a catalyst known as J14 made from a mixture of 3 parts hydrated $Al(NO_3)_3$ and 1 part hydrated $Ni(NO_3)_2$ on china clay is much better than a pure Ni catalyst for the synthesis of CH_4. In either case, the catalyst is precipitated by Na_2CO_3 and reduced in H_2. Reduction starts at 350° and is completed at 450°. If, after such a treatment, a synthesis reaction is carried out at 250° with an H_2: CO ratio of 3:1, it is found that equal volumes of H_2O and CH_4 are not produced in accordance with the equation $3H_2+CO \rightarrow CH_4+H_2O$, but that no water vapor is present in the gas phase, it being retained on the Al oxide part of the catalyst and not by the Ni. It is not known whether this retention of H_2O by the Al_2O_3 affects the synthesis reaction or not, but it is possible that this sorption of H_2O forms an integral part of the main synthesis reactions, and this may partly account for the great activity of the Al-containing catalyst. The general features of the synthesis reaction are interpreted.

3305. STRIMBECK, G. R. Use of Oxygen in Production of Synthesis Gas. Chem. and Eng. News, vol. 28, 1950, p. 1922.

Paper presented at the chemical conference of the American Gas Association. Operation of a Bureau of Mines pilot plant in Morgantown, W. Va., is described in which fluidized, 200-mesh coal had been gasified at efficiencies of up to 88% of the C converted. The process was run continuously on strongly coking coal at feed rates of 200–450 lb. of coal per hr. at temperatures of about 240°, 1,800°, and 3,000° F. The O_2 consumption was lowest in the high-temperature runs, requiring only about 170 cu. ft. per 1,000 cu. ft. of CO and H_2 produced. It is believed that this is the lowest O_2 consumption ever reported for a continuous synthesis-gas process. Coal consumption was reported as lowest in the hottest runs also, being only about 34 lb. per 1,000 cu. ft. of product, but steam consumption at 81 lb. per 1,000 cu. ft. was more than 2.5 times that for the lowest temperature and the % of C gasified was down to 83%. The process is thought to be adaptable to commercial production of synthesis gas, particularly since additional work indicated that the ratio H_2: CO could be adjusted within limits, and the type of coal is not critical to the performance of the process, thus permitting purchase of fuel on heat content considerations alone.

3305a. STRIMBECK, G. R., CORDINER, J. B., TAYLOR, H. G., PLANTS, K. D., AND SCHMIDT, L. D. Pressure Technique Lowers Cost for Synthesis Gases. Chem. Eng. News, vol. 30, 1952, p. 2392.

In a paper read at the American Gas Association meeting in May 1952, a report was made of the progress in the development, at the Bureau of Mines experimental plant, Morgantown, W. Va., of the direct coal gasification process. The plant is designed to gasify coal dust entrained in O_2 and steam at pressures up to 450 p. s. i. g. Test runs on pulverized Sewickley-bed coal at pressures of 100, 250 and 300 p. s. i. g. resulted in surprisingly large throughputs. Material requirements have been low per 1,000 $ft.^3$ of CO and H_2 produced. At 300 p. s. i. g. gasifier pressure, over 500 lb. of coal per hr. per $ft.^3$ of gasifier volume have been gasified. The material requirements at these throughputs were about 340 $ft.^3$ O_2 and 35 lb. of coal per 1,000 $ft.^3$ of CO and H_2, and with comparatively small heat losses per lb. of fuel. The process promises an excellent source of synthesis gas. Generation of the gas under pressure greatly lowers its cost by cutting the gas volumes to be compressed by ⅔ as only the O_2 needs to be compressed.

3306. STRIMBECK, G. R., HOLDEN, J. H., ROCKENBACK, L. P., CORDINER, J. B., AND SCHMIDT, L. D. Pilot-Plant Gasification of Pulverized Coal With Oxygen and Highly Superheated Steam. Bureau of Mines Rept. of Investigations 4733, 1950, 41 pp.; Bib. of Tech. Repts., vol. 15, 1951, p. 43; PB 101,855; Proc. Am. Gas Assoc., 1950, pp. 501–563.

Pilot-plant data are reported for 31 runs on the gasification of 90% through 200-mesh of a strongly coking Sewickley-bed coal with O_2 and with superheated steam in 3 temperature ranges 2,700°–3,400° F., 1,600°–2,000° F., and 230°–250° F. at feed rates of 200–450 lb. per hr. Average requirements per 1,000 std. cu. ft. of $CO+H_2$ produced are:

Steam temperature, °F.	Coal, lb.	O_2, std. cu. ft.	Steam, lb.
2, 904	33. 3	171	81. 1
1, 899	37. 3	326	42. 5
238	42. 3	394	29. 1

In general, the pilot plant performed very well. Continuous operation was possible, the runs being terminated voluntarily. The performance data indicate that the process could furnish low-cost synthesis gas on a commercial scale. The % gasification of the coal was very satisfactory. Average % C gasified was 88.9, 89.9, and 85.2 in the high-, medium-, and low-temperature steam runs, respectively. The O_2 requirement per 1,000 std. cu. ft. of $CO+H_2$ produced in the high-temperature steam runs was lower than for any other continuous process known. Correlations are presented on steam decomposition, O_2 required per 1,000 cu. ft. of $CO+H_2$ in the make gas, % CO_2, and H_2: CO ratio in the make gas. Refractory materials suitable for use in superheating steam to the range of 2,700°–3,400° F. have been found to be available at a reasonable cost. Apparatus is described with the aid of flow diagrams.

STRONG, H. W. *See* abs. **2448.**

3307. STUART, A. T. Manufacture of Industrial and Domestic Gases by Means of Electricity (Complete Gasification of Coal With Oxygen). Am. Gas. Jour., vol. 147, 1937, No. 1, pp. 19–22; Gas World, vol. 107, 1937, pp. 8–10; Canadian Chem. and Met., vol. 21, 1937, pp. 283–285; Gas Jour., vol. 219, 1937, pp. 343–344; Chem. Abs., vol. 31, 1937, p. 6442.

Gas of normal CO content and having the present standards of B. t. u. value, specific gravity, and composition, without any complex secondary processing, can be made by utilizing electrolytic O_2 and H_2 in place of air. A plant is described.

3308. STUHLPFARRER, —. [Catalytic Cracking of Hydrocarbons.] FIAT Reel K–28, frames 6232–6259, Aug. 26, 1940, PB 70,185–s; TOM Reel 295.

It is desired to crack Diesel oils from the Fischer-Tropsch synthesis consisting of predominantly unbranched paraffins with 11–18 C atoms into hydrocarbons with 3–5 C atoms by polymerization by which antiknock gasolines can be obtained. The production of CH_4 and C_2 hydrocarbons is to be avoided. In the apparatus described, natural and synthetic Al hydrosilicates were tested as catalysts and compared. Best results were obtained with those of Al_2O_3–4 SiO_2 composition. For the production of large amounts of unsaturated hydrocarbons, the catalysts must contain dehydrogenating additions such as Cr and Ba oxides. 1 diagram, 12 tables.

STURKEY, L. *See* abs. **1390.**

SUCKSMITH, W. *See* abs. **635, 2694, 2695.**

3309. SULLIVAN, F. W. Fuel-Synthesis Byproducts As Source of Chemicals. Chem. Eng. Progress, vol. 43, No. 12, 1947, pp. 13–17; British Abs., 1948, B, I, p. 283.

Impact that the synthetic chemical development by way of the Hydrocol process will have upon organic chemical production is presented, and the estimated production from a probable 10 Hydrocol plants is compared with U. S. production. The fact is that the total weight of the chemicals from Hydrocol operation on this scale is more than ⅔ the weight of the present production of these chemicals. Furthermore, the total volume of products from 10 plants would be considerably greater than the present production of coal tar on which a large part of the organic chemical industry is based.

3310. SUSTMANN, H. [Attempts to Change Properties of Kogasin by Compression up to 12,000 Atmospheres.] Brennstoff-Chem., vol. 21, 1940, pp. 246–250; Chem. Zentralb., 1941, I, p. 850; Chem. Abs., vol. 35, 1941, p. 7694.

Attempt to produce lubricating oil by polymerizing unsaturated hydrocarbons in Kogasin (I) by applying pressure. A (I) fraction (b. 50°–250°) in a Pb- or Zn-plated Pb tube was compressed to 5,000 kg. per cm.^{2} and 11,700 kg. per cm.^{2} for 1–5 hr., and the change in n was noted. Inconclusive results were obtained. Experiments using thin Pt tubes are suggested as likely to yield more precise data.

SUTCLIFFE, H. T. *See* abs. **24.**

SWIFT, A. H. *See* abs. **622.**

3311. SYMONDS, F. L., LAUGHREY, P. W., SKINNER, L. C., BATCHELDER, H. R., AND DONATH, E. E. Synthetic Fuel Processes May Be Future Source of Utility Gas. Am. Gas Jour., vol. 171, No. 1, 1949, pp. 19–21; Am. Gas Assoc. Monthly, vol. 31, No. 7–8, 1949, pp. 18–20, 24.

Paper presented at the American Gas Association meeting, May 1949. The residual gas from both the coal-hydrogenation process and the Fischer-Tropsch is suitable for general use as a city gas. In the former case, the city gas produced in the normal operation of a 10,000-bbl.-per-day plant will amount to about 390,000 cu. ft. per hr. with a net heating value of 1,065 B. t. u. per cu. ft. To make this gas available for city gas consumption, the hydrocarbon steam-reforming section would be eliminated, and the size of the coal gasification section would be increased to such a point that it could produce an equivalent amount of H_2. With coal at $3.56 per ton, the actual cost of the city gas would be $0.44 per M. B. t. u. The value of the gas from the Fischer-Tropsch process roughly will equal that recovered from coal hydrogenation. Assuming that 1,000,000 bbl. per day of synthetic liquid fuels were to be produced and that 75% of this is suitable for city gas, 710,000,000 cu. ft. per day would be available, or about 90% of the total manufactured gas production of the entire United States in 1944.

3312. SZCZENIOWSKI, B. [Fuel Problems During 1935.] Przeglad Mechaniczny, vol. 2, 1936, pp. 5–6.

Characteristics of actual trends in various countries with special regard to polymerization of gases obtained by cracking, coal hydrogenation, Fischer-Tropsch synthesis, and from water gas are given.

SZEGO, P. *See* abs. **2447.**

T

TADA, M. *See* abs. **2501.**

TAGLANG, P. *See* abs. **2242.**

TAHARA, H. *See* abs. **1907, 1909, 1910, 1911, 1912, 1913, 1914, 1927, 1928, 1929, 1930.**

TAHARA, H., ISHIBASHI, T., and KODAMA, S. Preparation of Isobutanol From Carbon Monoxide and Hydrogen. III. Influence of Alkali on the Copper-Chromium Oxide Catalyst. *See* abs. **3316.**

TAHARA, H., ISHIBASHI, T., AND KODAMA, S. Preparation of Isobutanol From Carbon Monoxide and Hydrogen. IV. Results of Syntheses in Long Runs. *See* abs. **3317.**

3313. TAHARA, H., TATUKI, Y., AND SIMIZU, J. [Catalytic Reactions of Carbon Monoxide and Hydrogen Under High Pressure. I. Synthesis of Isobutyl Alcohol.] Jour. Soc. Chem. Ind. (Japan), vol. 43, 1940, p. 82 B (in German); Chem. Abs., vol. 34, 1940, p. 6929.

In order to synthesize iso-BuOH, a mixture of 1 part CO and 2 parts H_2, under a pressure of 180 kg. per cm.^{2}, is conducted with velocities 120–800 l. per hr. over 80 cc. of 10 various catalysts at 450° and 500°. The liquid product contains, at best, 30% iso-BuOH. The yield decreases with the velocity with which the initial gas mixture is led over the catalysts and is dependent to a high degree on the reaction temperature.

3314. TAHARA, H., SAWADA, Y., AND KOMIYAMA, D. [Catalytic Reaction of Carbon Monoxide and Hydrogen Under High Pressure. II. The Influence of High Pressure on the Iron Catalyst Employed in the Synthesis of Benzine.] Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 38, 1941, pp. 184–195 (in German); Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, suppl., pp. 77–82; Chem. Zentralb., 1941, I, p. 2891, Chem. Abs., vol. 35, 1941, p. 3416.

Brief review of some of the earlier work. The same experimental methods were used as on the previous low-pressure investigation. The reaction was studied at 10, 50, and 100 kg. per cm.^{2} The high pressures used with the Fe catalyst (composition: Fe+25% Cu+2% Mn+125% kieselguhr+15% H_3BO_3+2.8% K_2CO_3) formed considerable H_2O, which did not form in the low-pressure studies. At 10 kg. per cm.^{2}, the yield of benzine was greater than at atmospheric pressure, and the yield did not fall even when the stream volicity was doubled. The activity of the catalyst declined under this pressure even more rapidly than under atmospheric pressure. At pressures of 50 and 100 kg. per cm.^{2}, the yield of benzine fell very sharply, and a marked increase in the formation of CH_4 occurred.

3315. TAHARA, H., KOMIYAMA, D., KODAMA, S., AND ISHIBASHI, T. Preparation of Isobutanol From Carbon Monoxide and Hydrogen. II. Copper-Chromium Oxide Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, pp. 89–90; Chem. Abs., vol. 45, 1941, p. 2849.

Good yields (28–34%) of iso-BuOH were obtained when the catalyst contained 15–70 parts Cu per 100 parts Cu+Cr and 20 parts K_2CO_3. The best yield (34%) was with 25 parts Cu. This product also contained 29% MeOH and 6% EtOH and PrOH. (*See also* abs. **3313.**)

3316. TAHARA, H., ISHIBASHI, T., AND KODAMA, S. Preparation of Isobutanol From Carbon Monoxide and Hydrogen. III. Influence of Alkali on the Copper-Chromium Oxide Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, pp. 90–91; Chem. Abs., vol. 45, 1951, p. 2849.

Varying amounts of K_2CO_3 and other K salts were added to the Cu–Cr (1:4) catalyst. The best yield (37%) of iso-BuOH was obtained with 70 gm. K_2CO_3 per 100 gm. Cu+Cr. Higher yields of total reaction product were obtained with K_2ZnO_2 than with K_2CO_3, but the product contained more H_2O. Other K salts

gave poorer yields. With 248 gm. $K_6Mo_7O_{24}$, only CH_4 was recovered.

3317. ———. Preparation of Isobutanol From Carbon Monoxide and Hydrogen. IV. Results of Syntheses in Long Runs. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, pp. 91–92; Chem. Abs., vol. 45, 1951, p. 2849.

Catalyst of Cu 1, Cr 4, and K_2CO_3 4 parts was heated at 490° and the gases passed over it at a pressure of 180 kg. per 3 $cm.^2$ at the rate of 200 l. per hr. At the start, 44 cc. fluid per $m.^3$ gas was obtained and at the end of 48 hr., only 19 cc. The concentration of iso-BuOH fell from 37 to 30% in 10 hr. and to 24% of the product in 100 hr. The concentration of MeOH increased with time. The products contained about 10% C : O compounds with a ratio of aldehydes to ketones of 4 : 1, and 12–16% hydrocarbons.

TAKAGI, H. *See* abs. **1485.**

3318. TAKAHASHI, G. Equilibrium Between Austenite and the Carbon Oxides. Sci. Repts. Tôhoku Imp. Univ., vol. 15, 1926, pp. 157–175; Chem. Abs., vol. 20, 1926, p. 2810.

As the temperature rises, the C content of the austenite in equilibrium with a given mixture of CO and CO_2 decreases, and the CO concentration in the gas in equilibrium with austenite of constant C content, or with austenite and cementite, increases. As the CO concentration of the gas increases at constant temperature, the C content of austenite in equilibrium with it increases until free cementite appears. As the temperature rises, the C content of austenite in equilibrium with FeO decreases; and the CO concentration in the gas in equilibrium with austenite and α Fe decreases, while that in equilibrium with austenite and FeO increases. Cementation does not occur when the CO concentration in the gas is less than that with which austenite and α Fe are in equilibrium. By means of cementation in CO, the temperature of the A_1 point was determined to be 726°.

TAKAZAWA, T. *See* abs. **1918, 1919, 1920, 1921, 1922, 1923, 1924, 1925, 1926.**

TAKEGAMI, Y. *See* abs. **1904.**

3319. TAKEI, M. Preparation of Raw Gas for Fischer Synthesis at Miike. Jour. Fuel Soc. Japan, vol, 16, 1937, pp. 87–88; Chem. Abs., vol. 32, 1938, p. 5604.

Satisfactory synthesis gas is obtained by mixing water gas with coke-oven gas, which has been subjected to CH_4 cracking in a high-temperature vertical stove. The heat required for CH_4 cracking is provided by the waste gas resulting from the Fischer process.

3320. TAKENAKA, Y. Destructive Hydrogenation of Synthetic Petroleum. I. Effect of Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 658–662; Chem. Abs., vol. 43, 1949, p. 2415.

Kogasin oil (synthesized from CO and H_2 under pressure) was fractionated into 3 portions distilling at 100°–200°, 200°–300°, and above 300°, respectively. Each portion was hydrogenated 5 min. in a rocking autoclave at 480° by using 20% Ni_2O_3, MoO_3, MoS_3, or $Mo(PO_4)_2$, with or without kieselguhr as catalyst, and H_2 under 35 atm. initial pressure to yield gasoline. The effect of using various catalysts on the composition of the product was studied. The reaction yielded 53–67% oil containing 47–65% gasoline, which was composed of 5–9.5, 3.1–11.8, and 14–22%, respectively, unsaturated, aromatic, and naphthenic hydrocarbons, and the remainder was saturated hydrocarbons. With Ni_2O_3 on kieselguhr, a gasoline fraction containing mostly aromatic and naphthene hydrocarbons was obtained, although the total oil fraction yield was small. MoS_3 and Mo $(PO_4)_2$ were second to Ni_2O_3 in producing the same result. The effect of using a carrier varied according to the catalyst used. Among the different fractions of Kogasin oil, that which distilled at the highest temperature gave a product containing the largest amount of cyclic hydrocarbons.

3321. ———. Destructive Hydrogenation of Synthetic Petroleum. II. Effect of Reaction Conditions. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 658–662; Chem. Abs., vol. 43, 1949, p. 2415.

Similar experiment was carried out by using 20% $Mn(PO_4)_2$ on kieselguhr as a catalyst and varying the initial pressure of H_2, reaction temperature, and time to find the optimum conditions for obtaining gasoline of high octane no. Higher temperatures and less H_2 or a longer reaction time at a lower temperature yielded a high-octane gasoline. By treating a fraction, boiling 200°–300°, with 2.85% H_2 under 44 atm. initial pressure 3 min. at 500°, gasoline having an octane no. of 75.4 was obtained. Gasoline having a high octane no. can be obtained from oil rich in normal paraffins by proper treatment.

———. *See* abs. **2017, 2018.**

TAKEZAKI, Y. *See* abs. **1894.**

TAKIGUCHI, K. *See* abs. **1910.**

3322. TAMMANN, G. [Transformation of Cementite at 210°.] Stahl u. Eisen, vol. 42, 1922, pp. 772–775; Chem. Abs., vol. 16, 1922, p. 3847.

Lack of linear change of properties in steel with C content raises the question whether primary cementite and pearlitic cementite are the same kind of crystals. In order to answer this question the transformation point of the 2 kinds is studied and found to be the same; the difference of the 2 kinds of cementite is, accordingly, one of grain size. In the discussion this conclusion is confirmed as a result of X-ray analysis of the 2 kinds of cementite.

3323. TAMMANN, G., AND BANDEL, G. [Heat Content and Specific Volume of Iron–Carbon Alloys.] Arch. Eisenhüttenw., vol. 7, 1934, pp. 571–578; Chem. Abs., vol. 28, 1934, p. 4356.

Literature on heat content, specific heat, and specific volume of Fe–C alloys and their changes in melting is compiled. Diagrams of state in 3 dimensions are constructed showing dependence of heat content and specific volume on C content and temperature. The γ-solid solutions must be considered, by their lattice parameters, as embedded solid solutions; the C atoms are situated between the lattice points, which are occupied only by Fe atoms, whereby the lattice is widened. The specific volume of Fe–C alloys 1,100°–1,650° increases slightly with C content. Pressure has little influence on the temperature of the pearlite transformation.

3324. TAMMANN, G., AND EWIG, K. [Contribution to the Knowledge Concerning Cementite.] Ztschr. anorg. Chem. vol. 167, 1927, pp. 385–400; Chem. Abs., vol. 22, 1928, p. 570.

Temperature-magnetization curves of C steels, ranging 0.15–3.9% C, indicate an abrupt lowering in magnetizability at 200°–220°. This lowering is proportional to the C content and, therefore, to the Fe_3C content. Lowering of the magnetizability during the pearlitic transformation becomes less with increasing C content. Since Fe_3C loses its magnetic properties at 210°, some of it was heated to various temperatures and temperature-magnetization curves were obtained. After heating Fe_3C for 5 hr. at 500°, the curves showed no noticeable decrease at 210°. This indicates that after heating at 500° for 5 hr., Fe_3C is completely decomposed into Fe and C. The probable effects of dissolved gaseous impurities, and of including the Fe_3C in a structure of ferrite (as in steel), upon the decomposition temperature of Fe_3C are discussed. The heat of transformation of Fe_3C (magnetic⇌nonmagnetic variety) cannot exceed 0.02 cal. per gm. With a dila-

tometer the increase in volume at the temperature of the magnetic transformation (200°–215°) was 0.0714 mm.^{3} per gm. of Fe_3C. This change in volume should produce noticeable changes in the physical properties of steels and, also, in white cast Fe. A study of the effect of the addition of Si, Mn, Ti, Al, and B upon the magnetic transformation temperature was undertaken. Al and Ti were without effect. 5% Si has little effect; 14% Si lowers the transformation temperature 100°; 3% Mn lowers this temperature 100°; 0.5% B lowers the temperature 200°.

TARAMA, K. *See* abs. **1892, 1915, 1916, 1917, 1918, 1919, 1920, 1921, 1922, 1923, 1924, 1925, 1926, 2196, 2197, 2200, 2201, 2202, 2203, 2204.**

TARAMA, K., TATSUKI, Y., KASAI, K., AND TAKEGAMI, Y. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXVIII. Analysis of the Synthetic Oil by Fractional Distillation. (2). *See* abs. **1904.**

TARAMA, Y. *See* abs. **1930.**

TARN, W. H. *See* abs. **46, 51, 53c.**

TASHIRO, E. *See* abs. **1896, 1900, 1901, 1902.**

TATARSKII, E. S. *See* abs. **3267.**

3325. TATIEVSKAYA, E. P. [Effect of Water Vapor on the Rate of Reduction of Magnetite and Hematite by Carbon Monoxide.] Jour. Phys. Chem. (U. S. S. R.), vol. 14, 1940, pp. 349–356; Chem. Abs., vol. 36, 1942, p. 3760.

2.5–20% of H_2O vapor added to CO strongly retards the reduction of Fe_3O_4 at 900°, and especially at 500°; the retardation is more pronounced if the Fe_3O_4 was already partly reduced. Reduction of Fe_2O_3 is not affected by H_2O at 500° or 900° unless Fe_2O_3 is already partly reduced. H_2O has no specific effect, it gives CO_2 and H_2 with CO on Fe oxide catalysts, and its apparent action is due to CO_2. CO_2 does not retard the reduction of Fe_2O_3 to Fe_3O_4. The inhibition of the reduction of Fe_3O_4 can be accounted for by considering the competition between CO and CO_2 for the magnetite surface.

———. *See* abs. **567, 568.**

3326. TATIEVSKAYA, E. P., AND CHUFAROV, G. I. [Effect of Carbon Dioxide on the Velocity of Reduction of Magnetite and Hematite by Carbon Monoxide.] Jour. Phys. Chem. (U. S. S. R.), vol. 13, 1939, pp. 495–501; Chem. Abs., vol. 34, 1940, p. 1284.

Experimental data over the temperature range 400°–900° and at gas pressures of 0.02–0.20 mm. Hg are given. The retarding effect of CO_2 on the initial stage of reduction of magnetite is considerable at 500° and negligible at 900°; CO_2 does not affect the initial reduction of hematite, but, after a Fe_3O_4 surface layer has once formed, hematite behaves the same as magnetite.

3327. TATIEVSKAYA, E. P., CHUFAROV, G. I., AND ANTONOV, V. K. [Rates of Reduction of Iron Oxides.] Jour. Phys. Chem. (U. S. S. R.), vol. 24, 1950, pp. 385–393; Chem. Abs., vol. 44, 1950, p. 8209.

Although the equilibrium pressure, calculated, of O_2 over Fe_2O_3 is much greater than over Fe_3O_4 or FeO, all 3 oxides are reduced by H_2 at similar rates, showing that reduction is independent of dissociation and that reduction of FeO is not the slowest stage in the reduction of higher oxides. The surface area of the oxides, from N_2 adsorption at −195°, was 0.85, 0.86, and 0.60 m.^{2} per gm. for Fe_2O_3, Fe_3O_4, and FeO, respectively. The oxides were heated in H_2, the H_2O formed was frozen out, and the rate v of reaction was calculated from the decrease in pressure p. In 1 experiment, v first increased to a maximum at 10–30% reduction and then decreased again. When the original p (p_o) was 200 mm. Hg, the maximum v of Fe_2O_3 was about 7, 16, 37, and 95×10^{-4} gm. O_2 per gm. Fe_2O_3 and minimum at 350°, 400°, 450°, and 500°, respectively; the maximum v of the other oxides were, for example, 10% less. At reductions below 10%, v was proportional to p_o^n, and the constant n was at 400° and 450° 0.68 and 0.83 for Fe_2O_3, 0.68 and 0.76 for Fe_3O_4, and 0.5 and 0.65 for FeO, when p_o varied 0–320 mm. Hg. The apparent energies of activation were 16,500, 13,500, and 14,000 cal. per mol.

TATSUKI, Y. *See* abs. **1893, 1904.**

TATUKI, Y. *See* abs. **3313.**

3328. TAUSSIG, J. H., JR. Theoretical Advantages of Low Air: Steam Ratios in Water-Gas Manufacture. Gas Age, vol. 85, No. 12, 1940, pp. 31–33, 40; Chem. Abs., vol. 34, 1940, p. 4886.

From the standpoint of generator fuel consumption, the lowest air: steam ratio that can be used and still supply enough heat for oil vaporization and fixing is most economical, because the lower ratios make cooler fires and promote the reaction: $C+2H_2O=CO_2+2H_2$, and retard the reaction: $C+CO_2=2CO$. The most economical point of operation may be found by plotting the cost of steam against the air: steam ratio and the cost of fuel against the air: steam ratio and selecting the air: steam ratio at which the sum of the costs is a minimum.

3329. TAYLOR, A. H. Sensitive Pressure Controller. Fuel, vol. 29, 1950, pp. 262–264.

An instrument for insuring close and reliable pressure control in the Fischer-Tropsch synthesis is described. It is also an efficient oil-fog separator. Graphs show the sensitivity at gas flows up to 2,500 cu. ft. per hr. over a pressure range up to 60 atm. Illustration.

———. *See* abs. **1333.**

3330. TAYLOR, E. H., AND TAYLOR, H. S. Hydrogenation of Ethane on Cobalt Catalysts. Jour. Am. Chem. Soc., vol. 61, 1939, pp. 503–509; Chem. Abs., vol. 33, 1939, p. 3755.

Rate of hydrogenation of C_2H_6 to CH_4 has been studied over a Co–ThO_2–Cu–kieselguhr catalyst and upon 4 Co–MgO catalysts. The results indicate that Co lies between Cu and Ni in its activity for this reaction. The rate is inhibited by H_2, but to a lesser extent than on Ni. The Co–MgO catalysts are markedly more active than the catalyst containing ThO_2.

3331. TAYLOR, G. B., AND STARKWEATHER, H. W. Reduction of Metal Oxides by Hydrogen. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 2314–2325; Chem. Abs., vol. 24, 1930, p. 3944.

Method is described for studying the rate of reduction of metal oxides at temperatures below 500° in which the volume of H_2 consumed is measured. The oxides of Ni, Cu, Fe, and Zn were studied by this method. Fe_2O_3 gels are reduced to ferroso-ferric oxide at 350° and to metallic Fe at 450°. Ignited Fe_2O_3 is not appreciably reduced at 350° but goes to metal at 450°. Foreign metal interfaces with Fe_2O_3 accelerate the reduction of Fe. Al_2O_3 and Cr_2O_3 greatly retard the reduction of ferroso-ferric oxide. Fe_2O_3 gels show the glow phenomenon in H_2 at fairly low temperatures but not in air or vacuum. The thermodynamics of ZnO reduction in the presence of Cu are worked out, giving an explanation of the formation of α-brass.

TAYLOR, H. G. *See* abs. **3305a.**

3332. TAYLOR, H. S. [Active Centers on Catalysts.] Ztschr. Elektrochem., vol. 35, 1929, pp. 542–549; Chem. Abs., vol. 23, 1929, p. 5395.

Measurements of heats of adsorption of gases on metal and metal oxide catalysts are discussed. The difficulty in explaining the observed maximum in heats of adsorption is considered. It is emphasized that the energy of activation of a surface reaction is dependent on the preparation of the contact substance. It is

possible that for a given reaction the energy of activation is smaller the more active the catalyst. Measurements of heats of adsorption together with reactions studied on poisoned and nonpoisoned catalysts demonstrate the existence of centers of different activity on a catalyst. A specific effect on the reacting molecules is exerted only by certain well-defined areas of the macroscopic surface.

3333. ———. Heterogeneity of Catalysts Surfaces for Chemisorption. Advances in Catalysis, Academic Press, Inc., New York, 1948, vol. I, pp. 1–26; Chem. Abs., vol. 44, 1950, p. 5690.

Examination of the adsorption of H_2 on various oxide and metal surfaces.

3334. ———. [Effect of the Heterogeneity of Catalysts on Chemisorption and Chemical Kinetics.] Jour. chim. phys., vol. 47, 1950, p. 1225; Chem. Abs., vol. 44, 1950, p. 7132.

Taylor presents his current views on the heterogeneity of surfaces; he points out that the Langmuir, Brunauer-Emmett-Teller, Hüttig, Harkins and Jura adsorption theories all assume a uniform surface and the absence of interaction between adsorbed molecules. Strictly speaking, this cannot be true, however, and on the basis of recent work in his and other laboratories Taylor reemphasizes the importance of the Freundlich isotherm $v=kp^{1/n}$.

———. *See* abs. **414, 415, 699, 1162, 1339a, 1639, 2321, 2322, 2547, 2994, 3330, 3339, 3746.**

3335. TAYLOR, H. S., AND BURNS, R. M. Adsorption of Gases by Metallic Catalysts. Jour. Am. Chem. Soc., vol. 43, 1921, pp. 1273–1287; Chem. Abs., vol. 15, 1921, p. 3922.

Measurements of the adsorption of H_2, CO, and CO_2 and C_2H_4 by finely divided Ni, Co, Fe, Cu, Pd, and Pt were made. Adsorption by a metallic catalyst is not like adsorption by such inert substances as charcoal and silica gels. It is specific, and saturation capacity is reached at low partial pressures of the gas. It is a surface phenomenon involving electronic rearrangements in both catalyst and adsorbed gas. Methods of preparation, which produce good metallic catalysts also produce metals with high powers of adsorption for gases whose reaction they catalyze, but the temperature of maximum adsorption is often lower than temperature of maximum chemical activity. This probably means that a free evaporation of both reactants and resultants is necessary for rapid chemical action. The greater the adsorption the lower is the temperature at which catalytic action begins.

3336. TAYLOR, H. S., AND KISTIAKOWSKY, G. B. Methanol Catalysts. I. Jour. Am. Chem. Soc., vol. 49, 1927, pp. 2468–2476; Chem. Abs., vol. 21, 1927, p. 3804.

Adsorptions of H_2, CO, and CO_2 on 2 MeOH catalysts, ZnO and ZnO–Cr_2O_3, were measured at 0° and 100°. In order to obtain reproducible results, it was necessary to clean the surface of H_2O and CO_2 by preliminary evacuation at 400°. Both these catalysts had adsorptive capacities considerably greater than those of most metal catalysts. The adsorption of both H_2 and CO is large at very low pressures and rapidly reaches saturation capacity independently of further pressure increase. The experiments indicate that the heat of adsorption is of the same order as that on metal catalysts. The mixed oxide catalyst shows greater adsorptive capacity than the ZnO. The results are consistent with the known facts concerning MeOH synthesis on these catalysts.

3337. TAYLOR, H. S., AND LIANG, S. C. Heterogeneity of Catalyst Surfaces for Chemisorption. I. Zinc Oxide. Jour. Am. Chem. Soc., vol. 69, 1947, pp. 1306–1312; Chem. Abs., vol. 41, 1947, p. 5772.

New technique for determining adsorption isobars was applied to the study of the adsorption of H_2 by ZnO over the temperature range 77°–600° K. It reveals desorption of chemisorbed H_2 on raising the temperature through certain temperature ranges, followed by readsorption at still higher temperature. The data indicate a marked heterogeneity of the ZnO surface for the adsorption of H_2 that must be taken into consideration in attempting to evaluate energies of activation for adsorption and catalysis.

3338. ———. Heterogeneity of Catalyst Surfaces for Chemisorption. II. Zinc Oxide–Chromic Oxide, Manganous Oxide–Chromic Oxide, Chromic Oxide Gel. Jour. Am. Chem. Soc., vol. 69, 1947, pp. 2989–2991; Chem. Abs., vol. 42, 1948, p. 1793.

As described in the previous paper in this series, the techniques of measuring chemisorption with increasing and decreasing temperatures at constant pressure were applied to a study of ZnO–Cr_2O_3 catalysts and Cr_2O_3 gel. These substances reveal heterogeneity of surface. MnO–Cr_2O_3 catalysts do not show desorption-readsorption phenomena on raising the temperature. The isobar on decreasing temperature consequently was horizontal over a considerable temperature range. The surface, nevertheless, exhibits a partial heterogeneity. The criterion of "pumping-off at temperature" was shown to be doubtful in distinguishing van der Waals' and chemisorption of H_2 in certain temperature ranges with these catalysts.

3339. SADEK, H., AND TAYLOR, H. S. Heterogeneity of Catalyst Surfaces for Chemisorption. III. Metallic Nickel. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 1168–1175; Chem. Abs., vol. 44, 1950, p. 5199.

Heterogeneity of the surfaces of 6 different Ni catalyst preparations was confirmed with the technique devised by Taylor and Liang (abs. **3338**) and H_2 as the adsorbate. The adsorption at −195° were analyzed to determine the relative amounts of van der Waals adsorption and chemisorption of H_2 and to show that different preparations adsorb different relative amounts of the 2 types. The velocity of the H–D exchange reaction on Ni–Cr_2O_2 and Ni–ThO_2 was studied to support these findings. There are marked differences in rates with activation energies of 0.45 and 2 kcal., respectively. The data do not support an interpretation based either on solubility of H_2 in the lattice or an exothermic entry of H_2 into the Ni lattice at temperatures −195° to −78°.

3340. TAYLOR, H. S., AND NEVILLE, H. A. Catalysis in the Interaction of Carbon With Steam and With Carbon Dioxide. Jour. Am. Chem. Soc., vol. 43, 1921, pp. 2055–2071; Chem. Abs., vol. 16, 1922, p. 522.

Steam was passed over C at 490°, 525°, and 570° and the volume, and composition of the gases evolved were determined both in the presence and absence of catalysts. The reaction is (*a*) $C+2H_2O=CO_2+2H_2$. The amount of CO in the emergent gases was hardly measurable. This reaction takes place in 2 steps (*b*) $C+H_2O=CO+H_2$ and (*c*) $CO+H_2O=CO_2+H_2$, of which (*c*) is the slower. Good catalysts for (*c*) such as Fe oxide do not affect the velocity of (*a*); hence (*c*) reaches equilibrium under these conditions even in the absence of catalysts. Many substances of which K_2CO_3 is best are powerful catalysts for (*a*). The same substances are found to catalyze the reaction (*d*) $C+CO_2=2\,CO$. Adsorption measurements show that these catalysts increase the adsorption of CO_2 by charcoal. The results conform to the view that a surface complex C_xO_y is formed and the catalysts hasten the decomposition of this complex, thus cleaning off the surface for further adsorption of CO_2.

3341. TAYLOR, H. S., AND OGDEN, G. Adsorption of Hydrogen and of Carbon Monoxide on a Surface of Zinc and Molybdenum Oxides. Trans. Faraday Soc., vol. 30, 1934, pp. 1178–1190; Chem. Abs., 29, 1935, p. 2418.

Mixture of ZnO with excess of Mo oxide exhibits van der Waals' adsorption in a low-temperature range and activated adsorption in a high-temperature range with both H_2 and CO. The decreased extent of activation adsorption and the increased activation energy when Mo oxide is mixed with the ZnO explains why the Mo oxide reduces the catalytic action of ZnO in the MeOH synthesis.

3342. TAYLOR, H. S., AND SICKMAN, D. V. Adsorption and Reactions at Surfaces of Zinc Oxide. Jour. Am. Chem. Soc., vol. 54, 1932, pp. 602–613; Chem. Abs., vol. 26, 1932, p. 1852.

Difficulties in measurement of the velocity of decomposition of alcohols on ZnO surface are discussed. The importance of the adsorption of H_2O in the decomposition of alcohols is shown. Evidence for an activated adsorption of H_2O on ZnO is given. The velocity of adsorption of H_2 by ZnO was measured in the range 0°–360°; isotherms were obtained at —191° and —78.5°. The heats of adsorption of 2 types of adsorption of H_2 by ZnO were determined. A theory of activated adsorption is developed mathematically, which gives expressions for the temperature of maximum adsorption. Methods of calculating the activation energy and heat of adsorption are given.

TAYLOR, J. *See* abs. **2041.**

TAYLOR, P. S. *See* abs. **1099.**

3343. TAYLOR, R. Present Position as Regards Production of Liquid Fuels From Water Gas. Chem. and Ind., vol. 50, 1931, pp. 580–584; Chem. Abs., vol. 25, 1931, p. 4383.

Review of the development of the synthetic liquid fuel processes—MeOH, higher alcohols, synthol, gasoline.

3344. ———. Catalytic Syntheses With Carbon Monoxide and Hydrogen Under Pressure. Jour. Chem. Soc., 1934, pp. 1429–1431; Chem. Abs., vol. 29, 1935, p. 115.

With 3 catalysts [Mn–Cr–Rb oxide (I), Zn–Mn–K–Co oxide (II), and Cu–Mn oxide–Co sulfide (III)] the weights of the constituent alcohols per kgm. of crude product were found as follows (the data for (III) were obtained with product that had been hydrogenated, and aldehydes and acids had been removed from the other 2 products before distillation of the alcohols) (the order is (III), (I), (II)): MeOH 220, 420, 198; EtOH 200, 12, 86; PrOH 50, 43, 17; iso-BuOH 3, 69, 11; BuOH 16, ——, 4; β-methylbutyl alcohol 2, 8, 1.5; AmOH, 6, ——, 1; β-methylamyl alcohol ——, 6.5, ——; hexyl alcohol 2, ——, ——; heptyl alcohol <1, ——, ——; residue 1, 89, 1.5. (III), which contained Co but no alkali, produced alcohols higher than C_2, the majority of which had straight chains, and (I), which contained alkali but no Co, gave higher alcohols, a large proportion of which had branched chains, while (II) gave both alcohols.

3345. ———. High-Pressure Synthesis of Aliphatic Compounds. Gas World, vol. 104, No. 2696, Coking Sec., 1936, pp. 38–42; British Chem. Abs., 1936, B, p. 440.

Review of the patent literature and of work carried out at the Chemical Research Laboratory on the high-pressure synthesis of MeOH from CO and H_2, of BuOH from EtOH and CO, and of AcOH from MeOH and CO.

———. *See* abs. **2316, 2317, 2319.**

TAYLOR, R. S. *See* abs. **1744.**

TAYLOR, W. J. *See* abs. **3589.**

3346. TEBBOTH, J. A. Decomposition of Carbon Monoxide by Nickel Catalysts. Reaction Mechanism Between 250° and 450°. Jour. Soc. Chem. Ind., vol. 67, 1948, pp. 62–66.

Principal factors involved in the catalytic formation of CH_4 from water gas have been described recently. A major difficulty encountered was the progressive deposition of C on the Ni–ThO_2–kieselguhr catalyst used. An attempt is made here to ascertain the mechanism of the formation of C and how to minimize it. It was found that unsupported and unpromoted Ni catalysts, derived from precipitated $NiCO_3$, showed little activity for the decomposition of CO at all temperatures between 250° and 450°. The presence of ThO_2 and kieselguhr in a Ni catalyst prepared from the precipitate $NiCO_3$ caused a marked increase in the rate of decomposition of CO at the same temperatures. Elementary C formation occurred on Ni catalysts at all temperatures from 250°–450°, being least at 250° and greatest at 325°–350°. The Ni of such promoted and supported Ni catalysts was converted almost quantitatively to Ni_3C at 250°. Above this temperature, carbide formation was incomplete. Decomposition of Ni_3C in the presence of ThO_2 and kieselguhr occurred above 250° and was rapid at 300°. The proportion of C combined as carbide decreased with increasing temperature, but some persisted at 450°. When using promoted and supported catalysts for CH_4 synthesis from CO and H_2, the conditions prevailing at the inlet end of the catalyst bed were very favorable for elementary C formation. The results were accounted for by 2 reactions: $3\,Ni + 2\,CO = Ni_3C + CO_2$ and $Ni_3C = C + 3\,Ni$. The latter reaction may have occurred in 2 stages with the formation of a lower carbide Ni_6C, but evidence here was incomplete.

———. *See* abs. **304.**

3347. TECHNICAL OIL MISSION. [Operation Costs in the Synthesis-Gas Production in Rheinpreussen.] TOM Reel 43, 1942, pp. 260–267; Bureau of Mines Transl. T–154, 1946, 6 pp.; TOM Reel 237.

Operating costs are computed for 4 different types of plants and are broken down for each item of operating expense.

I. Water-gas plant—1,440,000 m.³ water gas per day.
  Coke at 20 RM per ton:
    Water gas, 1.818 pf. per m.³
    $CO + H_2$, 2.075 pf. per m.³
  Coke at 17.50 RM per ton:
    Water gas 1.635 pf per m.³
    $CO + H_2$, 1.875 pf. per m.³

II. Gasification of coal fines—1,440,000 m.³ water gas per day.
  Coal at 14 RM per ton and O_2 at 0.025 RM per m.³
    Water gas, 1.045 pf. per m.³
    $CO + H_2$, 1.69 pf. per m.³

III. Reforming of coke-oven gas—356,000 m.³ reformed gas per day.
  Gas at 0.017 RM per m.³:
    Reformed gas, 1.69 pf. per m.³
    $CO + H_2$, 1.98 pf. per m.³
  Gas at 0.013 RM per m.³:
    Reformed gas 1.375 pf. per m.³
    $CO + H_2$, 1.61 pf. per m.³
  A. 65% water gas + 35% reformed gas.
    Coke at 20 RM per ton and coke-oven gas at 0.017 RM per m.³:
      Synthesis gas, 1.769 pf. per m.³
      $CO + H_2$, 2.035 pf. per m.³
    Coke at 17.50 RM per ton and coke-oven gas at 0.013 RM per m.³:
      Synthesis gas, 1.543 pf. per m.³
      $CO + H_2$, 1.775 pf. per m.³
  B. 70% water gas from powdered bituminous coal + 30% reformed gas.
    Coke-oven gas at 0.017 RM per m.³:
      Synthesis gas 1.487 pf. per m.³
      $CO + H_2$, 1.770 pf. per m.³
    Coke-oven gas at 0.013 RM per m.³:
      Synthesis gas, 1.392 pf. per m.³
      $CO + H_2$, 1.660 pf. per m.³

IV. Gasification of powdered coal—direct production of synthesis gas $CO:H_2=1.2-1,440,000$ m.^{3} per day, coal at 14 RM per ton and O_2 at 0.025, RM per m.^{3}:
Synthesis gas 1.37 pf. per m.^{3}
$CO+H_2$, 1.69 pf. per m.^{3}

3348. ———. Fischer-Tropsch Use of Iron Catalyst. TOM Reel 26, bag 2463, document 9, frames 900,000,232–900,000,333 (particularly 286), Mar. 31, 1943.

X-ray investigations, made by Dr. Herbst and Dr. Halle on the Fe catalyst containing Cu, revealed that the Cu, besides aiding in the reduction of the catalyst, played another quite important role in the synthesis. It was found in examining the standard catalyst that a new hexagonal carbide Fe_2C occurred, not yet described in the literature, which appeared to be necessary to the high activity of the catalyst. This new hexagonal carbide, as Dr. Herbst discovered, becomes transformed in course of time, particularly at the higher temperatures, into the carbide Fe_2C already identified by Hägg. This transformation is retarded greatly by the addition of Cu so that it is regarded as a stabilizer in one of the intermediate states of the catalyst occurring during the synthesis. For example, the addition of 2% Cu raises the conversion temperature about 50°.

3349. ———. [Experience With the Semicommercial Synol Research Plant ME 458, Leuna Works, Oct. 10, 1944.] Transl. of German documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis. Part II, 1946, pp. 41–59; TOM Reel 86, bag 3979, item 78.

Detailed descriptive matter covering catalyst reduction, synthesis apparatus, CO_2 extraction, activated C adsorption, and distillation units. The catalyst is the standard fused Fe type (WK 17) of particle size 0.5–1.0 mm. and reduced at 450° at a space velocity of 1 : 2,000 of H_2. The synthesis is performed by recycling at a throughput of 1 : 2,000 or 3,000 m.^{3} of gas per m.^{3} of catalyst per hr. with a gas conversion of 150 m.^{3} per m.^{3} of catalyst per hr. The yields amount to 170 gm. of products heavier than C_2 per m.^{3}, of which 35 gm. are gasol and 30 gm. paraffins boiling above 400°. The alcohol content in the lower-boiling fractions is 50–65%; from about C_{14} upward the alcohol content declines, at C_{18} about 30–40% of alcohols are obtained. The sum of the alcohols and olefins declines from 80% in the lower fractions to 65% in the boiling range of C_{18} alcohols. The alcohols are primary and straight chain, the olefins likewise. The higher fractions contain esters to about 10% in the region of C_{10} alcohols to 20% in the region of C_{18} alcohols. The content of the aldehydes and ketones in all fractions amounts to 1–2%.

3350. ———. Combined Intelligence Objectives Subcommittee Investigation of Ruhr Synthetic Oil Plants. TIIC Rept. 17; Nat. Petrol. News, vol. 37, No. 45, 1945, pp. R–861–864.

Summary report of the visit to 7 plants using the Fischer-Tropsch process and to 3 using the hydrogenation process. No new developments were found to offset the economic disadvantages of both processes. Indications were that the German government had discontinued the construction of Fischer-Tropsch plants and was planning to build additional hydrogenation plants. The Ruhr plants were found to be using the ordinary Co–Th–Mg–kieselguhr catalyst. It seems clear that no German plants have been using the Fe catalyst but that it was to be used in a projected Italian plant. The Fe catalyst consists of 100 parts Fe, 2.5–4 Cu, 10 lime, and 15 kieselguhr and is prepared from the nitrates by precipitation with CO_2. Something was learned of the Oxo process for making alcohols by the Fischer-Tropsch process. Fischer-Tropsch C_{12}–C_{17} olefins are treated at 140° and 150 atm. over a Co catalyst to produce aldehydes, which are reduced to alcohols over a Ni catalyst at 180° and 150 atm. The alcohols are converted into sulfonic ester soaps.

3351. ———. Thyssen-Galocsy Process. TOM Reel 65, frames 1–4, May 1945; Bureau of Mines Transl. T–402, Aug. 21, 1947, 3 pp.; TOM Reel 274, frames 1113–1115.

This process applies O_2 instead of air-blast for the complete gasification of solid fuel. It carries out the combustion in 2 stages with regulation of temperature, so that the refractory lining of the shaft is not destroyed by excess heat. An industrial-scale producer was installed and operated during the war and gave full satisfaction. Many advantages are quoted, among which are highly increased output in comparison with other plants (100,000–1,000,000 m.^{3} per day in a single unit), high thermal efficiency, continuous working, utilization of cheap fuels, recovery of large amounts of low-temperature tar, and cheap gas for industrial heating and synthesis purposes. It is especially applicable in blast furnaces for the reduction of Fe ore.

3352. ———. [Hydrocarbon Synthesis With Iron Catalysts, Leuna Works, Apr. 5, 1940.] Transl. of German documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis. Part II, 1946, pp. 27–40; TOM Reel 134, item IB–23 (1st half).

Details are presented of the experimental investigation of 3 Fe catalysts: A fused Fe catalyst (997); a sintered Fe catalyst (Michael); and a Leuna NH_3 catalyst (WK 17), each reduced with H_2 at atmospheric pressure at temperatures 450°–850° for relative periods of 5–15 days. The converters were tube furnaces (the tubes 15 mm. diam.) with Dowtherm as the heat transfer medium. A synthesis gas of composition $CO:H_2=1:2.6$ was used, except when operating at 20 atm. when the composition was 1.2 : 1. Reduction at the lower temperatures produces more active catalysts, although not much is gained by going below 450°. When 2 catalysts of the same composition but reduced at 2 different temperatures were used, the one reduced at the lower temperature gave a lower-boiling product than the one reduced at the higher temperature. Higher space velocity and synthesis temperature also have a tendency to increase the yield of low-boiling constituents. In comparing the products formed on Co catalysts at middle and atmospheric pressures and a space velocity of 100 with those produced from a sintered Fe catalyst at 20 atm. and a space velocity of 200, it is seen that the latter gives better benzine yields than the former. An essential feature in the synthesis with Co is the comparatively high yield of paraffins in the benzine fraction (86% paraffins, 14% olefins), whereas the products from the Fe catalyst contain considerably greater amounts of unsaturates (approximately 50% olefins, 45% paraffins). The effect of this increased olefin content is to raise the octane number of the benzine fraction. Of 3 catalysts examined, a Co catalyst, WK17 and 997, the latter produced the highest olefin content with the highest octane number (71%, as compared with 15 and 48% and 63.5%, as compared with 25 and 57%). It is pointed out, however, that factors other than the olefin content influence the octane number. In general, for the same olefin content of the benzine fraction, a high reaction temperature, a high space velocity, and an active catalyst, in other words, all factors that favor the formation of low-boiling constituents, will yield a product having the highest octane number. Also, an increase in the olefin content is accompanied by a decrease in the boiling point of the product. Some data

are presented on the behavior of several fused Fe catalysts under specific synthesis conditions of 19 atm. pressure and 200 space velocity, and X-ray investigations were made to determine the nature of C deposition on the catalyst. It is believed that it takes place according to the equation $2CO \rightarrow CO_2 + C$ and $4CO + 3Fe \rightarrow Fe_3O_4 + 4C$. A 2-stage operation was performed with a Co catalyst in the second stage at atmospheric pressure. The result was a conversion of 86% and a total yield from both stages of 135–150 gm. per $m.^3$ of water gas.

3353. ———. [Middle-Pressure Synthesis With Iron Catalysts, Sept. 9, 1939.] Transl. of German documents on the Development of Iron Catalysts for the Fischer-Trousch Synthesis. Part II, 1946, pp. 11–21; TOM Reel 101, Doc. PG–21, 578–NID.

Reviews historical development of the Fe catalyst. It is possible to point out that Fe catalysts, which are properly pretreated with CO and are operated at slightly elevated pressures, are capable of converting a theoretical mixture of CO and H_2 into hydrocarbons over a very long period. The total yields compare very closely to those obtained from Co catalysts, therefore, it now appears feasible to replace Co by Fe in the synthesis of hydrocarbons from CO and H_2. Except for traces of alkali, the new Fe catalyst contains no additional material. It must, however, be inducted at approximate atmospheric pressure and above 250° over a period of 24 hr. The synthesis itself is best carried out at pressures 10–20 atm. and at maximum working temperatures of 230°–240°, with a synthesis gas containing CO and H_2 in the ratio of 3:2. Higher pressures necessitate higher operating temperature, and, with water as the cooling liquid, heavier pressure apparatus is required. Without regeneration of the Fe catalyst, constant yields of 150 gm. of liquid, gasol, and solid hydrocarbons per N $m.^3$ of synthesis gas are obtained indefinitely. The liquid hydrocarbon products contain approximately 66% of a benzine fraction boiling below 180° and 20% at 180°–300°. The content of solid paraffin is about 5%. In general, ⅔ of the benzine fraction consists of unsaturated hydrocarbons and ⅓ of saturated hydrocarbons, density 0.7 at 15°, octane number (I. G. Farbenindustrie-test engine) about 60. The benzine can be improved materially by following the synthesis with a polymerization of the primary unsaturated hydrocarbons, thus raising the octane No. to 67; by adding 0.7 cc. of tetraethyl lead per l., the octane No. is raised to 77.

3354. ———. [Middle-Pressure Synthesis With Iron Catalysts.] Transl. of German documents on the Development of Iron Catalyst for the Fischer-Tropsch Synthesis. Part II, 1946, pp. 21–24; TOM Reel 101, Doc. PG–21,578–NID.

This summary was made some time after September 1940, when plans were being made to modify the equipment for use with the Fe catalyst at temperatures below 225° and pressures not above 10 atm. Certain factors influencing the synthesis at lower temperatures are presented. A very active catalyst must be used, such as can be obtained by precipitation from an Fe-salt solution, having added thereto a promoter such as 1% or less of Cu and about 0.25% of alkali. Proper induction of the catalyst is required by using CO-rich gases at low pressures and a higher-than-synthesis temperature. The synthesis temperature should be carried out at a maximum pressure of 8–10 atm. and with a H_2-rich synthesis gas. Under such conditions, conversion takes place at lower temperatures. For example, with a gas mixture of $CO : H_2 = 1 : 10$ conversion took place at 130°, and, at 140°, it amounted to 38% with a gas contraction of 12%; with a ration of 1:4, the synthesis temperature varied between 180°–200°, therefore quite comparable to the conditions of the CO synthesis. Fe catalysts produce reaction products that contain larger quantities of gasol and oxygenated organic compounds, than do Co catalysts. Multistage operation or recycling is the most economical method; the higher the H_2 content of the gas, the more stages are recommended.

3355. ———. Thermodynamic Expressions for the Formation and Stability of Hydrocarbons. TOM Reel 134, Item Ib–1; Bureau of Mines Transl., February 1947, pp. 1–8; TOM Reel 259, item 16.

Temperature range for which the formation of various hydrocarbons, saturated and unsaturated, from $CO + H_2$ is possible, is determined by consideration of the free energies of formation of the reactants and products. Calculations are carried over a range of pressures 1–100 atm. The conditions of thermodynamic stability are applied to consideration of condensation and decomposition reactions.

3356. ———. Thermodynamics of the Fischer–Tropsch Synthesis. TOM Reel 134, item Ib–2; Bureau of Mines Transl., February 1947, pp. 9–31; TOM Reel 259, item 16.

Theoretically obtainable yields at equilibrium for the synthesis of butane and octane from CO and H_2 were computed by standard thermodynamic methods. The effect of variations of temperature, pressure, and synthesis-gas composition on the theoretical yield were investigated.

3357. ———. Translations of German Documents on Mathematical Expressions for Thermodynamic Relationships and the Calculation of Yields in the Fischer–Tropsch Synthesis. Bureau of Mines Transl., February 1947, 78 pp; TOM Reel 259, item 16.

Report consists of 4 translations of Technical Oil Mission Reel 134, Documents Ib–1, Ib–2, Ib–3, and Ib–4, identified, respectively, as: Thermodynamic Expressions for the Formation and Stability of Hydrocarbons, 8 pp.; Thermodynamics of the Fischer-Tropsch Synthesis, 23 pp.; Calculation of Gas Consumption and Synthesis Course in the Hydrogenation of CO, 38 pp.; Calculation of Yield for Higher Hydrocarbons Based on Recent Methods, 9 pp.

3358. ———. Winkler Method of Gasification. TOM Reel 118, LU II 84; Bureau of Mines Transl. T–400, Aug. 14, 1947, 6 pp; TOM Reel 274, frames 1,095–1,100.

Theory and operation together with operating data are presented. This process permits the gasification of a wide range of fuels with maximum efficiency. Its specific gas production amounts to 1,000–4,000 $m.^3$ per $m.^2$ of cross section of the shaft per hr., as compared with, at most, 800–1,000 $m.^3$ in the modern rotating-grate gas producer. It has the further specific advantage of permitting the production of various types of gases, depending on the choice of gasifying agent and the style of operation. A diagram is shown.

3359. Teichner, S. [Evolution of Surface Area of Fischer Catalysts During Reduction.] Compt. rend., vol. 227, No. 8, 1948, pp. 478–480; Chem. Abs., vol. 43, 1949, p. 27.

It has been shown by other workers that interaction between Ni or Co oxides and kieselguhr used as catalyst support occurs to some extent. Visser and de Lange found evidence for the formation of Ni hydrosilicate bonds by X-ray diffraction studies. Data are presented in this paper for surface area changes of a Ni-kieselguhr catalyst on heating in vacuum and reduction:

Treatment	Weight loss, percent	Surface area	
		$M.^2$ per gm. of catalyst after pretreatment	$M.^2$ per gm. original catalyst
Evacuated 26 hr. at 20° C.	4.3	28	27
Evacuated 16 hr. at 180° C.	11.0	39	35
Reduced in H_2 at 450° C. for 18 hr., followed by evacuation at 180° C. for 48 hr.	22.8	87	67

The authors postulate a laminar or montmorillonite structure for the metal oxide-kieselguhr complex of the unreduced catalyst. The increase is area on heating or reduction is not a direct consequence of this structure but is due to holes formed by removal of O_2, H_2O, and CO_2 during the heating or reduction. However, the laminar structure does tend to prevent the collapse of the pore system and sintering. These catalysts are prepared as basic carbonates of the active metals, and H_2O and CO_2 result from their decomposition.

3360. ——— [Choice and Role of Kieselguhr as Support of Fischer Catalysts.] Compt. rend., vol. 228, 1949, pp. 1,644–1,646; Chem. Abs., vol. 43, 1949, p. 8,830.

Three commercial kieselguhrs—crude Filter-Cel, acid-treated Filter-Cel, and crude Hyflo-Super-Cel—were subjected to thermal and alkaline treatment and loss in weight, density, and specific surface were determined. As the result of such considerations, the reactivity of a kieselguhr may be defined as the % of silica capable of being dissolved warm in a 5% solution of Na_2CO_3, which dissolves the amorphous or very finely divided silica. The efficiency of the kieselguhr in a Fischer catalyst is linked to the quantity of reactive silica that it initially contains or which it is possible to generate by acid treatment, as well as to the real surface of this reactive silica. The formation of hydrosilicates with foliated structure can, in fact, be promoted only by this type of silica.

3361. ———. [Analogies of Texture Between Activated Montmorillonites and Certain Catalysts.] Jour. chim. phys., vol. 47, 1950, pp. 244–252; Chem. Abs., vol. 44, 1950, p. 7635.

Adsorption results are summarized. Adsorption studies with N_2 and hydrocarbons were made of 6 Fischer-Tropsch catalysts. The loss in weight, the density as determined by He, and the surface areas are given for the following thermal treatments: Desorption under vacuum at 20°, desorption under vacuum at 150°, and reduction at 450° and desorption under vacuum at 150°. In 4 cases, the reduced catalysts exhibited much greater surface areas than the catalysts subjected only to a vacuum treatment at 20° or 150°. Results are tabulated for the surface area of the support, and the surface area of the catalysts impregnated on these supports before and after reduction for kieselguhr subjected to the following treatments: Treated with mineral acids, untreated support, treated with 5% Na_2CO_3. The surface area of the catalysts was greater than those of the supports. The initial surface areas of the support did not determine the surface area of the catalyst after reduction. The difference between the total adsorption of N_2 and CO at −195° was utilized to determine the fraction of metal exposed at the surface. The results are given for 4 catalysts. The fraction of surface covered by metal atoms ranged 0.35–0.65.

3362. ———. [Kieselguhrs of the Type Utilized as Support for Catalysts.] Jour. chim. phys., vol. 47, 1950, pp. 229–232; Chem. Abs., vol. 44, 1950, p. 7635.

Following properties of raw kieselguhr, kieselguhr treated with HCl and HNO_3 and calcined kieselguhr were determined after different thermal treatments: Loss in weight after etching in Na_2CO_3, density, and specific surface as determined by adsorption of N_2 and CO at −195° and C_4H_{10} at 0°. The kieselguhr treated with acids had approximately 50% greater specific surface than the raw kieselguhr. The specific surface of the calcined kieselguhr was only 11% as great as that of the untreated kieselguhr. Treatment with 5% Na_2CO_3 reduced slightly the surface area of the raw kieselguhr, but the same treatment decreased by 50% the surface area of the acid-treated kieselguhr. Presumably the acid treatment caused the formation of siliceous gel, which was soluble in Na_2CO_3. Discusses significance of the results to the activity of supports for catalysts used in the Fischer-Tropsch process.

3363. Teichner, S., and Pernoux, E. [Ultrasonic Fractionation of a Kieselguhr Carrier of a Fischer Catalyst.] Compt. rend., vol. 230, 1950, pp. 1063–1064.

Suspension of an acid-treated kieselguhr (Filter-Cel) in distilled H_2O was subjected to an ultrasonic treatment (ν=970,000). 2 fractions were obtained: One (12% of the initial weight of the kieselguhr) was a stable dispersion; the other remained precipitated on the bottom of the vessel. The specific surface, determined by absorption of N_2 at 195°, of the dispersed fraction was 40 $m.^2$ per gm., that of the initial acid-treated kieselguhr 27 $m.^2$ per gm. Besides, treatment with a 5% H_2O solution of Na_2CO_3 involved losses in weight of 21.6 and 14.5%, respectively. Examination under the electronic microscope revealed an extensive flocculent appearance for the dispersed fraction and considerably less so for the same fraction treated with carbonate. The precipitated fraction had a specific surface of 15.2 $m.^2$ per gm. and a loss in weight by the carbonate treatment of 9%. The properties were similar to those of a kieselguhr untreated with acid. The ultrasonic treatment, thus, furnishes further proof of the formation by the acid treatment of kieselguhr of a silica gel of flocculent appearance with a broad specific surface, and easy reaction with Na_2CO_3. Such a gel is formed for the most part in the dispersed phase of ultrasonic treatment.

3363a. ———. Texture and Surface Area of Kieselguhrs After Various Treatments. Clay Minerals Bull., vol. 1, 1951, pp. 145–150; Fuel Abs., 1952, abs. 4949.

Properties of raw and acid-treated Filter-Cel and Hyflo-Super-Cel characterize their ability to combine with the other constituents of catalysts. Their degree of "reactivity" was determined and compared with specific surface and appearance in the electron microscope. Densities and adsorption isotherms of N at −195° were determined experimentally and surfaces calculated by the methods of Brunauer, Emmett and Teller. Attack by hot 5% Na_2CO_3 solution, which was used to measure the "reactivity," had not the same effect for all samples. Loss of silica, brought about by a small part of the kieselguhr dissolving in the carbonate solution, was nearly proportional to the initial specific surface of the samples. The specific surface of acid-treated Filter-Cel fell from 27–14 $m.^2$ per gm. but after alkaline attack, that of crude Filter-Cel was only slightly reduced. In the 1st case, the treatment had caused departure of a "reactive" silica with large surface formed by the acid treatment; in the 2d case, the "reactive" but low surface silica removed by alkaline treatment probably owed its solubility only to its finely divided state. Photographs of Filter-Cel treated with mineral acids and then by Na_2CO_3 are very different from those of Filter-Cel treated with mineral acids alone. The appearance of Filter-Cel treated by Na_2CO_3 alone is little different from that of the initial Filter-Cel. Thus acid treatment of crude kieselguhr causes the formation of a large surface silica gel which increases the total specific surface of the carrier. This

gel is eliminated during alkaline treatment and the specific surface of the substance diminishes by 50% and approaches that of the crude product. Formation of a hydrosilicate with flaky structure similar to that of montmorillonite is related to the possibility of combination of this "reactive" fraction of the kieselguhr which is used as a carrier. The conditions of formation of hydrosilicates in the catalyst mass of the Fischer process are different from the ordinary conditions of hydrothermal synthesis; hydrosilicate appears at atmospheric pressure and temperatures as low as 200° in the almost dry catalyst.

TEJIMA, T. *See* abs. **1918, 1919, 1920, 1921, 1922, 1923, 1924, 1925, 1926.**

TELEGIN, V. G. *See* abs. **2030, 2033, 2034.**

3364. TELEGIN, V. G., AND SIDOROV, N. V. [Utilization of Artificial Magnetite as a Raw Material for the Prepafation of the Catalyst for Ammonia Synthesis.] Jour. Appl. Chem. (U. S. S. R.), vol. 11, 1938, pp. 1064–1070 (in French, p. 1070); Chem. Abs., vol. 33, 1939, p. 4386.

Magnetite was prepared from commercial Fe (containing C, 0.12; Si, 0.09; and Mn, 0.05%) by oxidation with O_2 at 1,470°–1590°. The magnetite obtained was mixed with Al_2O_3 and KNO_3, and the mixture was used for the preparation of catalyst by electric fusion. The activity of the catalyst obtained was higher than that prepared from the concentrates of natural magnetite; this is explained by the small amount of SiO_3 in the artificial magnetite. The activity of catalyst prepared from an artificial magnetite, after heating at 625° for 8 hr. in the N_2–H_2 atm., was changed as follows: The activity corresponding to 400°, 450°, and 475° decreased, but that corresponding to 500° and 525° increased. 9 refs.

3365. ———. [Siderite as a Catalyst for Ammonia Synthesis.] Jour. Appl. Chem. (U. S. S. R.), vol. 12, 1939, pp. 1769–1774 (in French, p. 1774); Chem. Abs., vol. 34, 1940, p. 8,188.

Bakal (Ural) siderite contained FeO, 38.50; Fe_2O_3, 1.60; Al_2O_3, 2.20; SiO_2, 2.80; MgO, 13.25; CaO, 0.92; CO_2, 38.70; As, none; P, 0.001; S, 0.12 (as sulfate), and H_2O, 1.15%. The synthesis of NH_3 was attempted at normal pressure and under 300 atm. The sample of siderite containing ferrous oxide was inactive at atmospheric pressure and only slightly active at 300 atm., while samples containing the catalyst in the form of ferric oxide were more active. The highest activity was reached with a catalyst containing the Fe in the form of Fe_3O_4. 15 refs.

3366. TELEGIN, V. G., SIDOROV, N. V., AND SHPULENKO, K. B. [Effect of the Content of Aluminum Oxide in the Iron Catalyst for Synthesis of Ammonia Upon Its Activity at Atmospheric Pressure.] Jour. Appl. Chem. (U. S. S. R.), vol. 13, 1940, pp. 823–830 (in French, p. 830); Chem. Abs., vol. 35, 1941, p. 2287.

Chemical compositions of NH_3 catalysts were FeO, Fe_2O_3, Al_2O_3, and K_2O, respectively, (1) 32.05, 64.40, 3.55, and 0%; (2) 27.75, 63.00, 9.25, and 0%; (3) 25.15, 46.60, 28.25, and 0%; (4) 13.40, 25.50, 61.10, and 0%; (5) 20.40, 71.10, 5.20, and 2.94%; (6) 20.30, 52.70, 25.00, and 2.50%; and (7) 14.50, 43.60, 39.60, 2.10%. The catalysts were prepared by fusion of magnetite with Al_2O_3 and with Al_2O_3 and KNO_3 in the electric furnace. The activity of catalysts was determined at a volume velocity of N_2–H_2 gas mixture of 15,000 l. per hr. per. l. of catalyst at 310°–500°; for the last 3 catalysts also at a volume velocity of gas mixture of 2,000, 5,000, and 10,000. In all cases, activity decreased with an increase of Al_2O_3 content. A minimum amount of Al_2O_3 necessary for the stabilization of microstructure and activity of reduced Fe in the NH_3 catalyst should be determined by the working conditions. Thus, if a catalyst containing 0.1% Al_2O is stable enough at a temperature below 450° at atmospheric pressure, then for stable activity at 500° and 300 atm. the catalyst should have up to 5% Al_2O_3. The binary catalysts (Fe–Al oxides) were more active than ternary catalysts (Fe–Al–K oxides), probably because of the poisonous effect of K_2O.

TELLER, E. *See* abs. **389, 2230.**

TEMKIN, M. *See* abs. **1773.**

3367. TEMKIN, M., AND KIPERMAN, S. [Kinetics of Synthesis and Decompositon of Ammonia on Various Catalysts.] Jour. Phys. Chem. (U. S. S. R.) (in Russian), vol. 21, 1947, pp. 927–952; Chem. Abs., vol. 42, 1948, p. 2501.

Equation for the rate v of reaction, $v=k_1P_1(P^3_2/P^2_3)^{\alpha}-k_2(P^2_3)^{1-\alpha}$, in which P_1, P_2, and P_3 are the partial pressures of N_2, H_2, and NH_3, respectively, and k_1, k_2, and α are constant, is integrated by assuming the total pressure to be constant. The energy of activation is expressed as a function of α. The best composition of the gas mixture is given by $P_2:P_1=3\alpha$. The above equation is valid only when the system is not too far removed from the equilibrium state. Variations of the adsorbed amount of N_2 may cause the decomposition of NH_3 to be a zero-order reaction at very low NH_3 concentrations. Consideration of earlier experiments shows that the equation is valid for various catalysts (Fe, Mo, W, U, Ce, Mn, Os, Ru, Cu, and Pt), that α usually is 0.5, and that the activation energy is almost independent of the nature of the catalyst. This proves that the reaction mechanism is identical on various catalysts. The rate of synthesis should depend on the degree of uniformity of the catalyst surface. 57 refs.

3368. TEMKIN, M., AND PYZHEV, V. [Kinetics of the Synthesis of Ammonia on Promoted Iron Catalysts.] Jour. Phys. Chem. (U. S. S. R.), vol. 13, 1939, pp. 851–867; Chem. Abs., vol. 34, 1940, p. 6512.

From experimental data on the synthesis and decomposition of NH_3 technical Fe catalysts promoted by Al_2O_3 and K_2O at 400°–450° and 1 atm. pressure and $H_2:N_2$ ratios of 0.5 up to 8.5, the rate constants are $k=1.04\times10^3$ at 400° and 7.78 at 450°. The rate of formation of NH_3 is given by $v=k_1P_{N_2}(P^3_{H_2}/P^2_{HN_3})^{\alpha}$ with $\alpha=0.5$. The determining factor in the forward process is the rate of activated adsorption on the N_2-free surface. For the reverse process, the rate of NH_3 desorption is the rate-determining factor. For the complete process, the equation

$$dP_{NH_3}/dt=k_1(P_{N_2}P^{1.5}_{H_2}/P_{NH_3})-k_2(P_{NH_3}/P^{1.5}_{H_2})$$

holds both for the experimental data of Temkin and Pyzhev and for those of other authors. The apparent energy of activation for NH_3 formation is ~14 cal. and for decomposition ~40 cal. per mol.

3369. TEMKIN, M. I., KIPERMAN, S., AND LUK'YANOVA, L. I. [Flow-Circulation Method of Investigation of the Kinetics of Heterogeneous Catalytic Reactions.] Doklady Akad. Nauk. S. S. R., vol. 74, 1950, pp. 763–766; Chem. Abs., vol. 45, 1951, p. 1854.

This is an adaptation of the idea of Denbigh, subsequently utilized by Hammett for homogeneous reactions. The reacting gas is admitted to the catalyst zone at a constant velocity v, is made to circulate through the reaction zone, and is led out at exactly the velocity v. Provided the velocity of the circulation through the reaction zone is very much greater than the velocity v of inflow and outflow, the variation of the composition of the reacting gas in each single pass is negligible, and that composition can be taken as stationary. A check is provided by splitting the outgoing gas stream into 2 portions led out of the system just before and after the catalyst zone, with the sum of the 2 outgoing gas streams equal to v; fulfillment of the constancy of composition in each single pass is indicated by closeness of the compositions in the 2 branches

of the outgoing gas. The method was applied to the synthesis of NH_3 from a stoichiometric N_2+3H_2 gas mixture on 1 cc. of a synthetic NH_3 catalyst at 451°, with rates of circulation of 360–500 l. gas per hr., and v varies between about 9 and 110 l. gas (STP) per hr. With U=volume of gas flowing in and out per unit time, c=concentration of the product in the total outgoing gas, W=volume of the catalyst, f=free fraction of the catalyst volume. The rate k of the reaction can be expressed by cU/fW, or in terms of the partial pressure pA' of NH_3 in the initial gas mixture, $pA'U/fW$, or, on account of the insignificant volume change, $r=pAU/fW$, where pA=partial pressure of NH_3 in the outgoing gas. The previously established Temkin (abs. **3367**) kinetic law for the catalytic synthesis of NH_3, $r=k_1pH(pH^3/pA^2)^{0.5}-k_2(pA^2/pH^3)^{0.5}$ (with the exponent 0.5 valid for the particular catalyst), gives $k=\gamma^{1.5}P^{0.5}(U_0/W)x^2/(1-x^2)$, where $\gamma=pH/^{0.75}pA'$; P=total pressure; $U_0=U$ reduced to 0° and 1 atm.; $k=273fk_2/0.75^{1.5}P_oT(P_o=1$ atm.); x=yield of NH_3 in fractions of the equilibrium NH_3 content (=0.210%). Experimental data (U_0/W=8960, 20,000, 46,900, 69,800, 86,200, 110,000 ml. gas (STP) per ml. catalyst per hr., x=0.726, 0.603, 0.461, 0.388, 0.355, 0.302) give k(av.)$\sim 12\times10^3$, fairly close to the previously determined $k=7.8\times10^3$ by the simple flow method.

3370. TENENBAUM, M., AND JOSEPH, T. L. Reduction of Iron Ores Under Pressure by Carbon Monoxide. Am. Inst. Min. and Met. Eng., Tech. Pub. 1134, 1939, 18 pp.; Chem. Abs., vol. 34, 1940, p. 2752.

Most rapid rate of reduction was obtained with H_2. Rate was increased 40% by doubling pressure. With pure CO, the rate was about ¼ that with pure H_2. Doubling the pressure increased rate of reduction by 23%. Dilution of CO with N_2 to form bosh gas lowered reduction rate by ½. Doubling the pressure increased the rate about 20%. Substitution of 8.2% CO_2 for an amount of CO in bosh gas reduced rate still further. Pressure is most effective when applied to strongly reducing gases, rather than to those approaching equilibrium composition. Theoretical considerations are discussed.

TENNEY, R. F. *See* abs. **155, 156.**

TENTSCHART, H. *See* abs. **1948.**

TERASAKI, Y. *See* abs. **3174.**

3371. TERMINASOV, Y. S., AND BELETSKIĬ, M. S. [X-Ray Investigation of the Structure of the Nickel Skeleton Catalyst.] Doklady Akad. Nauk S. S. S. R., vol. 63, 1948, pp. 411–413; Chem. Abs., vol. 44, 1950, p. 9784.

Catalyst obtained after leaching out the Ni_2Al_3 with alkali and subsequent self ignition of the Ni residue consists of a mixture of cubic Ni (lattice constant a=3.52 Å.) and NiO (a=4.15 Å.). If, after leaching, the catalyst is stored under H_2O to prevent oxidation, X-ray patterns reveal hexagonal Ni, with a=2.56, c=4.16 Å. These lattice constants are distinctly lower than those of the hexagonal Ni of Bredig and Allolio (abs. **337**), evidently as a result of occlusion of H_2 in leaching. The grain size of the hexagonal Ni in the skeleton catalyst is of the order of 10^{-5}–10^{-6} cm. Self ignition and the accompanying heating-up evidently result in a conversion of the hexagonal Ni into cubic Ni.

TER-NEDDEN, W. *See* abs. **1047.**

3372. TERNISIEN, J. [Catalytic Oxidation and Influence of Catalyst Surface.] Chim. et ind., vol. 58, 1947, pp. 234–237.

Because of the ease with which H_2 is more or less adsorbed between 300° and 700° C., it was used in the study of surface. Adsorption by catalyst, with or without support is compared. Calculation using the Brunauer-Emmett-Teller equation showed the supported catalyst to be far superior to the nonsupported. The active surface of the supported catalyst lost 5% of its efficiency at 500° C., 26% at 600°, and 75% at 650°. After several hours use at the last temperature it lost 39%. The dimensions of surface for the same quantity of metal catalyst deposited are determined by comparing them to a standard surface magnified and photographed by the electron microscope.

3373. TERRES, E., AND PONGRACZ, A. [Reactions in the Blast-Furnace Equilibrium.] Ztschr. Elektrochem., vol. 25, 1919, pp. 386–407; Chem. Abs., vol. 14, 1920, p. 919.

Reversible reaction represented by the equation $Fe+CO_2\rightleftharpoons FeO+CO$ has been studied and the equilibrium ratio of the gases determined at temperatures 550°–950° by approaching the equilibrium from both sides and varying the quantities of the starting materials. On plotting the ratio of the initial gas concentration, CO_2 or CO, to the equilibrium concentration of the mixed gases, CO_2+CO, at equilibrium against the equilibrium temperature, a curve is obtained, which, in agreement with the results of Schenck and his coworkers and in disagreement with those of Baur and Glaessner, shows no minimum and is almost linear. It has been found that the quantity of Fe exerts an influence on the system, the position of equilibrium being displaced so as to favor the formation of CO as the amount of metal is increased. An analytical method and special apparatus have been developed for determining quantitatively in a mixture the amounts of Fe in the different states of oxidation. The action of CO_2 on Fe in a closed vessel results in the formation of both FeO and Fe_2O_3, from which the existence of solid solution is deduced by means of the phase rule. In conclusion, it is shown that at higher temperatures Fe can probably absorb considerable quantities of CO_2 and CO.

3374. TERRES, E., PATSCHEKE, G., HOFMANN, H., KOVACS, S., AND LÖHR, O. [Formation of Water Gas and the Behavior of Brown-Coal and Bituminous-Coal Cokes and Semicokes in Water-Gas Generation.] Gas u. Wasserfach, vol. 77, 1934, pp. 585–587, 628–636, 650–655, 666–669, 681–684, 703–706; Chem. Abs., vol. 29, 1935, p. 577.

Cokes and semicokes from the bituminous coal Unser Fritz and from several brown coals were prepared at various temperatures 300°–1,200° and gasified at slightly lower temperatures in N_2 containing H_2O vapor. Merck wood charcoal also was gasified. The water-gas analyses were used to calculate the extent of steam decomposition, $CO:CO_2$ ratios, and the water gas and Boudouard equilibrium; similar calculations were made for the theoretical steam-C equilibrium at temperatures 400°–1,200° with the N_2 0–100% saturated with H_2O. At 1,200°, the bituminous coal coke gave a steam decomposition, $CO:CO_2$ ratios, and the C gasification distinctly lower than the corresponding equilibrium values, and lower than wood charcoal. The reactivity of the bituminous-coal cokes decreased with increasing carbonizing temperatures. The brown-coal cokes and semicokes reached no consistent gasification equilibrium. Steam decomposition increased with increasing gasification temperature and with decreasing saturation and lower rate of flow of the gasifying medium. The reactivity with steam of the carbonized product increased with carbonizing temperature up to 700°, decreasing at higher temperatures. This is attributed to a progressive uncovering of the C structure at the lower temperatures followed by the production of a coarser structure at higher temperatures. Steam decomposition is initially, more or less proportional to the time of contact, then increases more or less rapidly according to the reactivity of the material, and then at a lower rate, probably without reaching an equilibrium value in a reasonable time. Carbonized materials can be arranged in the following order with

respect to increasing water gas formation and increasing reactivity: Graphite, lamp black, bituminous-coal coke and semicokes, wood charcoal, and brown-coal cokes and semicokes. The water gas equilibrium was approached in the gasification of the wood charcoal and bituminous-coal cokes at about 600° and attained above 750°. This equilibrium was obtained slowly in an empty porcelain tube at 600°. The brown-coal cokes and semicokes showed no regularity in attaining this equilibrium. The Boudouard equilibrium $C+CO_2=2\ CO$ was not fulfilled in any of these experiments. By using the Ostwald gasification triangle, it was shown that the reaction of steam with bituminous-coal coke and wood charcoal was free from secondary reactions, but that the brown-coal semicokes results showed an excessive and unexplained O_2 action. The use of the gasification triangle showed that the results of Harries and of Gwosdz with wood charcoal and coke were free from secondary reaction effects, but that the results of Bunte and Giessen (abs. **407**), on various cokes showed a surprising excess of H_2. An attempt was made to correlate surface activity, as determined by the heat of wetting of several brown-coal cokes and semicokes, with reactivity, but there appeared to be no distinct relationship. The influence of carbonizing temperature, gasification temperature, steam content, and time of contact of the gasifying medium on the gasification of the coke S content was investigated. Various views as to the nature of the primary action of steam on C are contrasted. When the reaction of steam with carbonized materials does not follow the water gas equilibrium, the principal reaction is believed to be largely, if not entirely, $C+H_2O=CO+H_2$, as larger amounts of CO are formed than can be accounted for by the water gas equilibrium. 57 refs.

3375. TERWEN, J. W. [Contribution to the Theory of the Water-Gas Process.] Chem. Weekblad, vol. 19, 1922, pp. 400–401; Chem. Abs., vol. 17, 1923, p. 1542.

Among some errors in the work of Kohn (abs. **1938**) the chief is the assertion that in the 2 equations, $C+2H_2O=CO_2+2H_2$ and $CO_2+C=2CO$, the fraction of steam transformed according to the 1st equation should be equal to the quantity of CO_2 that disappears according to the 2d equation.

3376. ———. [Adsorption of Hydrogen by Nickel.] Chem. Weekblad, vol. 21, 1924, pp. 386–389; Chem. Abs., vol. 18, 1924, p. 3507.

Gauger and Taylor found that the amount of H_2 adsorbed by Ni decreases with rising temperature. This is explained by assuming that H_2 molecules as well as H atoms are bound by the Ni atoms and that for every temperature a dynamical equilibrium between both forms is established. A typical $T-x$ curve for this equilibrium can be drawn from Gauger and Taylor's data, showing that at the higher temperatures the adsorbed quantity of H_2 approaches asymptotically half the amount of H_2 adsorbed at the lowest temperature.

3377. TESTUT, R. [Chromium Carbides.] Compt. rend., vol. 203, 1936, pp. 1007–1009; Chem. Abs., vol. 31, 1937, p. 332.

Powdered Cr and excess C heated in an electric furnace above 1,700° form Cr_3C_2, which is not attacked by O_2 below 1,000°, and so is separated from excess by heating in O_2 at 900°. It is insoluble in hot concentrated HCl, and is slowly volatile above 1,900°. Between 1,500° and 1,700° Cr_5C_2 is formed with some Cr_3C_2; this is less as temperature is nearer 1,500°. Cr_5C_2 is soluble in concentrated HCl but not in the 10% acid; it also is not attacked by O_2 below 1,000°. Below 1,400°, some Cr_2O_3 is formed. Cr_5C_2 also is formed by heating Cr in C_2H_2. CO passed over Cr at a temperature above 1,350° reacts according to $19\ Cr+6\ CO \rightarrow 3\ Cr_5C_2+2\ Cr_2O_3$, the rate rapidly increasing with temperature. Below 1,350° some C also is formed.

3378. THAU, A. [Large-Scale Low-Temperature Carbonization and Production of a Gas Mixture for Synthesis of Fuels.] Oel u. Kohle Erdoel Teer, vol. 11, 1935, pp. 815–822; Brennstoff-u. Wärmewirt., vol. 17, 1935, pp. 167–176; Chem. Abs., vol. 30, 1936, p. 3969.

Various phases of operation are discussed in describing the Lurgi, Didier, and Fischer-Tropsch processes.

3379. ———. Motor Spirit From Coke. Colliery Guard., vol. 150, 1935, pp. 335–337; Chem. Zentralb., 1936, II, p. 785.

Lengthy abstract of an article by Fischer (abs. **962**).

3380. ———. Synthetic Motor Spirit. Coal Carbonisation, vol. 2, 1936, pp. 159–163; Chem. Abs., vol. 30, 1936, p. 7815.

It is uneconomical to produce less than 20,000 tons of gasoline per yr. The whole production of coke and coke-oven gas can be converted into a gas suitable for synthesis of gasoline. Current processes, especially those used in Germany, are described in detail with drawings and plant photographs.

3381. ———. [Gasoline and Oil Synthesis From Water Gas.] Gas-u. Wasserfach, vol. 80, 1937, pp. 911–913.

Brief descriptions of the Schmalfeldt-Wintershall process for making synthesis gas from raw brown coal, and its application to the Fischer-Tropsch synthesis of gasoline and oil. A flow diagram and a heat chart of the latter.

3382. ———. [German Coals as a Starting Material for Refined Chemicals.] Brennstoff-u. Wärmewirt., vol. 19, 1937, pp. 17–25, 41–45; Chem. Abs., vol. 31, 1937, p. 4084.

Review of methods for converting coals to liquid hydrocarbons.

3383. ———. [Synthesis of Benzine by the Bindley Process.] Oel u. Kohle, vol. 13, 1937, pp. 350–353; British Chem. Abs., 1937, B, p. 750.

S content of the initial gas is reduced to 0.002 gm. per $m.^3$ by 1st removing the H_2S over Fe oxide, hydrogenating the organic S compounds over a $CuO–PbCrO_4$ catalyst, and finally removing the H_2S so produced by means of Fe oxide, followed by washing with aqueous $K_3Fe(CN)_6$. The synthesis itself is carried out at 200° per atm. in presence of a $Ni–Mn–Al_2O_3$–kieselguhr catalyst. The latter is agglomerated by mixing it with Et orthosilicate and exposing it to moist air before reduction. Ordinary water gas (CO, 42; H_2, 48%) may be used as the initial gas. The process is preferably carried out in stages, the hydrocarbons formed being removed after each stage. The course of the reaction may be represented by $9\ CO+18H_2=(CH_2)_9+9\ H_2O$.

3384. ———. [Oil Production From Coal. Its Technical and Economical Valuation From an Australian Viewpoint.] Brennstoff-u. Wärmewirt., vol. 20, 1938, pp. 87–92; Chem. Abs., vol. 32, 1938, p. 6835.

Discussion of the economics of coking, hydrogenation, and benzine synthesis.

3385. ———. [Treatment of Coal for the Production of Power Materials.] Ztschr. Ver. deut. Ing., vol. 82, 1938, pp. 129–138; Coal Carbonisation, vol. 4, 1938, p. 64; Chem. Abs., vol. 32, 1938, p. 3124.

Review of all the principal methods of coal processing for the production of fuels from coal. The methods that have been developed for the low-temperature carbonization of hard coals and brown coal are enumerated, and descriptions are given of the Lurgi internally heated ovens and the Borsig-Geissen rotary alloy-steel retorts. Particulars are given of the Bubiag-Didier, Koppers, Wintershall-Schmalfeldt, Pintsch-Hillebrand, Lurgi, Schmidt and Groh, and Demag gasification processes for the production of synthesis gas. Processes for the synthesis of motor fuels by hydrogenation vary according to whether the hydrocarbon is treated in the

gaseous, liquid, or solid phase. All the chief processes are described with flow diagrams and representative data. The paper concludes with notes on the processing of tar, the economics of the manufacture of motor fuels from coal, and a bibliography of 28 refs.

3386. ———. [Synthesis of Hydrocarbons From Water Gas.] Ztschr. Ver. deut. Ing., vol. 83, 1939, p. 906.

Review.

3387. ———. [Water-Gas Production With External Heating.] Gas- u. Wasserfach, vol. 84, 1941, pp. 509–513; Chem. Abs., vol. 36, 1942, p. 5334.

Water-gas reaction, being endothermic, requires a continuous supply of heat if it is to be maintained as a continuous process. Heat can be supplied in various ways, for example, continuous supply of O_2 in place of air, direct supply of superheated steam, and external heating of the generator. Processes involving an externally heated generator, for example, those of Heller, Herzberg and Bueb, are reviewed. The Didier-Bubiag process, in which an externally heated and continuous vertical retort is used, is described. In this the gas outlet is moved from the top of the retort to about halfway down. The raw, weakly or noncoking, coal before entering the retort passes through a drying chamber, which can also be adapted to submit the coal to a preliminary low-temperature carbonization. Superheated steam is introduced toward the bottom of the retort, the lowest section of which is not heated and serves to cool the issuing coke. The coal in passing down the retort is progressively carbonized in the zone above the gas outlet, and the carbonization gases must pass downward to reach the outlet; in doing so the tarry vapors are cracked. Water gas is produced in the lower half of the retort and passes upward to the same gas outlet. The operation is adjusted so that just enough coke leaves the retort to supply producer gas for external heating. Conditions can be varied to yield either a rich gas or synthesis gas. If lignite briquets are used, subjected to low-temperature carbonization in the pretreatment chamber, and the tarry vapors are led down through the top of the retort, C_6H_6 containing 16–25% of toluene can be recovered.

3388. ———. [Large-Scale Water-Gas Production for Chemical Synthesis.] Oel u. Kohle, vol. 38, 1942, pp. 589–601, 617–624, 685–690, 721–727, 749–765; Gas Times, vol. 44, 1945, p. 32; Gas Abs., Inst. Gas Technol., vol. 1, No. 7, 1945, p. 12 .

For the manufacture of NH_3, a synthesis gas containing H_2 and N_2 in the ratio 3 : 1 is required, while, for the production of MeOH and liquid fuels, a gas consisting of H_2 and CO in the ratio 2 : 1 is required. The production of synthesis gas of such required compositions has been achieved in Germany by 5 distinct systems of gasification processes. The method of supplying the required heat for the endothermic decomposition of steam by C has been chosen by the author as the basis of classification. (1) In the 1st class belong the gas generators, employing coke or brown coal as fuel, which operate with intermittent blast and make cycles, such as those built by the Bamag and Viag concerns. The Viag generators, however, combine this method of heating with the principle of recirculation. (2) The 2d group comprises those processes that employ O_2 for the internal supply of heat, which makes the operation continuous. The Winkler, Lurgi, and Thyssen-Galocsy processes belong in this class. (3) Among the processes using indirect heat transfer by recycling part of the produced gases that had been preheated to the required high temperature in intermittently operated regenerators, belong the Pintsch–Hillebrand, Koppers, and Wintershall–Schmalfeldt processes. (4) A group employing direct heat transfer by external heating comprises the Bubiag–Didier, Reiche Zeche, and Ahrens processes, although in the latter the principle of heat transfer by recirculation is combined with external heating. (5) The last class includes all other methods of heat transfer employed, such as heating of the reaction chamber by means of electricity as in the Hole and Stassano processes, the use of highly superheated steam in the Pattenhausen process, the use of molten salt bath proposed by Lichtenberger and Haiser. The gas produced by some of these methods needs further processing with steam, either to convert the excess CO into H_2, $CO+H_2O \rightarrow H_2+CO_2$, or to decompose the CH_4 into CO and H_2, as is done in the Wild, Gesent, Bamag, and Viag processes by means of a catalyst employed, which also removes the organic S compounds. In the Kuhlman, Linde, and Padovani processes, the same end is achieved by hot surfaces. For the removal of the excess CO_2 the alkazid process, pressure washing with water, or other processes have been used.

THENARD, A. *See* abs. **3389.**

3383. THENARD, P., AND THENARD, A. [Effect of Electricity on Mixtures of Marsh Gas and Carbon Dioxide and of Hydrogen and Carbon Monoxide.] Compt. rend., vol. 76, 1872, pp. 1049–1051; Jour. Chem. Soc., 1873, p. 864; Chem. Zentralb., 1873, p. 452.

In performing the same experiments as Brodie on the conversion of $CO+H_2$ by the electric current, it was found that the reaction goes farther than the production of CH_4 and that liquids of complex composition are obtained. Berthelot considers that they result from the condensation of CH_2O, which is the 1st product of the reaction between CO and H_2.

THIELE, E. W. *See* abs. **1366.**

3390. THIESSEN, G. Bituminous Coal. A Source of Gaseous and Liquid Fuels. Chem. Inds., vol. 38, 1936, pp. 349–353; Chem. Zentralb., 1936, II, p. 565; Chem. Abs., vol. 30, 1936, p. 3965.

Review of carbonization, high-pressure hydrogenation, and synthesis from CO and H_2.

THODOS, G. *See* abs. **1959.**

THOMAS, B. *See* abs. **3556.**

3391. THOMAS, B. W., AND SEYFRIED, W. D. Mass-Spectrometer Analyses of Oxygenated Compounds. Anal. Chem., vol. 21, No. 9, 1949, pp. 1022–1026.

By means of special techniques, mass spectrometric methods have been developed for the quantitative determination of individual oxygenated compounds containing 5 or less C atoms per mol. In mixtures containing 6 or less components the average accuracy is better than ±1% based on the total sample; for more complex mixtures, the accuracy is in the order of ±2% or less. H_2O in moderate concentrations has a negligible effect on the accuracy of the oxygenated compound determinations, and H_2O is determined with an average deviation of ±1%. A complete analysis of a 6-component mixture can be performed in about 2 hr., and only a few drops of sample are needed. Calibration data for 10 alcohols, 3 ketones, 6 aldehydes, 3 esters, 4 acids, and 2 ethers are presented.

3392. THOMAS, P. R., DOWN, L., AND LEVIN, H. Determination of Carbon Monoxide in Hydrocarbon Gases Containing Olefins. Anal. Chem., vol. 21, No. 12, 1949, pp. 1476–1480.

Studies of hydrocarbon synthesis and catalytic cracking make it necessary to determine CO in gases containing large amounts of olefins. All hydrocarbons except CH_4 are removed rapidly by condensation in liquid N_2 from which the uncondensed gases—CO, H_2, N_2, O_2 and CH_4—are removed by Toepler pump. Orsat apparatus is used to remove O_2 from this mixture and to determine CO. The major part of the CO is absorbed in acid cuprous chloride and the remainder in cuprous sulfate–2–naphthol. CO is determined in con-

centrations from 0.1–100% with an average error of less than 0.5% of the CO in the samples containing 10% CO. The accuracy is somewhat less for lower concentrations. The total time required for the determination is less than 1 hr.

THOMAS, R. W. *See* abs. **2489.**

THOMAS, V. *See* abs. **299, 300.**

3393. THOMAS, W. H., AND FARAGHER, W. F. Interrogation of Dr. C. H. N. Bensmann. BIOS Final Rept. 597, 4 pp.; PB 44,946.

In October 1945, an account was made of contacts with The Texas Co. and the events leading up to the appointment of the company as agent for the Fischer-Tropsch process in the United States.

THOMPSON, J. K. *See* abs. **1418.**

3394. THOMPSON, M. DEK. Specific-Heat Equations for Carbon Dioxide, Carbon Monoxide, Steam, Hydrogen and Oxygen, and the Free-Energy Equation for the Water-Gas Reaction. Trans. Electrochem. Soc., vol. 82, 1942, pp. 397–402; Chem. Abs., vol. 36, 1942, p. 6388.

Least-square solutions for the specific-heat equations of the above gases are worked out for the forms $C(p)=a+bT+cT^2$, $C(p)=a+bT+cT^{-2}$, and $C(p)=a+bT+cT^{-1/2}$, and the sums of the squares of the deviations of $C(p)$, Σ dev.^{2}, calculated by each equation, from the experimental values are compared. The equation giving the smallest Σ dev.^{2} being the best, it is found that, for the temperature range 300°–3,000° or 3,500° K., the T^2 equation is the best for CO and steam, the T^{-2} equation is the best for H_2, and the $T^{-1/2}$ equation is the best for CO_2 and for O_2. The equation for $\Delta G°$ of the water-gas reaction is then computed, and the values of log K computed by this equation are compared with the values obtained directly from spectroscopic observations.

THOMPSON, O. F. *See* abs. **451, 452, 453.**

3395. THOMPSON, S. O., TURKEVICH, J. AND IRSA, A. P. Reaction of Deuterium With Hydrocarbons Over a Cobalt–Thoria Fischer-Tropsch Catalyst. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 5213–5215.

H exchange reactions were observed between D_2 and C_2H_6, C_3H_8, C_4H_{10} and iso-C_4H_{10} when a mixture of 6 vol. of D_2 and 1 vol. of each of the hydrocarbons was passed over a Fischer-Tropsch Co catalyst under conditions of temperature and flow rate similar to those for hydrocarbon synthesis. The exchanged products were found to be extremely deuterated and the mole % of hydrocarbon molecules undergoing exchange was $< 10\%$ in the case of the ethanes and propanes, 45% for n-butane and 51% for isobutane. Cracking of the hydrocarbon gases to produce deuterated CH_4 was also observed. The exchange reaction of CH_4 and D_2 and CD_4 and CH_4 was also studied.

3395a. ———. Study of the Fischer-Tropsch Reaction Using Deuterium Gas. Jour. Phys. Chem., vol. 56, 1952, pp. 243–250.

Description is given of an apparatus for the production of deuterocarbons from deuterium and CO. The various deuterocarbons and waxes are examined for their mass spectrum patterns and infrared spectra.

3396. THOMSON, G. H. Hydrocarbon Synthesis. British Coal Utilisation Research Assoc. Bull., vol. 8, 1944, pp. 191–201; Chem. Abs., vol. 38, 1944, p. 6513.

Work is reviewed on the Fischer-Tropsch synthesis and the preparation and properties of the secondary products, motor spirit, diesel oil, lubricating oils, and paraffin wax. 111 refs.

3397. THOMSON, G. H., AND GIVEN, P. H. Hydrocarbon Synthesis. Butterworth's Sci. Publication, "Progress in Coal Science", London, 1950, pp. 332–352; Fuel Abs., vol. 8, No. 6, 1950, abs. 4602.

Synthesis processes for production of motor fuel and aliphatic compounds for the chemical industry are reviewed. Production of synthesis gas and S removal; catalysts, their life, regeneration, and recovery; plant design and operation; primary products; and effect of pressure and other operating variables are outlined. Secondary products include high-grade motor fuel, lubricants, synthetic soaps and edible fats, sulfate detergents, and alcohols. Related processes described include isosynthesis, Oxo synthesis, use of Ru catalysts, and oxidation of hard wax. Theories of catalyst structure and reaction mechanism are given. Recent developments include the modified Fischer-Tropsch process, use of fluidized bed, Fe catalysts, and lower H_2: CO ratios giving modified products. All these plus cheaper synthesis gas production are necessary before the process can become a commercial proposition.

3398. THONON, C., AND JUNGERS, J. C. [Dehydrogenation of Secondary Alcohols in the Liquid Phase With Nickel as a Catalyst.] Bull. soc. chim. Belg., vol. 58, 1949, pp. 331–349; Chem. Abs., vol. 44, 1950, p. 3876.

Ketone produced during the dehydrogenation of secondary alcohols has a strong inhibitory action on the further reaction. It has a markedly higher adsorption coefficient than the alcohol. The factors influencing the ratio of the adsorption coefficients of the ketone and alcohol are examined; for example, the temperature, the solvent, and the catalyst. 2-Propanol and 2-butanol are dehydrogenated under various conditions. The temperature increases the rate of reaction and changes the ratio in favor of the alcohol. No obvious influence of the solvent on the ratio has been observed. Different samples of Ni and Cu are used as catalysts. Cu is less active than Ni, but it changes the ratio slightly in favor of the alcohol.

3399. THOREN, F. [Activity and Temperature Relationships for Nickel Catalysts. I.] Ztschr. anorg. Chem., vol. 163, 1927, pp. 367–395; Chem. Abs., vol. 21, 1927, p. 3804.

Activities of Ni catalysts prepared in various ways were measured by a static method. The reactions used were: $C_2H_4+H_2\rightarrow C_2H_6$; $C_6H_6+3H_2\rightarrow C_6H_{12}$; $O_2+2H_2\rightarrow 2H_2O$. The activity of the catalysts increased stepwise with increase in temperature. The mean values for the temperatures at which marked increase in activity was evidenced were 9.7°, 40.1°, 60.2°, 80.7°, 100.3°, 119.4°, 134.7°, 170.0°. The actual % increase in activity at the various activation temperatures was not reproducible. The activation temperatures were almost the same for all reactions and for different Ni catalysts. The activation of the H_2 is considered to be the cause of the phenomenon.

3400. ———. [Activity and Temperature Relationships for Nickel Catalysts. II.] Ztschr. anorg. Chem., vol. 165, 1927, pp. 171–191; Chem. Abs., vol. 21, 1927, p. 3804.

Previously reported experiments on the hydration of C_2H_4, C_6H_6, and O_2 using the static method, indicated a stepwise increase in activity of Ni catalysts with increase in temperature. Further experiments on the hydration of C_2H_4, using the dynamic method and a single catalyst, confirmed the earlier results. The average temperatures at which the irregular increases in activity occurred, appeared to be —18°, 10°, 41°, 61°, 81°, 100°, 120°, 139°, and 163°. The results were not reproducible with different samples of the same catalyst.

3401. THORNTON, D. P. Petrochemical Industry in the Southwest Builds for Growing Peacetime Markets. Nat. Petrol. News, Tech. Sec., vol. 38, No. 1, 1946, pp. R3–R8.

Among the many plants mentioned as producing and preparing to produce chemicals from petroleum is

Carthage Hydrocol, Inc., owned by several oil companies and Hydrocarbon Research, Inc., which is planning the construction and operation of a $15,000,000 Fischer-Tropsch plant in the Panola gas fields of Panola Co., east Texas. It is reported that this plant will produce 5,000 bbl. per day of +80 octane gasoline, 1,000 bbl. per day of diesel fuel, and 200,000 lb. per day of crude alcohols (MeOH and EtOH) and acetone. It is stated that gasoline can be made for $0.05 per 1,000 cu. ft. gas in competition with conventionally produced gasoline from $1.00 crude. Study of the best features of the Fischer-Tropsch process in German plants plus research in this country will make this process competitive with conventional refinery production of gasoline. Byproducts can be converted relatively cheaply into chemicals and thus make Fischer-Tropsch gasoline and gas oils still more competitive with similar products from petroleum.

3402. ———. Japanese Research on Fuels. Petrol. Processing, vol. 2, No. 11, 1947, pp. 815–820.

Summary of the principal sources of fuels and lubricants and of the research work performed by the Japanese in obtaining supplies for war activities. The data are taken from the reports of the United States Naval Technical Mission to Japan. The peak year of the Seven-Year Plan to achieve a yearly production of about 1,000,000 kl. (6,300,000 bbl.) each of synthetic gasoline and fuel oil by 1943 occurred in 1944 when 114,000 kl. were produced, divided as follows: Hydrogenation 700 kl., Fischer-Tropsch 17,800 kl., low-temperature carbonization 95,400 kl.

3403. ———. Higher Propane Yields in Gasoline Plants by Hypersorption Process. Petrol. Processing, vol. 3, No. 11, 1948, pp. 1052–1054.

Summary of a paper by H. Kehde at the California Natural Gasoline Association meeting. Compare abs. **1070** and **1708.** Basically the process depends on the adsorption of selected components of the gas by activated charcoal, 10–40 mesh, flowing continuously from the top of the hypersorption tower under controlled flow. The operation of a hypothetical plant is described. Investment and operating cost data for a plant recovering 98.5% propane are given. With a capital investment of $542,000 and total operating expense, including amortization in 5 yr., of $355,100, the cost per lb. of propane with a yearly production of 18.1 million gal. is $0.0153. At a market value of $0.068 per gal. for the propane, a payout time of 0.61 yr. before taxes is obtained.

———. *See* abs. **1207.**

3404. THRING, M. W. Underground Gasification and British Coal Measures. Inst. Fuel, Wartime Bull., February 1944, pp. 103–104; Chem Abs., vol. 38, 1944, p. 2471.

Review of recent Russian methods of underground gasification, including the chamber, sloping seam, gallery, and radial methods. The sloping seam method, applicable to seams inclined as much as 70°, appears most practical. Gas produced varies 115–210 B. t. u. and is said to contain, during the suction phase, H_2 and CO in the proper proportions for hydrocarbon synthesis.

TIBIRICA, J. *See* abs. **2240.**

TIKHONOVA, Z. T. *See* abs. **1789.**

3405. TIMASHER, A. S. [Reduction of Complex Chemical Compounds in Relation to Their Dissociation.] Metallurg., vol. 14, 1939, No. 3, pp. 19–28; Jour .Iron Steel Inst. (London), vol. 140, 1939, A, p. 257.

Reduction of ferric, ferroso-ferric, and ferrous oxides with CO at 500° was studied in an apparatus in which a stream of CO was passed over the heated oxides, provision being made for continuous and automatic recording of the temperature and the CO_2 content of the exit gases. Preliminary tests had shown that at the temperatures used, Fe had a negligible catalytic effect on the reaction $2\ CO=CO_2+C$. The reduction of the ferric oxide took place in 2 stages, the 1st being irreversible and leading to the formation of 100% CO_2 ($3\ Fe_2O_3+CO=2\ Fe_3O_4+CO_2$). The 2d stage corresponds to the reduction of the ferroso-ferric oxide with formation of a gas mixture of 47% CO_2 and 53% CO. The ferroso-ferric oxide is reduced directly to metallic Fe ($Fe_3O_4+4\ CO=3\ Fe+4\ CO_2$). Under the experimental conditions the reduction of the ferrous oxide took place in 2 ways, namely, $FeO+CO=Fe+CO_2$ and by a complex reaction, the net result of which is represented by the reaction $4\ FeO=Fe_3O_4+Fe$. The whole of the ferrous oxide is decomposed at the beginning of the reduction, which afterwards consists of the reduction of the ferrosoferric oxide.

3406. TIMELL, T. [Liquid Fuels From Synthesis Gas.] Tek. Tid., vol. 46, 1948, pp. 813–818; Chem. Zentralb., No. 3, 1949, p. E234.

Review of the Fischer-Tropsch process for producing hydrocarbons from CO and H_2 and of the production of synthesis gas by the method developed in the United States by the oxidation of natural gas with O_2 under pressure. Natural gas preheated to about 650° is oxidized at 20 atm. and 1,300° according to the equation $CH_4+\frac{1}{2}\ O_2=CO+2H_2$. The CO_2 formed is washed out and a part of the residual gas is converted at 300°–400° over Fe oxide into the desired ratio of $CO:H_2$. The synthesis itself is carried out at 17–35 atm. and about 300° in presence of finely pulverized Fe catalysts suspended in the synthesis gas and steam. From 3,000,000 $m.^3$ of natural gas there are produced daily 700 tons of gasoline (octane No. 80), 150 of light oil, and 130–160 of byproducts, such as alcohols, ketones, aldehydes, and carboxylic acids. The production cost per l. of liquid hydrocarbons is 5 öre, as compared with 19 by the German process. A simplified process for synthesis from coal is under development in the United States.

3407. TINGEY, H. C., AND HINSHELWOOD, C. N. Catalytic Decomposition of Formic Acid on Surfaces of Platinum and Silver. Jour. Chem. Soc., vol. 121, 1922, pp. 1668–1676; Chem. Abs., vol. 16, 1922, p. 4115.

TITZENTHALER, E. *See* abs. **1836, 2692.**

3408. TIXIER, C. [Gasification and Application in the Chemical and Gas Industry.] Jour. usines gaz, vol. 73, 1949, pp. 186–189; Chem. Zentralb., 1950, I, p. 472.

Basic equations for C gasification. Its application to the production of synthetic NH_3, the Bergius pressure hydrogenation, and the synthesis of oils and alcohols by the Fischer–Tropsch process is shown. The importance of gasification to modern processes for the production of high calorie gas is considered also.

TOJO, T. *See* abs. **1903.**

TOMILOV, V. I. *See* abs. **2709.**

TOMITA, N. *See* abs. **2514.**

3409. TOMPKINS, F. C. Adsorption Isotherms for Nonuniform Surfaces. Trans. Faraday Soc., vol. 46, 1950, pp. 580–586; Chem. Abs., vol. 45, 1951, p. 18.

With certain restrictions regarding the magnitude of certain entropy changes, 4 well-known isotherms are deduced from variation of heat of adsorption with coverage. If the variation of net heat of adsorption with coverage is known either from theoretical calculations or experimentally from calorimetric measurements, the isotherm can be reasonalby well characterized. If the concept of nonuniformity of surfaces is accepted, then the interpretation of transformations of state in adsorbed films on solids must be reconsidered.

3410. ———. Physical Adsorption on Nonuniform Surfaces. Trans. Faraday Soc., vol. 46, 1950, pp. 569—580; Chem. Abs., vol. 45, 1951, p. 18.

Nonuniformity of an adsorbent surface affects the isotherm obtained in physical adsorption both for localized and nonlocalized monolayers. Subject to the approximation that the internal partition function of the adsorbed molecule is independent of the adsorption potential of each site, it is shown that the log pressure versus log amount adsorbed is a linear plot, whether the adsorbed film is regarded as a polyphase or a monophase system.

———. *See* abs. **636.**

3411. TONGUE, H. Design and Construction of High-Pressure Chemical Plant. Chapman & Hall, London, 1934, 420 pp.

3412. ———. Practical Manual of Chemical Engineering. D. Van Nostrand Co., New York, 1939, pp. 178–241.

Design and construction of pressure vessels for the chemical industry are included.

TOPLEY, B. *See* abs. **1422, 1423.**

TOPP, N. E. *See* abs. **555.**

3413. TORPOV, N. A., AND BORISENKO, A. I. [Solid Solutions in the System NiO-Fe_2O_3.] Doklady Akad. Nauk. S. S. S. R., vol. 63, 1948, pp. 705–708; Chem. Abs., vol. 43, 1949, p. 4552.

(1) Thermograms of Ni_2O_3 show 3 endothermal effects, the 1st 2, at 180° and 340°, corresponding to loss of hygroscopic and crystal H_2O, respectively, the 3d, at 815°, to $Ni_2O_3 \rightarrow 2\ NiO + \frac{1}{2}\ O_2$. On account of this dissociation, it is irrational to use Ni_2O_3 to produce Ni ferrite. (2) Firing $NiO + Fe_2O_3$ mixtures prepared by drying the precipitated hydrates and pressing under 3,000 kg. per $cm.^2$, at high temperatures is accompanied by deoxidation of the Fe_2O_3; thus, with the molecular ratios NiO: Fe_2O_3=2:3, 1:3, and 1:5, the amount of FeO after 3.5 hr. firing at 1,100°, 1,200°, 1,300°, 1,500°, was, respectively, 0, 0.70, 1.75, and 3.18; 0, 0.66, 2.67, 5.46; 0.08, 0.86, 4.32, 5.88%. (3) Products obtained by 40 hr. firing of $NiO + Fe_2O_3$ mixtures at 1,100°±10° showed, in petrographic examination, 1-phase structure only at the initial molecular ratios 1:1 and 2:3; at the latter ratio, crystallization of the ferrite is somewhat less distinct. With the molecular ratios 3:2, 2:1, and 3:1, product shows 2 phases, one of which is identified as Ni ferrite, the other NiO. Products of mixtures 1:2, 2:5, and 1:3 are equally 2-phase. (4) Debyegrams show disappearance of the Fe_2O_3 lines in the 2:1 product, and also of NiO lines in the 1:1 and 2:3 products. Combination of the results shows that the 3:1, 2:1, and 3:2 products are mixtures of Ni ferrite and NiO, 1:1 is the pure ferrite, 2:3 is a solid solution of Fe_2O_3 in Ni ferrite, whereas, 1:2, 2:5, 1:3, and 1:4 are all mixtures of that solid solution and Fe_2O_3.

3414. TOROPOV, N. A., PORAL-KOSHITS, E. A., AND BORISENKO, A. I. [Solid Solutions in the System CoO–Fe_2O_3.] Doklady Akad. Nauk. S. S. S. R., vol. 66, 1949, pp. 905–908; Chem. Abs., vol. 43, 1949, p. 7314.

In an equimolecular mixture of the precipitated hydroxides, ferritization is complete on 40 hr. heating at 1,100° of pellets dried at 120° and pressed under 3,000 kg. per $cm.^2$ The thermal dissociation $6\ Fe_2O_3 \rightarrow 4\ Fe_3O_4 + O_2$, in mixtures with CoO, is less intense than in mixtures with NiO. In the presence of excess CoO, the product obtained is porous, and contains, on microscopic examination, 2 phases, 1 dark gray, the other dark yellow. The amount of the former decreases with decreasing CoO. With increasing Fe_2O_3 content, the color of the crystals seen in specimens etched with HNO_3 changes from dark yellow in the equimolecular composition to yellow for $2\ CoO + 5\ Fe_2O_3$. With further increasing excess of Fe_2O_3, a new, light phase appears along with the yellow crystals, attaining 45–50% in $CoO + 6Fe_2O_3$. By X-ray examination, free Fe_2O_3 is present in samples of the composition $CoO + 3Fe_2O_3$ and with higher Fe_2O_3 contents. The pure spinel structure of $CoO + Fe_2O_3$ persists up to Fe_2O_3, contents corresponding to $2\ CoO + 5\ Fe_2O_3$. With excess CoO, from $3\ CoO + 2\ Fe_2O_3$ upward, CoO lines appear along with those of the spinel $CoO \cdot Fe_2O_3$. The latter is, consequently, the only compound occurring in this system. Fe_2O_3 is soluble in this ferrite to the extent of 1.5 mol. per mol. ferrite at 1,100°. CoO is not soluble in the ferrite.

3415. TORREY, P. D. Possibilities for Production of Liquid Fuels From Shale, Natural Gas, and Coal. I. Petrol. Eng., Refining and Gas Processing Sec., vol. 22, No. 3, 1950, pp. A39–A44.

General review of present and future developments in the building of a synthetic liquid fuels industry. The long-range objective is considered, rather than immediate prospects.

3416. ———. Possibilities for Production of Liquid Fuels From Shale, Natural Gas, and Coal. II. Petrol. Eng., Refining and Gas Processing sec., vol. 22, No. 4, 1950, pp. A45–A48.

Discussion of coal reserves and the costs and possible production of liquid fuels from coal in the United States.

TORREY, R. M. *See* abs. **3227.**

TOSHIMA, S. *See* abs. **1910.**

3417. TOTZEK, F. Communication to the Power Commission, June 12, 1942. TOM Reel 238; Bureau of Mines transl. T–489, 1950, 20 pp.

Report on the complete gasification of powdered coal by the Koppers-Totzek process operating under fluidized conditions with the help of O_2 and steam. Experiments are described using both powdered lignite and bituminous coal for the production of synthesis gas. The results were particularly favorable. Using lignite, a gas of the following composition was obtained: CO_2, 14; CO, 35; H_2, 50; N_2, 1%; $CO + H_2$ concentration 85%. Gas yield was 1.9 $m.^3$ per kg. of raw coal corresponding to an ideal gas yield of 1.62 N $m.^3$ O_2 consumption per kg. of coal was 1.304 N $m.^3$ corresponding to 0.16 N $m.^3$ per N $m.^3$ synthesis gas or 0.188 N $m.^3$ per N $m.^3$ ideal gas. The computed production cost of the synthesis gas was 1.32 pfg. per N $m.^3$ With bituminous coal, the gas had the composition: CO_2, 11; CO, 54; H_2, 34; N_2, 1%, $CO + H_2$ concentration 88%. Gas yield was 2.1 N $m.^3$ per kg. coal, corresponding to an ideal gas yield of 1.85 N $m.^3$ O_2 consumption amounted to 0.525 N $m.^3$, corresponding to 0.25 N $m.^3$ per N $m.^3$ of synthesis gas or 0.284 N $m.^3$ per N $m.^3$ ideal gas. The cost was 1.72 pfg. per N $m.^3$ synthesis gas. Similar calculations are made for the production of fuel gas from lignite char, lignite, and bituminous coal but without the use of O_2.

3418. TOWNEND, D. T. A. Gasification of Coal. Gas World, vol. 127, 1947, pp. 79, 406–418; Chem. Age, vol. 57, 1947, pp. 357–360, 399–400.

Paper presented at the St. Andrews symposium. An account is given of modern coal gasification developments with special attention to the Lurgi process as being typical of a pressure-operated process. Gasification uses internal heat normally by burning part of the charge with air or O_2. In the production of water gas, it is possible to combine the flow and make runs by using steam mixed with O_2 instead of air. Two main reactions may occur according to the temperature:

(*a*) $C + H_2O = CO + H_2 - 29$ cal.
(*b*) $C + 2\ H_2O = CO_2 + 2\ H_2 - 19$ cal.

Reaction (*a*) occurs at 1,100° and (*b*) at 600°–700°. The temperature may be regulated by the rate of steam

flow. Working at a pressure of 20 atm. increases the amount of CH_4, which is formed by a direct hydrogenation of the coal and not by synthesis, and this gives a higher calorific value to the gas; it also enables any CO_2 to be removed by scrubbing with H_2O. Such treatment gives a uniform gas independent of the type of coal used. The Lurgi process goes best with lignitic coal. The Lurgi process may be operated to produce synthesis gas for use in the Fischer-Tropsch reaction.

3419. ———. Recent Developments in Gasification. Gas Times, vol. 52, 1947, pp. 416–418; vol. 53, 1947, pp. 33–34, 37, 38.

William Young Memorial Lecture discusses the 2 main methods of producing gaseous fuels—carbonization and gasification. In the latter connection the discussion is confined mainly to the use of O_2=steam blasts, the typical processes being the Lurgi pressure process, the Winkler boiling bed at atmospheric pressure, and the Leuna-type and Thyssen-Galocsy slagging producers operating at high temperatures with removal of the ash as slag. Some reference also is made to the Pintsch-Hillebrand and the Bubiag-Didier processes, the Imperial Chemical Industries fluidized gas generator, and the Koppers powdered-fuel gasification process.

TRAEGER, B. *See* abs. **2693.**

3420. TRAENCKNER, K. [Gas Sources for the Present and Future Supply of Germany.] Gas- u. Wasserfach, vol. 82, 1939, pp. 590–595; Chem. Abs., vol. 33, 1939, p. 9592.

Various suggestions as to methods of gas manufacture are reviewed after giving data as to present supply sources. The % of gas from brown coal has increased very little in the last 10 yr. in spite of much experimental work; the most successful plant is that at Kassel. Disadvantages of brown-coal carbonization processes are briefly reviewed, as well as the important features of a number of gasification processes. One of the more promising of these processes is that of gasification with O_2 under pressure. Results are given for 3 brown coals, showing gas and byproduct yields and net costs. This process also can use bituminous coals, which are noncaking when heated under pressure. The flexibility of this process is stressed, as well as the possibility of combining gas manufacture and hydrogenation or synthesis. In such cases, the rich residual gases can be used as an enriching medium for the manufactured gas.

3421. TRAMBOUZE, Y. [Chemical Changes in Fischer Catalysts During Their Preparation.] Compt. rend., vol. 227, 1948, pp. 971–972; Chem. Abs., vol. 43, 1949, p. 2853.

Catalysts were prepared by several methods, and the chemical nature of the Ni was determined by extraction with NH_4OH, with HNO_3 and by fusion. Before reduction, Ni generally is found in 3 forms: The free oxide or combined with the CO_3 ion, hydroaluminate, and hydrosilicate of Ni.

3422. ———. [Study of Fischer Catalysts by X-ray Diffraction.] Compt. rend., vol. 228, 1949, pp. 1432–1433; Chem. Abs., vol. 32, 1949, p. 7313.

Further study has been made of the Fischer Ni catalyst in an attempt to confirm the presence of both a hydroaluminate and a hydrosilicate of Ni. It is confirmed that the former coexists with the hydrosilicate at 450°.

3423. ———. [Chemical Changes in Fischer Catalysts During Their Preparation.] Jour. chim. phys., vol. 47, 1950, pp. 258–261; Chem. Abs., vol. 44, 1950, p. 7638.

Ni, Al, Mn, kieselguhr catalysts were prepared by the following methods, and the % of the Ni removed by ammoniacal treatment, extraction with HNO_3, and with HCl, respectively, are: Precipitation at low temperature, 100, —, —; boiling of the precipitate, 63, 37, —; desorption under vacuum at 150° to constant weight, 63, 37, —; heating for 2 hr. at 220° in N_2, 59, 13, 28; heating at 320° to constant weight in N_2, 18, 46, 36; heating at 450° to constant weight in N_2, 16, 40, 44; heating for 48 hr. at 220° in N_2, 33, 59, 8; heating at 450° after the preceding treatment, 20.5, 59.5, 20. An X-ray diffraction study of these catalysts is summarized.

3424. ———. [Relation of the Chemical Composition and Structure of Fischer Catalysts to Their Synthesis Activity.] Thesis, Univ. Lyon, France, 1950, 87 pp.

Previous discussions on the origin, structure, and reaction mechanism of the Fischer synthesis catalysts are reviewed. The paper consists of 2 parts. The 1st discusses the chemical changes that occur in the development of Ni base catalysts. The presence of the oxide and hydroxide of Ni, basic carbonates and hydroaluminate and -silicate of Ni was detected. These were measured by a polarographic method. The relative proportions of these various types of compounds can be changed markedly by changing the conditions of the thermal treatment preceding the reduction. For example, reheating for 48 hr. at 220° in a stream of N_2 strongly diminishes the content of silicate and may even prevent its formation totally. The 2d part discusses the effect of various chemical compositions on the catalytic activity of Fischer-Tropsch catalysts. The specific role of each individual compound mentioned above, and particularly those of Ni hydrosilicate and Ni hydroaluminate, are discussed, the latter being found particularly important.

3425. ———. [Study of Fischer Nickel Catalysts by Differential Thermal Analysis.] Compt. rend., vol. 230, 1950, pp. 1169–1171; Chem. Abs., vol. 44, 1950, p. 7132.

Ni hydroxide and the gel formed by precipitating Ni with K_2CO_3 are heated to 500° for 1.5 hr. Both show the dehydration of the hydroxide at 360°–380° by a strong endothermic reaction; the second also shows the loss of adsorbed H_2O at 100° and the decomposition of the basic carbonates into CO_2, H_2O, and NiO at 220°–240°. Four other studies, one with a 1:1 mixture of kieselguhr and Ni hydroxide heated slowly, the other with catalysts heated variously to produce a silicate content of 15%, 8% and 0%, do not show the dehydration curve but do show the carbonate decomposition and, in the pertinent cases, another reaction at 400°, presumably hydrosilicate formation. When the contact mass is heated for a long time at 220°, the total decomposition of the basic carbonates and complete dehydration of the hydroxide make further combination impossible. A close relation between the precipitation conditions and the activity of a Fischer catalyst can now be established.

3426. TRAMBOUZE, Y., AND PERRIN, M. [The Effect of Preheating During the Course of Thermal Reduction of Nickel Catalysts on the Yield in the Fischer Synthesis.] Compt. rend., vol. 228, 1949, pp. 837–839; Chem. Abs., vol. 32, 1949, p. 8831.

It is clear that preheating clearly improved the activity of the 2 catalysts studied, the yield of hydrocarbons being tripled in the 1st case and doubled in the 2d. The % of reagents consumed is likewise maintained at a higher rate for a longer period. Furthermore, the active life of the catalyst is prolonged before poisoning takes place. It is established also that preheating not only raises the activity of the catalyst, which ordinarily is only medium, but also makes it superior to that of all catalysts not preheated. All these advantages result evidently from modifications occurring during the preheating. This is being investigated.

3427. ———. [Influence of the State of Combination of the Constituents of Nickel Catalysts on Their Activity in the Fischer Synthesis.] Compt. rend., vol. 228, 1949, pp. 1015–1017.

Ratio of uncombined Ni to that present as the hydroaluminate is a determining factor in the activity of the Fischer synthesis, whereas the presence of the hydrosilicate is unfavorable to this activity. On the other hand, the more Ni there is combined in forms susceptible of easy reduction at 450°, oxides, carbonates, aluminate, the less is the hydrogenating activity. It is logical to admit that each compound of Ni put to use exerts its catalytic activity in a given direction, since it possesses a crystalline structure favorable to such a reactive process at the interface.

3428. ———. Effect of the Chemical Composition of Fischer Catalysts and Their Constituents on the Synthesis Activity. Jour. Chem. Phys., vol. 47, 1950, pp. 474–482; Chem. Abs., vol. 44, 1950, p. 9783.

Ni–Al_2O_3–kieselguhr catalyst was shown to contain Ni aluminate and Ni silicate after being heat-treated to 450°. The aluminate is active in synthesizing higher hydrocarbons; the silicate forms CH_4 primarily. The distance between the Ni atoms in these 2 compounds is believed to be the factor responsible for the specificity of their catalytic properties.

3429. TRAMM, —. [Manufacture of Ethyl Benzene.] FIAT Reel K24, frames 3,127–3,130, Oct. 23, 1935; PB 70,215. TOM Reel 291.

Residue gas of the Fischer synthesis, the refuse gases of the gas-oil compression and the gases obtained in the cracking of gasolines are named as sources of ethane for manufacturing ethyl benzene. The % of ethane obtained and the cost for 1 ton of ethyl benzene are calculated.

3430. ———. [Plan of Pressure-Water Gas-Circulating Synthesis and the Low-Pressure Synthesis.] FIAT Reel K24, frames 3,069–3,076, Nov. 11, 1940.

Explains the scheme of the 2 types of synthesis in detail. The output of the obtained products is calculated. Two flowsheets.

3431. TRAMM, —., AND CLAR, —. [Preparation of Oils From Primary Products of the Gasoline Pressure Synthesis.] FIAT Reel K29, frames 6,634–6,701, 1940–1941; PB 70,218; TOM Reel 296.

Preparation of lubricating oils from gasolines of the pressure synthesis is described extensively. Primary materials are gasolines, which have been prepared partly by Co and partly by Fe catalysts. In any case, a preliminary treatment of the gasolines is necessary. The best way is to conduct the gasoline vapor through hot concentrated phosphoric acid with following neutralization. 26 tables, 3 graphs.

3432. TRAMM, H. [Gas Reactions in the Heavy-Chemical Industry.] Rundschau deut. Tech., vol. 18, No. No. 23, 1938, p. 3; Chem. Abs., vol. 32, 1938, p. 6809.

Reviews modern methods for the synthesis of technical products with the help of catalytic gas reactions, using especially H_2; CO, N_2, O_2, C_2H_2, C_4H_6, C_2H_4, C_3H_6 and C_4H_8. Illustrations.

3432a. ———. [Development of the Fischer-Tropsch Synthesis in Germany.] Chem.-Ing.-Tech., vol. 24, 1952, pp. 181–182; Chem. Abs., vol. 46, 1952, p. 6,361.

Bibliographical treatise in memory of F. Martin.

3432b. ———. [Industrial and Economic Possibilities of Carbon Monoxide Hydrogenation.] Chem.-Ing.-Tech., vol. 24, 1952, pp. 237–247; Bureau of Mines Transl. K–34, 1952.

Recent developments of the Fischer-Tropsch process with fixed bed catalysts are presented. The report is limited to the work done by the Ruhrchemie-Lurgi partnership. Great improvements in yield and quality of products and in gas-synthesis plant design have resulted from the development of high-activity catalysts and from the solution of important problems in reaction kinetics and heat transfer inside the reactors. As a result, the economic prospects of the process appear favorable for operation under German conditions. American prospects are discussed. The production of synthetic lubricants from the synthesis products is discussed in detail.

3432c. ———. [Technique of Carbon Monoxide Hydrogenation.] Brenntoff-Chem., vol. 33, 1952, pp. 21–30; Erdöl u. Kohle, vol. 5, 1952, pp. 10–17; Chem. Abs., vol. 46, 1952, p. 3,731.

Various types of converters used for hydrocarbon synthesis are illustrated and described. A graphic comparison shows the great improvement due to the modern high-capacity Fe catalyst as compared with the older Co catalyst. A graphic comparison of the total cost of gas manufacture by the blue-gas process with and without O_2 and with the producer-gas process, indicates that the water gas without the use of O_2 is the cheapest. For maximum gas utilization (96–97% conversion with low CH_4 formation) multiple-step conversion is required. Physicochemical investigations show that the gas for synthesis purposes should have a low CO_2 and H_2O content, but that N_2 is not as objectionable. CO_2 is chemisorbed on the catalyst but N_2 is only physically absorbed and is readily replaced. The undesirable effect of H_2O and CO_2 is shown graphically. A wide variety of products can be made by this process, ranging from gasoline to heavy wax, and including alcohols and their derivatives, solvents, and wetting agents. This wide range of products makes the process economically attractive in many countries.

———. *See* abs. **2591.**

TRAPNELL, B. M. W. *See* abs. **2820.**

3433. TRAUTZ, M., AND BADSTÜBNER, W. [Vapor Pressure and Heat of Vaporization of Iron Pentacarbonyl.] Ztschr. Elektrochem., vol. 35, 1929, pp. 799–802; Chem. Abs., vol. 24, 1930, p. 3690.

Vapor pressure of $Fe(CO)_5$ was measured 47.56°–104.26°, by means of the apparatus of Trautz, Baisch, and Dechend. Calculations of the heat of vaporization, by the Clausius-Clapeyron equation, showed that it gradually decreased from 9.65 kcal. at 23.78° to 8.79 kcal. at 98.98°. From the pressures at 0° and 104.2°, a value of 9.38 kcal. is obtained—a value much higher than that of Dewar and Jones (Proc. Roy. Soc., vol. 76, A, 1905, pp. 558–577). The lower values corresponding with the higher temperatures are attributed to the presence of $Fe_2(CO)_9$ dissolved in $Fe(CO)_5$, reducing its vapor pressure and raising its boiling point.

3434. TRAVERS, A. [Liquid-Fuel Problem and Proposed Solutions.] Chim. et ind., vol. 13, 1925, pp. 373–382, 722–730; Chem. Abs., vol. 19, 1925, p. 2398.

Discussion of the nature and distribution of petroleum, the processes of production of motor spirits from heavy oils or coal, cracking, berginization, synthesis from gaseous C compounds, and the situation in France.

3435. ———. [Methods of Increasing the Yield of Gasoline From Crude Petroleum. Substitute for Gasoline.] Rev. ind. minerâle, vol. 15, No. 353, 1935, pp. 403–428; Glückauf, vol. 71, 1935, pp. 1277–1280; Chem. Abs., vol. 29, 1935, p. 8304.

Nature of detrimental secondary reactions in the synthesis of MeOH from CO and H_2 is discussed together with the requirements of various catalysts. The energy consumption is about 1.8 kw.-hr. per kg. of pure MeOH. Theoretically, it is possible to form synthetic hydrocarbons representing 75–80% of the calorific value of water gas.

3436. TRAVERS, A., AND DIEBOLD, R. [Decomposition of Pure Cementite by Acids.] Compt. rend., vol. 205, 1937, pp. 916–918; Chem. Abs., vol. 32, 1938, p. 895.

Large proportion, sometimes 78%, of C from cementite is liberated in the free state, while of the hydrocarbons evolved, paraffins (CH_4, C_2H_6) form only 3–4%, the rest being olefins (C_3H_6 sometimes 50%). It is suggested, therefore, that cementite is $(Fe_3C)_n$ with n not less than 3, and that the linkage: C: C: is present, and that the H replacing the Fe on solution does not produce more than a small amount of saturated hydrocarbons on account of the absence of any catalyst. This view is shown to be consonant with several reactions and to explain the impossibility of determining $(Fe_3C)_n$ by selective solution of Fe. The C separated is remarkably absorbent.

3437. ———. [Isolation of Pure Cementite by Acid Attack of Ferrous Materials and Some of Its Physical Properties.]. Compt. rend., vol. 205, 1937, pp. 797–799; Chem. Abs., vol. 32, 1938, p. 895.

Pure cementite, Fe_3C, was isolated from a white cast Fe (C, 3.4%; Si, 0.3; Mn, trace) by anodic attack in an acid medium or by simple acid (AcOH) attack (abs. **89**) and separated from C by treatment with C_2HCl_3 (d. 1.47), washing with EtOH and Et_2O and drying in N_2. Thus obtained, it forms fine grains, greasy to the touch, Curie point 210°. The electrolytic potential relative to the calomel electrode (saturated KCl) is —0.3200 for *p*H 2.3, —0.500 for *p*H 7.3. The potential of the couple Fe_3C–Fe is 0.230 at 18° in a neutral medium, but increases if the *p*H increases beyond 7.5.

3438. TREIBSTOFFWERK, RHEINPREUSSEN. [Sulfur in Synthesis Gas—Routine Analysis.] MIS VII, 67 g, 7003033, 1942, 310 pp; PB 17122.

Manuscript data of the analyses made on gas at this synthetic oil plant in Germany is given. The analyses show S content before and after scrubbing and before entrance into the contact chamber.

TREMEARNE, T. H. *See* abs. **150.**

3439. TRILLAT, J. J., AND OKETANI, S. [Electron-Diffraction Study of the Cementation of Iron. I. Action of Pure Carbon Monoxide.] Compt. rend., vol. 230, 1950, pp. 2,203–2,205; Chem. Abs., vol. 44, 1950, p. 10,631.

Extremely thin polycrystalline films were prepared by vaporizing from pure Fe or mild steel onto the surface of freshly cleaved rock salt; the salt was then dissolved in H_2O and the metallic film collected on a Ni grill. This was submitted to cementation in the presence of pure CO and then examined by electron diffraction. After cementation at 540°, orthorhombic crystals of cementite are present. Below 500° none is formed. At 540°, if the preparations are not exposed constantly to fresh CO_2, decomposition takes place forming Fe_3O_4. As the temperature is raised, graphite is deposited on the surface, and above 820° the diagrams of Fe and Fe_3C are masked.

3440. ———. [Electron-Diffraction Study of the Cementation of Iron. II. Action of $CO+H_2$ Mixtures.] Compt. rend., vol. 232, 1951, pp. 1116–1118.

Supplementary studies to those performed with pure CO (see abs. **2719**) and at slightly raised temperatures of 350°–400° have shown under the experimental conditions that only cementite Fe_3C and oxide Fe_3O_4 are formed. In the presence, however, of a mixture of equal parts $CO+H_2$ different results are noted. At 350° and for the duration of the reaction (1–2 hr.), the presence is indicated of α–Fe, a little cementite Fe_3C, and a compound characterized by a diagram different from that of cementite and sometimes appearing in the pure state. Detailed examination identifies it as the percarbide Fe_2C or Hägg carbide. At 400°, after a 1-hr. treatment by $CO+H_2$, only cementite Fe_3C and α–Fe appear. The percarbide may however be seen if the reaction is prolonged to 2–3 hr. Above 400° only cementite exists. The results thus seem to indicate that the percarbide ceases to be stable above 400° while the cementite exists up to at least 600°. In the stable regions of percarbide, the following reactions probably occur:

$$(1)\quad 3Fe+2CO \rightarrow Fe_3C+CO_2,$$

$$(2)\quad 2Fe_3C+2CO \rightarrow 3Fe_2C+CO_2.$$

The formation of percarbide follows that of cementite, which contains less C; up to 400° reaction (2) may occur but not above. The presence of H_2 accelerates the speed of the reaction considerably. Further studies will be made of the action of $CO+H_2$ at temperatures below 350° and above 600°.

3440a. ———. [Electron-Diffraction Study of Cementation of Iron by Carbon Monoxide.] Metaux et corrosion, vol. 25, 1950, pp. 263–264; Chem Abs., vol. 45, 1951, p. 9440.

One hour cementation in CO atmosphere at 540° forms the orthorhombic Fe_3C; however, at temperatures <500° no Fe_3C was observed. During cementation in CO or in air there is a spontaneous oxidation of Fe forming Fe_3O_4 film perpendicular to the prepared surface. During cementation at higher temperatures graphite is deposited on the prepared surface. Above 820° there is no evidence of either Fe_3C or Fe which without doubt are masked by the graphite. Samples previously oxidized in air and then carburized at 540° give the same results but the cementite grain size is greater.

TROELTZSCH, J. *See* abs. **1677.**

3441. TROESCH, A. [Inhibition by Carbon and Hydrogen of the Adsorptive Activity of Methane by Fischer Nickel Catalysts.] Compt. rend., vol. 228, 1949, pp. 1013–1015; Chem. Abs., vol. 43, 1949, p. 6064.

Previous work on the adsorption of CH_4 on Ni catalysts is reviewed, and new experiments are analyzed. The adsorption of CH_4 upon the Fischer Ni catalyst is inhibited both by C, the fixation of which by the catalyst diminishes the active surface without modifying the speed of adsorption, and by H_2, the presence of which in the adsorbent reduces simultaneously the active surface and the speed of adsorption.

3442. ——. [Kinetic Laws of Adsorption of Methane by Fischer Catalysts Containing Nickel.] Compt. rend., vol. 228, 1949, pp. 1126–1128; Chem. Abs., vol. 43, 1949, p. 6064.

Previously published results (abs. **3441**) were analyzed kinetically. The heat of adsorption of CH_4 on a Fischer catalyst approximated 17 kcal. per mol.

3443. ———. [Application of the Kinetic Laws of Adsorption and Desorption to the Study of Catalysts.] Jour. chim. phys., vol. 47, 1950, pp. 148–156; Chem. Abs., vol. 44, 1950, p. 8754.

Measurements of the rate of desorption of H_2 indicate 3 types of active centers for which energies of activation of desorption are 9, 12, and 16.8 kcal., respectively. The action of adsorbed H_2 and C on the kinetics of CH_4 adsorption on Ni as published previously (abs. **3441** and **3442**) is discussed.

3444. ———. [Dissociation of Methane in Presence of a Nickel Catalyst.] Jour. chim. phys., vol. 47, 1950, pp. 274–285; Chem. Abs., vol. 44, 1950, p. 7637.

Studies made in the absence and presence of a Ni catalyst indicate that no reaction took place between CH_4 and Ni at 112°–287°. No intermediate carbide is necessary to explain the decomposition. The evidence suggests that Ni carbide is not responsible for the efficacy of Fischer-Tropsch catalysts.

3445. ———. [Kinetic Equations for Adsorption and Desorption.] Jour. chim. phys., vol. 47, 1950, pp. 145–147; Chem. Abs., vol. 44, 1950, p. 8194.

Adsorption of CH_4 on a Ni–Al–Mn–kieselguhr catalyst (abs. **2608**) obeys a simple Langmuir rate equation in which desorption is neglected and the rate of adsorption is proportional to the fraction of the surface not covered by adsorbate. The rate of adsorption of H_2 does not follow such an equation but indicates that the surface is heterogeneous. Desorption of CH_4 from the Ni surface at 170° and a constant pressure of 10^{-4} mm. cannot be measured because the evolved gas is all H_2. The rate of H_2 desorption does not follow the simple Langmuir equation and again indicates surface heterogeneity.

TROITSKAYA, F. B. *See* abs. **3764, 3766.**

3446. TROPSCH, H. [Synthesis and Decomposition of Formates.] Ann. chim. phys., vol. 15, No. 9, 1921, pp. 42–60.

Investigation of CaO as a catalyst for reactions in water gas mixtures was extended, and a study was made of the synthesis and decomposition of formates. As regards the mechanism of CH_4 synthesis, it is assumed that at temperatures below the decomposition of $CaCO_3$ (900°) water gas reacts with CaO to give calcium formate. $CaO+2\ CO+H_2O=Ca(CHO_2)_2$. The formate in the presence of an excess of lime then reacts to give CH_4 and $CaCO_3$. $2\ Ca(CHO_2)_2+CaO=3\ CaCO_3+CH_4$.

3447. ———. [Decomposition of Synthol at Atmospheric Pressure.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 49–50; Chem. Abs., vol. 21, 1927, p. 1698.

Synthol, 5.8 gm., on heating to 400°–480° at atmospheric pressure yielded 3.9 gm. C, 0.3 gm. CO_2, 0.7 gm. CO, 0.5 gm. H_2, 0.2 gm. CH_4, and 0.1 gm. hydrocarbons, these products being different from those obtained by heating it under pressure in autoclaves (abs. **1014**).

3448. ———. [Higher Boiling Constituents of Synthol.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 75–77; Chem. Abs., vol. 21, 1927, p. 2779.

Higher-boiling constituents of Synthol contain small quantities of viscous oils, which can be acetylated and, therefore, contain hydroxyl groups. The least volatile constituents are solid and asphaltic. Traces of a solid, paraffinic substance are obtained also.

3449. ———. [Equilibrium Conditions in the Formation of Hydrocarbons and Alcohols From Water Gas.] Brennstoff-Chem., vol. 8, 1927, p. 376; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 336–337; Chem. Abs., vol. 22, 1928, p. 3976.

Smith states (abs. **3206**) that equilibrium calculations show that, as the temperature is increased, formation of higher rather than lower hydrocarbons is favored, whereas experimental work of Tropsch shows that high temperatures favor formation of CH_4. Smith also finds that increased pressure favors production of higher paraffins. This agrees with experimental results of Tropsch, except that oxygenated compounds are formed at temperatures high enough to drive from the catalyst the higher hydrocarbons, which have been formed.

3450. ———. [Equilibrium Conditions for Formation of Hydrocarbons and Alcohols From Water Gas.] Brennstoff-Chem., vol. 9, 1928, p. 250; Chem. Abs., vol. 22, 1928, p. 4773.

Comment on abs. **3208.**

3451. ———. [Manufacture of Butyl Alcohol, Acetone, and Methanol From Corn.] Brennstoff-Chem., vol. 9, 1928, pp. 1–2; Chem. Abs., vol. 22, 1928, p. 2635.

Description of the Commercial Solvents Co. process at Peoria, Ill. The mixture of 60% CO_2 and 40% H_2 liberated during fermentation is washed with water under pressure to bring the proportion to 25% and 75%, respectively, and is then compressed to 300 atm., and passed over a catalyst comprising 97.75% Zn or Mg oxide with 3.25% Fe_2O_3. From the mixture of 68% MeOH and 32% H_2O, pure MeOH is obtained by rectification. Thirteen tons of MeOH are produced per day.

3452. ———. [Conversion of Coal Into Oils.] Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 348–355; Chem. Zentralb., 1929, II, p. 3266; Chem. Abs., vol. 24, 1930, p. 5461.

Survey of the known methods of producing liquid fuels from mineral coals either directly or indirectly by primary gasification.

3453. ———. [Problems in Fuel Chemistry.] Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 393–406.

Review of the methods of producing liquid fuels.

3454. ———. [Composition of the Products Obtained in the Synthesis of Petroleum.] Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 561–570; Chem. Abs., vol. 25, 1931, p. 3806.

Benzine fraction, boiling at 60°–185°, of the synthetic petroleum obtained by the catalytic reduction of CO at ordinary pressures has been examined (abs. **1021**).

After fractionating at every 10°, the specific gravity, *n*, and I value of each fraction were determined. The olefins were determined by separation as the double compound with Hg acetate, being subsequently regenerated by dilute HCl. The benzine was found to consist almost entirely of a mixture of paraffins, *n*-pentane to *n*-nonane, also *iso*-nonane, with the corresponding olefins, the latter predominating, especially in the lower-boiling fractions. It was quite stable to air and light for at least 2 yr.

3455. ———. [Synthesis of Organic Compounds From Gases Obtainable From Coal.] Entstehung, Veredlung, und Verwertung der Kohle, Berlin, Bornträger, 1930, 359 pp., chap. V.

———. *See* abs. **1013, 1014, 1015, 1016, 1017, 1018, 1019, 1020, 1021, 1022, 1023, 1024, 1025, 1026, 1043, 1044, 1045, 1046, 1047.**

3456. TROPSCH, H., AND DITTRICH, E. [Analysis of Gaseous Hydrocarbons, Particularly Olefins.] Brennstoff-Chem., vol. 6, 1925, pp. 169–177; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 285–304; Chem. Abs., vol. 19, 1925, p. 2793.

Fractional condensation at liquid-air temperatures was applied in the analysis of complex mixtures of paraffins and olefins. Gases other than hydrocarbons are first determined (CO_2 by absorption in KOH, O_2 with alkaline pyrogallol, CO with ammoniacal $CuCl_2$ and H_2 by selective combustion over CuO heated to 240°, at which temperature it is shown the higher hydrocarbons are not affected) and the residual hydrocarbons are then condensed by liquid air in an apparatus built by Ströhlein Co. Düsseldorf. Condensation and fractionation are carried out in 4 U-tubes cooled to suitable temperatures by liquid air and also by Al blocks cooled by this medium. The fractionation is carried out under high vacuum maintained by a Töpler pump. A Gaede pump is used also to circulate gases. The fractions obtained are: *B* (CH_4), C_1 (ethane, propane, ethylene, and propylene), C_2 (propane, butane, propylene, and butylene), *D* (olefins and paraffins of higher molecular weight). From the individual fractions, ethylene homologs are absorbed by 87% H_2SO_4 and ethylene itself is absorbed by a mixture of solutions *a* and *b* in proportions 0.25 : 1.875, *a* being 87% H_2SO_4 saturated with $NiSO_4$ and *b* being 87% H_2SO_4 containing 0.6%

$AgSO_4$. The amount of C corresponding to each vol. absorbed is determined by oxidation of the acid solution with excess KIO_3 and back titration of the excess with $Na_2S_2O_3$. Paraffin hydrocarbons are determined by combustion in small quartz tubes containing heated CuO. Boiling curves of the hydrocarbons are given with numerous tables of analytical data for pure gases. Specimen analyses of (1) an oil gas, (2) a synthol gas, and (3) a gas from the Bergius hydrogenation process are given.

3457. TROPSCH, H., AND KASSLER, R. [Catalytic Properties of Rhenium.] Ber. deut. chem. Gesell., vol. 63 B, 1930, pp. 2149–2151; Chem. Abs., vol. 25, 1931, p. 22.

Reduced Re and Re-Cu catalysts act as hydrogenating catalysts in the reactions $CO \rightarrow CH_4$ and $C_2H_4 \rightarrow C_2H_6$. At 470°, Re carbide is formed by passing CO over a Re-Cu catalyst.

3458. TROPSCH, H., AND KOCH, H. [Synthetic Benzine From Water Gas.] Brennstoff-Chem., vol. 10, 1929, pp. 337–346; Petroleum (London), vol. 26, 1930, pp. 157–158; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 533–560; British Chem. Abs., 1929, B, p. 1003; Chem. Abs., vol. 24, 1930, p. 4919.

Synthetic benzine obtained from water gas by catalytic reduction at atmospheric pressures was a mixture of 65% olefins, 0.1% benzene, 0.4–0.5% toluene and paraffins. The saturated and unsaturated constituents were separated, isolated, and identified in various fractions of the carefully fractionated benzine; a modified Hg acetate method was used whereby pure olefins were obtained from mixtures containing saturated hydrocarbons. The hydrocarbons thus obtained were pentane, hexane, heptane, octane, 3-methyloctane, nonane, 1-pentene, 2-pentene, 1 hexene, 2-hexene, 3,3-dimethyl-1-pentene, heptene, 2-octene, and nonene. A long-needled crystalline substance melting 106°, of unknown composition but possibly a γ-pyrone derivative, separated from the 100°–120° fractions of the benzine.

3459. TROPSCH, H., AND KRÖNIG, W. [Observations on the Action of Carbon Monoxide on Iron Oxide.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 46–48.

It is concluded that the formation of synthol by way of the carbide from Fe and CO is not probable.

3460. TROPSCH, H., AND SCHELLENBERG, A. [Formation of Methane in the Water-Gas Process.] Brennstoff-Chem., vol. 3, 1922, pp. 33–37; Ges. Abhandl. Kenntnis Kohle, vol. 6, 1921, pp. 317–329; Chem. Abs., vol. 16, 1922, p. 2022.

Vignon's experiments (abs. **3560, 3561, 3562, 3563**), on the reduction of CO to CH_4 by means of H_2 in the presence of CaO and Fe, at 900°–1,000° have been repeated and only traces of CH_4 found. The presence of 25–30% CH_4 among the products of dry distillation of $Ca(HCOO)_2$ could likewise not be confirmed. Vignon apparently determined CH_4 by difference and did not allow for residual N_2 in the apparatus.

3461. ———. [Decomposition of Methanol by Iron, Tin, and Aluminum.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 13–14; Chem. Zentralb., 1926, I, p. 3298; Chem. Abs., vol. 21, 1927, p. 3530.

MeOH vapor was conducted over the metal heated and spread out with a combustion tube. At 520°, C was deposited on the Fe, decomposition of the MeOH to a gas containing 4–7% CO_2, 20–25% CO, 55–60% H_2, and 3–12% CH_4 occurring. The small quantity of condensate was neutral and contained HCHO. With tinned Fe, the decomposition of MeOH followed the same course but was only slight. With Al at 520°, the gas contained 5% CO_2, 23% CO, 60% H_2, and 4% CH_4, and, at 270°, it contained 2% CO_2, 5% CO, 52% H_2, and 30% CH_4. In a receiver cooled with liquid air, a reaction product containing Al, probably $AlMe_3$ condensed.

3462. TROPSCH, H., AND VON PHILIPPOVICH, A. [Comparative Experiments on the Decomposition of Carbon Monoxide by Contact Substances.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 44–45; Chem. Zentralb., 1926, I, p. 3298; Chem. Abs., vol. 21, 1927, p. 3530.

Purified and dried CO was conducted over contact substances at 400°. Its decomposition according to the reaction: $2CO \rightarrow CO_2 + C$, was measured by determining the CO_2. Ni was the most active catalyst, but this activity was almost completely destroyed by alloying the Ni with 50% Sn. Great differences were found among different types of Fe. With a CO current of 400 cc. per hr., the following % CO_2 were found in the issuing gas: with Ni, 36.4; Fe from Fe_2O_3, 10.4, *ferr. reduct.*, 2.3; ZnO, 0.9; MnO, 0.8; Cr_2O_3, 0.6; NiSn, 0.3–0.6; Al_2O_3, 0.4; $BaSO_4$, 0.4; tinned Fe, 0.4; MgO, 0.2; Cu, 0.0.

3463. ———. [Condensation of Methanol in the Presence of Contact Substances.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 78–83; Chem. Abs., vol. 21, 1927, p. 2870.

Catalysts examined were those used in the production of synthol, with a view to elucidate the mechanism of this reaction. In nearly all cases, a small quantity of an oil of terpenelike odor was obtained, and the possibility of the formation of higher boiling compounds was proved. With NaOMe, Me_2O was formed, and the reaction gas was composed almost exclusively of H_2. In all other cases, considerable quantities of CH_4 were produced. With an alkaline Fe catalyst, a considerable amount of oily products was obtained, proving the production of oils directly from MeOH to be possible.

3464. TROPSCH, H., SCHELLENBERG, A., AND VON PHILIPPOVICH, A. [Reduction of Carbon Monoxide.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 63–67; Chem. Abs., vol. 21, 1927, p. 2550.

Formation of CH_4 from a mixture of CO (1 vol.) and H_2 (3 vol.) in contact with Ni, which normally occurs quantitatively at 240°–250°, is greatly diminished by adding NH_3 to the gas mixture. Neither formaldehyde nor hexamethylenetetramine was formed, and the final mixture contained 13% CH_4, 15% CO, 64% H_2, and 8% Ni. With a Ni catalyst that had been treated with alkali, the same gas mixture yielded at 400° and atmospheric pressure, 53% CH_4 and 1.1% of unsaturated hydrocarbons, the only liquid reaction product being H_2O. The same reaction occurred with a Ni catalyst that had not been treated with alkali, except that no unsaturated hydrocarbons were formed. A mixture of equal volumes of CO and H_2 in contact with an alkaline Ni catalyst at 400°, deposited much C. With a feebly alkaline catalyst, the final gas contained 27% CO_2, 2% CO, 26% H_2 and 45% CH_4, while, with a more strongly alkaline catalyst, it contained 11% CO_2, 29% CO, 50% H_2, and 9% CH_4. With both alkaline and neutral catalysts, the CH_4 contained 1.5% of higher homologs, reckoned as ethane. A mixture of equal volumes of CO_2 and H_2, in contact with neutral Ni at 400°, gave a final gas containing 10% CO_2, 42% H_2, and 48% CH_4, while with alkaline Ni it gave 7% CO_2, 70% H_2, and 23% CH_4. In no case could MeOH be detected.

3465. TRUCHET, R. [Industrial Synthesis of Fat Acids.] Rev. sci., vol. 80, 1942, pp. 265–270; Chem. Zentralb., 1943, II, p. 1511; Chem. Abs., vol. 38, 1944, p. 6273.

Review of the development of processes, difficulties encountered, and means of overcoming them.

TSELLINSKAYA, T. F. *See* abs **703, 2887.**

TSUNEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXI. Relations of the Gas Compostion to the Working Temperature and to the Degree of Saturation of the Benzine, Respectively. *See* abs. **1857.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXII. Usefulness of a New Alloy Catalyzer. *See* abs. **1858.**

———. *See* abs. **1850, 1851, 1852, 1853, 1854, 1855, 1856, 1866, 1867, 1869, 1874, 1877, 1884, 1885, 1908.**

3466. TSUNEOKA, S., AND FUNASAKA, W. Purification of the Gaseous Raw Material Used for Benzine Synthesis. I. Removal of Organic Sulfur Compounds at Low Temperature. Jour. Soc. Chem. Ind. (Japan), vol. 41, B, 1938, pp. 43–47; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1938, pp. 301–309 (in German); Chem. Abs., vol. 32, 1938, p. 3577.

Researches were undertaken to find a satisfactory method of S removal, with known or new materials, from a gas to be used further for the synthesis of benzine, its S contents to be less than 0.2 gm. per 100 m.³ city gas, with a total S content of 24.0 gm. S per 100 m.³, of which 22.6 gm. S is organic, was freed of CO_2 and H_2S and, as such, used over adsorbent materials, dry purificants, and H_2S extraction materials at room temperature. As adsorbent materials were used active C, SiO_2 gel, Japanese acid earths, and Adosol. Active C was found the most efficient but not active enough to produce a highly purified gas. As dry purificants, Fe_2O_3 on a pumice support and Luxmasse were used; as H_2S scrubbing materials, Thylox soluble and $(C_2H_5)_3N$, to which Fe_2O_3 was added, were used. 80% S removed was obtained with the dry purificants. Thylox failed to extract the organic S, while, with $(C_2H_5)_3$ N, 67.7%, S removal was obtained; it was further improved by addition of Fe_2O.

3467. ———. Purification of the Gaseous Raw Material Used for Benzine Synthesis. II. Removal of Organic Sulfur Compounds at High Temperature. Jour. Soc. Chem. Ind. (Japan), vol. 41, B, 1938 pp. 47–51; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1938, pp. 310–320 (in German); Chem. Abs., vol. 32, 1938, p. 3577.

The same city gas was used for S removal at high temperature by passing the gas through heated pipes without and in the presence of catalysts. Fe, Cu, and V2A steel pipes were used. At 500°, Fe pipe gave the best results but desulfuration is only 77%. Ag catalysts, 1% Ag by weight, CuO–CrO_4–Pb, Ni, Fe–Cu, Ag catalysts, 10% metal, and active C were used in an effort to eliminate the organic S by transforming it into H_2S, by contact. With CuO–CrO_4–Pb, Ni, Fe–Cu catalysts, 10% metal, at temperatures 450°, 350°, 300°, 330 cc. per hr. per cc. contact (Ges. Abhandl. Kenntnis Kohle, vol. 10, p. 313) in each case, the organic S content was reduced to less than 0.2 gm. per 100 m.³ of gas. The amount of organic S changed into H_2S was very small, the major part of it being fixed on the catalyst. A preliminary extraction of H_2S from the gas is necessary, otherwise the amounts of total S, remaining in gas, are 0.66, 3.12, 0.82 gm. per 100 m.³, respectively. With Fe_2O_3 on a pumice support, 30% Fe_2O_3, and Luxmasse, at 350° and 330 cc. per hr. per cc. contact, the organic S was completely removed from the gas. No preliminary extraction of H_2S is necessary, and the S is economically removed to less than 0.2 gm. S per 100 m.³, organic S less than 0.07 gm. per 100 m.³, total S less than 0.07 gm. per 100 m.³, or 99.7% S removed. The Luxmasse used by the authors was a byproduct obtained in the manufacture of Al, red mud, often used in city gas plants for H_2S removal, which in muddy form contained 38.2% of H_2O. The material was dried for 12 hr. at 105° and then crushed to 3–5 mm. granules.

TSUNEOKA, S., AND FUNASAKA, W. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLII. Purification of the Gaseous Raw Material Used for Benzine Synthesis. 1. Removal of Organic Sulfur Compounds at Low Temperature. *See* abs. **1878.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLIII. Purification of the Gaseous Raw Material Used for Benzine Synthesis. 2. Removal of Organic Sulfur Compounds at High Temperature. *See* abs. **1879.**

TSUNEOKA, S., AND KURODA, R. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXIV. Analytical Studies of Alloy Catalysts. *See* abs. **1870.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXV. Microscopic Study of Alloy Catalysts. *See* abs. **1871.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXVII. Cobalt Alloy Catalysts. *See* abs. **1863.**

TSUNEOKA, S., AND MURATA, Y. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXIII. Extraction and Leaching Treatment of Alloy Catalysts. *See* abs. **1859.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXVI. Gas Contraction and Benzine Synthesis. *See* abs. **1862.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXV. General Properties and Constituents of the Benzine Prepared With an Alloy Catalyst. *See* abs. **1861.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXIX. Influence of Bore and Length of the Reaction Tube. *See* abs. **1865.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXIV. Influence of the Particle Size and the Hydrogen Treatment or Oxidation Conditions of the Alloy Catalysts. *See* abs. **1860.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXVIII. Nickel-Alloy Catalysts. *See* abs. **1864.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXIX. Properties of a Precipitated Nickel–Cobalt Catalyst. *See* abs. **1875.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XL. Proportions of Nickel and Cobalt, and the Influence of the Addition of Copper to the Precipitated Nickel–Cobalt Catalysts. *See* abs. **1876.**

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXII. Studies on the Material of the Reaction Furnace. *See* abs. **1868.**

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXVI. Relation of the Activity of the Catalyst to the Synthesis Requirements at too High a Temperature. *See* abs. **1872.**

TSUNEOKA, S., AND NISHIO, A. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXVII. Volume Velocity of the Gas. *See* abs. **1873.**

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLVII. Composition of Starting Gases with New Iron Catalyst. *See* abs. **1883.**

TSUNEOKA, S., MURATA, Y., AND MAKINO, S. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLVI. Preparation of New Iron Catalysts and Their Superior Properties. *See* abs. **1882.**

3468. TSUNEOKA, S., MURATA, Y., FUNASAKA, W., AND NISHIO, A. Fischer Process—Japan. Jour. Fuel Soc. Japan, vol. 18, 1939, p. a7.

Continuous investigations were carried out by the Imperial Fuel Research Institute on:

(1) Studies on gas space velocity. The yield of gasoline was maximum at a certain gas velocity, either when the amount of the catalyst and the length of the catalyst zone or the gas space velocity and the length of the catalyst zone were maintained constant. The content of unsaturated hydrocarbons in the synthesized gasoline increased with an increase of gas velocity.

(2) The relation between the degree of unsaturation of the synthesized gasoline and various conditions.

(3) Studies on Ni–Co catalysts prepared by the precipitation method. U_3O_8 and ThO_2 were found to be superior promoters both for Ni–Co (50 : 50) and Ni–Co–Mn (50 : 50 : 15) catalysts; the yield of gasoline was 166 cc. per m.^{3} with Ni–Co–Mn–U_3O_8–ThO_2–kieselguhr (50 : 50 : 15 : 5 : 3 : 125) and 179 cc. per m.^{3} with Ni–Co–Mn–U_3O_8–kieselguhr (50 : 50 : 20 : 20 : 125) catalysts. The optimum ratio of Ni : Co was found to be 50 : 50. The reduction temperature of a Ni–Co–Mn–U_3O_8–ThO_2–kieselguhr (50 : 50 : 15 : 5 : 3 : 125) catalyst was lowered from 400° C. to 300° C. owing to the addition of 10% of Cu, notwithstanding that the activity was depressed greatly.

(4) Removal of organic S compounds from industrial gas. The content of organic S compounds in coal gas was reduced from 22.6 gm. S per 100 m.^{3} to 0.2 gm. S per 100 m.^{3} and less by the use of CuO–$PbCrO_4$, Ni, and Fe–Cu catalysts at temperatures of 450°, 350°, and 300° C., and the same space velocity of 330. The organic S compounds in coal were quantitatively fixed with Fe_2O_3 on pumice and Luxmasse at a temperature of 350° C. and a space velocity of 330, the content of S being reduced to 0.2 gm. S per 100 m.^{3} and less.

(5) Activation of a gasoline catalyst by slow oxidation with air. The activity of a Ni-Co–Mn–U_3O_8–ThO_2–kieselguhr (50 : 50 : 15 : 5 : 3 : 125) catalyst was increased by about 10% and 8%, respectively, when the catalyst, after reduction at 400° C., was oxidized slowly with air directly or after the replacement by H_2 with CO_2.

(6) Studies on Fe catalysts prepared by the precipitation method. Fe–Cu catalysts, prepared by the precipitation method, were studied, and 94 cc. per m.^{3} ($CO : H_2 = 1 : 1$) of gasoline was obtained with a Fe–Cu–Mn–Al_2O_3–kieselguhr–K_2CO_3 (100 : 25 : 2 : 3 : 125 : 2) catalyst.

3469. TSUTSUMI, S. Synthesis of Benzine From Carbon Monoxide and Hydrogen. Jour. Fuel Soc. Japan, vol. 12, 1933, pp. 1383–1390 (in English, pp. 137–138); Chem. Abs., vol. 28, 1934, p. 1515.

Previous work of Fischer and Tropsch and of Fujimura is reviewed and the author's own data presented. The highest yield attained by Fujimura was 145 cc. of liquid product per m.^{3} mischgas with 33 parts CO and 67 of H_2. The catalyst consisted of Co : Cu : Th : U = 8 : 1 : 0.2 : 0.1. The author obtained a yield of 155 cc. per m.^{3} of mischgas. Details of the work and the composition of the catalysts will be presented in a later paper.

3470. ———. Synthetic Gasoline From Carbon Monoxide and Hydrogen. I. Rept. Imp. Fuel Research Inst. Japan, No. 31, 1935, 62 pp.; Jour. Fuel Soc. Japan, vol. 14, 1935, pp. 110–116 (in English); Brennstoff-Chem., vol. 17, 1936, p. 54; Chem. Abs., vol. 29, 1935, p. 7627; vol. 30, 1936, p. 845.

Gas mixture consisting of 1 part CO and 2 H_2 was used for the investigation. The effect of various factors on the course of the synthesis was investigated with a Co : Cu : U_3O_8 : kieselguhr (1 : 0.1 : 0.12 : 1) catalyst. With this catalyst the highest yield, namely 97 gm. per m.^{3} mischgas, was obtained at 210°. With rising temperature the formation of gaseous hydrocarbons decreased. The most favorable gas velocity was 3–6 l. per hr., using 3 gm. Co. A gas mixture of 1 CO and 2 H_2 gave the best yield per m.^{3} of synthesis gas. With a gas rich in H_2 the reaction temperature can be lowered; this reacts favorably on the life of the catalyst. A ratio of Co : kieselguhr = 1 : 1 or 3 : 4 made the most active catalyst. Besides kieselguhr, alumina, pumice, and silica gel were used as carrier material; in no case was the activity equal to that with kieselguhr. The best raw material for the preparation of the catalyst was the nitrate. The catalyst prepared from the acetate was equal in activity, whereas that made from the sulfate was less active. When the chloride was used, the catalyst was virtually inactive. Further tests were performed with Ni : Mn catalysts. The best results here were obtained with a Ni catalyst to which 20% Mn, 8% U_3O_8, and 4% ThO_2 were added. The maximum yield amounted to about 115 gm. of liquid product per m.^{3} of mischgas. With a mixed catalyst of Co : Ni : Cu the results were more unfavorable, the activity decreasing with increasing content of Ni and Cu. The reason for this behavior lies in the formation of mixed crystals between Ni and Cu. The mechanism of the reaction is discussed from the standpoint of carbide formation. Mention is made in this connection that with mixtures of CO_2 and H_2 higher hydrocarbons are not formed, only CH_4. No carbide formation was observed.

3471. ———. Promoting Action of a Catalyst Promoter and Carrier. I. Jour. Chem. Soc. Japan, vol. 57, 1936, pp. 685–691; Chem. Abs., vol. 30, 1936, p. 7436.

Synthesis of liquid hydrocarbons from CO and H_2 is studied. For catalysts that require no high temperature before reduction of CO with H_2 and cause reaction at approximately 200°, no accelerating action of the carrier is noticed, but it has a tendency to decrease the activity of the catalyst. For catalysts that require high temperature before the reaction, the presence of carrier gives much acceleration, increases the resistance to heat, and increases the activity of the catalyst. There is no fundamental difference between carrier and accelerator in increasing the resistance of the catalyst to heat. The temperature of reduction increases with an increase in amount of carrier and accelerator, and an increase in small amount of accelerator gives the result of using a large amount of carrier when it is estimated by an increase in the temperature of reduction.

3472. ———. Studies of the Promoting Action of a Catalyst Promoter and Carrier. II. Jour. Chem. Soc. Japan, vol. 58, 1937, pp. 63–70; Chem. Abs., vol. 31, 1937, p. 2915.

Effect of the calcining temperature upon the gas-absorbing power of the mixtures Co+Cu+U_3O_8 in the range 200°–300°, and Co+U_3O_8, Co+ThO_2 in the range 250°–450° containing various amounts of diatomaceous earth was studied. The gas used was the mixture CO+H_2 in the ratio 1 : 2. The proper temperature to get the maximum absorbing power does not change much with the amount of the diatomaceous earth.

3473. ———. Studies on the Promoting Action of a Catalyst Promoter and Carrier. III. Selection of the Catalyst for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. Jour. Chem. Soc. Japan, vol. 58, 1937, pp. 996–1001; Chem. Abs., vol. 32, 1938, p. 735.

It has been stated that, in the reaction between CO and H_2, the active power of the catalyzer greatly depends on the mode of preparation.

3474. ———. Studies on the Promoting Action of a Catalyst Promoter and Carrier. IV. Activity of the

Catalyst for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. Jour. Chem. Soc. Japan, vol. 58, 1937, pp. 1002–1006; Chem. Abs., vol. 32, 1938, p. 735.

3475. ———. Promoting Action of Promoter and Carrier. V. Changes on the Catalyst Surface Caused by the Addition of Promoter and Carrier. Jour. Chem. Soc. Japan, vol. 59, 1938, pp. 893–898; Chem. Abs., vol. 32, 1938, p. 7332.

Most suitable % of Cr and of diatomaceous earth in the catalyst Ni–Cr–diatomaceous earth, for the synthesis of liquid hydrocarbons from CO and H_2 are 7.5% and 50%, respectively.

3476. ———. Promoting Action of Promoters and Carriers. VI. Relation Between the Dispersity of Catalysts and the Catalytic Activity. Jour. Chem. Soc. Japan, vol. 59, 1938, pp. 1407–1411; Chem. Abs., vol. 33, 1939, p. 2290.

In the catalytic reduction of C_6H_6 the catalyst prepared by the following method is most effective. To the solution of $Co(NO_3)_2$, a slight excess of K_2CO_3 is added. The precipitate is dried at 200°, mixed with kieselguhr and H_2O in a mortar, and dried at 100°. The ratio of Co to kieselguhr is 1 : 40. This method of preparation can be applied to the catalyst having the composition (4 Ni+Co)+7.5% Cr in the synthesis of liquid hydrocarbons from CO and H_2.

3477. ———. Preparation of Water Gas From Methane. Repts. Imperial Fuel Research Inst., Japan, No. 34, 1937, 50 pp.; Jour. Fuel Soc. Japan, vol. 17, 1938, pp. 24–28; British Chem. Abs., vol. 57, 1937, B, p. 751; Chem. Abs., vol. 32, 1938, p. 3125.

Experimental procedure and various factors, such as catalysts and temperature affecting the reactions, are given in detail with experimental data.

3478. ———. Production of Carbon Monoxide and Hydrogen by Means of the Methane-Steam Reaction. I. Action of a Nickel Catalyst on the Water-Gas Reaction. Jour. Chem. Soc. Japan, vol. 58, 1937, pp. 379–390; Chem. Abs., vol. 31, 1937, p. 5,135.

Water-gas reaction has been studied at 700° and 800° in the presence of Ni catalysts containing 10% each of Al_2O_3, MgO, SiO_2, ThO_2, CuO, MnO, CaO, Fe_2O_3, and ZnO. The catalyst Ni+10% MgO has the greatest activity for the oxidation of CO.

3479. ———. Production of Carbon Monoxide and Hydrogen by Means of the Methane-Steam Reaction. II. Effect of Temperature Upon the Catalytic Activity of Nickel Catalyst for the Hydrogenation of Benzine. Jour. Chem. Soc. Japan, vol. 58, 1937, pp. 593–597; Chem. Abs., vol. 31, 1937, p. 6443.

Change of catalytic activity of the catalyst Ni+10% various oxides has been studied at the temperature range 500°–700° for the hydrogenation of benzene. It has been found that Ni+10% Al_2O_3 is most active within this temperature range.

3480. ———. Production of Carbon Monoxide and Hydrogen by Means of the Methane-Steam Reaction. III. Action of Nickel Catalyst Upon Methane-Steam Reaction. Jour. Chem. Soc. Japan, vol. 58, 1937, pp. 610–620; Chem. Abs., vol. 31, 1937, p. 6443.

Activity of the catalyst Ni+10% various oxides has been studied for the CH_4-steam reaction at 700° and at 800°, and the results are reviewed in comparison with those of the previous articles.

3481. ———. Production of Carbon Monoxide and Hydrogen by Means of the Methane-Steam Reaction. IV. Nickel Sulfate as a Catalyst. Jour. Chem. Soc. Japan, vol. 58, 1937, pp. 1007–1012; Chem. Abs., vol. 32, 1938, p. 735.

3482. ———. Production of Carbon Monoxide and Hydrogen by Means of Methane-Steam Reaction. V. Effect of Potassium Nitrate Upon the Catalytic Activity of a Nickel Catalyst. Jour. Chem. Soc. Japan, vol. 59, 1938, pp. 29–39; Chem. Abs., vol. 32, 1938, p. 3098.

Catalytic actions of Ni and Ni+ promoter for the reactions are retarded by the presence of KNO_3. The degree of retardation differs with different kinds of promoter.

3483. ———. Production of Carbon Monoxide and Hydrogen by the Methane-Steam Reaction. VI. Effect of Potassium Carbonate on the Catalytic Activity of Nickel Catalysts. Jour. Chem. Soc. Japan, vol. 60, 1939, pp. 191–198; Chem. Abs., vol. 33, 1939, p. 4499.

When 3.3–33% K_2CO_3 is added to Ni catalysts, the reaction rate of CH_4-steam reaction decreases.

3484. ———. Researches on the Synthesis of Gasoline From Carbon Dioxide and Hydrogen at the Imperial Fuel Research Institute. Jour. Fuel Soc. Japan, vol. 16, 1937, pp. 481–496 (in English, pp. 55–60); Chem. Abs., vol. 31, 1937, p. 6857.

Many experiments were carried out with Ni and Co catalysts. The activity of a Ni and Co catalyst is increased enormously by adding a small amount of irreducible oxides, such as oxides of Al, Mn, Cr, U, and Th. The promoting action of these catalysts mainly is due to their preventing the sintering of the reduced Ni and Co at the higher reduction temperature. A number of synthetic experiments under pressure also were carried out. One of the factors accelerating the formation of solid paraffin was due mainly to the elevation of the catalyst temperature by the heat of reaction as well as the increase of added amount of the oxides of U and Th to Ni and Co catalysts.

3485. ———. Synthesis of Gasoline From Carbon Monoxide and Hydrogen at the Imperial Fuel Research Institute. Jour. Fuel Soc. Japan, vol. 16, 1937, pp. 55–60; British Chem. Abs., 1937, B, p. 1005.

Promoting action of Th, Al, U, and Mn oxides on the activity of Co and Ni catalysts mainly is due to their preventing the sintering of the reduced Co and Ni at the higher reduction temperature. Formation of solid paraffin, which occurs when the synthesis is carried out under pressure, can be ascribed in part to raising the catalyst temperature by the heat of reaction.

3486. ———. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. I. Catalysts Prepared by the Precipitation Method. (1). Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1939, pp. 435–440; Jour. Chem. Soc. Japan, vol. 59, 1938, p. 140; Chem. Zentralb., 1939, I, p. 4752; Chem. Abs., vol. 33, 1939, p. 4747.

In the synthesis of liquid hydrocarbons from CO and H_2, the rate of the consumption of CO with a U_3O_8 catalyst containing Co 5% and Cu 12%, which need not be reduced at a high temperature, was scarcely increased owing to the addition of kieselguhr. The yield of liquid hydrocarbons increased gradually with an increase of the amount of kieselguhr. This fact shows that the proper amount of kieselguhr added to the catalyst suppresses the too violent hydrogenating power of the catalyst for production of liquid hydrocarbons and retards formation of gaseous hydrocarbons and CO_2.

3487. ———. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. II. Catalysts Prepared by the Precipitation Method. (2.) Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1939, pp. 441–446; Jour. Chem. Soc. Japan, vol. 59, 1938, p. 140; Chem. Zentralb., 1939, I, p. 4752; Chem. Abs., vol. 33, 1939, p. 4747.

Activities of Co catalysts, which must be reduced at high temperature, were greatly increased by adding

kieselguhr, and the depression in the activities caused by the elevation of the reduction temperature was decreased greatly by a proper amount of kieselguhr, although the optimum reduction temperature was raised with an increase of the amount added. The rates of elevation of the optimum reduction temperature for Co catalysts, with an increase of the amounts of promoter (Th, U, and Mn oxides) and carrier (kieselguhr) added, differed considerably; a small addition of promoter corresponded to the case where a larger amount of carrier was added. This fact may be attributed to a difference between the incorporated states of promoter and carrier with Co, the former being more intimately incorporated with Co than the latter. The difference between promoter and carrier is not so great.

3488. ———. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. III. Catalysts Prepared by the Roasting Method. (1). Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1939, pp. 481–486; Chem. Zentralb., 1939, II, p. 3044; Chem. Abs., vol. 33, 1939, p. 6535.

Catalysts containing 5% Co and 12% Cu or 5% Co and 4% Cu, activated with U_3O_8, are less active and have lower optimum reduction temperatures when prepared by roasting below 300° than when prepared by precipitation. More kieselguhr must be added to the roasted catalysts to obtain the activity of the precipitated material.

3489.———. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. IV. Catalysts Prepared by the Roasting Method. (2). Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 36, 1939, pp. 47–52; Chem. Zentralb., 1939, II, p. 3044; Chem. Abs., vol. 33, 1939, p. 6535.

Optimum reduction temperature for Co catalysts prepared by roasting is lower and the decrease in activity from using high reduction temperatures is greater than for precipitated Co catalysts. The amount of kieselguhr in the roasted catalysts must be increased to raise their activity. The decrease in activity of roasted Co catalysts is greatest when Mn is used as a promoter, less with heavier ThO_2, and least with the heaviest U_3O_8.

3490. ———. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. V. Selection of Catalysts for the Synthesis. (1). Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 36, 1939, pp. 178–182; Chem. Abs., vol. 33, 1939, p. 8934.

Ni catalysts containing 10% of various oxides were prepared by roasting the nitrates and reducing the Ni in H_2 at temperatures 300°–700°. Their activities in the hydrogenation of C_6H_6 at 190° were compared. The loss of activity resulting from elevation of the reduction temperature was least for Ni–Al_2O_3, followed by Ni–ThO_2, Ni–SiO_2, and Ni–MgO. The loss for Ni–CuO, Ni–Fe_2O_3 and Ni–ZnO was less than for a Ni catalyst at 300°–550°, but greater at 550°–600°. Ni–MnO and Ni–CaO lost their activity rapidly as the reduction temperature increased. The activities of the Ni-metallic oxide catalysts for the synthesis of liquid hydrocarbons from CO and H_2 were only 20% of that of Ni–10% Al_2O_3 catalyst at 210°.

3491. ———. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. VI. Selection of Catalysts for the Synthesis. (2). Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 36, 1939, pp. 251–261; Chem. Abs., vol. 34, 1940, p. 314.

Activity of a Ni catalyst, prepared by precipitation from nitrate solution by K_2CO_3, followed by reduction of the oxide by H_2, diminished more rapidly with increase of temperature of reduction than that of a similar catalyst prepared by roasting. Apparently, K_2CO_3 and KNO_3 were absorbed on the active spots. A Ni–10% Al_2O_3–100% kieselguhr catalyst prepared by the precipitation method was fairly active for the CO–H_2 synthesis but showed a high optimum reduction temperature, 450°–500°. Reduction of the proportion of Al_2O_3 to 7.5%, or substitution of about 50% of the Ni by Co, lowered the optimum reduction temperature. Ni–10% Al_2O_3 and Ni–10% Al_2O_3–100% kieselguhr catalysts prepared by precipitation were about as active as a Ni–10% Al_2O_3 catalyst prepared by roasting, for the hydrogenation of C_6H_6 but were more active for the CO–H_2 synthesis.

3492. ———. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. VII. Activities of the Catalysts Used for the Synthesis. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 36, 1939, pp. 262–270; Chem. Abs., vol. 34, 1940, p. 314.

Addition of 0.2–0.3 gm. of $NiSO_4$ to a Ni–10% Al_2O_3–100% kieselguhr catalyst, prepared by precipitation, containing 6 gm. of Ni, almost completely suppressed its activity for the CO–H_2 reaction, but did not greatly affect its activity for the hydrogenation of C_6H_6, for the suppression of which 0.8–0.9 gm. of $NiSO_4$ was required. A catalyst containing 0.8–0.9 gm. of $NiSO_4$ retained its activity for the hydrogenation of nitrobenzene to aniline and of phorone to valerone, and for the water-gas reaction. When the catalysts were prepared by roasting, less $NiSO_4$ was required to suppress the activity for the hydrogenation of C_6H_6, 0.2–0.3 gm. for Ni (6 gm.)–10% Al_2O_3, and 0.04–0.05 gm. for Ni (6 gm.). It is inferred that the reaction of CO with H_2 is catalyzed by the most active spots, whereas the hydrogenation of C_6H_6 and the other reactions are accelerated by respectively less-active spots.

3493. ———. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. VIII. Changes on the Catalyst Surface Caused by the Addition of Promoter and Carrier. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 36, 1939, pp. 335–343; Chem. Abs., vol. 33, 1939, p. 9103.

Tests of Ni–Cr and Ni–Cr–kieselguhr catalysts showed the optimum ratios of Cr and kieselguhr to Ni to be 7.5% and 50%, respectively. A Ni–7.5% Cr–50% kieselguhr catalyst (Ni 7.5%, Cr 50%) was more active than a Ni–10% Al_2O_3–100% kieselguhr catalyst for the reaction of CO and H_2. For the hydrogenation of benzene, the activity varied in the opposite order. In the Ni-kieselguhr catalyst, the optimum ratio of kieselguhr to Ni was 1:2 for the CO–H_2 reaction and 50:1 for the hydrogenation of benzene. It was suggested that the action of the promoter does not differ greatly from that of the carrier, although a larger amount of the carrier is needed to prevent sintering during reduction of the catalyst.

3494. ———. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. IX. Relation Between the Surface Dispersity of Catalysts and the Catalytic Activities. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 36, 1939, pp. 344–351; Chem. Abs., vol. 33, 1939, p. 9103.

Co-kieselguhr catalysts for the hydrogenation of benzene were prepared by 3 methods: (*a*) $Co(NO_3)_2$ was treated with K_2CO_3 in the presence of kieselguhr. (*b*) $Co(NO_3)_2$ was treated with K_2CO_3, and the precipitate was dried and mixed with kieselguhr in a little H_2O. (*c*) $Co(NO_3)_2$ and kieselguhr were mixed and roasted. The products were dried and reduced by H_2 at various temperatures. The optimum ratios and reduction temperatures were determined. The activities of the catalysts prepared by these methods were in the order 2>1>3. Optimum ratios of Co to kieselguhr were

1:10 to 1:20 for (*a*), and 1:40 for (*b*) and (*c*). The rate of elevation of the optimum reduction temperature with increase in kieselguhr was largest for (*a*) and smallest for (*b*). The small rate for (*b*) was attributed to the high degree of surface dispersity of Co on kieselguhr. Corresponding results were obtained with a (4Ni+1Co)–7.5% Cr catalyst.

3495. ———. Fischer Process—Japan. Jour. Fuel Soc. Japan, vol. 18, 1939, p. a7.

Work at the Imperial Fuel Research Institute is reported on Ni and Ni–Co catalysts promoted by Cr oxide. Cr oxide was found to be a superior promoter both for Ni and Ni–Co catalysts, and 175 cc. per m.^{3} of gasoline was obtained with a Ni–Co–Cr-kieselguhr (80:20:7.5:100) catalyst. The activity of Ni–Cr catalysts for the synthesis was larger than that of Ni–Al catalysts, but in the case of the hydrogenation of benzene, a quite contrary relation was obtained, this being attributed to the change of the active surface of the catalyst according to the addition of promoter and carrier. Synthesis experiment under pressure showed that synthesis of pure liquid hydrocarbons, containing no O, was possible even under a high pressure of about 50 atm., this being quite contrary to the results obtained by F. Fischer and collaborators. Yield of gasoline up to 125 cc. per m.^{3} was obtained with a Co–ThO_2–kieselguhr (100:15:100) catalyst under 40 atm.

3496. ———. Nickel Catalysts for the Conversion of Water Gas. Jour. Chem. Soc. Japan, vol. 60, 1939, pp. 311–313; Chem. Abs., vol. 33, 1939, p. 4765.

Addition of KNO_3 to the Ni catalyst retards the formation of CH_4 in the water-gas reaction, $CO+H_2O \rightarrow CO_2+H_2$, at 400°.

3497. ———. (R. C. Grass, Ed.) Synthesis of Hydrocarbons. Bureau of Mines Inf. Circ. 7594, 1951, 60 pp.

This paper, among the documents obtained by the United States Naval Technical Mission to Japan, gives detailed data of research on the production of synthetic liquid fuels from coal by the Fischer-Tropsch or gas-synthesis process by the Imperial Fuel Research Institute of Japan between 1932 and 1935; also contains brief reviews of research on the gas-synthesis process before 1935 in Germany, Japan, Britain, United States, and France. Summary: Studies were made of the effects of reaction temperature, gas velocity, and synthesis gas composition on the yield of liquid hydrocarbons, and an optimum reaction temperature and gas velocity were found to exist. A compromise between the most desirable yield of liquid hydrocarbons and the greatest catalyst durability was established at a H_2:CO ratio of 2:1. A ratio of diatomaceous earth to the metals content of the catalyst was found to produce the best results between 1:1 and 3:4; silica gel also was found to be a fair carrier. In preparing catalysts acetates were found to be as good a source material as nitrates. Studies of Ni catalysts showed that by using 100 Ni:20 Mn:8 U_3O_8:4 ThO_2 catalyst, 168.8 ml. of gasoline was obtained per cu. m. of synthesis gas. Co–Cu catalysts and Ni–Co–Cu catalysts were investigated. The temperature at which Co is reduced does not impair its subsequent catalytic activity in any way. The reduction temperature of Co may be lowered from 350° to 200° by adding more than 5% Cu; to lower the reduction temperature of Ni from 450° to 250°, more than 100% Co and more than 10% Cu (relative to the Ni) must be added. Studies of catalysts containing Ag showed that, although Ag is inferior to Cu as a means of lowering the reduction temperature, it is superior to Cu as a promoter. The mechanism of the hydrocarbon synthesis was discussed.

3498. Tsyskovskii, V. [Synthesis of Fatty Acids From Fractions of Petrolatum.] Jour. Appl. Chem. (U. S. S. R.), vol. 19, 1946, pp. 428–434; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 655, 1946, 7 pp.

Previous attempts to use petrolatum as a raw material for oxidation to acids to be used for the manufacture of greases were unsatisfactory because of the unsuitability of the molecular weights of a substantial proportion of the charging stock and its contents of isoparaffins. Conditions of distillation were found during which isoparaffins contained in petrolatum are for the most part broken down into straight-chain paraffins. Fractions of the material amounting to 70% can then be oxidized to obtain acids of molecular weight not exceeding 322, which are quite suitable for the preparation of calcium-base greases.

Tur, E. V. *See* abs. **2709.**

3499. Turkevich, J. Electron Microscopy of Catalysts. Jour. Chem. Phys., vol. 13, No. 6, 1945, pp. 235–239.

Number of electron micrographs are presented: Pt oxide, Adams Pt catalyst, platinized asbestos, the same sintered, activated alumina, active silica gel, alumina silicate cracking catalyst, Zn oxide MeOH catalyst, and a Fischer catalyst of Ni–ThO_2 supported on kieselguhr. The kieselguhr is seen to be composed of diatoms, which are particles full of holes 1,300 A diam. These openings offer a large surface for support of the Ni and ThO_2.

———. *See* abs. **3395, 3395a.**

3500. Turkevich, J., and Selwood, P. W. Solid-Free Radical as Catalyst for Ortho-Para Hydrogen Conversion. Jour. Am. Chem. Soc., vol. 63, 1941, pp. 1077–1079; Chem. Abs., vol. 35, 1941, p. 3512.

Object of this investigation was to determine whether the list of solid substances catalytically active for this transformation could be extended to include solid free radicals. The organic free-radical chosen for the investigation was α, α–diphenyl-β–picrylhydrazyl (I). The magnetic characteristics of (I), the corresponding hydrazine, active ZnO and ignited ZnO were determined. H_2 adsorption at liquid-air temperature was determined on (I), active ZnO, and an intimate mixture of the 2. Ortho-para H_2 conversion at liquid-air temperature was slow on ZnO and slow on the free radical but very rapid on an intimate mixture of the 2.

3501. Turkevich, J., Schessler, D. O., and Irsa, A. P. Study of the Interaction of Ethylene and Deuterium. Nuclear Sci. Abs. 4, No. 19, Oct. 15, 1950, p. 842.

Interaction of C_2H_4 and D_2 can take place by addition or exchange. These reactions are studied by mass spectrographic analysis of the various deutero-ethylenes and deutero–ethanes and the H_2-D_2 gas during the catalytic conversion of ethylene into ethanes. The results obtained for the interaction of ethylene with 2 vol. D_2 on a Ni wire at 90° C. show that exchange is more rapid than addition, and that the concentration of light ethylene decreases exponentially, but that of the substituted ethylene goes through a maximum before it finally reaches O. A surprising result is the discovery of completely light ethane from the reaction of ethylene and D_2. These results suggest that the ethylene hydrogenation is effected by the H_2 that was previously on other ethylene, and only indirectly by the H_2 mol. The point is being further investigated, and the mechanism formulation is being reserved until the kinetic investigations are completed.

Turner, G. *See* abs. **329.**

3502. Tutiya, H. Catalytic Decomposition of Carbon Monoxide. I. Iron as Catalyst. Bull. Inst. Phys. Chem. Research (Tokyo), vol. 8, 1929, pp. 206–219; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 10, 1929, pp. 69–82; Chem. Abs., vol. 23, 1929, p. 3620.

Decomposition rate of CO was measured in presence of C, 2 kinds of Fe wire, reduced Fe, and a mixture of

Fe_3C and C, and the carbons produced were studied with X-ray. Conclusions: (1) Fe functions not as a catalyst but as a catalyst donor, that is, as a supporter of autocatalytic decomposition of CO. (2) When CO decomposes in presence of Fe, Fe_3C forms first, and the 2 reactions, $3Fe+2CO=Fe_3C+CO_2$ and $2CO=C+CO_2$, progress concurrently. (3) Fe_3C has a remarkable catalyzing ability and plays a chief role in the decomposition of CO. (4) C isolated from the catalytic decomposition not only has no catalyzing power but even hinders the catalytic effect of Fe_3C. (5) Fe_3C becomes very densely packed with the C, which is isolated by decomposition, till it ceases completely to catalyze. On this account Fe_3C in the C is very difficult to remove. This suggests a quality of C that is obtained catalytically by decomposition in presence of metal. (6) X-carbide of U. Hofmann is Fe oxide.

3503. ———. [Catalytic Decomposition of Carbon Monoxide. II. Is the So-Called X-Carbide Really Formed in the Iron Catalyst?] Bull. Inst. Phys. Chem. Research (Tokyo), vol. 8, 1929, pp. 609–613, abs. sec. 2, pp. 76–77; Chem. Abs., vol. 24, 1930, p. 3159.

X-ray spectograms of specimens of Fe carbide and Fe_2O_3 used as catalysts in the decomposition of CO gave no evidence of the formation of new compounds. The photograms of samples of Fe_2O_3 taken at suitable stages of the reaction showed evidence of the successive reduction to the oxides Fe_3O_4 and FeO and later to Fe_3C. It was found that almost all the lines of strong intensity, which Hofmann (abs. **1455**) ascribed to the X-carbide, agreed with those of Fe_3O_4, not only in position, but also in order of intensity; one of the weak lines, which was not common to Fe_3O_4, was due to FeO, and 2 were shown by Fe_2O_3.

3504. ———. Catalytic Decomposition of Carbon Monoxide. III. Behavior of Iron Carbides. Bull. Inst. Phys. Chem. Research (Tokyo), vol. 10, 1951, pp. 556–562, abs. 58–59 (in English); Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 16, No. 306–309, 1931; Chem. Abs., vol. 25, 1931, p. 5615.

In the catalytic decomposition of CO by Fe_3O_4 or Fe_3C, some relations between percarbide ($Fe\chi C$), cementite, and free C were determined. At 270°–320° Fe_3O_4 is reduced to $Fe\chi C$, and no FeO, Fe, or Fe_3C is found in the course of this reduction, which indicates equilibrium exists between Fe_3O_4 and $Fe\chi C$ in the solid phase and between CO and CO_2 in the gaseous phase. Reduction at 280°–320° gives a mixture of $Fe\chi C$ and Fe_3C and the amount of the latter increases with rise in reaction temperature. At 450°, $Fe\chi C$ decomposes rapidly into Fe_3C and C. At 270°, $Fe\chi C$ is formed not only from Fe and its oxides but from Fe_3C.

3505. ———. Catalytic Decomposition of Carbon Monoxide. IV. Behavior of Nickel Carbides. Bull. Inst. Phys. Chem. Research (Tokyo), vol. 10, 1931, pp. 951–973, abs. 83–84; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 16, No. 328–329, 1931; Chem. Zentralb., 1932, I, pp. 782–783; Chem. Abs., vol. 27, 1933, p. 1809.

An X-ray investigation of the catalytic decomposition of CO by Ni or NiO has confirmed the formation of Ni_3C and a percarbide, $Ni\chi C$. The percarbide is formed from NiO at 270° and rapidly decomposes into Ni_3C and C at 284°; it also is decomposed by atmospheric H_2O vapor. Ni_3C is quite stable at 285° and catalyzes the decomposition of CO. In the temperature range of stability of Ni_3C, the reaction $3Ni+2CO \rightleftharpoons Ni_3C+CO_2$ is possible, but not reaction $2CO=C+CO_2$. Free Ni is found in the earlier stages of reduction of NiO, but later changes completely to carbides.

3506. ———. Catalytic Decomposition of Carbon Monoxide. V. Behavior of Molybdenum Carbides. Bull. Inst. Phys. Chem. Research (Tokyo), vol. 11, 1932, pp. 1136–1149; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 19, No. 384–392, 1932; Chem. Abs., vol. 27, 1933, p. 1809.

CO was decomposed under various conditions in presence of metallic Mo, its carbides or solid solution of Mo_2C, and solid phases formed of carbides and C were examined by the X-ray method. Mo_2C is formed at 450°–600°; a very diffused diffraction line of C (002) is observed in the powder spectrogram of the reaction product at 600°. Mo and its carbides are not oxidized in CO at 450°–800°; CO flowing over the mixture of Mo_2C and C is decomposed at 600°, C itself having no catalytic property. A new carbide phase, most probably MoC, is formed at 750°. At 750°–800°, the mixture of Mo_2C, MoC, and C is formed, and CO is decomposed without the existence of metallic Mo; the reaction product at 650°–700° contains, besides Mo_2C, a metastable carbide phase.

3507. ———. X-Ray Observation of Molybdenum Carbides Formed at Low Temperatures. Bull. Inst. Phys. Chem. Research (Tokyo), vol. 11, 1932, pp. 1150–1156; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 19, No. 384–392, 1932; Chem. Abs., vol. 27, 1933, p. 216.

Mo atoms in Mo_2C have the dense hexagonal lattice, 1 atom being in the position (⅓ ⅔ ¼) and another in (⅔ ⅓ ¾). The C atom in the cell containing 1 mol. is perhaps in the position (0 0 0). Lattice constants are: a=2.994 Å. U., c=4.722 Å. U., c/a=1.577. The atoms of C and Mo in the unit cell of MoC have the following coordinates, respectively: C(⅓ ⅔ ½), Mo (0 0 0); the lattice constants are: a=2.901 Å. U., c=2.786 Å. U., c/a=0.960, and, thus, the C atom in MoC has a radius of 0.785 Å. U. No clear distinction between the lattice constants of MoC and of the metastable carbide phase was found; the reflections from the 2 carbides differ markedly in their relative intensities.

3508. TUTTLE, R. B. Two New Coal-to-Oil Plants Are Demonstrated by Mines Bureau. Oil Gas Jour., vol. 48, No. 1, 1949, pp. 58, 159.

Brief description of plants and operation of the coal-hydrogenation and the gas-synthesis units recently dedicated at Louisiana, Mo. The first is designed to operate at a pressure of 10,300 p. s. i. and temperature of 600°–900° F, and produce 200–300 bbl. of products per day. The actual production capacity is dependent on the coal and catalyst used. The gas synthesis unit is a designed modification of the Fischer-Tropsch process, and has a nominal rating of 80–100 bbl. of product per day, comprising 5–10 bbl. of propane, 55 bbl. gasoline, 10 bbl. diesel fuel, and 12 bbl. heavy oils and waxes. Two new-type Bureau-developed converters are to be used for the conversion of gas to liquid fuels. Each has a different cooling system: The first unit is cooled by circulating oil through a fixed bed of granular catalysts, the 2d by passing the gas through a rapidly circulating slurry of coolant oil and powdered catalyst. O_2 for processing operations is produced by a Linde-Fränkl generator at temperatures of more than 300° F. below O°. The synthesis gas is produced by O_2 steam gasification of pulverized coal at a temperature of 2,000° F. or more.

3509. TWIGG, G. H. Catalytic Isomerization of 1-Butene. Proc. Roy. Soc. (London), vol. 178, 1941, A, pp. 106–117; Chem. Abs., vol. 35, 1941, p. 5775.

Early work upon the isomerization of 1-butene to 2-butene on a Ni catalyst in the presence of H_2 is extended to D_2. The double-bond migration is examined simultaneously with the exchange and hydrogenation reactions. At 65°, the kinetics of double-bond migration are identical with those of hydrogenation, the rate of the reaction being proportional to the square

root of the pressure of the butene or H_2. The energies of activation are found for the temperature range 76°–126°. At the lowest temperature, the rate of double-bond migration is 6 times that of exchange. This is in agreement with the theory that the catalytic exchange between the olefins and D_2 takes place through the formation of an associative complex. The step that determines the rate in the double-bond migration is the 2d fast step of the exchange reaction. The accounts given for the double-bond migration by the dissociative theory of exchange must be regarded as inadequate; whereas the associative theory succeeds in giving a consistent picture of the whole reaction process.

3510. TWIGG, G. H., AND RIDEAL, E. K. Chemisorption of Olefins on Nickel. Trans. Faraday Soc., vol. 36, 1940, pp. 533–537; Chem. Abs., vol. 34, 1940, p. 4634.

Calculations were made that show that the previous view regarding the mode of adsorption is possible with very little distortion of the adsorbed molecule; namely, that olefins are chemisorbed on Ni with opening of the double bonds and adsorption on 2 Ni atoms. The interatomic spacing of the catalyst atoms is the important factor where 2-point contact is required in adsorption. There is little interaction between neighboring adsorbed ethylene molecules; for the higher olefins, however, the interaction is considerable, and these molecules cannot cover the whole surface.

3511. TYLER, F. Magnetization-Temperature Curves of Iron, Cobalt, and Nickel. Phil. Mag., vol. 11, No. 7, 1931, pp. 596–602; Chem. Abs., vol. 25, 1931, p. 2609.

Curves for σ/σ_0 against T/θ are almost identical for Fe, Co, and Ni. They are definitely incompatible with the classical curve and with quantum curves for j greater than, or equal to, 1. There is close agreement when $j=\frac{1}{2}$. The electron spin is to be regarded as the fundamental magnetic element operative for Ni, Fe, and Co. The value of $j=\frac{1}{2}$ means that electron spins are independent and that there is a tan h distribution. The electrons are not free but associated with ions as in Heisenberg's theory.

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3512. UBBELOHIDE, L. [Anthracite in German Motor-Fuel Economy.] Oel u. Kohle Erdoel Teer, vol. 12, 1936, pp. 353–359.

Various processes for motor-fuel production from coal are discussed: Coking, distillation, hydrogenation, Fischer-Tropsch, Pott and Broche, and Uhde.

3513. ———. [Mineral-Oil Research.] Oel u. Kohle Erdoel Teer, vol. 12, 1936, pp. 983–988; Chem. Abs., vol. 31, 1937, p. 3247.

An up-to-date account of processes for obtaining motor fuels and oils from materials other than petroleum, such as from coal and lignite by distillation, hydrogenation, Fischer-Tropsch, Pott-Broche.

UHL, W. C. *See* abs. **268.**

ULICH, H. *See* abs. **3147.**

ULLMANN, D. *See* abs. **1954.**

3514. ULLRICH, A. [Most Recent Processes for the Catalytic Production of Methanol From Carbon Monoxide and Hydrogen.] Metallbörse, vol. 19, 1929, pp. 1181–1182, 1238–1239, 1294–1295; Chem. Abs., vol. 23, 1929, p. 3898.

Review.

3515. ———. [Preparation of Methyl Ether From Oxides of Carbon by Means of Catalytic Hydrogenation.] Metallbörse, vol. 19, 1929, pp. 1741–1742; Chem. Abs., vol. 23, 1929, p. 5158.

Review.

UMEMURA, T. *See* abs. **1900, 1901, 1902.**

3516. UMINO, S. Specific Heat of Iron-Carbon System at High Temperatures, and the Heat Changes Accompanying Those in Phase. Sci. Repts. Tôhoku Imp. Univ., 1st ser., vol. 23, 1935, pp. 665–793; Chem. Abs., vol. 29, 1935, p. 4253.

Heat content of 19 Fe–C alloys containing 0.07–5.07% C was measured at numerous high temperatures up to and beyond the melting point. Electrolytic Fe and sugar C were used in preparing the melts. The heat of fusion of the δ–alloy containing 0.03% C is 65.31 cal.; 0.07% C, 64.90 cal.; of the γ–alloy containing 0.13% C, 67.19 cal.; 1.70% C, 57.8 cal. The heat of fusion of the eutectic is 60.91 cal. That of cementite, by extrapolation, is 65.0 cal., its melting point being estimated to be 1,600°. The heats of transformation of the α– into the γ–Fe at the A_3 point are calculated to be 5.59 cal. for pure Fe and 16.60 cal. for the eutectoid at 720°. The heat of solution of Fe_3C in γ–Fe of 0.90% C is 11.15 cal. at 720°; it decreases with rise in temperature and C concentration. The heat of the A_0 transformation of Fe_3C is estimated to be 9.35 cal.

3517. UNDERWOOD, A. J. V. Oil From Coal. Chem. and Ind., 1938, pp. 360–364; Chem. Abs., vol. 32, 1938, p. 4308.

Review covering carbonization, hydrogenation, gas synthesis, and liquefaction.

3518. ———. Oil From Coal. Fuel Econ. Rev., vol. 17, 1938, pp. 14, 16–21, 31; Chem. Abs., vol. 33, 1939, p. 1122.

Reviews developments during 1937 in connection with the Fischer-Tropsch process, coal hydrogenation, and the recovery of benzol from coal gas.

3519. ———. Utilization of Oil Shales and Cannel Coals in Connection With Production of Synthetic Oils. Inst. Petrol. Conf., June 1938, pp. 468–473; Chem. Abs., vol. 33, 1939, p. 3571.

Possibilities of combining the carbonization of oil shales and cannel coals with processes for the production of synthetic oils by the Bergius or Fischer-Tropsch processes are discussed. An outline is given of various schemes in which the solid residue from the carbonization of cannel coal is utilized for these synthetic processes, and the scale of operation that would probably be necessary is indicated.

3520. ———. Industrial Synthesis of Hydrocarbons From Hydrogen and Carbon Monoxide. Ind. Eng. Chem., vol. 32, 1940, pp. 449–454; British Chem. Abs., 1940, B, p. 427; Chem. Abs., vol. 34, 1940, p. 3045.

Hydrocarbons in about 70% yield are obtained from $2\,H_2+CO$ using a Co catalyst—kieselguhr at 190°–200°, 5–15 atm.; yields are decreased and catalyst is impaired at higher pressures. A main controlling factor is the rate of removal of the products of reaction from the catalyst. Removal of wax from the surface of the catalyst maintains its activity. Various raw materials and processes for making synthesis gas are given. Conversion of CH_4 into synthesis gas (H_2: $CO=2:1$) by the process: $3CH_4+CO_2+2H_2O=4CO+8H_2$; $CH_4+O_2=CO+2H_2$, using a Ni catalyst at 760°, is discussed. Accurate temperature control is necessary, and indirect watercooling is used. S is removed by passing the gas over an alkaline Fe oxide or Ni catalyst at 177°–299°. Commercial plant is described. Straight-chain hydrocarbons with gasoline fraction of low octane number, a Diesel oil fraction with high octane number, and waxes (for example, those of m. p. 90.6°) are obtained.

———. I. G. Farbenindustrie A.-G. Works at Leuna. XVI. Mersol Process. *See* abs. **1480.**

3521. UNITED STATES ARMY ENGINEER CORPS. Survey of Southeastern Montana for Areas Suitable for

Synthetic Liquid Fuel Plants. Summary of Report to Bureau of Mines, December 1948, 4 pp.

Survey showed that there are enough minable coal reserves and water supplies to support some 362 10,000-bbl.-per-day plants for a 40-yr. period, and there is enough low-cost strip coal to operate 15 such plants for 20 yr. The North Central States would be the nearest and most logical potential market area for any liquid fuels produced. The comparative costs of liquid fuel, not including processing, based on the gas-synthesis process and on the most desirable and largest area, are calculated at \$1.80–\$2.37 per bbl. The mining cost alone is calculated at \$2.77–\$3.28 per ton of coal.

3522. ———. Survey of Western Kentucky, Northwestern Colorado, and Southeastern Texas for Areas Suitable for Synthetic Liquid Fuel Plants. Summary of Report to Bureau of Mines, December 1948.

Sample surveys of 4 States have indicated that they alone have enough coal, shale, and natural gas to produce 9,000,000–10,000,000 bbl. of synthetic liquid fuels for 40 yr. Western Kentucky has coal reserves of 16,768 million tons or enough to meet the requirements of either 138 10,000-bbl-per-day synthine plants or 164 hydrogenation plants of the same size. Water supplies are adequate, and the area is favorably situated with respect to markets. Northwestern Colorado has coal reserves yielding 25 gal. or more per ton of easily minable coal, which will support 105 10,000-bbl.-per-day synthine plants for 40 yr., together with available coal reserves adequate to supply 279 synthine plants or 336 hydrogenation plants. Water supplies available by 1963 for all new uses would limit the synthetic-fuel capacity to 1,050,000 bbl. per day from shale, plus 510,000–840,000 bbl. per day from coal, depending on the process used. Southeastern Texas has an estimated 9.5 trillion cu. ft. of natural gas, enough to support 15 10,000-bbl.-per-day synthine plants for 20 yr. Its availability, however, depends on economic and conservation considerations, which could very definitely limit the consumption.

3522a. ———. Synthetic Liquid Fuel Potential of the United States. Report for the Bureau of Mines, March 3, 1952. Chem. Eng. News, vol. 30, 1952, p. 2,101.

Report based on a survey of the United States and Alaska by Ford, Bacon and Davis, Inc. to the Army Corps of Engineers. The survey reveals that there are sufficient available supplies of coal, oil shale, and natural gas in suitable general areas in 25 States to produce 226.4 billion bbl. of synthetic liquid fuels by the hydrogenation of coal, or 195.3 billion bbl. by the synthine (Fischer-Tropsch) process. An additional 781.1 million bbl. of liquid fuels could be obtained from natural gas by the Fischer-Tropsch method, while 99.4 billion bbl. are obtainable by retorting oil shale. In other words, available coal supplies could yield 15.5 million bbl. of liquid fuels per day by hydrogenation or 13.4 million bbl. per day by the synthine process, plus 6.8 million bbl. per day by retorting oil shale, for a period of 40 yr. Natural gas could add 107,000 bbl. per day by the synthine process for 20 yr. Plant sizes adapted are 10,000 bbl. of synthetic liquid fuels per day for coal hydrogenation, Fischer-Tropsch process for coal, and retorting of oil shale; and 5,000 bbl. per day of natural gas for the Fischer-Tropsch plant for natural gas. The report indicates that there are 37 States with significant resources of these 3 raw materials plus oil-impregnated material. The following factors were considered in selecting suitable areas: H_2O supply, power, access transportation, labor, housing, marketing and products transportation, waste disposal, plant investment, processing costs and strategic considerations. Only those areas with respect to coal were selected which had 60 million ton of recoverable coal in a 3-mile radius. The coal must have a minimum calorific value of 4,500 B. t. u. per lb. Other limitations included thickness of beds and depth of overburden. Because of these limitations, the suitable areas include only about 10% of the minable coal as estimated by the Federal Geological Survey. Basic criteria for oil shale were the existence of 200 million ton in a 5-square-mile area. The primary shale also must yield 25 gal. of oil per ton with 15 gal. per ton for the secondary shale. Bed thickness was limited to 25 ft. or more. The natural gas minimum requirements were 225 trillion B. t. u. in a 40-mile radius (primary) and 225 trillion B. t. u. (secondary). The gas in a 20-mile radius must have a minimum calorific content of 700 B. t. u. per $ft.^3$ and that in the 40-mile radius must have a content of 400 B. t. u. per $ft.^3$ The report also covers estimated costs of plants, manufacturing, and coal production. It also includes a large number of charts and tables.

3523. United States Bureau of Mines. Production of Synthesis Gas From Wyoming Subbituminous Coal. General Investigation of Methods and Flowsheet for Plant to Process 8,000,000 Cubic Feet per Day. Special Report, November 1946, 23 pp.

To obtain general information on the advantages and disadvantages of various methods of producing synthesis gas from a coal like the Wyoming coal, 4 methods are considered suitable for treating this coal, and calculations are made of the investment and production costs for a plant with a capacity of 100,000 N $m.^3$ per hr. of synthesis gas. The high content of H_2 of Wyoming coal promises very high tar content and, consequently, very favorable conditions for utilizing it for the production of motor fuels by combining carbonization and byproduct gasification with the synthesis of hydrocarbons and hydrogenation of tar. The 4 methods investigated are: Lurgi pressure gasification; combined carbonization-gasification with O_2 and with burning of coke and cracking of carbonization gas; the same with use of air in the 1st step and O_2 in the 2d with burning of the carbonization gas and gasification of the coke; and the Koppers complete gasification of powdered coal. Cost of equipment is taken from figures available from German sources. Corresponding figures for the United States are calculated with the ratio of 1 RM : \$0.50 for the investment cost and 1 RM : \$1.00 for the cost of labor, with a rough adjustment for special work.

Further calculations on 3 so-called pioneer plants A, B, and C: Carbonization-gas producer plant; Koppers pulverized-coal gasification; and Lurgi pressure gasification give production costs per 1,000 N $m.^3$ on the basis of capacities of 8,000,000 cu. ft. of ideal gas per day and 320 operating days, respectively, of \$9.30, \$11.80, and \$11.50. Here again the combined carbonization-gasification method is found to be the most favorable one. It is proposed to erect 2 units of the carbonization-gasification type with the necessary equipment for operating each of the units for the production of gas as well as for the carbonization of coal and the production of coke, as this seems the safest, cheapest, and most-flexible method with respect to the requirements of a pilot-experimental plant, which should be able to handle various types of coal from such standpoints as tar recovery and alteration of the $CO : H_2$ ratio. It might also prove an economical method for the treatment of oil shales with more than 10% of oil.

Investment costs and production figures for 100,000 N m.³ per hour of synthesis gas

	I Gasification of pulverized coal (Koppers)		II Lurgi pressure gasification		III Carbonization with O_2; gasification with O_2		IV Carbonization with air; gasification with O_2	
Investment cost:								
Million RM	49.5		54.0		50.2		46.6	
Million dollars		24.75		27.0		25.1		23.3
Coal consumption, tons per year		740,000		945,000		995,000		925,000
Laborers		420		600		550		450
Wages:								
Million RM	1.05		1.5		1.37		1.13	
Million dollars		1.05		1.5		1.27		1.13
Percent of production cost	11.0	20	13.5	24.5	12.8	23.4	11.5	21.5
Production cost per year:								
Million RM	9.6		11.14		10.66		9.79	
Million dollars		5.18		6.13		5.81		5.27
Tar production, tons per year				44,200		65,800		60,500
Value of tar:								
Million RM			4.86		6.58		6.05	
Million dollars				1.33		1.65		1.51
Percent of production cost			43.5	21.6	62.0	28.3	62.0	28.5
Production cost, 1,000 N cu. m.:								
Million RM	10.9		7.2		4.60		4.24	
Million dollars		5.9		5.40		4.70		4.25

3524. UNITED STATES BUREAU OF SHIPS, NAVY DEPARTMENT. Bibliography of Synthetic Liquid Fuels. Bib. 35, Apr. 2, 1945, 65 pp.; PB 1752.

Subject list of articles compiled for the Special Fuels Section of the Research and Standards Branch in connection with investigations of synthetic liquid fuels from oil shale, low-temperature carbonization of coal, Fischer-Tropsch synthesis, and Bergius high-pressure liquefaction of coal.

3525. UNITED STATES CONGRESSIONAL COMMISSION ON PUBLIC LANDS AND SURVEYS. Synthetic Liquid Fuels. 1944, 469 pp.

3526. UNITED STATES INDUSTRIAL CHEMICALS, INC. American Hydrocarbon Synthesis. U. S. Industrial Chemical News, I–XII, January–December 1948; Chem. and Eng. News, vol. 26, 1948, adv. sec., pp. 153, 391, 683, 1057, 1341, 1757, 2059, 2343, 2747, 3035, 3331, 3611.

Series of articles deals with various aspects of the chemical development of products of the Fischer-Tropsch synthesis to be manufactured by Hydrocol, Inc. at its Texas plant following the entrance of the United States Industrial Chemicals, Inc., into the field of marketing.

3527. UNITED STATES NAVAL TECHNICAL MISSION IN EUROPE. Thoria–Alumina Catalyst for Isoparaffin Synthesis. Tech. Rept., 110–45, 1945. 8 pp.; Oil Gas Jour., vol. 44, No. 37, 1946, pp. 86, 89; CIOS Rept., XXV–27; PB 289, 890.

Digest of the report, Wartime Research on Synthetic Fuels by the Kaiser Wilhelm Institut für Kohlenforschung. A catalyst of ThO_2–Al_2O_3 (1 : 4) gives the best yields of all catalysts investigated. Higher gas velocities may be used, the tendency for alcohol formation is low but high for C deposition. Increasing the Al_2O_3 content increases CH_4 formation, and addition of 0.5–1% K_2CO_3 raises the yield slightly. ZnO–Al_2O_3 catalyst shows slightly lower yields but better commercial prospects. Both catalysts are prepared by precipitation from the respective nitrate solution by means of Na_2CO_3. For synthesizing isoparaffins, pressures of 300 atm. and temperatures of 420°–450° are best. Yield drops rapidly below 300 atm., but, as pressures increase above this, the % of O-containing products increases until at 1,000 atm. the entire product is dimethyl ether. Temperatures below 450° show increases of alcohol and unsaturates and a decrease in C deposition. Above 450°, the reaction rate increases rapidly with mainly naphthenic products and excessive C deposition. The best synthesis gas is $CO : H_2 = 1.2 : 1$ and the best gas velocity 10 l. per hr. per 20 cc. of catalyst. Operating with a ZnO–Al_2O_3 catalyst (1 : 4) with a $CO : H_2$ ratio of 1 at 300 atm. and 450°, the yields per m.³ of gas were: Total yield C_3 and higher 120–130 gm., C_4 (90% isobutane) 50–80 gm., C_5+ (97% iso-) 30–60 gm.

3528. ———. Methane Cracking by Partial Combustion With Oxygen or Air in Germany. Bib. Sci. Ind. Repts., vol. 6, No. 12, 1947, p. 1050; PB 23,076–S, November 1945.

Descriptive list of 12 documents extending the subject matter of the original report by Lyon and Crawford (abs. **2155**).

3529. UNITED STATES NAVAL TECHNICAL MISSION TO JAPAN. Japanese Fuels and Lubricants. Article 7. Progress in the Synthesis of Liquid Fuels From Coal. X–38(N)–7, February 1946, 333 pp.; PB 58,701; BIOS Final Rept., 1305; PB 79,230; Fuel Abs., vol. 5, 1949, abs. 237; TOM Reel 232.

This report, containing more than 30 separate papers, summarizes the findings of the Petroleum Section of the U. S. Naval Technical Mission to Japan relative to research and industrial development in the fields of high-pressure hydrogenation, Fischer-Tropsch synthesis, and low-temperature carbonization. A general history (pp. 9–22, 321–326) of the synthetic fuels program in Japan also is presented. Numerous flowsheets, charts, and tables explain the extent and nature of the developments. It is revealed that Japan, in its acute need for oil, plunged into industrial coal hydrogenation without acquiring an adequate background of experience with the intermediate-scale equipment. Also materials, particularly heat-resistant alloy steels, were not available for the construction of suitable equipment, and manufacturing facilities did not exist for fabricating reaction vessels of proper size. All evidence indicates that only 2 commercial-scale coal-hydrogenation plants were installed in Japan, and it may reasonaby be interpreted that they did not have a perfected process. Also, according to information obtained, only 5 Fischer-Tropsch plants were ever put under construction; of these, only 3 were placed in operation, the 2 others being under construction at the end of the war. The Japanese 7-Year Plan called for production of 2,000,000 kl. of liquid fuels from coal by 1943, but actual production in the peak year 1944 was only 113,000 kl.

3530. ———. Japanese Fuels and Lubricants. Article 7. Progress in the Synthesis of Liquid Fuels from Coal. Location and Output of Japanese Synthetic Oil Plants. X–38(N)–7, February 1946, pp. 14–19, 23; PB 58,701.

Company	Location	Designed capacity	Type of operation	Catalyst	Actual fuel output, kl.				
					1941	1942	1943	1944	1945
Coal hydrogenation:									
1. Manshu Jinzo Sekiyu Co., Fushun Works.	Fushun, Manchuria.	2.5 ton/hr.; 10,000 tons per year.; nominal throughout, Oyama coal.	Liquid-phase, 200 atm. 430°; vapor phase, 200 atm., 430° and 440°, 1st and 2d stage, respectively: coal:vehicle=2:3 by weight.	Liquid phase—precipitated FeS; vapor phase—40% MoS_3+60% acid clay; Fe_2O_3; Fe_2O_3:S:$Sn(OH)_2$ 100:17:1; $ZnCl_2.2H_2O$; $MoO_3.Sn(OH)_2$.	------	770	--------	690	------
2. Chosen Jinzo Sekyu Co., Agochi Works.	Agochi, Korea..	5 tons per hr., paste; 50,000 tons per yr.; Agochi brown coal; nominal production 10,000 kl. heavy oil.	200-250 atm.; Unable to function as coal-hydrogenation unit: Converted to MeOH synthesis.	*See* No. 1	------	--------	--------	--------	------
Total coal-hydrogenation oil					------	770	--------	690	------
Fischer-Tropsch:									
1. Nippon Jinzo Sekiyu Co., Miike works.	Omuta, Kyushu.	30,000 tons per yr. oil output; 1,000 m.³/hr. converter-gas throughput.	Actual production, 16,000 tons; Ruhrchemie license 56 converters; atmospheric pressure, 180°–200°,2-stage; actual throughput gas, 750 m.³	Co:ThO:MgO:kieselguhr=21.2:1.2:2.4:75.2; Catalyst life, 120 days.	7,200	9,290	13,870	11,070	1,720
2. Amagasaki works.	Amagasaki, Honshu.	30,000 tons per yr..	Atmospheric pressure; 24 double-tube Ruhrchemie-type converters.	Co----------	------	--------	200	130	------
3. Takikawa works.	Takikawa, Hokkaido.	50,000 tons per yr..	10 atm. pressure; 36 double-tube, 32 single Ruhrchemie-type converters; 4 Japanese design.	Co and precipitated Fe catalyst and natural Fe catalyst.	------	1,550	1,600	6,610	2,480
4. Manshu Jinzo Sekiyu Co., Chielin works.	Chielin, Manchuria.	1,000 kl. per yr.---	----------	----------	------	Under construction.			
5. Chinchu works.	Chinchu, Manchuria.	40,000 kl. per yr---			------	Under construction.			
Total Fischer-Tropsch oil					7,200	10,840	15,670	17,810	4,200

3531. ———. Report on Research on the Fischer-Tropsch Process at the Kyoto Imperial University. X–38 (N)–7, encl. (D), 1946, pp. 227–248; PB 58,701.

Summarizes technical information pertaining to research on the Fischer-Tropsch process by Prof. G. Kita and staff at the Kyoto Imperial University. Serves only to outline the scope of the work and to present certain significant points covered in the interviews with Prof. Kita, Prof. S. Kodama, and Prof. K. Tarama. The report deals briefly with the history of the work, normal and middle pressure catalyst studies, and catalyst preparation and presents a list of papers, published for the greater part in the Journal of the Institute of Physical and Chemical Research, and a list of about 20 Japanese patents relating to the Fischer-Tropsch process.

3532. ———. Research Activities of the Imperial Fuel Research Institute, Kawaguchi. VII. Fischer-Tropsch Process. X–38 (N)–7, encl. (E), 1946, pp. 258–262; PB 58,701.

Key man in the organization was S. Tsutsumi, 1933–39. The plant ceased operation in 1940 when the plant at Miike was begun. The plant never attained more than 30% of design capacity, which was 200 kg. of total crude-oil product daily. Failure was due to poor catalysts and to faulty and cumbersome converter design. Only Ni catalysts were used, and the one giving the best results had the approximate weight composition Ni : Co : Cr : kieselguhr=40 : 10 : 7.5 : 50.

It was prepared by precipitation from the nitrates and reduced at atmospheric pressure with H_2. Flowsheet of the plant is shown.

3533. ———. Report on Miike Synthetic Oil Co., Omuta, Kyushu. X–38 (N)–7, encl. (G), 1946, pp. 283–305; PB 58,701.

Miike plant was constructed in 1936–40. It utilizes the conventional low-pressure Fischer-Tropsch process with Co–ThO_2 catalyst. Synthesis gas (H_2: CO=2 : 1) is obtained by blending water gas and reformed coke-oven gas. The process is licensed by Ruhrchemie and most equipment was constructed by Koppers. Plant capacity was rated at 30,000 tons of product per yr., but actual production during the peak year 1943 was only 16,000 tons. This primarily was due to decreased production of synthesis gas from the high–S, low-melting-point-ash Miike coal and to the low yield of oil per unit of synthesis gas because of low catalyst activity. Details on the history, organization, process flowsheets, plant layout, product quality, and output are presented.

Fuels Act covering calendar year 1945. A progress re- Synthetic Liquid Fuels in the United States. Rept. on the Synthetic Liquid Fuels Act, 1945, 44 pp.; Fuel, vol. 25, 1946, pp. 134–137.

Comprehensive summary of the Report of the United States Secretary of the Interior on the Synthetic Liquid Fuels Act covering calendar year 1945. A progress report on the investigations already made in the fields of coal hydrogenation, liquid fuels from water gas by the Fischer-Tropsch synthesis, synthesis-gas production, oil-shale research, and the production of fuels from agricultural residues.

3535. UNITED STATES SENATE COMMITTEE ON PUBLIC LANDS AND SURVEYS. Synthetic Liquid Fuels. Hearings Before a Subcommittee, 78th Cong., 1st sess., on S. 1243, Washington, 1944, 469 pp.

Reports of testimony and hearings of the Senate Committee on the possibilities of producing synthetic liquid fuels in the United States by the hydrogenation of coal and water gas.

UPJOHN, T. E. *See* abs. **1460.**

3536. URAZOVS'KII, S. S., AND YAKIMKIN, N. A. [Reactivity of Gaseous Nickel Carbonyl.] Ukrain. Khem. Zhur., vol. 10, 1935, pp. 44–50; Chem. Abs., vol. 30, 1936, p. 2476.

Reactions $CO+3H_2 \rightarrow CH_4+H_2O$ and $2CO \rightarrow CO_2+C$ are more powerfully catalyzed by $Ni(CO)_4$ at its decomposition temperature (150°) than by other Ni catalysts. The reaction $CO+CH_4 \rightarrow MeCHO$ is not catalyzed by $Ni(CO)_4$.

3537. UREN, L. C. Impact of Wartime Conditions on the Petroleum-Producing Industry. Petrol. Eng., vol. 17, No. 4, 1946, pp. 203, 204, 206.

Discussion of technologic developments during the war period and their effect on the petroleum industry. One of the most notable is the large-scale production of synthetic oil products from natural gas, coal, and shale oil. The Fischer-Tropsch process for synthesis of hydrocarbons from CO and H_2 is particularly promising and is said to be successful in producing motor fuels from natural gas at costs competitive with present day costs of petroleum fuels. Natural-gas reserves have assumed new significance as a result of this development. Hydrogenation of coal also has advanced economically and technologically.

3538. USACHEV, P. V. [Conference on Heterogeneous Catalysis, Moscow, May 13–16, 1940. Mechanism of the Catalytic Synthesis of Ammonia.] Jour. Phys. Chem. (U. S. S. R.), vol. 14, 1940, pp. 1246–1249; Chem. Abs., vol. 35, 1941, p. 3882.

Addition of 7% Al_2O_3 to an Fe catalyst gives optimum results.

3539. UTILIZATION. Synthetic Liquid Fuels From Coal. Vol. 1, December 1947, pp. 37–41.

Review.

V

3540. VALLETTE, F. [Synthetic Methanol.] Chim. et ind., Special No., April 1928, pp. 235–238; Chem. Abs., vol. 22, 1928, p. 4461.

Theoretical discussion of the possibilities of the synthesis of MeOH from CO and H_2, from which it is concluded that the experience gained in the synthesis of NH_3 would enable the production of MeOH, independently of the manufacture of synthetic NH_3, to be readily established, that the cost would be approximately 1.18 francs per l., that the cost of MeOH equivalent to 1 l. of gasoline would be about 1.77 francs, and that it would be feasible to produce enough MeOH to replace the whole of the gasoline now being imported into France.

3541. ———. [Synthetic Products Derived From Béthune Coals.] Rev. ind. minérale, No. 302, 1933, pp. 299–308.

Production of MeOH from water gas by the catalytic method developed by the Mines de Béthune is discussed briefly. Describes special apparatus.

3542. ———. [Hydrogenation of Coal.] Bull. soc. encour. ind. nat., vol. 135, 1936, pp. 353–365; British Chem. Abs., 1936, B, p. 965.

Describes plant at Béthune and compares Bergius and Fischer-Tropsch processes.

3543. VALØTA, G. [Industrial Production of Gas Mixtures for Large-Scale Chemical Syntheses.] Industria (Milan), vol. 56, 1942, pp. 191–193; Chem. Zentralb., 1943, II, p. 1036; Oel u. Kohle, vol. 40, Sch. 5, 1944; Chem. Abs., vol. 38, 1944, p. 6520.

Review of the various systems for the production of H_2–N_2 and H_2–CO mixtures by the water-gas process for use in the synthesis of NH_3, MeOH, and fuels. The production of gas for use in syntheses from gas mixtures such as coke-oven gas or natural gas is discussed.

VAN ARSDELL, P. M. *See* abs. **775.**

VAN BAVEL, T. *See* abs. **1739.**

VAN DINGENEN, W. *See* abs. **3547, 3548.**

3544. VAN DYKE, B. H. Low-Pressure Oxygen Cycle. Chem. Eng. Progress, vol. 44, No. 10, 1948, pp. 20, 38, 42 (News Sec.); Chem. and Ind., vol. 63, No. 4, 1948, pp. 604–607; Petrol. Refiner, vol. 27, No. 10, 1948, pp. 540–544; Blast Furnace Steel Plant, vol. 36, 1948, pp. 1212–1215.

Elliott Co. plant, described by the help of a simplified flow diagram, is designed to produce approximately 114 tons per day of 95% purity gaseous O_2, plus approximately 6 tons per day of 99.5% high-purity gaseous O_2, plus 332 tons per day of 99.5% purity dry N_2. The recovery of O_2 from the air charged to the plant is approximately 97.5%.

3545. VAN ITTERBEEK, A. [Relation Between Adsorption and the Catalytic Activity of Metals.] Mededeel. Koninkl. Vlaam. Acad. Wetenschap., Belg., Klasse Wetenschap., vol. 3, No. 10, 1941, pp. 3–20; Chem. Zentralb., 1942, II, p. 742; Chem. Abs., vol. 37, 1943, p. 4958.

On the very pure Ni film the adsorption of H_2 and CO at temperatures up to 500° and pressures below 1 mm. was studied with the help of a thermal-conductivity gage. At ordinary temperature, activated adsorption of H_2 occurs; at higher temperatures, this increases and is apparently not to be attributed to diffusion adsorption. Comparison of the H_2 and CO isobars shows that at 167° and 329° the ratio of H_2: CO is 3 : 1 and at 2 other temperatures the ratio is 2 : 1, corresponding, respectively, to the synthesis of CH_4 and benzene. It is concluded that the occurrence of this stoichiometric surface ratio is related to the surface reaction. On a copper film, neither H_2 nor CO is adsorbed until a small quantity of Th is electrodeposited. In this instance also, temperatures exist at which the H_2: CO ratio is 3 : 1 and also those in which it is 2 : 1.

3546. ———. [Prospects of the Problem of Synthetic Oils in Belgium.] Techn. Wetenschap. Tijdschr., vol. 11, 1942, pp 37–44; Chem. Zentralb., 1942, I, p. 2955; Chem. Abs., vol. 37, 1943, p. 3586.

Discussion of future possibilities of oil synthesis in Belgium includes a review of synthetic oils, Bergius and Fischer-Tropsch processes, catalysis as the basis of the oil synthesis, relationships between catalysis and adsorption, recent determinations of adsorption at extremely low pressures and extremely pure adsorbing surfaces of Ni, Cu, and Cu activated with ThO_2 (carried out in the Laboratory of Natural History at Louvain), comparison of the results obtained with the velocity of reaction of the gas mixture CO–H_2, discussion of the regions of reaction for CH_4 and heavy oils with the aid of so-called stoichiometric temperatures, influence of pressure on the stoichiometric points, and practical importance of the empirical determination of the properties of catalysts with the aid of adsorption measurements.

3547. VAN ITTERBEEK, A., AND VAN DINGENEN, W. [Catalytic Action of Nickel and Copper–Thorium in the Formation of Methane and Heavy Gases.] Ztschr. physik. Chem., vol. 50, B, 1941, pp. 341–360; Chem. Abs., vol. 37, 1943, p. 1917.

Adsorption of H_2–CO mixtures by Ni foil was determined at low pressure, less than 2 mm. Hg, and over a wide temperature range. At 167° and 329°, H_2 and CO are adsorbed in the ratio 3 : 1, corresponding to CH_4 formation, and, at 125° and 378°, they are adsorbed in the ratio 2 : 1, corresponding to higher paraffin forma-

tion. The reaction rates also show maximum at these temperatures. Cu adsorbs H_2 and to a smaller extent CO only if it contains traces of Th. At 250° and 325°, H_2 and CO are adsorbed in the ratio 3 : 1. Similar experiments with D are described.

3548. ———. [Formation of Methane in Connection With the Activated Adsorption of Hydrogen and Carbon Monoxide by Nickel and by Copper.] Physica, vol. 8, 1941, pp. 810–824; Chem. Abs., vol. 36, 1942, p. 6062.

CH_4 forms when H_2 and CO are adsorbed on Ni. Cu acts in the same way when activated by a trace of Th. It was found that Ni shows 2 temperatures, 165° and 300°, at which the ratio of H_2 : CO adsorbed is 3 : 1, correct ratio for CH_4 formation and, also 2 temperatures, 125° and 370°, at which the ratio is 2 : 1, correct ratio for benzene formation. At these exact temperatures, the reaction rate showed sharp maxima. The reaction product at 200°–300° was found to be nearly pure CH_4, but, at 165° and 400°, heavier products also occurred, which contained benzene. The same type of behavior was found for Cu; the best temperature range for CH_4 formation is 250°–525°.

VAN LOON, W. *See* abs. **677.**

3549. VAN NOY, C. W., DUNVILLE, T. C., DRESSLER, R. G., AND CHAFFEE, C. C. Guide for Making Cost Estimates for Chemical-Type Operations. Bureau of Mines Rept. of Investigations 4534, 1949, 64 pp.

Procedure suggested in this report is intended for the use of engineers, estimators and accountants, in estimating the cost of chemical-type operations, such as the production of synthetic liquid fuels, anhydrous NH_3, and the like. It is intended to cover operating, not investment, costs.

VAN RAAY, H. *See* abs. **1836a.**

3550. VAN VOORTHUIJSEN, J. J. B. VAN E. Isomerization Equilibria of the Butanes, Pentanes, Hexanes, and Heptanes. Rec. trav. chim., vol. 66, 1947, pp. 322–334 (in English); Chem. Abs., vol. 42, 1948, p. 439.

Isomerization equilibria for the butanes were determined by passing C_4H_{10} and HCl over $AlCl_3$ (on Norit CC) at 100°, 150°, and 200°. For the higher alkanes the determination was made in an autoclave: 100 gm. hydrocarbons, 5–10 gm $AlCl_3$ (sublimed through active C at 250°), HCl, and H_2 were heated for 24 hr. as high as 80°. The products were analyzed by fractionation. Neopentane, neoheptane, 3, 3–dimethylpentane, and 3–ethylpentane were not produced under these conditions, and neoheptane failed to isomerize. The results for the heptanes deviated considerably from the thermodynamic predictions.

3551. VAN WINSEN, A., AND BROWN, E. A. Superfine Asbestos. Canadian Chem. Process Ind., vol. 32, 1948, pp. 129–132.

Superfine is the term applied to asbestos when opened to a degree where the individual fibers are exceedingly fine and so minute in diam. that most of them are invisible under the optical microscope. Electron microscopical study reveals the presence of fibers approximately 20 mμ diam. It is produced by wet milling in a ball or pebble mill and by subsequent spraying through a nozzle with compressed air. Its heat-resisting nature, fibrous form, and large surface area suggest the use of superfine asbestos as a catalyst or inert carrier upon which very finely divided catalyst could be deposited.

3551a. VARGA, J. [Manufacture of Motor Fuels by the Fischer-Tropsch Synthesis.] Magyar Kém. Lapja, vol. 5, 1950, pp. 363–368.

Summary.

VASKEVICH, D. N. *See* abs. **2092.**

VAUGHAN, W. E. *See* abs. **1469.**

VEDARAMAN, S. *See* abs. **1194.**

3552. VELDE, —. [Gasoline Synthesis According to Fischer-Tropsch Ruhrchemie Middle-Pressure Process.] FIAT Reel K–25, frames 003,957–003,978, Mar. 15, 1938; PB 70,216.

Survey of gasoline synthesis and calculation of the operating and installation costs for the 2-stage pressure method. (Several papers of the same content, FIAT Reel K–25, frames 3,974–3,978, contain the English translation of FIAT Reel K–25, frames 3,966–3,970). The synthesis gas ($CO : H_2 = 1 : 2$), is carried over Co catalysts at 175°–200° C. and raised pressure. The products are: 30% gasolinelike hydrocarbons, 30% Diesel oil, and 40% paraffinlike hydrocarbons that can be converted into gasol under weak thermal treatment with 80% yield.

3553. ———. [Oxidation of Paraffin With Nitrous Gases.] FIAT Reel K–25, frames 003,951–003,952, July 7, 1945; PB 70,216.

Process was carried out to produce highly molecular waxlike acids, taking care that the chain length of the paraffin hydrocarbons is spared as much as possible. After further processing, these waxlike acids can be used as substitutes for Montan waxes or I. G. Farbenindustrie waxes and emulsifiers. The starting material for the production of wax acids (straight-chain fatty acids with C numbers above 18–20) was Ruhrgasoline hard wax in refined and crude condition. It is a paraffin mixture of b. p. 400°–450° and mol. weight of about 600. At 100°–125°, paraffin is subject to the action of nitrosyl sulfuric acid and nitrous gases that are formed by NH_3 oxidation. A product that contains still unaltered starting material is formed. The pure acid can be separated by a treatment with caustic alkali solution and extraction with gasoline.

3554. VELDE, H. [Methods for Working Up the Primary Products of the Synthesis Process and Their Application to the Treatment of Petroleum.] Oel u. Kohle, vol. 37, 1941, pp. 143–148; British Abs., 1948, B, I, p. 280; Chem. Abs., vol. 35, 1941, p. 8268.

Special refining method worked up by Ruhrchemie is similar to ordinary vapor-phase refining. Raw gasoline before or, preferably, after final stabilization is heated to a high temperature below the cracking temperature and led over a special catalyst, unnamed, after which the vapors are cooled and passed over the same catalyst in a 2d step at a lower temperature. Octane no. was improved by 8–24 points, the increase being independent of the original octane no. It is indicated that this effect results from an isomerization of the original material, including both branching and a change in the position of the double bond. A gasoline of 35% olefin content had an octane no. of 44, whereas, of 55% olefin content had an octane number of 41, other properties being substantially the same. The octane nos. were increased to 52 and 61, respectively, by the method discussed. The method increased the octane no. of a cracked gasoline from petroleum from 66 to 71.5. Other methods, polymerization, aromatization, and cracking are briefly discussed.

3555. ———. [Relation of Octane Number and Peroxide Content of Synthetic (Fischer-Tropsch) Gasoline.] Oel. u. Kohle, vol. 40, 1944, pp. 10–15; Petrol. Refiner, vol. 25, No. 6, 1946, pp. 137–140; Chem. Abs., vol. 38, 1944, p. 5067.

Storage tests in brown and transparent bottles with and without exposure to light showed a considerable accelerating effect of light on the peroxide formation, peroxides determined by the method of Yule and Wilson, in primary synthetic gasoline (I), vapor-phase cracked synthetic gasoline (II), and a 1 : 1 blend of (I) and (II), (III). All the gasolines were obtained by

the Fischer-Tropsch synthesis, (abs. **1018** and **1021**) or by processing material primarily made by this process. The octane numbers of samples containing an appreciable amount of peroxides decreased noticeably; the research octane number of (I) dropped from 58.0 to 37.0 when the peroxide content had reached 325 mg. O_2 per l., the octane no. of (II) fell from 68.1 to 45.0 at a peroxide content of 350 mg. O_2 per l., and (III) decreased from 65.0 to 38.5 at a peroxide number of 305 mg. O_2 per l. The same gasolines with and without the addition of alcohol, cresol, $PbEt_4$, or a mixture of all these additives were stored in Fe drums, and it was found that cresol inhibited the peroxide formation almost completely during a storage period of 2 yr. A definite inhibitor effect was found for alcohol with (I) and (III). $PbEt_4$ acted as inhibitor for gasolines stored in galvanized Fe drums but was without effect in bare Fe drums. The relation of octane no. and peroxide no. for the types of gasolines tested is shown in a diagram. Removal of peroxides by acidic $FeSO_4$ solution did not completely restore the original octane no.

3556. VELLINGER, E., AND THOMAS, B. [Ultraviolet Absorption Spectra of Synthetic Petroleum.] Compt. rend., vol. 209, 1939, pp. 882–884; Chem. Zentralb., 1940, I, p. 2455.

Spectrum of Fischer synthetic oil shows the presence of a considerable amount of aromatics. Oils obtained by the polymerization of olefins showed the same behavior. Oils were investigated that had been produced by the Fischer process and distilled in a cathodic vacuum. It was noted that as the distillation temperature increased the absorption and the density likewise increased. It appears that a part of the aromatic nuclei had become concentrated in the residue. From the position of the bands it was evident that the product consisted of napthalene or other highly condensed nuclei.

VELTISTOVA, M. V. *See* abs. **728.**

3557. VELTISTOVA, M. V., DOLGOV, B. N., AND KARPOV, A. Z. [Synthesis of Methanol From Water Gas Under Pressure.] Jour. Chem. Ind. (U. S. S. R.), vol. 10, No. 9, 1934, pp. 24–32; Chem. Abs., vol. 29, 1935, p. 1059.

Best catalyst is prepared by mixing ZnO and Cr_2O_3 and stirring with CrO_3 solution to produce $8ZnO \cdot Cr_2O_3 \cdot CrO_3 \cdot xH_2O$. This is heated in a stream of H_2O and forms $8ZnO \cdot 1.5\ Cr_2O_3$. At 390°–400°, 250 atm., and a gas speed of 10,000 l. per hr., this yields 1,150–1,200 gm. of MeOH per l. of catalyst per hr. Pure CO_2 and H_2 in the ratio 1 : 2 should be used, and no inert gas or S compound should be present, though H_2S can be reversibly desorbed from the catalyst.

VENKATESEN, C. *See* abs. **1189.**

VERESHCHAGIN, L. F. *See* abs. **3559.**

3558. VERESHCHAGIN, L. F., AND ZELINSKIĬ, N. D. [Chemical Reactions at High Pressures and Temperatures. I. Apparatus for the Study of Chemical Reactions at Pressures up to 5,000 Atmospheres and High Temperatures.] Bull. acad. sci. U. R. S. S., Classe sci. chim., 1943, pp. 443–452 (English summary); Chem. Abs., vol. 39, 1945, p. 1587.

Apparatus is described (with diagrams) for the study of reactions up to 5,000 atm. and 400°. The use of hydraulic compressors in conjunction with gas pressure as the generator of pressure permits considerable improvement in the technique of work of this type. The use of Hg as the hydraulic fluid (as previously used) is undesirable for several reasons, 1 of which is the entry of Hg into reactions under the experimental conditions.

3559. ZELINSKIĬ, N. D., AND VERESHCHAGIN, L. F. Chemical Reactions at Superhigh Pressures and High Temperatures. II. Reactions of Polymerization of Cyclohexene and Vinylcyclohexene. Bull. acad. sci. U. R. S. S., Classe sci. chim., 1945, pp. 44–51 (in English, pp. 51–52); U. O. P. Survey Foreign Petroleum Literature Transl. No. 535; Chem. Abs., vol. 40, 1946, p. 5025.

Reactions of polymerization of cyclohexene, vinylcyclohexene, and unsaturated compounds of synthine under pressures up to 4,000 kg. per $cm.^2$ and at temperatures up to 300°, 350°, and 360°, respectively, were studied. The polymerization of synthine ($n^{20}D$ 1.3969; boiling up to 150°; $d^{20}=0.7143$; I no. 80.0) leads to the formation of oily products with a gently sloping viscosity-temperature curve. The oily product obtained in the experiment in which P=4,000 kg. per $cm.^2$ T=360°, and t=3.5 hr. was distilled under vacuum; 2 gm. were obtained, $b_{0.5}$ 150°–255°. The viscosity of the oil was slightly less than that of the turbine oil; $n^{21}D$ 1.4836. It congealed at 40°–45°.

VERNON, C. E. *See* abs. **141.**

VIALLE, J. *See* abs. **759.**

VIDT, E. J. *See* abs. **15a.**

3560. VIGNON, L. [Action of Water Vapor on Carbon in the Presence of Lime.] Compt. rend., vol. 152, 1911, pp. 871–874; Chem. Abs., vol. 5, 1911, p. 2044.

If water vapor is allowed to act upon a mixture of C and CaO at 600°–800°, H_2, CH_4, and some C_2H_4 are formed besides CO and $CaCO_3$. The mixture of CaO and C decomposes H_2O more rapidly and at lower temperature than C alone. Much H_2O and long heating reduce the amount of CH_4 as the latter is decomposed by the H_2O to CO and H_2. The above reactions may explain the formation of marsh gases and natural gases as well as formation of petroleum in nature.

3561. ———. [Formation of Hydrocarbons From Carbon Monoxide.] Bull. soc. chim. (4), vol. 9, 1911, pp. 18–20; Chem. Abs., vol. 5, 1911, p. 1088.

CO is converted into CH_4 by conducting CO over a mixture of CaO and $Ca(OH)_2$ at about 400°. The reaction takes place with the intermediate formation of Ca formate, which decomposes to give CH_4 and C_2H_4. This salt at 360°–370° gives a gas containing 20% CO_2, 27% CO, 51% H_2, and 2% hydrocarbons.

3562. ———. [Composition of Water Gas.] Compt. rend., vol. 156, 1913, pp. 1995–1998; Chem. Abs., vol. 7, 1913, p. 3405.

Water gas prepared by conducting H_2O vapor over coke, the ash of which contained 7–8% CaO, contained 3.45% CH_4, whereas water gas from C obtained from sugar, the ash of which contained 0.8% CaO, gave less than 2% CH_4, CO and CO_2 having been removed. Mixing coke with CaO and passing H_2O vapor over the mixture, there were obtained, with 11% CaO at 1,000°, 12% CH_4; with 13% CaO at 1,000°, 19% CH_4; with 33% CaO, 23% CH_4, CO and CO_2 removed. Following reactions take place: (1) $4CO+2H_2O=3CO_2+CH_4$; (2) $2CO+2H_2=CO_2+CH_4$; (3) $CO_2+4H_2=CH_4+2H_2O$.

3563. ———. [Formation of Methane by Catalysis From Carbon Monoxide and Water Vapor.] Compt. rend., vol. 157, 1913, pp. 131–134; Chem. Abs., vol. 7, 1913, p. 3602.

Substances studied as catalyzers were Fe, Ni, Cu, and the oxides of Si, Al, and Mg. The catalyzers were placed in a glazed porcelain tube and heated at different temperatures in the electric furnace, the temperature being taken from the midst of the catalyzer by a Le Chatelier couple. The temperatures at which a maximum yield of CH_4 was obtained and the % present in the resulting gas after deducting CO_2 and CO are as follows: Al_2O_3, 950°, 39.1%; MgO, 900°, 58.7%; SiO_2, 750°, 43.5%; Fe, 950°, 35.5%; Ni, 400°, 89.3%; Cu, 700°, 74.1%. With Fe, Al_2O_3, and SiO_2, carbides are evidently an intermediate product and these carbides, as soon as formed, are acted upon by H_2O vapor with

the formation of CH_4: for example, $12CO+2Al_2O_3=C_3Al_4+9CO_2$; $C_3Al_4+6H_2O=3CH_4+2Al_2O_3$. Another explanation for the formation of CH_4 is that under the influence of catalyzers the following reactions take place: $CO+H_2O=CO_2+H_2$; $3H_2+CO=CH_4+H_2O$; $4H_2+CO_2=CH_4+2H_2O$.

3564. ———. [Water Gas.] Ann. chim., vol. 15, 1921, pp. 42–60; Chem. Abs., vol. 15, 1921, p. 2712.

It has been found that moist CO and H_2 react to form small amounts of CH_4, the proportions at 400°, after absorption of CO and CO_2, being H_2 99.8% and CH_4 0.2% and at 1,300°, 98.65% and 1.35%. The catalytic effect of various mineral constituents of the ash of gas coke on the formation of CH_4 is discussed.

VILESOVA, G. F. *See* abs. **569.**

3565. VINCENT, J. W. Aspects of the Synthetic Fatty Acid and Synthetic Fat Industries in Germany. Chem. Trade Jour., vol. 119, 1946, pp. 635–637; Petrol. Times, vol. 51, 1947, p. 283; BIOS Final Rept. 805, 1946, 99 pp.; PB 49,196.

During the war Germany operated 3 synthetic fatty acid plants: Witten (Ruhr), now in the British zone with intake capacity 40,000 tons per yr.; Oppau (Ludwigshafen), now in the French zone, 20,000 tons; and at Heydebrech, now in the Russian zone, 20,000 tons. A 4th plant, 12,000 tons, also was completed toward the end of the war at Leuna, now in Russian zone, but was not operated during the war. There was a synthetic fat plant at Witten. The raw material was Fischer-Tropsch gatsch b. 320°–450° C. or paraffin from hydrogenation of brown coal. A report of Mersol and Mersolate manufacture is given. I. G. Farbenindustrie's Mersol plants were located at Leuna (Merseburg), 50,000 tons, and Wolfen, 35,000 tons, both now in the Russian zone. The Witten plant owned by the Deutsche Fettsäurewerke, and the Oppau plant owned by I. G. Farbenindustrie have recently been operated, Witten, 20,000 tons, Oppau, 10,000 tons, with full capacity promised in 6 months. The Oppau plant is being repaired in anticipation of an offer from the Russian zone of 500–1,000 tons per month of brown-coal hydrogenation wax from Saxony. The Trade and Industries Division of the British Military Government is considering repair of Krupp and Victor Fischer-Tropsch plants to provide gatsch for the Witten plant. It is proposed to use the Ruhrchemie Fe catalyst and to examine the possibility of cracking the high-melting-point gatsch. As a result of laboratory work, Witten has reported favorably upon use of a rather oily slack wax from spindle oil refining at the Deurag-Neurag refinery at Misburg (near Hanover) and unfavorably upon a similar sample from neutral oil refining. Oppau has reported favorable results with these 2 slack waxes. Based on German data, costs for operating similar plants in the United Kingdom have been worked out. The figures are £96 10 s. 2 d. (Oppau) and £91 0 s. 4 d. (Witten) per metric ton of mixed fatty acids, which compare unfavorably with current market values. The cost of imported wax accounts for nearly ⅔ of this cost, however. The synthetic-fat plant is in operation, 350 tons per mo. Estimated costs of production in England was £205 4s. 1 d. per ton. The Oxo plant at Oberhausen has been 90% repaired. The usual feed stock for the mersol plants was mepasin or hydrogenated Fischer-Tropsch kogasin with b. p. 230°–320° C., though Witten also operated at times on heavy Fischer-Tropsch fractions. The hostapon process at Leuna is in direct production of alkyl sulfonic acids by sulf-oxidation of mepasin using SO_2 and O_2, the reaction being promoted either by ultraviolet light or by the use of acetic anhydride as catalyst. The I. G. Farbenindustrie chemists favored acetic anhydride.

VITTIKH, M. V. *See* abs. **2658.**

3566. VLUGTER, J. C. Manufacture of Mersolate in Germany. BIOS Final Rept. 1130, February 1947, 29 pp.; PB 75,845.

Mersolates are sodium alkyl sulfonates and are prepared by reacting a paraffinic-base material (a saturated gas-oil fraction from Fischer–Tropsch products) under influence of light with SO_2 and Cl and saponifying the resulting intermediate product, Mersol, by means of NaOH. A description of the process and the reaction conditions of the sulfochlorination and saponification are given. Several plant installations are described and translation is made of a report by Dr. Hagge and Dr. Korn on the preparation and saponification of Mersol with recommendations for the design of a Mersolate plant with a capacity of 15,000 tons of active material per yr.

3567. ———. [Synthetic Detergents, Production of Mersolates in Germany.] Chem. Weekblad., vol. 45, 1949, pp. 198–199.

Digest of a paper presented to the Netherlands Chemical Society, July 1948. 3 sources of detergents by way of the Fischer–Tropsch process are mentioned. The Fischer-Tropsch paraffins b. 320°–450° were utilized to produce 40,000 tons of synthetic soap per yr. The gasol fraction b. 240°–320° from the Mersol process produced a capacity of 80,000 ton of mersolate per yr. The Oxo process by preparation of primary alkylsulfates from C_{12}–C_{18} olefins gave a possible production of 10,000 tons. The mersol process is considered the most important source of detergents and, therefore, is described at greater length.

3568. VOGEL, H. [Synthesis and Polymerization of Formaldehyde.] Helv. Chim. Acta, vol. 11, 1928, pp. 370–371; British Chem. Abs., 1928, A, p. 508; Chem. Abs., vol. 22, 1928, p. 1756.

When a mixture of equal volumes of CO and H_2 was passed at 150°–180° over a mixture of pumice and Zn dust with 2% of MgO and 1% of PbO, formaldehyde was formed together with caramellike polymerization products.

3569. VOGEL, J. C. Oil From Coal in South Africa. South African Min. and Eng. Jour., vol. 51, 1940, pp. 107–109; Coke Smokeless-Fuel Age, vol. 3, 1940, p. 48.

Describes the essential features of the 3 types of processes—carbonization, hydrogenation, and synthesis—with special reference to South African conditions. There is no low-temperature-carbonization plant and little promise of an adequate market for the semicoke. Coal carbonization cannot be regarded as a major source of indigenous oil fuel. The establishment of a coal-hydrogenation industry in South Africa is mainly a question of economics. As regards synthesis, bituminous coal would have to be the fuel used. Separate carbonization of the coal and gasification of the coke probably would be too expensive and some form of direct gasification would have to be used. Coals of the Vereeniging and Breyten areas, seams 1 and 4 of the Witbank area, and the semianthracites of Natal all appear to meet the requirements. From the standpoint of raw material, the synthetic process has much wider scope than the others in the Union, and the investment required may be much less than for a hydrogenation plant.

3570. VOGEL, R., AND DÖRING, W. [Iron–Cementite–Manganese Carbide–Manganese.] Arch. Eisenhüttenw., vol. 9, 1935, pp. 247–252; Chem. Abs., vol. 30, 1936, p. 710.

Former investigations of this system and parts of it were enlarged and completed by establishing the constitutional diagrams on the basis of heats of reaction and structure. Mn and Mn_3C do not form, as indicated previously, an uninterrupted series of solid solutions with a maximum temperature; a transition

equilibrium occurs at solidification between 1.5 and 2.9% C, which leads toward higher C contents, to a minimum temperature. A new transformation of Mn carbide was observed at 1,050°. Four kinds of crystals were found in the system Fe–Fe_3C–Mn_3C–Mn: Ternary solid solutions of $\alpha(\delta)$–Fe with C and Mn, which are restricted to a small range in the Fe-corner; ternary solid solutions of γ–Fe with C and Mn with a very extended range; ternary solid solutions of γ–Mn with C and Fe (area+$\beta_4\nu_3$); and solutions Fe_3C and Mn_3C (area C $\beta_4\nu_3\nu_1$). The cementite does not form solid solutions with the excess Fe but the Mn_3C does with excess Mn. The conditions are explained in detail by the diagram. A table shows the location of the characteristic points α, β, γ, δ, and ϵ for the equilibria of the Fe–Mn–C alloys in solid state. Various structures ilustrated in photomicrographs.

3571. VOIRET, E. G. [Motor-Fuel Problem in France.] Chim. et ind., vol. 56, No. 5, 1946, pp. 423–428.

Discusses main means by which the motor-fuel requirements of France can be met from internal resources. By utilization of gas producers, distillation or gasification of lignites, coal and bituminous shales, and manufacture of certain synthetic fuels, at least the vital minimum of motor fuels can be produced from native resources on an economic basis, and probably a large measure of independence of foreign supplies be secured. It is considered that the synthesis of liquid fuels by the Bergius, Pott–Broche, Fischer, and Mines of Béthune methods is not economically attractive under normal circumstances, but a partial exception is made in favor of the synthesis of MeOH from Fuveau lignites. The requisite mixture of CO and H_2 also may be obtained by processing coke or by converting CH_4.

VOLKOVA, A. A. *See* abs. **849.**

3572. VOLMER, W. [Fischer-Tropsch Hydrocarbon Synthesis.] Ztschr. Elektrochem., vol. 54, 1950, pp. 252–254; Chem. Abs., vol. 45, 1951, p. 1749.

Attempt to obtain information on the mechanism of the Fischer-Tropsch synthesis by studying the statistical distributon of hydrocarbons in the product.

VOL'NOV, Y. N. *See* abs. **1795, 1796.**

3573. VON FREDERSDORFF, C. Continuous Gasification of Powdered-Coal Suspensions by Air–Oxygen and Air–Oxygen–Steam Mixture. Proc. Am. Gas Assoc., vol. 31, 1949, pp. 705–724; Chem. Abs., vol. 44, 1950, p. 8,623.

Describes operation and results of a laboratory-scale coal-gasification unit. Results define the variables affecting the process and indicate the magnitudes of the effects. It is indicated that (1) a slagging operation can be applied successfully to suspension gasification at atmospheric pressure, (2) low gas-residence time is advantageous in increasing the make-gas calorific value, (3) tangential firing can remove more than 50% of the ash in the form of slag, and (4) the use of a combustion tube in the center of the gasifier does not yield any thermal advantage over operation without a tube. Although a satisfactory gasification was accomplished from the standpoint of gas calorific value, it will be necessary to use steam superheated to at least 2,000° F. to decrease the make-gas CO_2 content, decrease the O_2 required for gasification, increase the C conversion, and shift the point of maximum thermal efficiency to closer correspondence with the point of maximum calorific value. Anticipated benefits of the process for the industry include the production of a low-cost base or carrier gas for blending purposes, a gas of intermediatae calorific value by oil carburetion of the hot exhaust of the gasification furnace, and a gas of adjusted H_2: CO ratio suitable for synthesis purposes.

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3573a. VON FREDERSDORFF, C. G., AND PYRCIOCH, E. J. Pressure-Gas Oxygen Coal Gasifier. Am. Gas Assoc. Monthly, vol. 34, September 1952, pp. 33–35, 46–47.

Series of some 20 successful runs were made to explore the effects of O_2 enrichment, O_2: coal ratio and gasification pressure on the gas heating value and conversion efficiency of the continuous, pulverization-pressure gasification process developed at the Institute Gas Technology. Using a high-volatile C Illinois No. 6-seam bituminous coal containing approximately 8% ash, a range of pressure from 2–5 atm., O_2: coal ratios from 0.7–1.0 lb. per lb. and O_2 concentrations 21–70% were explored. The gasification results are summarized. Gases produced varied from a 150 B. t. u. producer gas using 30% O_2 concentration to a 240 B. t. u. synthesis gas with 70% O_2 concentration. The gas heating value generally increased by 5 B. t. u. per $ft.^3$ with each atm. increase in gasification pressure. Gas heating value reached a maximum in the range 0.7–0.85 lb. per O_2 per lb. coal. With a constant steam: coal ratio of 1.0 lb. per lb., the ratio H_2: CO varied 0.95–1.4 depending on the O_2: coal and O_2 concentration used. Maximum values of steam decomposition of >50% occurred when the O_2: coal ratio was approximately 0.9 lb. per lb. The % C gasified increased rapidly with O_2: coal ratio and attained values of over 90% at 0.85 lb. O_2 per lb. coal. C gasification increased generally by 4% for each atm. increase in gasification pressure. The cold gas efficiency increased with both O_2: coal ratio and gasification pressure and attained maximum values of nearly 75% based on heating value of the coal. The O_2, coal and steam requirements per 1,000 $ft.^3$ synthesis components (CO+H_2) were greatly influenced by both the O_2: coal ratio and gasification pressure. Minimum requirements were as low as 33 lb. steam, 33% coal and 300 $ft.^3$ total O_2. The coal ash removed in the process as dust and slag was as high as 100% of the total ash fed in the coal. On the basis of \$0.06 per 1,000 $ft.^3$ compressed air, \$5.00 per ton O_2, \$4.00 per ton slack coal and allowing \$0.30 per 1,000 lb. process self-generated and self-superheated steam, the synthesis gas raw material cost varies 14.5–16.2 cents per 1,000 $ft.^3$ of CO+H_2 depending on the amount of O_2 enrichment.

VON PHILIPPOVICH, A. *See* abs. **998, 3462, 3463, 3464.**

VON RENNENKAMPFF, J. *See* abs. **1180, 1181.**

3574. VON SELASINSKY, A. [Soap From Coal.] Rundschau deut. Tech., vol. 18, No. 1, 1938, p. 9; Chem. Abs., vol. 32, 1938, p. 3179.

Historical review, especially describing the Imhausen-Troschke process and its importance for Germany's economic situation.

VON SETH, R. *See* abs. **1622, 1623.**

3575. VON STACKELBERG, M. [Investigations on Carbides. I. Crystal Structure of Carbides MeC_2.] Ztschr. physik. Chem., vol. 9, 1930, B, pp. 437–475; Chem. Abs., vol. 25, 1931, p. 11.

X-ray investigation by the powder method of a series of carbides of formula MeC_2 shows that they have a face-centered tetragonal lattice with 4 mol. in the unit cell and lattice constants as follows, recording a, c, and the density in order: CaC_2, 5.48, 6.37, 2.21; SrC_2, 5.81, 6.68, 3.26; BaC_2, 6.22, 7.06, 3.90; LaC_2, 5.54, 6.55, 5.35; CeC_2, 5.48, 6.48, 5.56; PrC_2, 5.44, 6.38, 5.75; NdC_2, 5.41, 6.23, 6.08; ThC_2, 5.85, 5.28, 9.3; $NaHC_2$, 5.40, 8.17, 1.33; KHC_2, 6.05, 8.42, 1.37. The C–C distance in the C_2 group is 1.4 Å. U., agreeing with band spectra data. With the help of the polarizing microscope the tetragonal symmetry was confirmed for CaC_2, SrC_2, and BaC_2. An electron configuration similar to that of the N_2 molecule is postulated for the C_2 and HC_2 groups. The possible space-group classifications are discussed. These

carbides appear to show a new lattice type somewhat similar to that of pyrite.

3576. ———. [Crystal Structures of Several Carbides and Borides.] Ztschr. Elektrochem., vol. 37, 1931, pp. 542–545; Chem. Abs, vol. 25, 1931, p. 5812.

In order to form a carbide of the CaC_2 type, hydrolyzing to C_2H_2 with H_2O, a minimum metal-ion size is necessary. The metallic properties of most carbides of this formula are due to the presence of 2 extra valence electrons. Ca, Sr, Ba, La, Ce, and Th form borides of formula MeB_6 with CsCl-type cubic lattice.

3577. ———. [Structural Principle of Carbides, Silicides, Nitrides, and Phosphides of Electropositive Metals.] Ztschr. physik. Chem., vol. B 27, 1934, pp. 53–57; Chem. Abs., vol. 29, 1935, p. 657.

Compounds of Be, Al, Mg, Ca, Si, Ti, and Zr with C, Si, N, and P are considered as forming ionic-crystal lattices. The anions assemble in a lattice of the closest spherical packing. The cations are embedded in the tetrahedral or octahedral gaps in the lattice

3578. Von Wartenberg, A., Muchlinski, A., and Riedler, G. [Investigation of Formaldehyde.] Ztschr. angew Chem., vol. 37, 1924, pp. 457–459; Chem. Abs., vol. 19, 1925, p. 769.

Attempts were made to synthesize CH_2O by subjecting a mixture of $CO+H_2$ to the silent electric discharge in an ozonizer. The voltage, pressure, temperature, and time of contact were varied over wide limits, but only traces of CH_2O were ever obtained; indeed, a mixture of CH_2O+H_2 was decomposed by the electric discharge. From the Nernst heat theorem, it appears that the equilibrium is favorable for the formation of CH_2O from $COCl_2+2\ H_2$. The best yield obtained, at 300° with Ni catalyzer, was 3.6%. The chief reaction was decomposition of the $COCl_2$ to CO and HCl. The oxidation of CH_4 with O_3 to give CH_2O was tried with a large number of catalyzers, of which $PbCrO_4$ proved to be the best; but the highest yield obtained, at 650°, was only 2% based on CH_4.

3579. Von Wartenberg, H., and Lerner-Steinberg, B. [Heat of Formation of Formaldehyde.] Angew. Chem., vol. 38, 1925. pp. 591–592; Chem. Abs., vol. 19, 1925, p. 3202.

For the heat of formation from $CO+H_2+1.4$ cal. is obtained.

3580. Von Waugenheim, F. [Preparation of Carbon From Carbon Monoxide.] Brennstoff-Chem., vol 8, 1927, pp. 385–388; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 227–233; Chem. Abs., vol. 22, 1928, p. 2641.

Attempt was made to prepare pure C by passing CO over a pure Fe_2O_3 catalyzer at temperatures under 650°. The reduced Fe was removed from prepared C by vaporization in a current of Cl. The recovered C was not entirely Fe-free, but it was nonmagnetic. It was a good conductor of electricity.

3581. Von Waugenheim, F., and Winkelmann, —. [Production of Pure Carbon at Low Temperature.] Thesis, Cologne, 1924; Ges Abhandl. Kenntnis Kohle, vol. 8, 1929, p. 235.

Formation of C on a reduced Fe catalyst proceeds only to a definite point, beyond which the activity of the catalyst virtually ceases. The limit was established by a reduction in concentration of the Fe to about 1%. The breakdown in the catalyst activity at a definite reduction of the Fe was believed to be due to the formation of a solid solution of a higher carbide and C, from which the catalytically active Fe_3C could not be regenerated.

3582. Von Weber, U. [Determination of Branched Isomers in Mixtures of Paraffin Hydrocarbons.] Angew. Chem., vol. 52, 1939, pp. 607–610; Chem. Abs., vol. 34, 1940, p. 365.

Information on the isomeric composition of Fischer-Tropsch hydrocarbons. The method is explained in detail. By determining boiling points and molecular weights of fractions, it is estimated that the mole fractions of branched hydrocarbons are 0.15, 0.27, and 0.40 for the C_6, C_8, and C_{10} ranges, respectively.

3583. Von Wettberg, E. F., Jr., and Dodge, B. F. Methanol Equilibrium. Ind. Eng. Chem., vol. 22, 1930, pp. 1040–1046; Chem. Abs., vol. 24, 1930, p. 5718.

Equilibrium in the reaction $CO+2\ H_2 \rightleftharpoons CH_3OH$ was determined at 170 atm. and temperatures ranging 258°–329°. Zn–Cr and Zn–Cu catalysts were used. The new data differ considerably from results by theoretical methods, and various sources of error in the latter are pointed out. The results of various investigators are summarized in tabular form.

3584. Voos, W. [Manufacture of Catalysts for the Synthesis.] FIAT Reel K 21, no date, frames 893–898; PB 70,212; TOM Reel 288.

Invention is discussed for making catalysts of the metal group Co–Ni–Fe possessing a surface activity as yet unattained elsewhere. Because of the very fine distribution, they provide immeasurable possibilities for being used in the synthesis of fuels or catalysis in related fields, as well as in the hydrogenation of vegetable and animal oils.

3585. Vorbach, —. [Experiments With Silica Gel as a Carrier for Cobalt Catalysts in the Synthesis of Gasoline From Carbon Monoxide and Hydrogen.] FIAT Reel R–20, June 3, 1940, frames 7537–7540; PB 73,564.

Report from the I. G. Ammonia Laboratory, Oppau, deals with experiments to determine the influence of the size of pores in silica gel used as a carrier substance in the synthesis of gasoline. It is obvious that the size of pores is important. Small-size silica gel ignited at 1,000° proved to be an easily reproducible carrier substance, which can fully replace diatomaceous earth in synthesizing gasoline from CO and H_2.

3586. Vorberg, G. [Problems of the Production of Liquid Fuels From Coal.] Seifensieder-Ztg., vol. 72, 1946, pp. 146–149, 166–168; Chem. Abs., vol. 43, 1949, p. 6390.

Most important processes are discussed, including high-pressure hydrogenation, low-pressure synthesis, the Fischer-Tropsch process, and the extraction process of Pott and Broche.

3587. Voss, —. [New Syntheses in the Solvent Industry.] Kunststoffe, vol. 17, 1927, pp. 79–80, 132–134, 205–207; Chem. Abs., vol. 21, 1927, p. 3993.

Recent patents are reviewed on processes dealing with the generation of MeOH from water gas, direct oxidation of CH_4 to MeOH, manufacture of MeCl and MeBr from CH_4 and the oxidation of these to MeOH, and the manufacture of MeOH from CO.

Voss, D. J. *See* abs. **3153a.**

Vvedenskii, A. A. *See* abs. **2030.**

W

3588. Wachs, W., and Reitstoetter, J. [Synthetic Fats in Germany.] Angew. Chem., vol. 20, B, 1948, pp. 61–68; British Abs., 1948, B, II, p. 547; Chem. Abs., vol. 42, 1948, p. 7,067.

Fatty acids are produced by oxidation of paraffins from brown coal and from synthetic wax with air at 100° and 1 atm. in presence of a catalyst, $KMnO_4$, which accelerates the formation of peroxides on which

the chain reaction depends. The treatment is stopped when about 40% of the paraffins have been attacked in order to reduce secondary oxidations. The purification by vacuum fractionation at 2–5 mm. Hg and esterification with glycerol of the C_{12}—C_{18} fraction to produce edible fat are outlined. Acids from Fischer-Tropsch wax include branched-chain members, which must be removed for physiological reasons. Fatty acids and sulfonate detergents and wetting agents from the lower fractions obtained by this process are used to replace soaps from natural fats for washing and industrial purposes.

3589. WAGMAN, D. D., KILPATRICK, J. E., TAYLOR, W. J., PITZER, K. S., AND ROSSINI, F. D. Heats, Free Energies, and Equilibrium Constants of Some Reactions Involving O_2, H_2O, C, CO, CO_2, H_2, CH_4. Jour. Research, Nat. Bureau of Standards, vol. 34, 1945, pp. 143–161, Research Paper 1634; Chem. Abs., vol. 39, 1945, p. 2449.

Values are given for: The heat-content function, $(H°-H°_o)/T$, the free-energy function, $(F°-H°_o)T$, the entropy, S°, the heat content, $H°-H°_o$, and the heat capacity, $C°_p$, for: $O_2(g)$, $H_2(g)$, $N_2(g)$, $CO(g)$ all to 5,000° K.; H_2O (g) to 3,000° K.; $CO_2(g)$ to 3,500° K.; $CH_4(g)$ to 1,500° K.; C (solid, graphite) to 1,500° K.; C (solid, diamond) to 1,200° K. Also given are: The standard entropy, S°, for H_2O(liq) at 25%; the heat of formation, the free energy of formation, and the equilibrium constant of formation from the elements, for H_2O(liq) at 25° and for $H_2O(g)$, $CO(g)$, $CO_2(g)$, and $CH_4(g)$ at 1,500° K.; the increment in heat content and free energy for the transition of graphite into diamond at 1,200° K. and 20,000 atm. From the foregoing, values were calculated for $\Delta H°$, $\Delta F°$, and the equilibrium constant to 1,500°K. for the following reactions, most of which are important in connection with the production of liquid hydrocarbon fuels from natural gas or coal and H: C (solid, graphite) $+CO_2(g)=2\ CO(g)$; C(solid, graphite) $+H_2O(g)=CO(g)+H_2(g)$; $CO(g)+\frac{1}{2}O_2(g)=CO_2(g)$; $CO(g)+H_2O(g)=CO_2(g)+H_2(g)$; $CH_4(g)+\frac{1}{2}\ O_2(g)=CO(g)\ 2\ H_2(g)$; $CH_4(g)+CO_2(g)=2\ CO(g)+2\ H_2(g)$; $CH_4(g)+H_2O(g)=CO(g)+3\ H_2(g)$; $CH_4(g)+2\ H_2O(g)=CO_2(g)+4\ H_2(g)$.

WAGNER, E. O. *See* abs. **2576, 2577.**

3590. WAGNER, K. H. Synthetic Fats. Bib. Sci. Ind. Repts., vol. 7, No. 6, Nov. 7, 1947, pp. 535–536; PB 85,791, 1947, 157 pp.

This comprehensive report deals essentially with 4 viewpoints: Production of synthetic fats to be used as food; changes of fats during storage; physiology of the fat metabolism; and synthetic fat in animal experimentation and human pathology. The starting materials for the production of synthetic fats are the fatty acids, which are obtained from the paraffins of the Fischer-Tropsch process by catalytic oxidation with atm. O_2 subsequently esterified with glycerol. Data necessary for cost calculations are given.

WAINWRIGHT, H. W. *See* abs. **144a, 3023, 3024, 3025.**

3591. WAINWRIGHT, H. W., AND LAMBERT, G. I. Colorimetric Method for the Determination of Thiophene in Synthesis Gas. Bureau of Mines Rept. of Investigations 4753, 1950, 11 pp.

Study of the isatin method is reported. Variables investigated included aging of reagent, temperature, influence of oxidizing agents, and interference due to the presence of CS_2, C_2H_5SH, and olefins. A procedure was developed for carrying out the analysis, and its applicability to synthesis gas containing low concentrations (less than 2%) of olefins was proved valid. It is claimed that as little as 0.0001 grain of thiophene S per 54.5 ml. of test reagent can be detected by determining color intensity with a Beckman spectrophotometer at a wavelength of 580 mμ, using a 10-mm. light path.

WALENDA, H. *See* abs. **2687.**

WALKER, J. *See* abs. **9, 10.**

3592. WALKER, J. C., AND MALAKOFF, H. L. Basic Oxygenated Chemicals From C_1, C_2, and C_3 Paraffins and Olefins. Petrol. Refiner, vol. 25, 1946, pp. 607–612; Oil Gas Jour., vol. 45, No. 33, 1946, pp. 59, 60, 62, 65; Chem. Abs., vol. 41, 1947, p. 1598.

Four methods for producing oxygenated hydrocarbons are discussed briefly: (1) Direct oxidation; (2) dehydrogenation followed by oxidation and hydration; (3) oxidation to CO and H_2 followed by hydrogenation of the CO; (4) chlorination followed by hydrolysis. With the aliphatic gases as raw materials in the direct-oxidation process, a typical oxygenated crude liquid will contain about 35% MeOH, 20% HCHO, and 5% AcH as principal products. Partial oxidation of natural gas to CO and H_2 for production of MeOH, which by further oxidation yields HCHO, has been the impetus to the development of the bakelite-type plastics industry. The production of EtOH from C_2H_4 illustrates commercial production by hydration, which is displacing older established methods. C_2H_4, which is expected to be available at $0.02 per lb., will reduce the cost of synthetic EtOH to $0.10 per gal. Future oxidation processes now in the pilot-plant stage include the Fischer-Tropsch, nitration, thermal cracking plus hydration, and electric discharge plus hydration.

3593. WALKER, S. W. Manufacture of Synthetic Gasoline. Oil Gas Jour., vol. 46, No. 8, 1947, p. 126; Nat. Petrol. News, vol. 39, No. 26, 1947, p. 44.

Paper presented at Midwest Regional Meeting, American Chemical Society, Kansas City. Improvements in the Fischer-Tropsch process and use of low-cost natural gas and O_2 have resulted in an economic process for the synthesis of gasoline and byproduct chemicals. The substitution of a fluidized Fe catalyst for the German fixed Co catalyst has resulted in better heat control, higher-quality gasoline, fewer undesirable products, and lower investment costs. Production of the synthesis gas by partial combustion of natural gas is an innovation which depends on cheap O_2 from the modified Linde-Fränkl process and is a more efficient process than CH_4 reforming or the steam and coke method. It is estimated that 360,000 lb. per day of crude, H_2O-soluble chemicals will be produced in each of the 2 plants now under construction. These consist primarily of alcohols, aldehydes, acids, and ketones and are found mostly in the H_2O stream from the oil-recovery section from which they may be separated into the various components. The oil stream also contains oxygenated compounds of the same general type having 4 or more C atoms; these are less important industrially at the present time, since their availability in quantity is limited. However, the development of satisfactory recovery and separation processes for these compounds will encourage investigation of their commercial uses. The chief end product of the process is, of course, gasoline, which can be produced in the form of an approximate 80-octane no. fuel in competition with natural petroleum products of equivalent quality, taking into account operating and amortization costs with natural gas at prevailing prices. It is indicated that the investment for a synthetic oil plant is approximately $3,000–$3,500 per daily bbl. of hydrocarbon products, or less than half the corresponding figure for the German plants.

———. *See* abs. **2069.**

WALLIS, A. E. *See* abs. **2308.**

WALTER, K. *See* abs. **1088, 1089.**

3594. WALTHER, C. [Technique of Oil Synthesis.] Arch. Wärmewirt., vol. 15, 1934, pp. 23–24.

Discusses liquefaction of coal and other synthetic processes for production of hydrocarbons, synthetic lubricating oils, and liquid fuels from gases.

WANGENHEIM, F. *See* abs. **1027, 1028.**

3595. WARD, C. C., SCHWARTZ, F. G., AND ADAMS, N. G. Composition of Fischer-Tropsch (Cobalt Catalyst) Diesel Fuel. Ind. Eng. Chem., vol. 43, No. 5, 1951, pp. 1117–1119.

Sample of diesel fuel prepared by the German modification of the Fischer-Tropsch process, using a Co catalyst, was fractionated and analyzed by use of refractometric and spectrographic methods. The sample contained about 2% of oxygenated material, which was removed by percolating the sample through silica gel. 80 gal. of the percolate was fractionated at reduced pressure, and 177 0.5% fractions were collected. The density, refractive-indexes, Br number, and cetane number were determined on each fraction and the infrared spectra on selected fractions. The approximate composition of the fuel was as follows, in %: Oxygenated compounds, 2; α-type olefins, 1.5; internal-type olefins, 8.5; paraffins, 88. Engine tests on several of the fractions indicated ratings higher than cetane, showing the need for a standardized method of rating Diesel fuel components that have a cetane number of more than 100.

3596. WARD, S. G. Coal—Its Constitution and Utilization as a Chemical Raw Material. Canadian Chem. Process Ind., vol. 31, 1947, pp. 626–636.

First Westman Memorial Lecture. Includes discussions of the formation and composition of coals, thermal decomposition, action of solvents, action of chemical reagents, methods of utilizing and processing coal, such as complete gasification, coal hydrogenation, Pott-Broche process, Fischer-Tropsch synthesis process, and direct utilization of coal gas as a chemical raw material. Bibliography with 68 refs.

3597. WARDEN, C. P. Production of Oils From Coal. Jour. Chem. Met. Min. Soc. South Africa, vol. 38, 1937, pp. 1–21; vol. 38, 1938, pp. 342–347; Chem. Abs., vol. 31, 1937, p. 8886; vol. 32, 1938, p. 4752.

Conversion of coal into oils requires 2 operations: (a) Reduction in molecule size from more than 2,000 to 100–400, and (b) the H_2: C ratio must be increased—for coal from 0.65 to 1.90 and for tar from low-temperature carbonization from 1.25 to 1.90. To do this, 3 types of operations may be used: (1) Carbonization, (2) hydrogenation; or (3) catalytic synthesis. Each is discussed. Flow sheets for 4 types of plants to produce oil from South African coal are presented and discussed.

3598. WARDENBURG, F. A. High-Pressure Synthesis as Applied to the Manufacture of Things in Everyday Use. Jour. Franklin Inst., vol. 221, 1936, pp. 449–464; Chem. Abs., vol. 30, 1936, p. 3950.

Synthesis of NH_3 and MeOH is described with historical and economic comment.

3599. WARNER, B. R., DERRIG, M. J., AND MONTGOMERY, C. W. Catalytic Synthesis of Hydrocarbons and Oxygenated Compounds From Ketene and Its Relation to the Fischer-Tropsch Synthesis. Jour. Am. Chem. Soc., vol. 68, 1946, pp. 1615–1617; Chem. Abs., vol. 40, 1946, p. 7149.

The fact that CH_2 and CO can combine to form ketene (CH_2CO) indicates the possibility that ketene may form and may be intermediate in the Fischer-Tropsch synthesis. Experiments determined that CH_2CO in the presence of H_2 reacts on a Co–ThO_2–kieselguhr catalyst at 200° to yield hydrocarbons and oxygenated compounds, which are similar to the products of the Fischer-Tropsch synthesis. A reasonable assumption to explain the experimental results involves preliminary catalytic decomposition of $CH_2CO \rightarrow CH_2 + CO$ followed by polymerization of CH_2, or by reactions involving higher ketenes and formation of oxygenated compounds. A reaction mechanism for the Fischer-Tropsch synthesis might be postulated as follows: (a) $CH_2CO \rightarrow CH_2 + CO$; (b) $CH_2 + CH_2CO \rightarrow CH_3CH{=}C{=}O$; (c) $CH_3CH{=}C{=}O \rightarrow CH_2{=}CH_2 + CO$; (d) $CH_2 + CH_3CH{=}C{=}O \rightarrow CH_3CH_2CH{=}C{=}O \rightarrow CH_3CH{=}CH_2 + CO$.

3600. WARREN, T. E. Inspection of Hydrogenation and Fischer-Tropsch Plants in Western Germany During September 1945. BIOS Final Rept. 82, 1945, 28 pp.; PB 7,917 and PB 27,316; TOM Reel 199.

General survey of plants and processes largely covered in other reports already abstracted.

3601. ———. Factors Influencing Establishment of a Synthetic Liquid-Fuel Industry in Western Canada. Canadian Chem. Process Ind., vol. 31, 1947, p. 644.

Paper presented at the 3d annual meeting of the Chemical Institute of Canada. The situation regarding supply and requirements of petroleum in western Canada is considered in conjunction with the raw materials and processing methods that might conceivably be used for the production of petroleum substitutes. 2 basic methods, direct hydrogenation and hydrocarbon synthesis, are considered in their application to 3 types of raw material, natural gas, asphaltic oil, including bitumen, and coal. There is uncertainty at present regarding several factors that should be taken into consideration in planning the establishment of a synthetic liquid-fuel industry.

3602. ———. Petroleum Substitutes in Canada. Chem. and Eng. News, vol. 25, 1947, p. 1857.

Paper presented at the meeting of the Chemical Institute of Canada. Discusses the processing methods that might be used for the production of petroleum substitutes. The natural-gas reserve in Alberta is estimated at 1–2.5 trillion cu. ft., enough to last a minimum of 22.8 yr. at the present rate of consumption or 16.1 yr. with a synthesis plant of 5,000 bbl. per day capacity. There also is enough coal in western Canada to supply a Fischer-Tropsch plant of 30,000 bbl. per day capacity for 2,000 yr. Coal hydrogenation is considered too expensive a method to be used in Canada unless the equipment could be simplified by the use of higher pressures. The deposits of tar sands in western Canada containing 350,000,000 bbl. of bitumens would supply a 30,000 bbl. per day hydrogenation plant for 25–30 yr.

3603. ———. Factors Influencing the Establishment of a Synthetic Liquid-Fuel Industry in West Canada. Canadian Chem. Process Ind., vol. 32, 1948, pp. 318–321; British Abs., 1950, B, I, p. 173.

Methods and materials that might be used by a synthetic-oil industry in the prairie area of Canada are reviewed; including hydrocarbon syntheses from natural gas and coal, and the hydrogenation of coal, heavy crude oils, and bitumen.

3604. WATANABE, M. Equilibrium in the Reduction of Cobaltous Oxide by Carbon Monoxide. Bull. Inst. Phys. Chem. Research (Tokyo), vol. 9, 1930, pp. 676–682 (abs. 62–63, in English); Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 14, No. 262–263, 1930; Chem. Abs., vol. 25, 1931, p. 3224.

Equilibrium $CoO(s) + CO \rightleftharpoons Co(s) + CO_2$ was studied by a static method over the range 563°–861°. The observed values of the equilibrium constant $K_p = p_{CO_2}/p_{CO}$ range between 174.4 (at 563°) and 23.2 (at 861°) and agree over the entire range (within 1%) with the following formula, which was derived with the aid of specific heat data: $-RT \ln K_p = \triangle F^\circ = -11544 + 8.06\,T \log T - 0.00305\,T^2 + 0.00000031\,T^3 - 17.65\,T$.

3605. WATANABE, S. (R. C. GRASS, ed.) Bench-Scale Studies of the Fischer-Tropsch Synthesis Over Iron, Nickel, and Nickel-Cobalt Catalysts. Bureau of Mines Inf. Circ. 7611, 1951, 26 pp.

Digest of certain phases of Japanese research in the field of synthetic liquid fuel. The potentialities of Ni as a substitute for Co for the synthesis of hydrocarbons from CO and H_2 were investigated. Extended experiments were carried out to determine the durability of Fe catalysts, to study the yield and quality of the products, and to evaluate Fe catalysts as a potential substitute for Co catalysts in the hydrocarbon synthesis. The experimental procedure and the operating data are presented in considerable detail.

WATANABE, S. Synthesis of Benzine by Catalytic Reduction of Carbon Monoxide at Atmospheric Pressure. VI. Consumption of Carbon Monoxide in Passing Through Catalyst Layer. *See* abs. **3612**.

3606. WATANABE, S., AND MORIKAWA, K. Determination of the Activity of Catalysts Which Accelerate the Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. Jour. Soc. Chem. Ind. (Japan), vol. 36, 1933, B, p. 226; Brennstoff-Chem., vol. 14, 1933, p. 391.

Several catalysts, the composition of which is not specified, were investigated for their utility in the benzine synthesis. Their efficiency was determined in 2 ways. First, the speed of reaction was determined at certain fixed temperatures by a method of F. Thoren (abs. **3399** and **3400**). The catalyst is heated carefully with the reaction gas in a closed glass vessel provided with a Hg manometer and the temperature and pressure are read off at short intervals. The speed of reaction is, of course, not accurately determined, but it is close enough to determine at what temperature it changes suddenly. Second, the activity of the various catalysts is determined on the basis of the yields in liquid hydrocarbons obtained with them. The conclusion reached is that the efficiency of a catalyst is higher the lower the temperature at which the catalyst attains the maximum reaction velocity.

3607. WATANABE, S., MORIKAWA, K., AND IGAWA, S. Synthesis of Benzine (Gasoline) From Carbon Monoxide by Means of Catalytic Reduction at Atmospheric Pressure. I. Methods of Synthesis and Analysis. Jour. Soc. Chem. Ind. (Japan), vol. 37, 1934, B, pp. 142–146; Chem. Abs., vol. 28, 1934, p. 5648.

Experimental apparatus and procedure and the catalysts used are described. Experimental results are reported for reductions under the following conditions: (1) 197°, (2) 197° and 203°, and (3) 197° and 228°, with 32.9% CO and 63.8% H_2 in the raw gas for (1) and (2) and 32.7% CO and 64.5% H_2 for (3). The catalysts for the 3 runs had the compositions: Co : Cu : Th=8 : 1 : 0.3 for (1), and Co : Cu : ThO=9 : 1 : 2 for (2) and (3). Gasoline yields varied 50–65 mg. per l. of gas for (1), 51–76 mg. per l. for (2) and 36–115 mg. per l. for (3). Material balances for 2 runs are appended.

3608. ———. Synthesis of Benzine From Carbon Monoxide by Means of Catalytic Reduction at Atmospheric Pressure. II. Effect of Temperature Upon Synthesis. Jour. Soc. Chem. Ind. (Japan), vol. 37, 1934, B, pp. 385–389; Brennstoff-Chem., vol. 15, 1934, p. 413; Chem. Abs., vol. 28, 1934, p. 6982.

Plots are presented for yield, % of C, and % of H of the reaction products as functions of the reaction temperature, which show that, for benzine synthesis, it is most desirable to keep the reaction temperature nearly at the optimum temperature, in this case 220°, or somewhat below it, as a small rise above the optimum temperature usually promotes undesirable side reactions. The activity of the catalyst is a function of the location of the maximum point of the curve of gas contraction versus temperature of reduction, a greater activity being associated with a lower temperature value. The Co catalyst, containing Cu, prepared from the carbonate gave an optimum reduction temperature of 250°–300° and that prepared from the nitrate one of 190°–200°. The temperature rise during synthesis, if too great, may adversely affect the activity of the catalyst.

3609. ———. Synthesis of Benzine (Gasoline) From Carbon Monoxide by Catalytic Reduction at Atmospheric Pressure. III. Influence of the Gas Velocity. Jour. Soc. Chem. Ind. (Japan), vol. 38, 1935, B, pp. 70–73; Chem. Abs., vol. 29, 1935, p. 3495.

Yields of gasoline and water per l. of gas decreased with an increase in gas velocity from 0.82 to 2.46 l. per hr., at a temperature of 197°, CO : H_2=33.1 : 64.7 and 1.33 gm. of catalyst (Co : Cu : ThO_2=9 : 1 : 2). At velocities up to 1.13 l. per hr., the rate of gas contraction and the yields of H_2O, CO_2, and gaseous hydrocarbons became constant, whereas the gasoline yield continued to decrease. The optimum gas velocity, which seemed to depend upon the activity of the catalyst, was found to be 1.1 l. per hr. for 1 gm. of catalyst. Higher gas velocities resulted in an increased density of the product. The catalytic reaction was influenced only very slightly by changes in the gas velocity but considerably by temperature changes. Experimental data are reported with 5 refs.

3610. ———. Synthesis of Benzine From Carbon Monoxide by Means of Catalytic Reduction at Atmospheric Pressure. IV. Influence of the Mixing Ratio of Carbon Monoxide and Hydrogen. Jour. Soc. Chem. Ind. (Japan), vol. 38, 1935, B, pp. 328–331; Chem. Abs., vol. 29, 1935, p. 6401.

Ratio H_2 : CO was varied from 0.97 : 1 to 2.96 : 1. The experimental data are reported. When CO is present in excess of the optimum ratio of CO : H_2=1 : 2, the production of gaseous olefins and CO_2 is accelerated, but that of gaseous paraffins is retarded. When an excess of H_2 is present, the reverse is the case. The oil production is increased with increasing CO concentration. A theoretical explanation of the reaction mechanism is attempted. Dilution of the raw gas with N_2 increased gaseous olefins and CO_2 and decreased the oil production owing to lowering of the partial pressure of CO.

3611. ———. Synthesis of Benzine by Catalytic Reduction of Carbon Monoxide at Atmospheric Pressure. V. Effect of Adding Lower Hydrocarbons to the Feed Gas. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 967–971; Chem. Abs., vol. 43, 1949, p. 2406.

Fischer synthesis was carried out with 2 vol. CO and 1 vol. H_2 mixed with 8–13% hydrocarbon, and the result was compared with that for feed gas having no admixture. A catalyst of composition of Co : Cu : ThO_2=9 : 1 : 2 was used. When the feed gas contained saturated hydrocarbons, the rate of consumption of CO and the formation of CO_2 were lowered and the formation of olefins was slightly increased. With an increase in molecular weight of the added saturated hydrocarbons the number of C atoms in the gaseous saturated hydrocarbons formed was increased. When the feed gas contained unsaturated hydrocarbons, the consumption of CO was lowered but the production of oil was not decreased, about 50% of olefin added being hydrogenated and 30% taking part in polymerization. C_2H_2 yielded a liquid product by self-polymerization.

3612. WATANABE, S. Synthesis of Benzine by Catalytic Reduction of Carbon Monoxide at Atmospheric Pressure. VI. Consumption of Carbon Monoxide in Passing Through Catalyst Layer. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 1128–1130; Chem. Abs., vol. 43, 1949, p. 2406.

Synthesis of benzine was carried out using gas containing CO and H_2 in the ratio 1:2 and a catalyst of the composition of CO : Cu : ThO_2=9 : 1 : 1 at 197° under pressure of 7–369 mm. It was found that the relation $x=ap^b$ holds between the reaction pressure, p, and x, which represents the yield of oil, contraction of gas volume, or consumption of CO, with a and b as constants. As the above formula is of the same form as that of Freundlich's adsorption isotherm, $y=ap^n$, it is observed that there is a direct relation between the consumption of CO and the adsorption of CO. The formula $x=ap^b$ holds only when p is 30–200 mm. Below 30 mm. b increases gradually to 1 at a very low value of p, whereas, above 200 mm. b gradually decreases to zero at a large value of p. When the feed gas passes through the catalyst layer, the relation between the distance traversed L_i and the partial pressure P_i can be expressed by a general formula $1/bp_1{}^b-1/bp_i{}^b=aL_i$. Since this is a hyperbola, the rate of reaction in the catalyst layer can be represented by a hyperbola.

3613. WATANABE, T. Poisoning Effect of Certain Substances on the Iron Catalyzer in the Decomposition of Carbon Monoxide. Bull. Inst. Phys. Chem. Research (Tokyo), vol. 7, 1928, pp. 1078–1087 (abs. I, 102–103); Chem. Abs., vol. 23, 1929, p. 1560.

CO from formic acid is decomposed in an Fe pipe on Fe gauze, and the gas is analyzed. The effects of H_2O, N_2, H_2, CH_4, C_2H_2, C_6H_6, $C_{10}H_8$, H_2S and C_4H_4S on the catalysis are investigated. N_2,CH_4, C_6H_6 and C_2H_2 have no effect, except that C_2H_2 liberates C. H_2O gives some CO_2, H_2, and CH_4. H_2 gives CH_4. Naphthalene causes a progressive drop in the catalysis efficiency, but the fall is temporary; by passing pure CO over the poisoned catalyst, the initial efficiency is recovered. S compounds kill the catalyst.

3614. WATASE, T. Heat of Formation of Cementite. Sci. Repts. Tôhoku Imp. Univ., vol. 17, 1928, pp. 1091–1109; Chem. Abs., vol. 23, 1929, p. 1046.

Cementite prepared by subjecting plates of C steel (2% C) to electrolysis with N HCl and a current density of 0.075 amp. per cm.,^{2} was burned in a Berthelot-Mahler bomb calorimeter, and its heat of combustion was determined. From the observed amount of heat evolved and the composition of the combustion residue, the heat of the reaction $Fe_3C+3\ O_2=Fe_3O_4+CO_2$ was found to be 366.3 kcal. From this figure and those found in the literature for the formation of Fe_3O_4 and for CO_2, the heat of formation of cementite is calculated to be −4.8 kcal. at 20°.

3615. ———. [Heat of Formation of Cementite.] Ztschr. physik. Chem., vol. 147 A, 1930, pp. 390–395; Chem. Abs., vol. 24, 1930, p. 3702.

Previous value (abs. **3614**) for the heat of combustion of Fe_3C was recalculated as 362.5±0.1 cal. and the heat of formation as −2.5 cal., by using the latest thermochemical data of Roth (abs. **2908**).

3616. ———. Studies on the Equilibrium: $Fe_3C+2\ H_2\rightleftarrows 3\ Fe+CH_4$. Jour. Chem. Soc. Japan, vol. 54, 1933, pp. 110–132; Chem. Abs., vol. 27, 1933, p. 2368.

Equilibrium $Fe_3C+2\ H_2\rightleftarrows 3\ Fe+CH_4$ was studied at 450°–603°. The values $\triangle F_{298.}=-15{,}803$ cal. and $\Delta H_{298.}=-21{,}822$ col. were obtained.

WATSON, K. M. *See* abs. **1498a.**

3617. WEBER, G. Carthage Hydrocol Project. Oil Gas Jour., vol. 47, No. 47, 1949, pp. 248–250.

First commercial application of the Hydrocol process for converting natural gas to liquid hydrocarbons is slated for initial operation late this year. It was ⅓ completed at the end of March. The plant location is described, and the company stockholders and officers are listed. Some details of plant operation are presented. Flowsheet outlines process.

WECK, H. I. *See* abs. **3153a.**

3618. WECK, H. I., MEYERSON, S., AND SEELIG, H. S. Hydrocarbon Synthesis Catalyst Studies. Use of Deuterochloric Acid. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 2331–2333.

Fe catalysts that have been used in hydrocarbon-synthesis studies liberate H_2 and hydrocarbons when dissolved in HCl. By the use of DCl instead of HCl, it has been proved that these hydrocarbons are derived from Fe_2C and the acid and are not adsorbed synthesis products that were liberated when the catalyst dissolved. From an examination of the methanes formed, it has been concluded that stable Fe alkyls do not exist on the catalyst. No exchange was observed between the H_2 in a sample of n-pentane absorbed on metallic Fe and the D in the acid used to dissolve the Fe.

3619. WEDEKIND, E. [Magnetic Microbalance.] Ztschr. angew. Chem., vol. 41, 1928, pp. 771–774; Chem. Abs., vol. 23, 1929, p. 3.

Modification of the well-known Pascal set-up for measuring the properties of weakly diamagnetic or paramagnetic compounds. The balance is replaced by a microbalance, and the magnet is improved. The principle of the Pascal method remains unchanged. Gives details and diagrams needed for practical use.

———. *See* abs. **2238, 3622, 3623.**

3620. WEDEKIND, E., AND ALBRECHT, W. H. [Distinguishing the Different Types of Ferric Oxides and Hydrated Oxides by Their Different Magnetic Properties. I.] Ber. deut. chem. Gesell., vol. 59, 1926, pp. 1726–1730; Chem. Abs., vol. 21, 1927, p. 526.

3621. ———. [Distinguishing the Different Types of Ferric Oxides and Hydrated Oxides by Their Different Magnetic Properties. II.] Ber. deut. chem. Gesell., vol. 60, B, 1927, pp. 2239–2243; Chem. Abs., vol. 22, 1928, p. 3090.

3622. ALBRECHT, W. H., AND WEDEKIND, E. [Distinguishing the Different Types of Ferric Oxides and Hydrated Oxides by Their Different Magnetic Properties. III. Hydrated Ferric Oxide from the Decomposition of Iron Pentacarbonyl.] Ztschr. anorg. Chem., vol. 202, 1931, pp. 205–208; Chem. Abs., vol. 26, 1932, p. 1535.

3623. ———. [Distinguishing the Different Types of Ferric Oxides and Hydrated Oxides by Their Different Magnetic Properties. IV.] Ztschr. anorg. Chem., vol. 202, 1931, pp. 209–226; Chem. Abs., vol. 26, 1932, pp. 2630–2631.

Data previously reported are correlated and explained. Both natural and pure synthetic oxide hydrates exhibit low magnetic susceptibilities. Although these are normal, they do not always show well-defined X-ray interference patterns. Some preparations with poor X-ray interference patterns are normal, whereas others with characteristic patterns exhibit magnetic abnormality.

3624. WEGHOFER, H. [Addition of N_2O_4 to Olefinic Double Bonds.] Erdöl u. Kohle, vol. 4, 1951, pp. 1–3; Brennstoff-Chem., vol. 30, 1949, p. 440.

Addition of N_2O_4 to 2-methylbutene-2 was investigated to clarify the structure of the reaction products. In connection therewith, Fischer-Tropsch olefins were converted, and the composition of the reaction products as well as several of the reactions were described. By adding N_2O_4 to olefins, such as 2-methylbutene-2, there are formed, besides crystallized nitrosonitrate, an oily fraction, which, like the nitrous ester of 3-nitro-2-methylbutanol-2, is changed by treatment with NaOH into 3-nitro-2-methylbutanol-2 (nitronitrite). In performing the reaction, saponification with NaOH takes place at once, the nitrosonitrate yielding oximes and the nitronitrite nitroalcohols. The % division of the reaction products depends

largely upon the reaction temperature, furthermore a very definite effect of peroxide addition exists. For example, the division at 0° without peroxide gives 73% oxime and 27% nitroalcohol; with 1% benzoyl-peroxide, 40% oxime and 60% nitroalcohol. The addition of N_2O_4 to a Fischer-Tropsch heptene in butanol solution yields, among other compounds, a dioxynitro compound. There are, thus, 3 reaction products available: A nitrosonitrate, a nitronitrite and a dinitro compound, the proportion of each depending upon the chosen reaction conditions (temperature and additives), the solvent agents, and the structure of the olefins.

3625. WEIBERG, M. [Reduction of Iron Ores With Carbon Monoxide, Hydrogen and Methane.] Jernkontorets Ann., vol. 124, 1940, pp. 179–212; Chem. Zentralb., 1940, II, p. 3315; Chem. Abs., vol. 34, 1940, p. 6903; vol. 36, 1942, p. 6968.

Review of the equilibrium conditions in reductive Fe oxides with CO, H_2, and CH_4. The approximate relation between the O_2 content of the wüstite and the gas composition at equilibrium in the wüstite region was calculated. On the basis of these calculations, the equilibrium diagram for the systems Fe–C–O and Fe–H–O were extended to include the O curves and the limits of the wüstite region in the phase diagram for the system FeO were corrected. Further, the relation between the equilibrium constants and the temperature was calculated for the reaction $H_2O+CO=H_2+CO_2$ for temperatures up to 2,000° and for the reaction $C+2H_2=CH_4$ for temperatures up to 1,200°, as well as for the formation of CH_4 by reduction with a mixture of CO and H_2. In the reduction with pure CO, the temperature increases about 100°–150°; in the reduction with pure H_2, it drops about 350°. There is no change in temperature with a mixture of 64% CO and 36% H_2. Reduction with CH_4 or coke-oven gas requires addition of so much heat that it can only be carried out in a retort furnace or other equipment with special provision for supplying heat, unless the CH_4 is first converted into a CO–H_2 mixture by oxidation with O_2, H_2O, or CO_2. Because of its greater rate of diffusion, H_2 reduces more vigorously at 1,000° than CO until about 75% of the O contained in the ore has been removed. Beyond this point the reduction velocity with H_2 drops considerably more rapidly than that with CO. Reduction time is shortest with a mixture of CO and H_2. Microscopic investigations showed that the greater reduction velocity of CO toward the end of the reduction probably is due to its carbonizing action on the reduced Fe, which surrounds the remaining small grains of wüstite as a thin scale. As a result of the reaction between the C in the austentite and the O in the wüstite, a gas is formed under high pressure in the boundary region, which ruptures the Fe scale and permits further reduction by the CO. In reduction with H_2, a similar condition may develop, except that only H_2 and not H_2O vapor is able to diffuse through the Fe scale, so that less excess pressure is developed in this case. In the reduction with pure CO at 1,000°, the Fe can be carbonized up to cementite, which does not show the constant composition Fe_3C but rather possesses a certain solvent power for C or Fe so that if forms a homogeneous region in the phase diagram. Upon longer carbonization of reduced Fe at 1,000° with CO, the cementite disintegrates with the separation of C; a heavy deposition of C from the gas phase also takes place. Reduction of a pure magnetite crystal at 1,000° results in the formation of 3 layers: a nucleus of Fe_3O_4, an intermediate layer of wüstite, and a surface layer of pure Fe. This shows that the O_2 passes through the wüstite layer by diffusion in solid solution; no porosity develops in the wüstite layer, only large fissures.

3626. WEIL, B. H. Shale Oil and Other Substitutes for Petroleum. Nat. Petrol. News, vol. 35, No. 31, 1943, p. R–348; U. O. P. Co. Lib. Bull, No. 33, 1943.

Approximate costs of motor fuels from sources, other than petroleum, are as follows: Fischer-Tropsch gasoline from coal, $0.18 per gal.; from natural gas, $0.09–$0.12 per gal.; coal-hydrogenation gasoline, $0.16, with the possibility that this will be lowered to $0.12 at some future time; 10% alcohol blend gasoline, $0.10. This involves alcohol at over $0.40 per gal., and moreover only 10% of the fuel would be a substitute. These figures represent costs without profit and correspond to about $0.05 per gal. for petroleum gasoline.

3627. ———. Shale Oil, Other Petroleum Substitutes, and Oil Shortage. Interstate Oil Compact Commission, Quart. Bull., July 1943; Gas Age, vol. 92, No. 13, 1943, pp. 36, 62, 64; Gas, vol. 20, No. 1, 1944, pp. 36, 38.

Approaching depletion of petroleum reserves makes it desirable to supplement United States petroleum production with the production of oil from shale, the Fischer-Tropsch synthesis, the hydrogenation of coal, or the blending of hydrocarbon fuels with alcohol. Discussion deals chiefly with shale oil.

3628. ———. Economic Factors to Determine Fuels of the Future. World Petrol., vol. 16, No. 2, 1945, p. 49.

At present rates of production, United States known reserves of petroleum would last 14 yr., coal 3,000, and natural gas 30. Synthesis of gasoline is at present uneconomic, but fundamental research should be carried on in case of future emergencies. Processes discussed are the Fischer-Tropsch, pyrolysis of oil shale and oil sands, carbonization and hydrogenation of coal, of which the first seems the most attractive. No future shortage of gaseous fuels is expected. Gasolines of 85–90 octane no. will be produced, and car design will undergo relative improvement. Diesel fuels are becoming more important, but it is difficult to predict the future of heavy fuel oil and natural gas.

3629. ———. Fuels of the Future. Petrol. Eng., vol. 16, No. 5, 1945, pp. 156, 158, 160, 162, 164, 166.

Review of our present fuel resources and their possible future development. The Fischer-Tropsch, using natural gas, is almost competitive with crude petroleum. Even with the eventual use of coal as the raw material, this process appears attractive as it may be possible to bring down the cost of synthetic gasoline to as low as $0.09 per gal., which would be competitive with petroleum at $2.00 per bbl. A combination of coal carbonization with this process appears possible. Although coal constitutes the best raw material for use in any process for the long-term synthesis of petroleum-like oils, its hydrogenation is so complex and requires such expensive and elaborate equipment that it appears likely to be less attractive than the Fischer-Tropsch process using the same raw material.

3630. ———. Synthetic Lubricating Oils. Nat. Petrol. News, vol. 37, No. 27, July 4, 1945, pp. R–512, 513, 516, 518, 520, 522.

Review containing 204 literature and 376 patent refs. Included are many refs. to the hydrogenation of coal and tar and to the Fischer-Tropsch process.

———. *See* abs. **2054, 2055, 2056, 2057.**

WEINBERGER, E. B. *See* abs. **2309, 2310.**

3631. WEINGÄRTNER, —. [Regeneration of Cobalt Catalysts of the Gasoline Synthesis by Hydrogenation.] FIAT Reel K25, frames 3,918–3,924, Mar. 21, 1938; PB 70,216.

On the basis of laboratory tests and working experiences, chemical and physical reactions in hydrogenation are explained. From that are developed the conditions for hydrogenation in the plant. It is stated

that 1,000 m.^{3} per hr. for the furnace brings an efficient regeneration and prolongation of the life of the catalyst affected by the paraffin. An increase of production in furnaces with hydrogenation and with more than 2,000 working hours is reported. The disadvantage is that the paraffin is not completely removed and a part is destroyed by catalytic splitting.

———. *See* abs. **3270.**

WEINIG, R. *See* abs. **1931.**

3632. WEINROTTER, F. Investigation of the Reaction Water Obtained From Middle-Pressure-Synthesis Experiments With Iron Catalysts and Hydrogen-Rich Starting Gas. TOM Reel 101, Doc. PG–21579–NID; transl. of German documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis, part II, 1946, pp. 24–26.

Analysis of the saponification fraction of the reaction water boiling below 100° revealed the presence of ketones and the absence of aldehydes. The % of pure alcohol was calculated and expressed in wt. % as follows: MeOH, 0.6, EtOH, 3.2, *n*-PrOH, 1.3, *n*-BuOH, 0.5. Analysis of the fraction boiling above 100° showed 1.7 gm. residue of pure fatty acid, or 0.23 wt. % of the total quantity of reaction water examined. For further identification, the fatty acids were esterified with MeOH in the presence of H_2SO_4. The only fraction obtained was 1.8 cc. of methyl acetate. Methyl formate was not present. The fatty acid mixture contained approximately 80% by wt. of acetic acid. The remainder was made up of the higher homologs of the fatty acid series. Formic acid was not present or at least only in very small traces. In the original reaction water, fatty acids were present in free form up to approximately 80%. (*See* abs. **936.**)

———. *See* abs. **1029, 2239a.**

WEINTRAUB, M. *See* abs. **2099, 2100, 2101, 2102, 2103, 2103a.**

3633. WEIR, H. M. Oxo Process for Alcohol Manufacture From Olefins. TOM Rept. 6, 1945, 30 pp.; PB 2,047; T. A. C. AIMI–1.

Report covers the essential features of the Oxo process for producing alcohols from olefins as compiled mostly from seized German documents and interviews with personnel. The 1st stage of the process is operated at 150 atm. and 140°, the 2d at 150–200 atm. and 180°. The standard Fischer-Tropsch catalyst (100 Co–5 ThO_2–8 MgO–180–200 kieselguhr) is used generally. The Co of the catalyst is converted partly to $Co(CO)_4$ in the 1st stage, and this dissolves in the liquid product. Subsequent hydrogenation breaks up the carbonyl leaving the Co in a catalytically active form. Apparently, almost any type of olefins may be used for the feed, but the sources mainly considered were the primary aliphatic olefins produced by the Fischer-Tropsch process and the olefins with double bond at the end of the straight chain obtained by mild cracking of Fischer-Tropsch paraffin gatsch. When diolefins are present, reaction occurs at only one of the double bonds with poor yields. Practically olefin mixtures from C_{11}–C_{17} were desired, mainly, since these gave C_{12}–C_{18} alcohols, which, after sulfonation, were most effective as detergents. The chemistry of the process is reviewed, and the practical operating conditions are outlined, with some attention being given to the engineering standpoint with flow sheet of the continuous process. The overall cost of alcohol product is calculated at 71 pf. per kg. for the batch process and 60 pf. per kg. for the continuous process or \$0.05–\$0.09 per lb.

3634. ———. High-Pressure Gasification of Coal in Germany. Ind. Eng. Chem., vol. 39, 1947, pp. 48–54; Chem. Abs., vol. 41, 1947, p. 1079.

Details of the construction of equipment, typical operation, and costs for the continuous production of city gas directly from solid fuel and at high pressure at Böhlen, the first commercial installation in Germany to operate under the conditions described. The fuel used was in the form of a 3–10 mm. brown-coal coke and local brown coal itself. The plant had a capacity equivalent to 15,000,000 cu. ft. of gas at normal temperature and pressure per day. The fuel bed, 1–2 m. deep, in the generator was continuously blasted with a mixture of steam and O_2. The crude gas produced contained some 30% CO_2 and was under some 18 atm. pressure. Suitable cooling, removal of tar and distillate, and other purification under pressure produced a gas with the following typical analysis: H_2, 48–49, CO, 22–24; CH_4, 25–29%; the remainder being higher hydrocarbons, N_2 and CO_2. It had a normal heating value of 470–490 B. t. u. per cu. ft.

WEISCHER, A. *See* abs. **1980.**

3635. WEISER, H. B., AND MILLIGAN, W. O. Constitution of Colloidal Systems of the Hydrous Oxides. Chem. Rev., vol. 25, 1939, pp. 1–30; Chem. Abs., vol. 33, 1939, p. 9088.

3636. ———. Electron-Diffraction Study of Hydrous Oxides Amorphous to X-Rays. Jour. Phys. Chem., vol. 44, 1940, pp. 1081–1094; Chem. Abs., vol. 35, 1941, p. 951.

Hydrous oxides that give X-ray-diffraction patterns of the amorphous type may be grouped in 2 classes: (*a*) Oxides that give relatively sharp ring electron-diffraction patterns and (*b*) oxides that give electron-diffraction patterns of the amorphous type. The oxides of the 1st class are crystalline, but the primary crystal size is so small that the X-ray-diffraction pattern consists of broad bands. The precipitated oxides of the following metals belong in this class: Fe^{III}, Al (from sulfate), Ga, Ti^{IV}, and probably Be. The oxide gels of the 2d class are amorphous in the sense that glasses are amorphous, the atoms arranging themselves in the form of a network lacking the periodicity and symmetry that characterize a crystal lattice. The following precipitated oxides belong in this class: Cr, Si, Cb^V, and Ta^V. Fe_2O_3 gel thrown down at room temperature consists of minute crystals of α–Fe_2O_3. The oxide gel from $Al_2(SO_4)_3$, like that from $AlCl_3$ and $Al(NO_3)_3$, is γ–$Al_2O_3.H_2O$. Gallia gel precipitated at room temperature is made up of minute crystals of α–Ga_2O_3.

3637. WEISS, —., AND HAASE, —. [Analysis of the Fatty Acids for Soaps Made From Riebeck Paraffin and Fischer Gatsch.] FIAT Reel R–19, frames 6,533–6,566, May 6, 1940; PB 73,594; TOM Reel 300.

Fatty acids obtained from the above sources were decomposed into their individual components. The method, therefore, is described fully. The content of monocarboxylic acids (straight chain, branched, unsaturated) and their quantitative distribution on the basis of the chain length are determined. The examination is made by fractional distillation of the methyl esters in vacuum after adsorption on silica gel of all other acids that are not included in the examination. Results presented in 17 graphs and figs.

WEISS, B. *See* abs. **2234.**

3638. WEISS, P. [Equation of Magnetic State and Variation of Atomic Moment.] Compt. rend., vol. 180, 1925, pp. 358–361; Chem. Abs., vol. 19, 1925, p. 1653.

By using data previously obtained for Ni, curves are given that establish a relation between the magnetization σ, the field H, and the absolute temperature T. Systematic divergences from the relation $H_m = n\sigma$, where n is a constant, are ascribed to an intra-atomic change by which Ni passes from 3 to 8 magnetons.

3639. WEISS, P., AND FORRER, R. [Magnetic Heat Phenomenon and the Specific Heat of Nickel.] Compt. rend., vol. 178, 1924, pp. 1347–1351; Chem. Abs., vol. 18, 1924, p. 1941.

Magnetic heat phenomenon is defined as the reversible emission of heat that accompanies magnetization. It is here considered as a function of the magnetic field that produces it, leaving to a later date its study as a function of the intensity of magnetization. The elevation of temperature ΔT as a function of the variation of the field ΔH is given by the magnetic analog of the Clapeyron formula: $C_H \Delta T = T(d\sigma/dT)\Delta H$, where C_H is the specific heat in a constant field and σ is the specific magnetization. Data and 2 graphs of ΔT versus H, and 1 graph of C_H versus T are given.

3640. ———. [Magnetic Isotherms of Nickel.] Compt. rend., vol. 178, 1924, pp. 1046–1049; Chem. Abs., vol. 18, 1924, p. 1941.

Magnetic isothermal diagrams for Ni are given and discussed for the range 20°–405° and H=0–21,000 gausses.

3641. ———. [Magnetization and the Magnetocaloric Phenomena of Nickel.] Ann. Physik, vol. 5, 1926, pp. 153–213; Chem. Abs., vol. 20, 1926, p. 1941.

Discussion of the experimental data relevant to the establishment of the equation of state of a magnetic substance. The following topics, in particular, are discussed: (1) Magnetization of Ni as a function of field and temperature in the range 20°–630°; (2) reversible temperature variations in relation to specific heat; (3) determinations of spontaneous magnetization; (4) the impossibility of a ferromagnetic equation of state. Interpretations of experimental data recently obtained (abs. **3638**) given.

3642. ———. [Absolute Saturation of Ferromagnetic Substances and the Law of Approach as a Function of the Field and of the Temperature.] Ann. Physik, vol. 12, No. 10, 1929, pp. 279–374; Chem. Abs., vol. 24, 1930, p. 2345.

Question of ferromagnetism is discussed in detail. The mathematical theory and the experimental work on Fe, Ni, magnetite, ferromagnetic sesquioxide of Fe, Fe_2B, cementite, pyrrhotine, and a series of ferrocobalts are described. Conclusions: The atomic moments of Fe and Ni are, respectively, 11 and 3 times 1125.6 c. g. s., with a precision of about 1 in 1,000. This value of the experimental magneton is approximately 0.19% higher than the older value (1,123.5) and 0.63% less than 1/5 of the Bohr magneton. It is very close to the value, 1,126, which was deduced in 1924 from the moments of the ions of the Fe family, calculated from the Curie constant by the classical Langevin formula. This is regarded as an experimental justification of that formula. For ferric Fe in magnetite, the moment is 10.10 magnetons. A part of this excess over an integer is attributed to the paramagnetism that accompanies ferromagnetism in a molecule containing both ferric and ferrous Fe. It is very difficult to obtain C. P. ferromagnetic sesquioxide, cementite, Fe_2B, and pyrrhotine, and the last 3 are extremely hard, magnetically. The experimental values found for the magnetic moments are 8.88, 9.10, 8.84, and 1.83, respectively, which, considering the difficulties just mentioned, are compatible with the integral moments 9, 9, 9, and 2, respectively. The frequency with which the moment 9 occurs here, as well as in α–Co in the ferrocobalts and γ–Co of the Ni–Co series, is remarkable. The value 2 for pyrrhotine is the smallest moment known. In the Fe–Co and Ni–Co alloys, the atomic moment varies linearly with the concentration in certain intervals, thus confirming the law of mixtures. The results also indicate that the metals exist in different states, characterized by different magnetic moments. Thus in α–Fe–Co rich in Fe, the moment of Co is 17, whereas in α–Fe–Co rich in Co, the Fe has a moment of 15 and the Co 9 magnetons. In γ–Fe–Co, the moment of Co is 8⅔. In γ–Ni–Co, the Co moment is 9 magnetons, whereas in H–Ni–Co it is 8½. In the Fe–Co alloys containing 13–50% Co, there is indication of at least 3 different atomic moments. For 35–45% Co, the saturation value at ordinary temperatures is about 12.4% higher than for pure Fe. The law of approach to saturation as a function of the field is given by the equation $\sigma_{H,T} = \sigma_{\infty T}\,[1-(a/H)]$. The constant a measures the magnetic hardness in strong fields and is sensibly independent of the temperature in the interval investigated. It differs from one specimen to another and is small for pure metals that crystallize in the cubic system. It is large for noncubic substances such as Fe_2B, cementite, and pyrrhotine. This law is valid for Fe and N at ordinary temperatures down to about 1,000 gausses, and this limit is displaced toward higher values as the temperature is lowered. The law of approach to saturation toward the limit of O abs. is given by the equation $\sigma_{\infty T} = \sigma_{0000K}\,(1-AT^2-BT^4-\ldots)$. Certain conditions that these 2 laws impose on the atomic model are not yet satisfactorily explained. The maximum magnetization at saturation of pyrrhotine is at 160° K., as already obtained by Zeigler. 2 new phenomena were observed. In most of the specimens of Ni, a feeble magnetization, proportional to the field, was found superimposed upon the regular phenomenon of approach to saturation. This parsitic magnetization is zero at 0° K. At 120° K., magnetite has a singular change in state. This does not affect its magnetic moment or the law of thermal variation of saturation but manifests itself at increasing temperatures by a discontinuous variation in magnetization, owing to an abrupt decrease in the coefficient of magnetic hardness, a.

WEISSBERGER, E. *See* abs. **1525.**

WEITKAMP, A. W. *See* abs. **420a, 420b, 3767, 3768.**

3642a. WEITKAMP, A. W., AND FRYE, C. G. Products of the Hydrogenation of Carbon Monoxide Over an Iron Catalyst. Relation of Product Composition to Reaction Mechanism. Am. Chem. Soc., 121st Meeting abs., March–April 1952, p. 11–M.

Evaluation of proposed reaction mechanisms for the hydrocarbon synthesis process was prompted by the availability of new product composition data and a knowledge of the effects of certain operating variables on product composition. The hydrocarbon synthesis process consists of several competing and concurrent reactions. The chemical steps in the formation of primary-product molecules are initiation, chain extension, and termination. The initiator of chain growth may be adsorbed radical, possibly formed by hydrogenation on surface carbide. The adsorbed radical is enlarged by repeated addition and hydrogenation of adsorbed CO molecules. The termination reaction produces mainly alcohols or aldehydes and olefins. Competition between growth and termination is responsible for the exponential decrease in yields of successive C-number fractions. Distributions of normal and branched isomers are explained on the assumption of a statistical distribution of growth on the 2 C atoms last added to the adsorbed radicals. Secondary reactions convert part of the original olefins to paraffins and may convert part of the alcohols or aldehydes to acids and ketones.

3642b. WEITKAMP, A. W., SEELIG, H. S., BOWMAN, N. J., and CADY, W. E. Products of the Hydrogenation of Carbon Monoxide Over an Iron Catalyst. Am. Chem. Soc., 121st Meeting abs., March–April, 1952, p. 9–M.

The general nature of the product from the hydrogenation of CO over an Fe catalyst has been investigated but not the detailed composition. In the present work the hydrocarbons were analyzed by distillation, chromatography, spectrometric methods, and other means. The wt. % yield reaches a maximum at 3 C's and then declines almost exponentially with increasing C number. In the aliphatic and alicyclic hydrocarbons,

olefins predominate and straight-chain structures are prevalent. The straight-chain content decreases exponentially with increasing C number. The branched isomers and the alicyclic hydrocarbons occur in increasing proportions in higher C-number fractions. Simple relationships among the structures and distributions of the open-chain and ring compounds reflect the mechanism of formation. Significant deviations from thermodynamic equilibria indicate that competing reaction rates control product composition. Knowledge of the composition not only aids in the efficient utilization of the product but also permits a better understanding of the process.

3643. WELLER, S. Kinetics of Carbiding and Hydrocarbon Synthesis With Cobalt Fischer–Tropsch Catalysts. Jour. Am. Chem. Soc., vol. 69, 1947, pp. 2432–2436; Chem. abs. vol. 42, 1948, p. 1483.

Rates of carbiding, of hydrogenation of carbide, and of hydrocarbon synthesis from CO–H_2 mixtures have been measured for a Co–ThO_2–kieselguhr catalyst (100 : 18 : 100) with the use of a circulating gas system. The initial carbiding rate is comparable with the synthesis rate, but the steady rate of bulk carbiding is about 10 times lower. The apparent activation energies for bulk carbiding and for the synthesis are 31 and 27 kcal. per mol., respectively. Within the pressure range 8–45 cm. Hg, the pressure dependence of the carbiding rate can be expressed as Rate$=kp^n$; where n is 0.20–0.25. Some of the implications of these results for the mechanism of the carbiding and synthesis are discussed.

3644. ———. Effect of Operating Variables Upon the Fischer–Tropsch Synthesis. Bureau of Mines Rept. of Investigations 4405, 1949, 8 pp.

Paper consists of 2 parts: First is a discussion, based chiefly on previously published information, of the probable effect of space velocity, temperature, pressure, and gas composition on the course of synthesis and the type and properties of the products. Some remarks are made also on the role that Co carbide, particularly bulk carbide, plays in the synthesis.

3645. WELLER, S., AND FRIEDEL, R. A. Isomer Distribution in Hydrocarbons From the Fischer–Tropsch Process. Jour. Chem. Phys., vol. 17, 1949, pp. 801–803; Chem. Abs., vol. 44, 1950, p. 1314.

Isomer distribution found experimentally for the saturated hydrocarbon products (pentane to octane range) from a Co Fischer–Tropsch catalyst has been deduced from probability considerations. With certain restrictions, it is assumed that the C skeleton is built up by addition to any terminal C atom (for which the priori probability has a constant valve a) or to any penultimate C atom (with a priori probability b). Values of a and b, determined from experimental data, led to deduced isomer concentrations in each molecular-weight cut agreeing with experimental concentrations with an average deviation of 0.7%. Peculiarities in the observed isomer distribution were reproduced also. If the same general mechanism described for Co catalysts holds for Fe catalysts, it should be possible to deduce the isomer distribution in the products from Fe catalysts also, when these data have been obtained. Furthermore, it may be anticipated that data for the skeleton isomerism of the olefinic products also will be describable in similar terms. In case of general agreement in enough cases, the validity of the assumed chain build-up mechanism for the Fischer–Tropsch reaction might be established and other schemes ruled out.

3646. ———. Isomer Distribution in Fischer-Tropsch Hydrocarbons. Jour. Chem. Phys., vol. 18, 1950, pp. 157–158; Chem. Abs., vol. 44, 1950, p. 4651.

An isomer distribution can be calculated by assuming that the various isomers of a given molecular-weight fraction add C atoms in proportion to their concentrations. (*See also* abs. **3645.**) It also can be calculated by assuming that the C-atom addition is proportional to the number of ways in which addition to the individual isomers can occur. An application of this calculation is given. Both schemes of calculation give results that agree well with experiment.

3647. WELLER, S., HOFER, L. J. E., AND ANDERSON, R. B. Role of Bulk Cobalt Carbide in the Fischer-Tropsch Synthesis. Jour. Am. Chem. Soc., vol. 70, 1948, pp. 799–801; Chem. Abs., vol. 42, 1948, p. 3550.

Evidence is presented that for Co catalysts, bulk Co carbide is neither an intermediate in the Fischer-Tropsch synthesis nor a catalytically active substrate for the synthesis: (1) The presence of extensive amounts of carbide in Co catalysts severely inhibits the Fischer-Tropsch synthesis; (2) used catalysts show no carbide by X-ray analysis, but samples carbided before synthesis show carbide to be present after synthesis; (3) the low-temperature unstable cubic Co produced by reduction of Co catalysts is not converted to hexagonal Co during the synthesis, although carbiding and subsequent hydrogenation of a reduced catalyst always result in this conversion.

WELLS, C. *See* abs. **3158.**

3648. WELLS, C., AND MEHL, R. F. Rate of Diffusion of Carbon in Austenite in Plain Carbon, in Nickel, and in Manganese Steels. Am. Inst. Min. and Met. Eng., Tech. Pub. 1180. 1940, 28 pp.; Chem. Abs., vol. 34, 1940, p. 7241.

Concentration-penetration curves for the diffusion of C in γ Fe were determined by diffusing C from high-C into low-C alloys. From chemical analysis of layers, diffusion coefficients (D) were calculated for 0.1–1.0 wt. % C and 750°–1,250°. At 0.7% C, D is accurate to ±5% and at 0.1% and 1.0%, to ±10%. From the variation of D with temperature, the activation heat of diffusion (Q) was determined graphically. At 0.7% C, $Q=32{,}000\pm500$ cal. per gm. atomic weight; at 0.1 and 1.0%, $Q=32{,}000\pm1{,}000$ cal. For the range 0.1–1.0% C, $D_c\ \gamma\ \mathrm{Fe}=0.12\pm0.07 \times e^{-32{,}008^\circ\pm1{,}000/RT}$; this is an average equation that does not give variation in D with concentration. At 0.7% C, $D_c\ \gamma\ \mathrm{Fe}=0.12\pm0.03.e^{-32{,}000\pm1{,}000/RT}$; this is more precise. The rate of diffusion increases with increasing C concentration by approximately 80%, 0.1–1.0% C; this is approximately independent of temperature. For an accuracy of ±10%, $D_c\ \gamma\ \mathrm{Fe}=(0.07+0.06 \times \%\ \mathrm{C}).e^{-32{,}000/RT}$. Rate of diffusion does not vary with grain size in the range of A. S. T. M. Nos. −3 to 8 within the experimental error given nor with impurities ordinarily present in commercial steels; O as high as 0.19% has no effect on D. Mn and Ni up to 20% increase the rate of diffusion, but the increase is inappreciable for the amounts of these elements ordinarily present in heat-treating or carburizing steels. The significance of these results for the study of carburizing and formation of pearlite from austenite is discussed.

3649. WELLS, C., BATZ, W., AND MEHL, R. F. Diffusion Coefficient of Carbon in Austenite. Jour. Metals, vol. 188, No. 3, Trans., 1950, pp. 553–560; Chem. Abs., vol. 44, 1950, p. 3421.

Diffusion-coefficient values for C in austenite covering a wide range of temperature and composition have been determined by employing statistical methods. In addition, the relation between concentration and each of the following, D (diffusion coefficient), Q (activation heat of diffusion), and A (the constant in the diffusion equation), has been obtained.

WEN, C. *See* abs. **468.**

WENDER, I. *See* abs. **3275a, 3656b, 3656c.**

3650. WENDER, I., AND ORCHIN, M. Critical Review of the Chemistry of the Oxo Synthesis for Production

of Alcohols From Olefins, Carbon Monoxide, and Hydrogen. Bureau of Mines Rept. Investigations 4270, 1948, 26 pp.

Reviews the developments that have taken place in the synthesis of the higher alcohols and discusses the chemistry of the process, the reaction mechanism, the nature and analysis of the products, and their uses. The practical importance of the Oxo reaction is clearly outlined. The industrial production of long-chain alcohols, aldehydes, and fatty acids from olefin fractions of Fischer-Tropsch products or of petroleum products appears now to be a matter of careful cost estimating and engineering design.

3651. WENDER, I., FRIEDEL, R. A., AND ORCHIN, M. Ethanol From Methanol. Science, vol. 113, 1951, pp. 206–207.

It has been found that, contrary to the usual order of reactivity of alcohols (tertiary>secondary>primary) MeOH reacts with synthesis gas ($CO:H_2$) more rapidly than secondary alcohols with EtOH as the chief product. The conversion was achieved by treating the alcohol with synthesis gas at 180°–185° in the presence of a Co catalyst such as dicobalt octacarbonyl $[Co(CO)_4]_2$. Pressures of 3,500–5,100 p. s. i. were employed. Analysis of the product mixture showed that 76.4% of the MeOH had reacted to yield a total of 70.3% of products (based on the converted MeOH) of which 38.8% was EtOH.

WENDER, I., GREENFIELD, H., AND ORCHIN, M. Chemistry of the Oxo and Related Reactions. IV. Reductions in the Aromatic Series. *See* abs. **3655.**

3652. WENDER, I., LEVINE, R., AND ORCHIN, M. Chemistry of the Oxo and Related Reactions. I. Homologation of Alcohols. Jour. Am. Chem. Soc., vol. 71, 1949, pp. 4160–4161; Chem. Abs., vol. 44, 1950, p. 2439.

Investigations at the Bureau of Mines have revealed that an alcohol can be converted to the homologous alcohol containing 1 C atom more than the original one by the Oxo or hydroformylation reaction without proceeding via an olefin intermediate followed by a 1-step hydroformylation-hydrogenation. The process is to treat the alcohol with synthesis gas, $1H_2:1CO$, at 160°–180° and 3,200 p. s. i. for 1–1.5 hr. in the presence of a Co catalyst, cobaltous acetate, or cobaltous oxide. By this means, benzyl alcohol is converted to β–phenylethyl alcohol, isopropyl alcohol to n–butyl and isobutyl alcohol, and t–butyl alcohol to isoamyl alcohol. It is believed that the homologation reaction is an acid, $HCoCO_4$, catalyzed reaction that proceeds via a carbonium ion according to a mechanism that will be discussed later.

3653. ———. Chemistry of the Oxo and Related Reactions. II. Hydrogenation. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 4375–4378.

Aldehydes and ketones can be reduced to alcohols by H_2 and CO in the presence of a Co catalyst, and the reaction can be applied to the reduction of compounds containing S. A free radical mechanism is proposed for the hydrogenation. When olefins are treated with 150–300 atm. of synthesis gas and a Co catalyst at 180°–185°, alcohols containing 1 C atom more than the olefin are the principal products. Double bonds in some compounds, when treated under these conditions, are hydrogenated rather than hydroformylated. (*See* abs. **3652.**)

3654. WENDER, I., ORCHIN, M., AND STORCH, H. H. Mechanism of the Oxo and Related Reactions. III. Evidence for Homogeneous Hydrogenation. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 4842–4843.

It has been shown that the hydroformylation reaction is often accompanied by hydrogenation; indeed, in some instances, hydrogenation proceeds to the exclusion of hydroformylation. Evidence is presented that strongly indicates that the great variety of hydrogenations that occur in the presence of Co and a high partial pressure of CO probably proceed by homogeneous catalysis in which $[Co(CO)_4]_2$ or $HCo(CO)_4$ functions as the catalyst.

3655. WENDER, I., GREENFIELD, H., AND ORCHIN, M. Chemistry of the Oxo and Related Reactions. IV. Reductions in the Aromatic Series. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 2656–2658.

Previous work has shown that certain aliphatic alcohols react with H_2 and CO in the presence of a Co catalyst to give an homologous alcohol; only in the case of MeOH is any of the alcohol reduced to a hydrocarbon. The present study is concerned with the reaction of alcohols and ketones in the aromatic series under the same conditions and shows that in all cases hydrocarbons are the principal products. Benzyl alcohol gives both 2-phenylethanol and toluene, but substituted benzyl alcohols of the type $C_6H_5CR_1R_2OH$, where R_1 and R_2 may be H_2, alkyl, or aryl groups, react to give hydrocarbons in excellent yields. The mechanism of hydrocarbon formation is discussed. A simple, convenient procedure for the preparation of dicobalt octacarbonyl is given.

3655a. WENDER, I., METLIN, S., AND ORCHIN, M. Chemistry of the Oxo and Related Reactions. V. Acid Catalysis With Pinacol. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 5704–5706.

Reaction of pinacol with CO and H_2 at 185° in the presence of a Co catalyst gives a complex mixture of products. 4 compounds more volatile than the starting material were identified; these were pinacolone, pinacolyl alcohol, 3,4–dimethylpentanol–1 and 2,2,3–trimethyltetrahydrofuran. The origin of these compounds is consistent with the formation and further reaction of a common carbonium-ion intermediate formed from pinacol under acidic conditions. The acid catalyst is probably Co hydrocarbonyl, $HCo(CO)_4$.

3655b. WENDER, I., GREENFIELD, H., METLIN, S., AND ORCHIN, M. Chemistry of the Oxo and Related Reactions. VI. Experiments With Meta- and Para-Substituted Benzyl Alcohols. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 4079–4083.

Nuclear-substituted benzyl alcohols react with synthesis gas ($2H_2:1CO$) in the present of a Co catalyst (dicobalt octacarbonyl) to give a mixture containing a substituted toluene derived from the hydrogenolysis of the hydroxyl group (reduction) in addition to a substituted 2-phenylethanol (homologation). The effect of the substituent on the overall rate of the reaction and on the product distribution was studied in a series of semiquantitative experiments. The rate of reaction decreased in the following order: p–OCH_3≫p–CH_3>m–CH_3, p–t–butyl>H>p–Cl>m–OCH_3≫m–CF_3. The proportion of homologation product as compared to reduction product also increased in the order in which the substituent is capable of releasing electrons but this effect was not nearly as pronounced as the effect on the reaction rate.

WENDER, I., LEVINE, R., AND ORCHIN, M. Chemistry of the Oxo and Related Reactions. II. Hydrogenation. *See* abs. **3653.**

WENDER, I., METLIN, S., AND ORCHIN, M. Chemistry of the Oxo and Related Reactions. V. Acid Catalysis With Pinacol. *See* abs. **3655a.**

3656. WENDER, I., ORCHIN, M., AND STORCH, H. H. New Modifications of the Oxo Process. Armed Forces Chem. Jour., vol. 4, October 1950, pp. 4–9.

It is pointed out, with reference to the work of Keulemans, Kwantes, and Van Bavel (abs. **1739**), that it is possible by the hydroformylation of olefins to predict the structure of the aldehydes or alcohols obtained from a given olefin. It also has been found that under regu-

lated conditions of pressure and temperature it is entirely feasible to produce alcohols from olefins by a 1-step synthesis or to isolate the aldehyde as the major product. It is indicated quite strongly as the result of experiments that hydrogenation reactions that occur in the presence of Co and a high partial pressure of CO proceed by homogeneous catalysis in which dicobalt octacarbonyl functions as the catalyst. It also is possible that the reductions that occur under Oxo conditions proceed via a free redical mechanism. If this is so, hydrogenation under such conditions should not be adversely affected by S compounds, as is the heterogeneous catalysis of hydrogenation over a solid catalyst. Under the conditions of the Oxo reaction, some types of unsaturated linkages are hydrogenated, whereas others react by hydroformylation. Several such reactions are described, and the yields of products obtainable are summarized. Of particular interest is the reaction of furan and its derivatives. The homologation of aliphatic alcohols and the hydrogenation and homologation of aromatic aldehydes, ketones, and alcohols are discussed. It is not yet proved, but it is assumed, that the Oxo reaction with olefins proceeds via a carbonium ion, and evidence is mounting that homologation may proceed through such an intermediate. Two recently discovered reactions are found to take place under Oxo conditions: HCHO reacts with synthesis gas to yield ethylene glycol and methylal with synthesis gas, and a Co catalyst yields methyl cellosolve. The synthesis of EtOH from coal or natural gas via synthesis gas and MeOH now is possible. Recent work indicates that EtOH may be an intermediate in the Fischer-Tropsch synthesis. Further assumptions have been made as to the possible mechanism of the Fischer-Tropsch hydrocarbon synthesis: The C skeleton is built up by the stepwise addition of 1 C atom at a time, and addition of the C atom occurs only at the terminal or next to the terminal C atom of the chain and does not occur at a tertiary C atom to form a product containing a quaternary C atom. As regards the Oxo synthesis these assumptions are already accepted as facts.

WENDER, I., ORCHIN, M., AND STORCH, H. H. Mechanism of the Oxo and Related Reactions. III. Evidence for Homogeneous Hydrogenation. *See* abs. **3654.**

3656a. WENDER, I., STERNBERG, H. W., AND ORCHIN, M. Chemistry of the Metal Carbonyls. I. New Concepts Applied to Carbonyls of Cobalt. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 1216–1219.

Reactions of a variety of organic compounds with dicobalt octacarbonyl, previously assumed to proceed by displacement of 1 or more mols of CO by the entering organic molecule, are explicable on a common basis: The entering organic group, which always has an available pair of electrons, effects a homomolecular disproportionation of the dicobalt octacarbonyl into catalyst (II) ion and Co carbonyl anion according to the generalized equation: $12\ B+3[Co(CO)_4]_2 \rightarrow 2[Co(B)_6][Co(CO)_4]_2+8\ CO$, where B is a base in the Lewis sense. The electrons necessary for the formation of the anion are secured at the expense of some of the Co. Situations are also described in which these electrons are furnished by an external source. The tendency to form the stable (rare-gas structure) Co carbonyl anion is probably the driving force for the reactions.

3656b. STERNBERG, H. W., WENDER, I., FRIEDEL, R. A., AND ORCHIN, M. Chemistry of the Metal Carbonyls. II. Preparation and Properties of Cobalt Hydrocarbonyls. Jour. Am. Chem. Soc., vol. 75, 1953, pp. 2717-2720.

New method for the preparation of Co hydrocarbonyl is based on the reaction between dicobalt octacarbonyl and pyridine whereby a Co salt of Co hydrocarbonyl is obtained readily and quantitatively:

$3[Co(CO)_4]_2+12\ Pyr \rightarrow 2[Co(Pyr)_6][Co(CO)_4]_2+8\ CO$

Addition of salt to excess dilute H_2SO_4 in a stream of inert gas over a period of about 45 min. gave pure Co hydrocarbonyl in a yield of 95%. Co hydrocarbonyl is stable in aqueous solution and behaves like a strong mineral acid. The half life in the gas phase and in hexane solution is dependent upon its concentration. The infrared spectra of Co hydrocarbonyl in the gas phase and in hexane solution were determined in the 2–15μ region. Neither of these spectra showed the presence of a conventional hydroxyl band. In addition the deutrocarbonyl was prepared to check for the expected shift of spectral bands, but the spectrum was identical to that of the hydrocarbonyl. Mass spectrometric analysis of Co hydrocarbonyl gave peaks for Co (CO), $Co(CO)_2$, $Co(CO)_3$ and $Co(CO)_4$ and H_2. The latter was not found as part of any other fragment.

3656c. ———. Chemistry of the Metal Carbonyls. III. Reaction Between Dicobalt Octacarbonyl and Dimethylamine. Jour. Am. Chem. Soc., vol. 75, 1953, pp. 3148–3152.

It has been shown that many Lewis bases react with dicobalt octacarbonyl: $3[Co(CO)_4]_2+12B \rightarrow 2[Co(B)_6]^{++}[Co(CO)_4]^-+8\ CO$. When excess dimethylamine is condensed onto dicobalt octacarbonyl at —80° and the solution is warmed to room temperature, no CO is evolved and equimolar amounts of Co cation and Co carbonyl anion are formed. Infrared and mass spectrometric analysis of the reaction product indicated the presence of dimethylamine, dimethylformamide and small amounts of tetramethyl urea. It appears from these data that the CO usually given off in the disproportionation of dicobalt octacarbonyl in this instance reacted with the amine: $3[Co(CO)_4]+20(CH_3)_2NH \rightarrow 2[Co[(CH_3)_2NH]_6]^{++}[Co(CO)_4]^-_2+8(CH_3)_2NCHO$. According to this equation, stoichiometric quantities of dicobalt octacarbonyl would be required to convert dimethylamine to dimethylformamide. However, if it were possible to reverse the first equation employing the proper conditions, only catalytic quantities of dicobalt carbonyl might be required to convert dimethylamine to dimethylformamide, especially since the latter can coordinate the cation in the form $[Co[(CH_3)_2NCHO]_6]^{++}$. Treatment of dimethylamine with 1 mole % of dicobalt octacarbonyl at 200°–210° and an initial pressure of 3000 p. s. i. of CO gave dimethylformamide smoothly and in good yield; no tetramethyl urea was formed. A possible mechanism for the formation of dimethylformamide from dimethylamine and dicobalt octacarbonyl is discussed.

WENDER, I., GREENFIELD, H., METLIN, S., AND ORCHIN, M. Chemistry of the Oxo and Related Reactions. VI. Experiments With Meta- and Para-Substituted Benzyl Alcohols. *See* abs. **3655b.**

3657. WENDT, G. L., AND EVANS, G. M. Equilibrium Between Hydrogen–Carbon Monoxide and Methane–Carbon Dioxide in the Corona Discharge. Jour. Am. Chem. Soc., vol. 50, 1928, pp. 2610–2621; Chem. Abs., vol. 22, 1928, p. 4335.

Gaseous phase in the reaction $2CC+2H_2=CO_2+CH_4$ reaches an equilibrium at a composition of 37.1% CO, 37.6% H_2, 13.3% CO_2, and 8.7% CH_4, corresponding thermodynamically to 900°–950° K. Contraction continues, however, and the end products are C and H_2O.

3658. WENNER, R. R. Prediction of Reaction Equilibria. Chem. Eng. Progress, vol. 45, 1949, pp. 194–207; British Abs., 1949, B, I, p. 546.

All predictions are ultimately based on heats of formation and reaction, and these are best determined experimentally. For example, methods of calculation from bond energies are only a substitute for rigid determination. A number of methods are listed both for these heats and for entropy determination. The

methods are applied to the reaction of $C_2H_4+CO+H_2 \rightleftharpoons$propionaldehyde. This, the Oxo reaction, is shown to go virtually to completion at 1 atm. The industrial use of higher pressures is presumably directed toward faster reaction rates by alteration of surface conditions. Other reactions discussed.

WENTZEL, K. *See* abs. **2881.**

3659. WENZEL, —. [State of the Synol Problem.] TOM Reel 134, sec. II, No. 10; Rept. 326, Apr. 10, 1942, 33 pp.

Since the Synol process was devised for producing high-molecular alcohols from CO and H_2, the problem has been to place it on an operating, commercial basis, 10,000 tons per yr., find the proper conditions for the synthesis, discover usable and economical methods for separating the hydrocarbons and alcohols in a pure enough state, and find applications for the products. These problems appear to have been solved. Alcohols can be obtained from synthesis or water gas of composition CO : H_2=1 : 0.75 or 1 : 1. For best results, overheating of the catalyst should be avoided. Pressures above 25 atm. are inadvisable. Four stages of gas conversion are best, care being taken that the formation of CO_2 does not exceed 10% in order to produce the best yield of alcohol. Temperature of conversion is about 190°–195° in the 1st stage, and not exceeding 210°–225° in the other stages. The layout for a Synol-synthesis plant with provision for a change over to diesel oil and gasoline production is described. A plate converter was the most efficient for heat removal. The best catalyst for the process appears to be the Leuna NH_3 fused Fe catalyst WK 17 of grain size 1–2 mm. reduced at 450° for 48 hr., with a H_2-load of 1:3,000 per hr. It was found that this catalyst during the conversion forms hexagonal Fe carbide, Fe_2C, which at temperatures above 290° is transformed into inactive Hägg Fe_5C. The 2d choice is a precipitation catalyst, No. 2643, with 3.7% Al_2O_3, 1% K_2O, and the remainder Fe. Recently an Fe catalyst of high activity has been developed at Leuna containing small additions, 0.1% Sb, Ni, which may surpass the precipitation catalyst previously obtained. The working up of the products is discussed at length to remove undesired impurities as acids, esters, aldehydes, and ketones. Alcohols up to C_6 are separated by washing with water or MeOH solutions, the higher alcohols by the boric acid method. Alcohols up to C_{22} have been obtained. The alcohols are thought to be mainly straight-chain and primary alcohols with the double bond at the end of the chain. The products are believed to be suitable for making detergents, solvents, softeners for plastics, and varnish solvents. Several patent applications listed.

3660. WENZEL, W. [Synol Process. New Synthesis of Aliphatic Alcohols.] Angew. Chem., vol. 20, 1948, B, pp. 225–230; Bureau of Mines Transl. K–8, 1949, 26 pp; Chem. Abs., vol. 43, 1949, p. 994.

Predominant production of alcohols from CO and H_2 was developed by using fused Fe catalysts permitting operating temperatures as low as 180°. This development with all of its attending variations in synthesis is summarized, and some general information is presented on material balances and separation of alcohols.

———. *See* abs. **1999, 2000, 2001, 2002.**

3661. WERNER, G. [Synthesis of Hydrocarbons by the Process of Fischer and Tropsch.] Ztschr. kompr. flüss. Gase, vol. 36, 1941, pp. 77–80, 89–94; Chem. Zentralb., 1942, I, p. 828; Chem. Abs., vol. 37, 1943, p. 3243.

Comprehensive presentation of the process of Fischer–Tropsch in its chemical principles and technique, with recent literature.

3662. WERT, C. A. Precipitation From Solid Solutions of Carbon and Nitrogen in Alpha–Iron. Jour. Appl. Phys., vol. 20, 1949, pp. 943–949; Chem. Abs., vol. 44, 1950, p. 508.

Formation of precipitates from the solid solutions of C and N in α–Fe was studied by means of the internal friction peak associated with the stress-induced interstitial diffusion of the solute atoms. A transformation law fits the experimental data. The data show the following: (1) Fe_3C precipitates in the shape of spheres; (2) an intermediate phase in the precipitation of N forms in the shape of disks; and (3) within the experimental error no continuous nucleation is indicated. From the results of a derivation made by Zener, the mean distance between nuclei is calculated for Fe_3C. For C concentrations of about 0.016 wt. %, this distance is about 800, 2,000, and 7,000 Å. at 27°, 102°, and 312°, respectively. With appropriate experimental conditions, the temperature dependence of the precipitation rate is about the same as the temperature dependence of the diffusion rate of the solute atoms.

3663. ———. Diffusion Coefficient of Carbon in Alpha–Iron. Phys. Rev., vol. 79, 1950, pp. 601–605; Chem. Abs., vol. 44, 1950, p. 9760.

Equation of the form $D=D_oe^{-\Delta H/RT}$ is developed for interstitial diffusion in cubic lattices. This development uses a classical statistical mechanical treatment. Measurements of D for C in α–Fe were made, −35° to 200°. Combined with earlier data they extend the knowledge of D in this system from $D=10^{-20}$ to $D=10^{-6}$ cm.^{2} per sec. The values of D_o and ΔH obtained by fitting this equation to the experimental points give D_o=0.02 cm.^{2} per sec. and ΔH=20,100 cal. per mol.

3664. ———. Measurements on the Diffusion of Interstitial Atoms in Body-Centered Cubic Lattices. Jour. Appl. Phys., vol. 21, 1950, pp. 1196–1197; Chem. Abs., vol. 45, 1951, p. 1835.

Rate of diffusion of C in Ta and Nb and of N in α—Fe was measured by effects on internal friction and an elastic aftereffect. Data covering a range of 10^4 in rate are reported.

3665. ———. Solid Solubility of Cementite in Alpha-Iron. Jour. Metals., vol. 188, Trans., 1950, pp. 1242–1244; Chem. Abs., vol. 44, 1950, p. 10,631.

By using the internal friction of C in α–Fe, the solubility of cementite in α–Fe has been measured down to a temperature of 150°. The yield strength of ingot Fe containing small amounts of cementite also has been determined as a function of C concentration.

WESSELKOCK, H. *See* abs. **3057, 3066, 3067, 3069.**

3666. WEST, H. L. Major Developments in Synthetic Lubricants and Additives in Germany. Jour. Inst. Petrol., vol. 34, 1948, pp. 774–820; BIOS Final Rept. 1611, February 1948, 128 pp.; PB 93,668.

By the end of the war, Germany had a well-developed synthetic-lubricating oil industry, which was rapidly expanding. On a quantity basis the products obtained from natural petroleum resources predominated, but from a quality standpoint the synthetic production was of more importance. The total production of lubricants in January 1944 was 70,000 tons per mo., of which about 12% were synthetic oils. The I. G. Farbenindustrie was obtaining 1,250 tons per mo. from the polymerization of C_2H_4 with $AlCl_3$, while they, together with Rhenania Ossag, were producing 2,100 tons from olefins obtained from the cracking of petroleum and Fischer-Tropsch waxes. In addition to these developments, Ruhrchemie was producing 1,500 tons from olefins obtained from Fischer-Tropsch gas oils and sweater oil from the manufacture of wax derived from the process. Rheinpreussen was obtaining 300 tons by a method analogous to that for Paraflow production with chlorinated Kogasin from the Fischer-Tropsch process as the main raw material. In addition, there

were about 3,000 tons of lubricating oils being produced by brown-coal hydrogenation. A very promising development, which had not come into production, was the use of the esters of fatty acids, particularly sebacic and adipic acids. Extensive bibliography.

———. *See* abs. **873, 874, 875, 876, 877, 878, 3729.**

3667. WESTGREN, A. [Crystal Structure of Cementite.] Jernkontorets Ann., vol. 114, 1932, pp. 457–468; Chem. Abs., vol. 27, 1933, p. 1301.

Grouping of Fe atoms suggested by Hendricks (abs. **1400**) is verified, but the parameters have been slightly adjusted as follows: $x=0.333$, $y=0.175$, $z=0.065$, $u=-0.167$, and $v=0.04$. The C atoms are surrounded by 6 Fe atoms at the distance 2.01 Å. U., which define a regular prism on a triangular isosceles base. 11 refs.

———. *See* abs. **1601.**

3668. WESTGREN, A., AND LINGH, A. E. [Crystal Structure of Iron and Steel.] Ztschr. physik. Chem., vol. 98, 1921, pp. 181–210; Chem. Abs., vol. 15, 1921, p. 3812.

Deals with an X-ray spectrographic investigation of the crystal structure of Fe and steel. The results of Hull (abs. **1516**) that the atoms of pure Fe at ordinary temperature (α–Fe) are arranged on a centered cubic lattice, have been confirmed. At 800°–830° that is, within the so-called β–Fe interval, the atoms are grouped in the same way as in α–Fe. Since allotropy of crystalline solids is synonymous with polymorphism, β–Fe cannot be regarded as a special modification of Fe. In both austenite and pure Fe, which is stable at 1,000°, the crystals have a plane-centered cubic lattice. This is also characteristic of γ–Fe, and constitutes a fundamental difference between α– and γ–Fe. In martensite the Fe appears in the form of the α modification. This is likewise the case in rapid-drawn steel of ordinary composition that has been hardened at 1,275°.

3669. WESTGREN, A., AND PHRAGMÉN, G. [X-Ray Studies on the Crystal Structure of Steel.] Ztschr. physik. Chem., vol. 102, 1922, pp. 1–25; Jour. Iron Steel Inst. (London), vol. 105, 1922, pp. 105, 241–273; Engineering, vol. 113, 1922, pp. 630–634; Chem. Abs., vol. 16, 1922, p. 2291.

X-ray photograms (according to Debye and Scherrer) of an Fe wire, heated to 800°, 1,100°, and 1,425°, have shown that the wire within the so-called β– and δ–ranges has a body-centered cubic structure and within the γ–range a face-centered structure. It is thus proved that the transformation that takes place at 900° (A_3) is reversed at 1,400° (A_4). The γ–Fe lattice of austenite steels is enlarged by the dissolved C. A steel with 1.98% C has a somewhat larger lattice when quenched from 1,100° than when quenched from 1,000°. Also, the α–Fe lattice in martensite seems to be influenced by the C present. The ranges of homogeneous α–Fe lattice in martensite are extremely small. A steel with 0.80% C, quenched in H_2O from 760°, is on the verge of being totally amorphous. Debye photograms of cementite and of the well-known crystal tablets of spiegel Fe are identical. A Laue photograph and investigations of an orientated rotating crystal of the latter type have made it possible to find out the crystal data of cementite. It belongs to the orthohombic system, its ratio of axis is 0.670 : 0.755 : 1, and the dimensions of its elementary parallelepiped are 4.53, 5.11, and 6.77 Å. The base group consists of 4 mol. Fe_3C, which corresponds to a specific weight of 7.62 for the cementite.

WESTRIK, R. *See* abs. **677.**

3670. WETZEL, L. A., MCKEEVER, C. H., AND LEVESQUE, C. L. Structures of the Oxo Aldehydes From Styrene. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 4939–4940.

Previous work (abs. **3** and **4**) reported the preparation of 2–phenylpropionaldehyde in 30% yield by the application of the Oxo reaction to styrene. There was no evidence, however, of the formation of 3–phenylpropionaldehyde. Additional evidence is now obtained that the primary product of the Oxo reaction on styrene is actually a mixture of the 2– and 3–phenylpropionaldehydes. The data indicate that at least 23% is the 2–isomer, at least 29% is the 3–isomer, while the remaining 47% cannot be assigned to either at present. Oxidation of the phenylpropionaldehyde produced by the Oxo reaction with styrene (46% yield) gives a mixture of acetophenone and 3–phenylpropionic acid. This indicates that both 2– and 3–phenylpropionaldehydes are formed in the Oxo reaction.

3671. WEVER, F. [Iron Carbide.] Mitt. Kaiser Wilhelm-Inst. Eisenforsch. Düsseldorf, vol. 4, 1922, pp. 67–80; Chem. Abs., vol. 18, 1924, p. 1460.

By X-ray analysis, it is proved that the forms of cementite shown in the Fe–C thermal diagram are not distinguishable by their lattice structure. Fe_3C crystallizes in a rhombic lattice denoted by the quadratic form $\sin^2\theta/2=0.0464x^2+0.0367y^2+0.0208z^2$. The edge lengths are $a=4.481$ Å., $b=5.034$ Å., $c=6.708$ Å. The density is calculated therefrom as 7.82. Data by the Debye-Scherrer method above 210° show that the magnetic transformation is not associated with a change in the type of lattice. The quadratic form is expressed by $\sin^2\theta/2=0.0456x^2+0.0362y^2+0.0203z^2$. The edge lengths are $a=4.52$ Å., $b=5.08$ Å., $c=6.77$ Å.

3672. ———. [Nature of the Magnetic Transformation of Iron.] Ztschr. anorg. Chem., vol. 162, 1927, pp. 193–202; Chem. Abs., vol. 21, 1927, p. 3871.

A_3 and A_4 transformations of Fe are shown to oe both polymorphic and phase transformations. In the magnetic A_2 transformation, neither the space group, the crystal structure, nor the space lattice orientation within the individual crystals is changed. Hence the magnetic transformation is not polymorphic. Further, the cooling curve for very pure Fe is interpreted as failing to establish the A_2 as a phase transformation.

3673. ———. [Thermodynamics of the Transformations of Iron.] Mitt. Kaiser Wilhelm Inst. Eisenforsch, Düsseldorf, vol. 9, 1927, pp. 151–155; Chem. Abs., vol. 21, 1927, p. 2245.

Discussion of polymorphic and phase transformations. The A_3 and A_4 transformations of Fe are clearly both polymorphic and phase transformations, whereas the magnetic A_2 transformation comes under neither class.

3674. WEVER, F., AND MÜLLER, A. [Binary Systems: Iron–Boron, Iron–Beryllium and Iron–Aluminum.] Mitt. Kaiser Wilhelm Inst. Eisenforsch., Düsseldorf, vol. 11, 1929, pp. 193–223; Chem. Abs., vol. 23, 1929, p. 5458.

Equilibrium diagram of Fe–B was studied thermally, microscopically, and by means of X-rays and was found to belong to that group of binary Fe alloy having a narrowly limited γ–phase. As a result of insufficient solubility, a closed γ–field was not obtained. Mixed crystals of α–Fe–B as well as the solid solution γ–Fe–B are formed by ordinary atomic substitution. The boride Fe_4B_2 has a tetragonal space lattice with 2 mol. per unit, while the boride FeB also exhibits tetragonal symmetry with 16 mol. per unit. The Fe side of the equilibrium diagrams of Fe–B and Fe–Al was studied, and both systems were found to have completely closed γ–fields. Mixed crystals of α–Fe and γ–Fe with both Be and Al are formed by atomic substitution.

3675. WEVER, F., AND NAESER, G. [Manner in Which Carbon Is Bound in Hardened and Tempered Steels.] Mitt. Kaiser Wilhelm Inst. Eisenforsch., Düsseldorf,

vol. 16, 1934, pp. 201–206; Chem. Abs., vol. 29, 1935, p. 2491.

Object was to determine, by analyzing the residues of tempered steels obtained by electrolysis in $FeCl_2$ solutions, the manner in which C is bound in steel at different temperatures. The residues are separated magnetically into 2 parts, one essentially highly dispersed C with H_2O and the other a gray-black powder, which, in dry state, ignites in air. The C content of the unseparated residues decreases with increasing tempering temperatures from very high values in untempered steels to that of the composition Fe_3C at 700°, whereas the C content of the purified residues is mostly FeC up to about 300° and Fe_2C between 300° and 600°–700°; the composition of cementite is reached above 700°. Residues of steels transformed directly from the austenite state have lower C contents than tempered steels and correspond to Fe_2C for transformation temperatures of 400°–500°. The existence of the carbides FeC and Fe_2C in tempered steels is considered to be established. 23 references.

3676. WEYGAND, C. [Modern Method of Manufacture of Gasoline.] Farbe u. Lack, 1926, pp. 599–600; Chem. Abs., vol. 21, 1927, p. 1004.

Synthetic process method of F. Fischer: CO, purified water gas, is hydrogenated in the presence of Co or Co–Cr_2O_3, Co–ZnO, Co–BeO, at 270° under atmospheric pressure, giving a reaction product of the following composition: (1) Gasol, C_2H_6, C_3H_8, C_4H_{10}; (2) gasoline, water-clear, not discoloring, boiling at 20°–180°; (3) petroleum boiling at 180°–330°; (4) paraffin wax.

3676a. WHEELER, A. Reaction Rates and Selectivity in Catalyst Pores. Advances in Catalysis, Academic Press, Inc., New York, vol. 3, 1951, pp. 249–327.

The review covers the physical picture of pore structure, mechanism of transport in catalyst pores, physical factors determining reaction rates on porous catalysts, reaction rates in single pores, reaction rates on practical catalyst pellets, reaction rates on poisoned catalysts and effect of pore structure on catalyst selectivity. 34 refs.

———. *See* abs. **178, 178a, 179, 181.**

WHEELER, R. V. *See* abs. **2813, 2814.**

3677. WHEELER, R. V., AND WOOD, W. L. Pyrolysis of Methane. Fuel, vol. 7, 1928, pp. 535–539; Chem. Abs., vol. 23, 1929, p. 3212.

Study of the thermal decomposition of CH_4 has been made. The results obtained agree, in general, with those of Fischer (abs. **954**). C_6H_6 is formed at 875°–1,100°, the optimum temperature (for the apparatus used) being about 1,050° with a yield of 0.2 gal. per 1,000 cu. ft. Quartz, porcelain, and Cu reaction tubes were all without catalytic effect on the decomposition. With an Fe tube only C and H_2 are formed. Dilution of the CH_4 with N_2 has little effect on the yield of aromatic hydrocarbons obtained at 1,000°, but dilution with H_2 rapidly decreases the yields. The apparatus is described and illustrated.

3678. WHITAKER, J. W. Fuel Research in India. Jour. Indian Chem. Soc., Ind. News Ed., vol. 12, 1949, pp. 9–17; British Abs., 1950, B, I, p. 396.

Program of the Indian Fuel Research Institute; includes a physical and chemical survey of the Indian coal fields and studies of the efficient burning of powdered high-ash coals, of the Fischer-Tropsch process, and of high- and low-temperature carbonization.

3679. WHITE, E. C., AND SHULTZ, J. F. Fused Cobalt Oxide as a Water-Gas Catalyst. Ind. Eng. Chem., vol. 26, 1934, pp. 95–97; Chem. Abs., vol. 28, 1934, p. 1505.

Catalysts made by the proper fusion and partial reduction with H_2 of Co oxide effectively catalyze the water gas reaction to equilibrium at temperatures as low as 283° and space velocities of 1,800 vol. of water gas per vol. of catalyst per hr. Adding suitable promoters, such as Fe up to 3% or Cr oxide, suppressed the simultaneous formation of CH_4. A Co catalyst containing 38% Cu was particularly active as a water-gas catalyst without significant synthesis of CH_4.

3680. WHITE, J. Equilibrium at High Temperatures in Systems Containing Iron Oxides. Iron and Steel Inst. (London), Carnegie Schol. Mem., vol. 27, 1938, pp. 1–75; Chem. Abs., vol. 33, 1939, p. 4496.

Dissociation of Fe_2O_3 into O_2 and other Fe oxides was studied up to 1,650° under O_2 pressures 2–76 mm. Hg. The reaction was followed by measuring the change in O_2 pressure in a sealed tube, by air quenching from the equilibrium temperature and determining the weight loss, or by measuring the weight change with a special balance while the sample was at high temperature. Dissociation increases with rising temperature and decreasing O_2 pressure. Addition of lime increases dissociation and addition of silica decreases it. In mixtures each acts independently of the other. Equilibrium constants were calculated and dissociation calculated from them was found to be in approximate agreement with the observed dissociation. Additional work was done on the mutual solid solubility of Fe_2O_3 and Fe_3O_4. 23 refs.

WHITE, R. R. *See* abs. **13, 258.**

WHITE, T. A. *See* abs. **199, 200.**

3681. WHITE, T. A., AND BENTON, A. F. Adsorption of Hydrogen by Nickel Poisoned With Carbon Monoxide. Jour. Phys. Chem., vol. 35, 1931, pp. 1784–1789. Chem. Abs., vol. 25, 1931, p. 3895.

H_2 adsorption at 0° on about 23 gm. of Ni is increased considerably by 0.038 cc. of CO at all pressures up to 1 atm.; larger amounts of CO seem to have little effect on the amount of H_2 adsorbed but decrease the rate of adsorption.

3682. WHITELEY, J. H. Observation on Martensite and Troostite. Jour. Iron Steel Inst. (London), vol. 111, 1925, pp. 315–349; Chem. Abs., vol. 19, 1925, p. 3462.

An investigation was made of the different structures of quenched and tempered steels, grouped under the terms martensite and troostite. The facts recorded indicate that martensite, like austenite, is a solid solution of carbide in a transitory form of Fe intermediate between γ–Fe and α–Fe of strong twining tendency. A series of photomicrographs (mostly X 850) accompanies the paper.

3683. ———. Solution of Cementite in α–Iron and Its Precipitation. Jour. Iron Steel Inst., No. 14, 1927, 11 pp.; Engineering, vol. 124, 1927, pp. 472–473; Chem. Abs., vol. 21, 1927, p. 3872.

Basic steel of the Armco type, acid-steel plate heated to 1,000° and air-cooled, and acid-steel plate heated to about 1,400° and cooled very slowly were the specimens examined. The results indicate that above 630°, α–Fe dissolves an appreciable amount of cementite, which is retained in solid solution on quenching. On tempering at or below 250°, precipitation of this cementite occurs in the ferrite grains, and on further heating, the cementite particles travel to the grain boundaries at high velocity. The solubility of cementite increases above 630°, being above 0.03% at 720°. Decrease in purity of the ferrite slightly raises the initial temperature of solution, the acid-steel samples showing no solubility below 750°. Photomicrographic examination shows that the carbide precipitated at lower temperatures was always uniformly distributed in the ferrite grains in parts well away from pearlite areas, indicating a very rapid rate of diffusion. During slow cooling, the dissolved carbide is deposited on existing crystals. The presence of dissolved C has a distinct

hardening effect. Thus the sample of basic steel untreated showed a Brinell number of 89, whereas heated to 680°, quenched, and reheated to 550° the Brinell number was 91, and quenched from 680° it was 105.

3684. WHITMAN, W. G. Liquid-Fuel Supplies and National Security. Petrol. Processing, vol. 4, No. 11, 1949, pp. 1222–1232; Petrol. Refiner, vol. 28, No. 11, 1949, pp. 97–107.

Paper presented at the annual American Petroleum Institute meeting, November 1949. Five measures are put forward to ensure adequate liquid-fuel supplies for national security. The 1st is to foster the continuing existence of reserve capacity to produce crude oil in an emergency. The 2d is to accumulate a reserve of refinery products by stockpiling, but not in such large volume as to offer exorbitant and unnecessary insurance premiums for short-range security. The 3d suggestion is to import as much oil as can be accepted without serious prejudice to domestic exploratory activity. The 4th is to develop synthetic liquid fuels by private enterprise, assisted by basic Government research. The 5th is to develop refinery flexibility to permit higher yields of distilled products and to reduce the output of residual fuels.

3685. WHITNER, T. C. Review of Hydrogenation. Oil and Soap, vol. 16, 1939, pp. 39–44; Chem. Abs., vol. 33, 1939, p. 2747.

Brief review of hydrogenation as applied to hardening of vegetable oils, conversion of glycerides or other esters of fat acids into alcohols of high molecular weights, reduction of CO to hydrocarbons or to alcohols and hydrogenolysis of petroleum. Some mention also is made of the types of catalysts, as well as the operating conditions employed in each instance. A short outline of various methods for the commercial production of H_2 and its purification is included.

3686. WICKE, E. [Theoretical and Practical Investigation of the Adsorption Velocity of Gases on Porous Substances.] Ztschr. Elektrochem., vol. 44, 1938, pp. 587–590; Chem. Abs., vol. 33, 1939, p. 1200.

For the velocity of adsorption and desorption of gases on porous solids, formulas are obtained, based on the following assumptions: Porous solids have a pile of spheres structure, the spaces between the solid fragments being the macropores; the micropores extend fjordlike into the solid particles and fill relatively rapidly, so that the velocity of sorption is determined solely by the transport of gases in the macropores. The effective diffusion coefficient for CO_2 calculated from the sorption velocity has the same order of magnitude as that calculated from the resistance to the flow of the gas through the solid absorbents.

3687. WIDEMANN, M. [Solubility of Hydrogen in Iron.] Anz. Maschinenwes., vol. 64, No. 11, suppl., 1942, pp. 17–19; Chem. Zentralb., 1942, II, p. 2194; Chem. Abs., vol. 38, 1944, p. 2603.

Absorption of H_2 by liquid Fe, by Fe products during heat treatment in H_2-containing atmospheres, and by Fe during pickling is explained. Dissolved and absorbed H_2 are partly lost during hot and cold working or by exposure of metal to the atmosphere. H_2 causes decarburization in Fe–C alloys and decreased watt loss in transformer steel sheets. X-ray examination shows H_2 is dissolved in the α– and γ-lattices, produces an increase in lattice constant, and acts especially on the intercrystalline material.

WIEDEKING, K. *See* abs. **1032, 1033.**

3688. WIELAND, H. [Combustion of Carbon Monoxide.] Ber. deut. chem. Gesell., vol. 45, 1912, pp. 679–685; Chem. Abs., vol. 6, 1912, p. 1409.

Combustion of CO in O_2 or air, in presence of Pd and H_2O, has been explained by assuming the formation of H_2O_2 and the simultaneous formation of CO_2 and H_2O_2 from CO, H_2O, and O_2. This oxidation is not dependent upon O_2 of air, but takes place thus: $CO+H_2O=CO_2+H_2$. The 1st product is HCOOH, which decomposes into CO_2 and H_2, the latter once more forming H_2O and O_2 of air. The presence of HCOOH may be shown by directing a CO flame upon ice, neutralizing the water formed with $Ba(OH)_2$, filtering, and testing with $AgNO_3$.

3689. ———. [Mechanism of Oxidation Process. III. Process of Combustion.] Ber. deut. chem. Gesell., vol. 45, 1912, pp. 2606–2615; Chem. Abs., vol. 7, 1913, p. 347.

Just as in the oxidation of CO to CO_2, HCOOH is an intermediate product, so, if the nonluminous Bunsen flame is allowed to burn on distilled H_2O, HCOOH can be detected. HCOOH also can be detected in the CH_4 flame; its formation probably is due to the decomposition of the CH_4 into C and H_2, and C with H_2O at once gives CO, the source of the HCOOH. (*See* abs. **2217.**)

WIEMER, H. *See* abs. **1966.**

WIENERT, F. *See* abs. **2909.**

3690. WIETZEL, G. [Preparation of Synthetic Fatty Acids for the Manufacture of Soap.] Klepzig's Textil–Ztschr., vol. 41, 1938, pp. 528–529; Chem. Abs., vol. 32, 1938, p. 9537.

Air is passed for 10–30 hr. through liquid paraffin at 90°–160° in the presence of suitable catalysts. The oxidized product is washed first with an aqueous solvent and later with a base. Any ingredients that cannot be saponified are removed either by extraction with a solvent or by distillation. The crude soap is treated with a diluted acid to liberate the fatty acid, which is then fractionally distilled. Soft soap, soap powder, household soap, and toilet soap can be obtained in this way.

3691. ———. [Synthesis of Fatty Acids by Oxidation of Hydrocarbons.] Angew. Chem., vol. 51, 1938, pp. 531–537; Brennstoff-Chem., vol. 20, 1939, p. 130; Chem. Age, vol. 39, 1938, pp. 278–280; Chem. Abs., vol. 33, 1939, p. 420.

General discussion with graphs and figures. The oxidation of synthetic paraffin from the Fischer-Tropsch process is carried out with air at temperatures of 80°–120°, under pressure and with catalysts. Overoxidation should be avoided by careful control of the temperature and the time of operation. The choice of catalysts is important also, since they may promote the oxidation at lower temperatures and prevent overoxidation. Oxidation takes place after the material has been suitably prepared, therefore, by saponification with caustic and separation of the unsaponified constituents either by selective solution or by distillation at 300°–400°. This treatment also clarifies and deodorizes the saponified portion of the fatty acids. The unsaponified portion is mixed with fresh paraffin and recycled. The crude soap does not yet meet the requirements for use but must be split by means of mineral acids into fatty acids and be subjected to vacuum distillation, whereby about 50–80% of the original raw material is preserved in a form pure enough for soapmaking. Some remarks are made also on the food fats made from synthetic fatty acids by esterifying with glycerin. The results thus far obtained have some appearance of success even though the work has not yet gone beyond the experimental stage.

3692. ———. [Preparation of Fatty Acids by the Oxidation of Paraffin.] Fette u. Seifen, vol. 46, 1939, pp. 21–25; Chem. Abs., vol. 33, 1939, p. 9024.

Fatty acid mixtures obtained by the commercial oxidation of paraffin contain, as a rule, all the products obtainable by breaking the C to C linkage between each adjacent pair of CH_2 groups and oxidizing them

to COOH groups. The composition of such fatty acid mixtures suggests that the CH_2 groups nearer the center of the paraffin chain are the ones most prone to oxidation. Usual analytical methods are suitable for determining the I, OH, ester, and carbonyl numbers of the fatty acid mixtures.

3693. WIGGINTON, R. Notes on Recent Developments in Fuel Technology. Fuel, vol. 7, 1928, pp. 1–3, 49–51; Chem. Abs., vol. 22, 1928, p. 2254.

Brief reviews of the following subjects: The Pittsburgh explosion, the Bergius method; calorific values of H_2 and C; chamber ovens for gas manufacture; synthetic gasoline; natural steam power; submerged combustion; the Benson boiler; pulverized fuel on ships; Smith tar extractor, water gas from vertical retorts.

WILEY, J. W. *See* abs. **2700.**

3694. WILFORD, A. T. Recent Fuel Developments. Bus and Coach, vol. 11, 1939, pp. 4–8, 34, 49–51.

Survey of British requirements with particular reference to production from domestic sources. The possibilities of obtaining fuels from the hydrogenation of coal and synthesis of gas are discussed.

WILHELM, R. H. *See* abs. **3749.**

3695. WILKE, G. [Production of Water Gas From Semicoke.] Tech. Mitt. Krupp, vol. 5, 1937, pp. 44–49; Chem. Abs., vol. 31, 1937, p. 8883.

Semicoke containing 8–10% of volatile matter yielded by the back-run process as gas containing H_2, 53 and CO, 36%, suitable for the Fischer–Tropsch synthesis.

3696. ———. [Production and Purification of Gas for the Synthesis of Benzine.] Chem. Fabrik, vol. 11, 1938, pp. 563–568; Chem. Abs., vol. 33, 1939, p. 1911.

For about 2 yr. 4 plants with a total yearly capacity of 300,000 tons of benzine have been operating the Fischer-Ruhrchemie process, and 5 more with a yearly capacity of 225,000 tons are under construction. Automobile and airplane lubricants of high quality have been made recently from the crude products of the process, and the paraffin fraction has been converted into fatty acids on a commercial scale for over a year. The ratio $CO:H_2$ must be held close to 1:2, and the gas be almost dust-free, contain not over 0.2 gm. H_2S or organic S per 100 $m.^3$, and contain no resin-forming substances. There is now no producer for the direct gasification of coking coal, but Krupp-Lurgi has recently developed a process for producing strong lump coke suitable for this synthesis. Producers for noncoking coals, brown coals, and others, by the Viag, Koppers, Pintsch-Hillebrand, Wintershall-Schmalfeldt, Bubiag-Didier, and Lurgi processes are described.

3697. WILKE, W. [Present Position of Synthetic Fuels and Their Importance to the World Oil Economy.] Schweiz. Bauztg., vol. 66, 1948, pp. 587–591; British Abs., 1949, B, I, p. 336.

Hydrogenation of coal (Bergius-Pier process) and direct synthesis (Fischer-Tropsch process) are discussed in detail and their merits compared. Elements of groups 5 and 6 make the best catalysts for the Bergius-Pier process. Economy in H_2 consumption is effected by using not only coal but also coal tar and petroleum residues. The specific gravity and octane number of the gasoline product are increased if the initial H_2 content of the hydrogenated tar is low. The Co–Th Fischer-Tropsch catalyst now has been substituted by cheaper Fe catalysts. The chief advantage of the process lies in the initial gasification of coal to CO, making possible the use of low-grade coals and coke. Care must be taken to remove S compounds. Recent improvements to the process in America are described. Natural gas is used as the raw material there instead of coal. This is oxidized by O_2 over Ni catalysts under controlled conditions to give CO and H_2. Flowsheets, diagrams, and graphs are shown, and special reference is made to the economy and heat economy of the various processes.

3698. WILKINS, E. T. Underground Gasification of Coal. Fuel Econ. Rev., vol. 23, 1944, pp. 14–18, 58; Gas World, vol. 121, 1944, pp. 545–550; Am. Gas Assoc. Monthly, March 1945, pp. 119–123.

Review of Russian prewar proposals. 3 methods of gasification are given: Stream method applicable only to steeply dipping seams and requiring some preliminary hand labor; percolation method intended for use with horizontal seams, eliminates all underground labor and depends on the development of shrinkage cracks and fissures in the coal when heated, so that part of the seam becomes readily permeable to gas; and borehole-producer method, a combination of the 2 preceding methods. A supply of O_2 for air enrichment is desirable for satisfactory gasification and would appear to add an appreciable, but not a prohibitive, amount to the cost of gasification. 3 different gases have been generated: Producer gas obtained by continuous blowing with air; water gas generated by alternate 20 min. blasts of air and steam; and H_2-rich gas. It is proposed to use the gas of lower calorific value as power gas for electricity generation and H_2-rich gas for chemical processes such as NH_3 synthesis and Fischer-Tropsch process. Available details are given of trials carried out on 5 different coal seams. No definite data have been obtained so far on the % of coal gasified. The cost of producing gas by this method is said to be about ⅓ of that with normal producers—1–2 d. per therm as against 4–6 d. Capital expenditure is about 60–70% of that of normal gas-producer plants, the principal costs being those of the blast- and power-supply installations.

———. *See* abs. **304.**

3699. WILKINS, E. T., AND JOLLEY, L. J. Catalytic Production of Methane. Coke and Gas, vol. 9, 1947, p. 245.

Paper presented at the 11th International Congress of Pure and Applied Chemistry, London, July 1947. The work of the British Fuel Research Station is reviewed. The process has reached such a perfected stage that no obstacle appears to stand in the way of building a full-scale plant whenever desired. The cost of synthetic CH_4 production is made up largely of the cost of making the necessary water gas. Catalysts of Ni, ThO_2, MgO, all supported on kieselguhr, have been used to promote the reaction. 4 primary difficulties have been met. (1) C deposition on the catalyst. Methods for prevention are: To add steam to the reaction gases; to increase the $H_2:CO$ ratio of the gases; to select a catalyst least susceptible to C deposition; and to study the correct design of the reaction vessel. (2) Sintering of the catalyst. This can be avoided by keeping the actual temperature of the catalyst below 600° C. The actual temperature is found to be about 150° below that of the temperature as measured. (3) Poisoning by S. This is the greatest single cause of catalyst deterioration and occurs when the Ni has absorbed 2–3% of S by weight. It can be avoided by using a gas of extreme purity, but it is preferred to use a cheaper method of using a gas of moderate purity (below 0.03 grain S per 100 cu. ft.) and secure a moderate catalyst life of 3 months. The above purity is secured by use of the well-known $Fe_2O_3 \cdot Na_2CO_3$ mixture at 200°. (4) Dissipation of the heat of reaction. This is secured by watercooling the shell of the reaction vessel to 200°. The catalyst is arranged to line the wall of the vertical tube, the outside of which is water cooled.

3700. WILLCOX, O. W. Cheap Oxygen Is Major Factor in United States Fischer-Tropsch Adaptation

World Petrol., vol. 18, 1947, 7th Ann. Refinery Issue, pp. 78–79, 104.

Value of cheap O_2 to the coal, steel, and oil industries is noted, and particular mention is made of the changes that have been effected by it in the Fischer-Tropsch synthesis technique. The development of the Linde, Fränkl-Linde, and M–7 (National Defense Research Committee and M. W. Kellogg Co.) processes for the manufacture of O_2 from air is outlined, and the advantages of the latter process are emphasized. A brief description of the Stanolind plant in Kansas is given, and the estimated costs of O_2 produced at this plant and at the Hydrocol plant in Texas are compared with recent estimates of costs at small O_2 plants.

WILLEKE, H. *See* abs. **3058.**

3701. WILLEMART, A. [Use of Carbon Monoxide in Organic Syntheses: Oxo Reaction.] Bull. soc. chim., 1947, pp. 152–157; Chem. Abs., vol. 41, 1947, p. 6527.

Review, especially of information obtained from the I. G. Farbenindustrie plant at Ludwigshafen-Oppau, concerning the reaction of an equimolecular mixture of CO and H_2 with olefins in the presence of a Co catalyst with primary formation of aldehydes. Primarily a review of patents.

3702. ———. [Use of Carbon Monoxide in Chemical Synthesis.] La Nature, No. 3156, April 1948, pp. 99–102.

Review of the Fischer-Tropsch process and its commercial development.

3703. WILLFROTH, —, AND GIESEN, —. [Improvement of Consistency and Durability of Catalyst Used in Methanol Synthesis.] Board of Trade, German Division, Technical Information and Documents Unit, F. D. 1030/47, Jan. 5, 1928, 9 pp.; Fuel Abs., 1948, No. 2388.

Experiments are described aiming at improving the consistency and durability of ZnO-base catalyst by adding Mg salts. Shows process for the manufacture of various types of improved catalysts, as well as their effects in the catalytic hydrogenation of CO and of other C compounds. Further research on ZnO–Mg–Cr catalysts is intimated.

3704. ———. [Use of Zinc and Chromium Minerals as Catalysts for Synthesis of Methanol.] Board of Trade, German Div., Tech. Information and Documents Unit, FD 1029/47, January 1928, 28 pp.; Fuel Abs., No. 2389, 1948.

Effect of various Zn- and Cr-containing catalysts is described in connection with operational data. ZnO was confirmed as the best basic substance for the catalytic hydrogenation of CO to O_2-containing C compounds.

3705. WILLIAMS, A. E. Food From Coal. Coke Smokeless-Fuel Age, vol. 3, 1941, pp. 187–189; Chem. Abs., vol. 35, 1941, p. 7682.

Coke is converted into water gas. The reaction gases are purified and separated and caused to react in presence of catalyst under pressure and at temperatures of 250°–420° to form hydrocarbons. The hydrocarbons are oxidized to form fatty acids. Glycerol is synthesized from acetylene and CH_4. Synthetic lard and butter are produced by combining the proper mixtures of fatty acids and glycerol.

3706. ———. Hydrogenation and War. Engineer, vol. 171, 1941, pp. 58–60; Chem. Abs., vol. 36, 1942, p. 5582.

Hydrogenation of fatty oils, the production and hydrogenation of water gas, synthesis of CH_3OH and faty acids, and hydrogenation of coal and tar are reviewed.

3707. ———. Synthetic Food Fats. Food Manuf., vol. 16, 1941, pp. 161–163; Chem. Abs., vol. 35, 1941, p. 7048.

Synthetic fats are produced from the hydrogenation of water gas (equal vols. CO and H_2) at 300° with metallic Pt and CrO_3 as catalysts, resulting in 10% CH_4 and 90% higher paraffin hydrocarbons. The latter are oxidized to solid fat acids at 140°–160° for 6–8 hr. in presence of oxides of Fe, Mn, or V. Esterification is carried out under vacuum at 200°–220° by use of glycerol with a sulfonic acid as catalyst. The synthetic product is not identical with the natural products, but is satisfactory as nutriment. Synthetic lard compares favorably in cost with the wartime price of true lard. Glycerol is hard to obtain in wartime, so in Germany it is synthesized by (1) Hydrogenation of water gas, chlorination resulting in trichloropropane, which, when treated with caustic alkali, produces glycerol or (2) fermentation of glucose with yeast and Na_2SO_3, then addition of lime and $CaCl_2$ and activated C, filtration, distillation of alcohol, leaving weak glycerol in the still, which is then concentrated and refined. Sometimes substitutes for glycerol are used, such as glycol or mannitol. Certain molds and yeasts synthesize fats.

3708. ———. Synthetic Hydrocarbons. Engineering, vol. 151, 1941, pp. 394–395; Chem. Abs., vol. 35, 1941, p. 6923.

Fischer-Tropsch process for synthesizing hydrocarbons from CO and H_2 in presence of a Co–Th–kieselguhr catalyst is described. The composition of the products depends on the H_2: CO ratio, the proportion of gases to catalyst, and the pressure. The yields of gaseous, liquid, and solid products at various pressures are tabulated. Waxes formed during the synthesis and impurities in the gases, especially S, reduce the activity of the catalyst. The synthesizing plant is described briefly, and the application of the products is discussed, with special reference to motor fuel and lubricating oil.

3709. ———. Synthetic Hydrocarbons From Water Gas. Paint Manuf., vol. 15, 1945, pp. 348–355; Chem. Abs., 40, 1946, p. 1005.

Hydrocarbon oils and alcohols produced synthetically from water-gas are of value to the paint and varnish industry in several ways. As alternatives to the volatile oils of paint, the higher flash point and lower price of the synthetic products give them an advantage. Synthetic oils are valuable as substitutes for glycerides in paints and sealing solutions for application to chemically active surfaces, for the synthetic product is inert to such surfaces.

3710. ———. Synthetic Lubricating Oils. Sci. Lubrication, vol. 2, 1950, pp. 2–5; Fuel Abs., vol. 8, No. 2, 1950, abs. 1082.

Processes used in production of synthetic oils from coal are noted, and the Fischer-Tropsch process is described in some detail. Olefins provide suitable raw material for lubricating oil manufacture. The catalysts and operations employed in the polymerization of olefins are noted, and the properties of the lubricants so obtained are enumerated. Details of the hydrogenation process, suggested as the most promising refinery treatment, are presented also.

3711. WILLIAMS, C. R. Gas Development and Trends in South Texas. Oil Gas. Jour., vol. 45, No. 36, 1947, pp. 68, 71; Petrol. Eng., vol. 18, No. 4, 1947, pp. 174, 176.

Abridged version of a paper presented before the Texas Section, American Institute of Mining and Metallurgical Engineers. Of the estimated natural-gas reserves of the United States of approximately 150 trillion cu. ft., South Texas alone has 25–30 trillion cu. ft. and the State of Texas about 58% of the total reserves. The potential supply is increasing annually through new discoveries, and it is probable that gas will continue to maintain a reserve ratio substantially in excess of consumption, which averaged approxi-

mately 2¾ trillion cu. ft. before the war and 4½ trillion cu. ft. at the close. Technical development and expansion of the Fischer-Tropsch process into actual commercial operation in Brownsville, Tex., indicate that natural gas may be worth $0.08–$0.12 per 1,000 cu. ft. for the manufacture of liquid fuels, although the ultimate realization of such a price will require accessibility to adequate gas reserves to afford a long-time operation and will depend largely on the duplication of small-scale results in larger commercial plants. Another factor influencing the value of natural gas is the proposed conversion of coal at the mines into synthetic natural gas having a heat value of approximately 1,000 B. t. u. per cu. ft. at a cost of $0.16–$0.20 per 1,000 cu. ft. Completion of such developments and the resulting competition in the transportation of gas from the Texas area will not justify a very high price at the wells, therefore, it would appear that the ultimate future price of natural gas will depend on its successful utilization by the Fischer-Tropsch synthesis of gasoline rather than by its export for industrial fuel.

3712. WILLIAMS, E. C., AND BEECK, O. Hydrogenation of Hydrocarbons. National Research Council Committee on Catalysis, 12th Rept., 1940, pp. 107–119.

A table of hydrogenation catalysts, including remarks on their preparation, properties, and uses, is of special interest. Nearly 50 compounds are listed suitable or used for destructive hydrogenation of coal, oils, and tars, MeOH synthesis, NH_3 synthesis, and hydrogenation of oils. Literature refs. appended.

3713. WILLIAMS, J. P. Manufacture of Motor Fuels and Synthetic Petroleum, Especially From Coal. Synthetic Liquid Fuels Hearings Before a Subcommittee of the Committee on Public Lands and Surveys, U. S. Senate, 78th Cong., 1st sess., on S. 1243, 1943, pp. 238–247.

Brief survey of motor-fuel sources: Byproduct coking, shale oil agricultural products, solid fuel engines, high-pressure hydrogenation, and Fischer-Tropsch synthesis. The cost of synthetic gasoline by the Fischer-Tropsch process is calculated from German data of 1938 and adapted to American prewar conditions. The estimated costs are as follows from 3 raw materials:

Cost estimates on Ruhrchemie process if operated in the United States in 1940

Raw material	Cost of synthesis gas per gal. of primary product	Cost of 1 gal. primary product	Cost of 1 gal. finished synthetic gasoline
Coke	$0.122	$0.186	$0.244
Subbituminous coal	.073	.136	.182
Natural gas	.066	.13	.174

The conversion cost of the primary product from synthesis gas is put at $0.0635 per gal. The estimates are for a plant making 2,424 bbl. of primary product per day. The total steel required is considered equivalent to 14 tons per bbl. of gasoline per day.

WILLIAMS, K. A. *See* abs. **87.**

WILLIAMS, N. H. *See* abs. **691.**

3714. WILLIAMS, P. N. Synthetic Fats. Chem. and Ind., No. 19, 1947, pp. 251–255.

Historical review of the process for producing synthetic fats by the oxidation of hydrocarbons to fatty acids; the method developed by the Deutsche Fettsäure Werke, Witten, Germany, for the manufacture of synthetic fatty acids from the Fischer-Tropsch wax (gatsch) is described in some detail. The total yield of crude fatty acids by this process is said to be 80% on the hydrocarbon oxidized. The margarine product obtained by the esterification of the fatty acids with glycerin is described and analyzed. The product was found to be palatable and suitable for human consumption, although its nutritional value is still considered doubtful. From information available it appears that not only was the cost of producing the acids considerably greater than the cost of natural fatty acids; namely, £65–£77 per ton at 10 RM to the £, but the synthetic fat was even more expensive, £177 per ton. It is further stated that if paraffin wax at £44 per ton could be obtained as raw material, the production of synthetic fatty acid in England would cost £91–£96 per ton and the synthetic fat £205 per ton.

3715. WILLIEN, L. J. Proposed Process for the Complete Gasification of Coal by the Use of Oxygen. Proc. Am. Gas Assoc., 1923, pp. 969–974; Chem. Abs., vol. 19, 1925, p. 1485.

Review of the possibilities of continuous blast gasification with 85–90% O_2. The process should be economically feasible if, as estimated, 90% O_2 can be produced for $0.45 per 1,000 cu. ft., with a plant investment of $1.00 per 1,000 cu. ft. per yr.

WILSON, D. W. *See* abs. **1723.**

WILSON, E. *See* abs. **1410.**

3716. WILSON, H. Production of Formalin From Digester Gas. Surveyor, vol. 105, 1946, pp. 27–28; Chem. Abs., vol. 40, 1946, p. 5861.

All S compounds are removed from the gas (70% CH_4 and 30% CO_2), H_2O vapor is added, and the mixture is passed over granular Ni catalyst at 950°. The CO and H_2 produced are converted to MeOH at 2,500 lb. pressure over a granular Zn chromite catalyst. The MeOH is dehydrogenated to give CH_2O, which is dissolved in H_2O.

WILSON, M. W. *See* abs. **3025.**

3717. WILSON, R. E. Technical and Economic Status of Liquid-Fuel Production From Nonpetroleum Sources. Nat. Petrol. News, vol. 36, 1944, pp. R 596–602; Chem. and Eng. News, vol. 22, 1944, pp. 1244–1250; Chem. Abs., vol. 38, 1944, pp. 5057, 6065.

Discussion of oil-from-coal law recently authorized by Congress.

3718. ———. Oil for America's Future. Petrol. Eng., vol. 17, No. 1, 1945, pp. 166, 171, 172, 174.

Digest of testimony presented October 3 before a special congressional committee investigating petroleum resources. Severe possibilities, which eliminate even a remote danger of a petroleum shortage, are discussed. One important possibility is the production of gasoline from natural gas by the Fischer or Synthol process at costs similar to the present costs of production from crude petroleum. By devoting only ⅓ of the present calculated reserves of natural gas to this process, about 500,000 bbl. per day over a period of 25 years could be produced; this amounts to about 30% of our prewar gasoline consumption. Another possibility is that of hydrogenation of our low-grade coals, the reserves of which are virtually inexhaustible. The cost of gasoline on a large-scale operation would be about $0.10–$0.15 per gal. above present gasoline costs. A 3d possibility is the application of the Fischer process to subbituminous and lignite coals. Recent research development enables this indirect method to produce good quality gasoline and diesel fuels at costs not more than $0.05–$0.06 per gal. above present costs. In addition to these methods, there are still the oil shales and oil sands of the United States and Canada to be considered. It is believed, however, that the accessibility and extent of our coal and lignite deposits will make them the most logical major source of petroleum, if and when crude petroleum becomes scarce. The industry regards the use of the above processes as a rather long-range alternative and is, therefore, not

likely to spend the large sums required for extensive research nor for building large-scale pilot plants or semicommercial units. The Bureau of Mines program of research and development seems, therefore, to be sound, though the opinion of the industry is somewhat divided on this point. It is urged that the building of semicommercial units should be postponed until much more research and pilot-plant work has been done and until commercialization of the process appears reasonably imminent.

3719. ———. Government Synthetic Fuel Program. Nat. Petrol. News, vol. 41, No. 23, 1949, p. 22.

It is felt that erection now of commercial-size synthetic liquid fuel plants would be premature. The wisest course at the present time would be to confine expenditures only to research and pilot-plant work to obtain the technical information essential as a sound basis for commercial-plant design and operation, if and when such plants are needed.

3720. WILSON, R. E., AND ROBERTS, J. K. Petroleum and Natural Gas—Uses and Possible Replacements. Nat. Petrol. News, vol. 39, No. 14, 1947, pp. 9–10.

Paper presented at a meeting of the American Institute of Mining and Metallurgical Engineers and the Western Petroleum Refiners' Association. The authors foresee a considerable expansion in the present main uses of liquid fuels. By 1970 the demand for crude oil or its equivalent will be 56% greater than in 1945. As a supplementary, or possibly as a replacement fuel, that produced by the Synthol or Hydrocol process appears to be the most promising. Gasoline made by this process will cost \$0.06–\$0.065 per gal. when made from natural gas, \$0.03–\$0.04 more when made from coal. Another process that may help extend crude supplies is the hydrogenation of cracked cycle stocks and residue. It appears more expensive than the Synthol process when using natural gas as the raw material, but it will become economically desirable as the price of crude rises. Alternatively, residue could be used as starting material for the Synthol process by converting it to CO and H_2. It is estimated that these processes will be in commercial operation as follows: Synthol using natural gas in 1948; Synthol using coal in 1970; and hydrogenation of heavy oil residue in 1965. Gasoline from coal hydrogenation and from oil shale will cost much more, but neither of these sources should be overlooked and investigation of them should be continued.

WILSON, S. P. *See* abs. **633.**

3721. WINDFELD-HANSEN, I. [Production of Motor Alcohol From Coal, More Particularly From the Standpoint of the Possibility of Creating a Synthetic Motor Alcohol Industry in Denmark.] Ingenioren, vol. 49, No. 6, 1940, A, pp. 17–25; Chim. et ind., vol. 43, p. 645; Chem. Abs., vol. 34, 1940, p. 5623.

3721a. WINFIELD, M. E. Adsorption and Hydrogenation of Gases on Transition Metals. Australian Jour. Sci. Research, vol. A 4, 1951, pp. 385–405; Chem. Abs., vol. 46, 1952, p. 1,939.

Behavior of gases chemisorbed at the surface of face-centered cubic crystals of transition metals is discussed by considering simple models of the surface and the possible arrangements of the gas molecules on them. Molecular, atomic and ionic adsorbates are considered. In using such bond energies and lattice parameters as are available, models are suggested for the structures of the adsorbates of O_2, H_2, C_2H_4, C_2H_2, and CO on Cu, Ni and Fischer–Tropsch catalysts. From the properties of these models, mechanisms are suggested for the hydrogenation of C_2H_4 on Ni and for the Fischer–Tropsch hydrocarbon synthesis.

WINKELMANN, —. *See* abs. **3581.**

WINKELMANN, H. *See* abs. **1606.**

3722. WINKLER, —. [Synthesis of Ethyl Alcohol—Preparation of Ethyl Alcohol From Carbon Monoxide and Hydrogen Under Pressure.] Ind. agr. aliment., vol. 66, 1949, pp. 159–160; British Abs., 1950, B, II, p. 2.

Mixture of CO and H_2 (3 : 1) is passed through a reaction tube at 300°–320° and 180–200 atm. in contact with a catalyst containing Fe_2O_3, K_2CO_3, and ZrO_2. Fractionation of the product yields an alcohol fraction equal to 25 gm. per $m.^3$ of gas and containing 60–70% of EtOH. The reaction tube of 120 mm. diameter produces 1,500 kg. of EtOH per month.

3723. WINKLER, H., AND JACQUE, L. [Synthetic Petroleum and the National Fuel.] La Nature, vol. 53, i, 1925, pp. 325–327, 346–347; Chem. Zentralb., 1925, II, p. 1002; Chem. Abs., vol. 19, 1925, p. 2734.

Review from the chemical standpoint of the liquid-fuel problem, including a discussion of cracking and hydrogenation of petroleum, carbonization of oils, and the possibilities of EtCH and MeOH as fuels.

3724. WINKLER, L. [Place of Gas in German Energy Supply.] Gas- u. Wasserfach, vol. 78, 1935, pp. 845–848, 876–880; Chem. Abs., vol. 30, 1936, p. 1208.

Discussion of competition of gas with electricity and with solid fuels. A gas of higher heating value than the present 430–450 B. t. u. gas is advocated, as offering a lower unit cost. Low temperature distillation is advocated to produce larger volumes of liquid fuel and a gas of higher heating value, which may be scrubbed to remove heavy hydrocarbons. Motor-fuel synthesis from manufactured gas by the Fischer process also is advocated, and attention is called to yield of gas of higher heating value from this process in addition to motor fuel.

WINSAUER, W. O. *See* abs. **1269.**

3724a. WINTER, E. [Catalytic Decomposition of Ammonia Over Iron.] Ztschr. physik. Chem., vol. 13, Abt. B, 1931, pp. 401–424; Chem. Abs., vol. 26, 1932, p. 364.

Catalytic decomposition of NH_3 in NH_3–H_2 or NH_3–H_2–N_2 mixtures was studied over Fe catalysts at 500°–700° by a flow system. On supported Fe catalysts the rate of decomposition was approximately proportional to the partial pressure of NH_3 and inversely proportional to the 3/2 power of the partial pressure of H_2. H_2 was without effect on the decomposition. One series of runs over a roll of Fe gauze indicated that the rate of decomposition was proportional to the first power of NH_3 partial pressure and inversely to the first power of H_2. The energy of activation over the temperature range studied is about 51,000–54,000 cal. The relation between catalytic activity and formation of Fe nitride is discussed. The results indicate that the reaction rate depends upon the concentration of atomic N on the surface of the catalyst.

3725. WINTER, H. [Catalysts and Materials of Hydrogenation.] Glückauf, vol. 73, 1937, pp. 420–424; Coal Carbonisation, vol. 3, 1937, p. 114.

Importance of catalytic research and investigations on hydrogenation reaction vessels in relation to the German 4-year plan is emphasized. The limitations of light metals (sp. gr. below 5) and their applications in binary catalysts are noted. For economic reasons, special interest attaches to the less expensive of the heavy metals. The degree of activity of catalysts is important in securing the desired product (for example, motor fuels and not CH_4). The stability, freedom from poisoning, and ready regeneration of catalysts are important factors. The present state of knowledge on these matters is reviewed with reference to original sources, and the various mechanical forms in which catalysts are used, ranging from sheets to colloidal sus-

pensions, are discussed. Methods of increasing the activity of catalysts and the various theories of catalytic action are considered. The special requirements of constructional materials for reaction chambers and the like are noted. Plain C steels are not satisfactory; instead, low-C special steels (Ni–Cr, W, and other alloys) are used. Many data relating to specified materials and reactions incorporated.

WINZER, K. *See* abs. **1035, 2624, 2625.**

3726. WIRGES, M. F., AND PALM, J. W. Production of Chemicals by Oxidation of Natural-Gas Hydrocarbons. Oil Gas Jour., vol. 48, No. 1, 1949, pp. 90, 92, 114; Petrol. Processing, vol. 4, No. 6, 1949, pp. 677–678.

Paper presented at the American Institute of Chemical Engineers meeting at Tulsa. Direct oxidation of natural-gas hydrocarbons is used for the commercial production of substantial quantities of formaldehyde, acetaldehyde, methanol, acetone, and other chemicals. The methods used in carrying out the various steps in the oxidation process are discussed by help of a flow sheet. The important variables in the process are temperature, pressure, makeup composition, recycle, catalyst, and reaction time. These variables are discussed and data concerning their effects on the reaction are presented. Use of a recycle system with commercial O_2 at elevated pressures instead of atmospheric induces increased yields (102% increase) of CH_2O. The preferred temperature range is 840°–880° F. Natural gas added as makeup in the recycle system gives optimum chemical yields within the range of 5–20% makeup. The reaction time is usually from 0.25–2 sec. Catalysts must be selected carefully.

3727. WIRTH, G. [Evaluation of Converters for Exothermic and Endothermic Catalytic Reactions Occurring Within Narrow Temperature Limits.] Tom Reel 134, sec. I–B, item 37, July 4, 1952; Bureau of Mines Inf. Circ. 7,587, 1950, 13 pp.

In exothermic and endothermic catalytic reactions, control of the temperature is of utmost importance. Basic calculations are developed for determining catalyst volumes of various types of reactors that give particular temperature distributions. With the help of the formulas evolved, the individual types of construction are compared with regard to cooling surface and space utilization. To select a converter of the proper size, it is necessary to consider still other factors that do not appear in the calculations; for example, height of the catalyst bed, linear gas velocity, ease of discharging, construction costs, and maintenance and operating costs. It is believed that the information contained in this paper may prove of value to workers in the field of catalytic reactor design.

3728. WIRTH, H. R., AND ETH, —. [Benzine and Oil.] Schweiz. Aero-Rev., vol. 17, 1942, pp. 139, 141, 226–228; Chem. Zentralb, 1942, II, p. 971; 1943, I, p. 116.

Brief review of the production of motor fuels from petroleum by cracking and polymerization, as well as by the benzine synthesis process of Fischer-Tropsch and high-pressure hydrogenation.

WITHERS, J. G. *See* abs. **259.**

3729. WITHERS, J. G., AND WEST, H. L. Interrogation of Dr. O. Roelen at Wimbledon. BIOS Final Rept. 511, 1946, 26 pp.; PB 28,883; TOM Reel 227.

Translation of 3 documents prepared by Dr. Roelen: (1) The Fischer-Tropsch Synthesis and Its Products; (2) Synthetic Lubricants Made by Ruhrchemie A.-G.; (3) Town Gas and Methanized Gas for Automotive Propulsion. (*See also* abs. **1334** and **1335.**)

3730. WITTKA, F. [Recent Advances in the Field of Paraffin Oxidation.] Seifensieder-Ztg., vol. 66, 1939, pp. 666–668, 699–700; Chem. Abs., vol. 33, 1939, p. 9603.

Review of patents.

3731. ———. Manufacture of Synthetic Fatty Acids by Oxidation of Paraffins Obtained From Water Gas by the Fischer-Tropsch Process. Soap Sanit. Chemicals, vol. 16, 1940, p. 28.

3732. ———. Moderne Fettchemische Technologie. Heft II. Gewinnung der höheren Fettsäuren durch Oxydation der Kohlenwasserstoffe, 1940, 167 pp. Lithoprint by Edwards Bros., Ann Arbor, Mich., 1945.

3733. ———. Synthetic Aliphatic Acids. Soap Sanit. Chemicals, vol. 16, 1940, No. 8, pp. 28–32, 73; No. 9, pp. 34–37, 73; Chem. Abs., vol. 34, 1940, pp. 7636–7637.

Raw materials used in the German process are synthetic paraffins prepared from water gas by the Fischer-Tropsch process, yielding up to 50%. The paraffins are distilled, and those having a b. p. above 350° are used. They are mixed with 0.1% of powdered $KMnO_4$ and heated to 150° for 10 min. By adding catalysts and blowing air through porous plates made of sintered metal, the temperature can be reduced to 100° and the time of oxidation shortened to about 20 hr. Various salts of Mn including $KMnO_4$, Mn stearate, and Mn soaps of unsaturated acids are used in quantities from 0.5–1%, depending on the quality of the soaps. The products of oxidation are gaseous, as well as volatile and nonvolatile liquids. The gases formed are CO_2 and rarely CO. The volatile liquid products are H_2O and low aliphatic acids of all kinds. Acetic acid is the main constituent of the soluble acids. The insoluble low-aliphatic acids make up 10–12% of the original weight of the paraffins and have an acid value of about 272 and a saponification number of about 370. The acids of low molecular weight have little value and are used in small amounts only industrially. The nonvolatile liquid products of the oxidation are used for making soaps after being separated from the large quantities of unsaponifiable substances with which they are mixed. If light-colored acids are desired, the oxidation is stopped when only 30–40% of the paraffins have been oxidized. Naphtha is used as the solvent in the continuous process for the removal of the unsaponified materials, and the soap solutions are first mixed with Et or isopropyl alcohol to prevent the formation of emulsions. Two solvent-extraction plants are described, both processes requiring 2 treatments for producing usable acids. Another process, the high-temperature and pressure method, consists in heating the soap solution at high temperature under pressure and dispersing the hot soap solution without a drop in temperature. The oxidized acids are dehydrated to form unsaturated acids, and the acid products are changed into neutral ones. The soap remains as a yellow liquid, which when cooled over rollers gives an odorless yellow powder. Approximately 0.1% of unsaponifiable remains in the soap. Aliphatic acids made from the Fischer-Gatsch paraffins have the following constants: Acid value, 261.8; I number, 7.0; oxidized acids, 0.2%; average molecular weight, 214. Separation of the acids in this mixture shows that virtually all from C_7 to C_{22} are present. For soap making all under C_{10} and over C_{20} are eliminated by fractional distillation. The fraction that can be used for soaps has the following properties: Solidification point, 26.2°–30°; acid value, 244.2–239; saponification number, 247.2; average molecular weight, 229.8=$C_{13}H_{27}COOH$; I number, 4.9; hydroxyl value, 3.7; unsaponifiable, 0.29%. Through esterification, the lower acids can be converted into a form that can be used in the perfume industry, but no use has been found for the higher acids, which are sent back to the oxidation tower.

3734. ———. [Modern Fatty Acid Synthesis.] Seifensieder-Ztg., vol. 40, 1943, pp. 50–51, 68–69; Chem. Zentralb., 1944, I, p. 717; Chem. Abs., vol. 39, 1945, p. 2211.

Production of fatty acids from CO, hydrocarbons, alcohols, aldehydes, ketones, nitro compounds, and

metal alkyls is discussed. The problem of fat acid synthesis by oxidation of paraffins has already been solved. The following 3 processes should be considered for commercial production: (a) Potash fusion of chlorinated hydrocarbons; (b) high-pressure hydrogenation of CO; and (c) saponification of aliphatic nitro compounds. The advantage of these is that the raw materials are of the gas-oil type and are byproducts, which are cheaper than paraffins.

3735. ———. [Production of Fatty Alcohols.] Allgem. Oel- u. Fett-Ztg., vol. 40, 1943, pp. 103–110; Chem. Zentralb., 1943, II, p. 74; Chem. Abs., vol. 38, 1944, p. 4461.

Patent literature on production of fatty alcohols by splitting sperm oil, by high-pressure hydrogenation of fat acids, and by oxidation of hydrocarbons is reviewed.

3736. WOLFF, B. [Synthetic Fatty Acids.] Przeglad Chem., vol. 3, 1939, pp. 45–51; Chem. Abs., vol. 33, 1939, p. 3759.

Concise description of the technical synthesis of fatty acids by oxidation of higher paraffins with air at higher temperatures, 140°–160°.

WOLFF, L. K. *See* abs. **3222, 3223.**

WOLLAN, E. O. *See* abs. **3182.**

WOOD, W. H. *See* abs. **432.**

3736a. WOOD, W. L. Production of Gaseous Hydrocarbons From Coals and Their Tars. Oil Shale Cannel Coal Conf., vol. 2, 1951, pp. 690–709; Chem. Abs., vol. 46, 1952, p. 11,630.

Cannel coals were studied as a possible source of olefinic gases to be used by the chemical industries in England. Low-temperature assays were conducted on samples from most of the major seams, and semicommercial tests were run on a high and a low oil-yield cannel. The light oils and tars were cracked at high temperatures and the carbonization and cracking gases analyzed. Some properties of the liquid products and the analyses and yields of gases are given. It is concluded that, even with simplified equipment charging high-grade cannel coals, the process could not produce olefins at a cost competitive with those available from petroleum cracking.

———. *See* abs. **2208, 2209, 3677.**

WOODDELL, J. S. *See* abs. **1049.**

3737. WOODRUFF, J. C. Synthetic Methanol and Ammonia From Butyl Fermentation Gases. Ind. Eng. Chem., vol. 19, 1927, pp. 1147–1150; Chem. Abs., vol. 21, 1927, p. 3702.

High-pressure NH_3 plant at Peoria has been adapted to the production of MeOH, for which purpose it is necessary to remove only a portion of the CO_2 content of the fermenter gas, the reaction employed being $CO_2+3H_2=CH_3OH+H_2O$. Investigations are in progress for the development of a suitable process for converting the CO_2 into CO in order to make use of the reaction $CO+2H_2=CH_3OH$ whereby the MeOH output for a given compressor capacity may be increased 33%.

WOODS, H. L. *See* abs. **1390.**

WOODWARD, L. A. *See* abs. **448, 449, 1409.**

3738. WORLD PETROLEUM. Humble Considers Erecting Gas-Conversion Plant on Gulf Coast. Vol. 17, No. 1, 1946, p. 63.

In addition to the Hydrocol plant now being built in Brownsville, Tex., 2 plants are being considered for construction in the Hugoton gas field extending from western Kansas to the Texas panhandle. Humble has not indicated the proposed location. In common with other operators of cycling plants in the Gulf coastal areas of Oklahoma and Texas, Humble is carefully conserving gas as a reserve of motor fuel raw material. At current prices, natural gas at the wellhead in Texas is bringing only about 10% of its B. t. u. value when compared with liquid fuel. In common with most other large companies in the oil industry, Standard Oil is devoting a considerable portion of its research and development work to gas- and coal-conversion processes. An extensive abstract of Murphree's recent talk before the American Gas Association (abs. **2344**) is included.

3739. ———. Centrifugal Compressors Completed for Carthage Hydrocol Plant. Vol. 20, 1949, pp. 58–59.

Two mammoth centrifugal compressors for the Hydrocol plant have been built by Clark Bros., Olean, N. Y. Each of the compressor units consists of 3 cases to be installed in tandem for drive through by a single steam turbine. Designed capacity is to compress 110,000 cu. ft. of air per minute to 100 p. s. i. g.

The 1st 2 cases operate in parallel, the 3d acting as a 2d stage. Power requirement is 23,000 b. hp. A total of 24 units with an installed hp. of over 80,000 will be used to compress 6 different gases involved in the Fischer-Tropsch synthesis. Some special nonferrous metals have been adopted in order to guard againt O_2 and to provide adequate intercooling between the various compressor cases. Internal parts of the O_2 compressors are made of bronze alloy and are water-cooled, a special bronze diaphragm being used to obtain a high rate of cooling. 2 photographs given.

WORTHINGTON, H. *See* abs. **607.**

3740. WRIGHT, C. C. Liquid Fuels From Coal. Canadian Min. Jour., vol. 64, 1943, pp. 792–794; Pennsylvania State Coll., Mineral Industries, vol. 13, 1943, No. 2, pp. 1, 3; Chem. Abs., vol. 38, 1944, p. 847.

Brief review of methods of obtaining liquid motor fuel from coal.

3741. ———. Liquid Fuels From Coal. Mineral Industries, vol. 13, No. 2, 1944, pp. 1, 3; Coke, vol. 6, 1944, pp. 59–60.

Review of the various methods of producing motor fuel from coal, indicating the present state of commercial operation of the Bergius process, the Fischer–Tropsch synthesis process, and extraction processes such as the Pott–Broche and Uhde. In current Fischer–Tropsch synthesis, the refined liquid products consist of 62% gasoline of low octane number and low lead susceptibility, 26% Diesel oil of very high cetane number, 10% gas, and 2% paraffin wax. The theoretical yield of liquid products is 13 lb. per 1,000 cu. ft. of gas treated; the actual yield is 7.5 lb. (1.2 gal.) but the modified Fischer–Pichler process yields 9.4 lb. In 1938 Germany was operating 14 Fischer–Tropsch plants with a capacity of 7,000,000 bbl. per yr.

3742. ———. Hydrogen or Synthesis Gas by the Oxygen Gasification of Solid Fuels. Mineral Industries, vol. 17, No. 3, December 1947, pp. 1, 3.

Basic processes for the conversion of coal to synthesis gas are: Gasification of lump or sized fuel in a fixed bed with steam and O_2 or air; gasification of fine coal in a fluidized bed using steam and O_2; and gasification of finely pulverized coal carried in a gas stream with steam alone or with steam and O_2. Economic consideration will be the deciding factor. The fixed-bed process developed by the Consolidated Mining & Smelting Co. of Canada has been investigated for the production of raw synthesis gas and of H_2 from both coke and anthracite. The process has probable interest for use in the United States. O_2, produced by the Claude process, is saturated with H_2O and then passes with steam through the fuel bed. The raw synthesis gas produced is scrubbed and passed through a converter where it reacts with steam in the presence of a catalyst to form H_2 and CO; the CO_2 being removed by scrubbing with H_2O at 225 lb. pressure. In terms of generator volume, the gasification rates for

coke exceed those of the conventional water gas process and compare favorably with most of the fluidized- and pulverized-coal processes. With small sizes of anthracite, gasification rates were only about 50% of those for large sizes. The efficiency of the fixed bed O_2 producer compares favorably with that of any other process yet developed as regards C, O_2, and steam consumption. The over-all economics depend largely upon the cost of O_2 and fuel suitable for the process.

———. *See* abs. **1163.**

3743. WRIGHT, C. C., AND NEWMAN, L. L. Oxygen Gasification of Anthracite in the Wellman-Galusha Producer. Chem. Eng., vol. 54, No. 6, 1947, pp. 114–115; Pennsylvania State Coll., Mineral Ind. Exper. Sta., Tech. Paper 122, 1947, 12 pp; Proc. Am. Gas Assoc., vol. 29, 1947, pp. 701–712.

Rice and Barley anthracites were gasified in the Wellman–Galusha producers used for the manufacture of synthesis gas from coke by O_2 gasification at Trail, B. C. Both sizes were satisfactorily gasified using O_2 and steam and at gasification rates considerably above 100% increase in capacity over that obtained with air and steam. The gas produced from the Rice anthracite was close to the compostion desired for synthesis gas; that from the Barley size was not so good. The coal consumption per 1,000 cu. ft. of raw gas was, respectively, 23.2 and 25.9 lb. The O_2 consumption per lb. of fuel gasified was appreciably lower for Rice coal and slightly lower for Barley coal than for large coke. Steam consumption per 1,000 cu. ft. of raw gas and per lb. of fuel gasified was higher for both Rice and Barley coal than for coke. Operating results are tabulated, a heat balance is shown, and a flowsheet is given.

3744. WRIGHT, C. C., BARCLAY, K. M., AND MITCHELL, R. F. Production of Hydrogen and Synthesis Gas by the Oxygen Gasification of Solid Fuels. Ind. Eng. Chem., vol. 40, 1938, pp. 592–600; Chem. Abs., vol. 42, 1948, p. 4329.

Information in this paper is additional to that reported recently by Mitchell and by Wright and Newman. The oxygen gasification of solid fuels in fixed-bed producer-gas equipment has been demonstrated as a practical commercial success. The construction and operation of the equipment is simple, its performance well known, and its cost relatively low. The results of plant-scale operations indicate that the overall C, O_2, and steam consumption for synthesis-gas production compare favorably with any fixed-bed, fluid-bed, or coal-suspension process thus far developed. Gasification efficiencies for synthesis-gas production are high. The gasification rates per unit of generator area are appreciably higher than those normally attained in air-blown producer operations and higher than those attained in the standard water-gas generator when using the same size fuel, but appreciably lower than the rates attained for the pulverized-fuel processes. The gasification rates per unit of generator volume are, however, comparable to those of the pulverized-fuel processes. The quality of the raw gas from O_2 gasification of anthracite was such that with a slight reduction in CO_2 content it could be used directly for the isosynthesis process. Raw gas from the coke at the highest steam : O_2 ratio approached this composition. For conversion to a gas of 2 : 1= H_2 : CO ratio, the shift reaction must be used. Removal of CO_2 from the gas by pressure scrubbing with water results in a substantial loss of CO and H_2. This loss may be reduced appreciably by 2-stage pressure letdown and by recycling part of the gas. Material and heat balances over the producer and over the converter system are shown for the production of H_2, and a calculated material balance is shown for the production of synthesis gas of 2 : 1=H_2 : CO ratio. These balances indicate some of the factors involved in the overall problem of synthesis-gas production from solid fuels. The economics of the O_2 gasification of solid fuels in fixed beds hinges largely upon the cost of the solid fuel suitable for the process and upon the cost of O_2, the relative efficiency, as compared with other processes, and the capital charges.

3745. WRIGHT, C. W. Germany's Capacity to Produce Petroleum. Survey of the Substitute Fuel Industry. Petrol. Times, vol. 37, 1937, pp. 46–50.

Statistical report on the German crude petroleum production and byproducts, the production of synthetic hydrocarbons from lignite in 1934 and 1935, and the total production, consumption, imports, and exports of oil products from all sources for 1913 and 1932–35.

3746. WRIGHT, M. M., AND TAYLOR, H. S. Interaction of Methane and Methane-d_4 on Nickel and the State of the Catalyst Surface. Canadian Jour. Research, vol. 27, 1949, B, pp. 303–317; Chem. Abs., vol. 43, 1949, p. 7802.

Mass spectrometer studies of the exchange reaction and the reaction of H_2 with catalyst surface residues support the concept of dissociative adsorption. Evidence of fragments, such as CX_3, CX_2, CX, C (X=H or D), was obtained. The first order disappearance of CD_4 has an activation energy of 20.9 kcal. at 100°–255°. Temperature increases the concentration of the more hydrogenated fragments (larger i for CD_4 and CH_4), and equilibrium between the fragments depends on the heats of adsorption of the fragments and H on the surface and, therefore, on the nature of the catalyst and on the strength of CH bonds formed. Experimental details, tables, and graphs.

3747. WRIGHT, S. R., DIMOCK, W. R., AND DAVIS, S. G. Evaluation of Catalysts Used in the Synthesis of Hydrocarbons. Canadian Chem. Process Ind., vol. 32, No. 1, 1948, pp. 53–54, 57; British Abs., 1948, B, I, p. 280.

Preliminary report on the methods used in evaluating Fischer-Tropsch catalysts at the University of Alberta. The evaluation is being done on a semipilot plant scale with synthesis gas prepared from natural gas and O_2 using a catalyst chamber of design similar to that used at the Bureau of Mines in Pittsburgh. Operating data are presented, activity tests of 3 Co catalysts tabulated, and optimum operating conditions indicated.

3748. WYCKOFF, R. W. G. R., AND CRITTENDEN, E. D. X-Ray Examination of Some Ammonia Catalysts. Jour. Am. Chem. Soc. vol. 47, 1925, pp. 2866–2876; Chem Abs. vol. 20, 1926, p. 526.

The effect of promoters in activated catalysts is studied by means of X-rays to show that certain additions produce their activating effects by favoring the formation of numerous active points and by stabilizing these specifically active metal particles. X-ray photographs, prepared in the usual way for powder photographs, were obtained (1) from various fused Fe oxides having compositions near to Fe_3O_4 and others richer in ferrous Fe than Fe_3O_4, (2) from artificial magnetites containing various amounts of Al_2O_3 and $K_2Al_2O_4$ as promoters, and (3) from the Fe catalysts obtained by reducing these fused oxides. One function of the promoters of Al_2O_3 and $K_2Al_2O_4$ in reduced Fe oxide catalysts for the synthesis of NH_3 is suggested. The length of the edge of the unit cube of magnetite was found to be $A_o=8.37\pm0.010$ Å. U. In magnetites containing an excess of FeO this substance occurs as a separate phase. This phase disappears when the equivalent amount of the promoter, Al_2O_3, is added. The composition of the oxide is thus adjusted toward Fe_3O_4 with the formation of $FeAl_2O_4$, which is apparently in solid solution in the magnetite. The value of

A_0 for magnetite containing $K_2Al_2O_4$ differs so little from A_0 for pure Fe_3O_4 that it is impossible to decide whether or not there is solid solution of one in the other. A_0 for the α-iron obtained by the reduction of Fe_3O_4 is 2.859 ± 0.004 Å. U. The size of the unit cell of Fe in the reduced material containing the promoters differs from that of pure Fe by less than 0.1%. The presence of the composite promoter, K and Al oxides, in the reduced catalysts has been found to maintain a large surface of Fe by preventing the rapid growth of the Fe crystals.

3749. WYNKOOP, R., AND WILHELM, R. H. Kinetics in Tubular Flow Reactor. Hydrogenation of Ethylene Over Copper–Magnesia Catalyst. Chem. Eng. Progress, vol. 46, No. 6, 1950, pp. 300–310. Chem. Abs., vol. 44, 1950, p. 6713.

Catalytic hydrogenation of ethylene over Cu–magnesia catalyst was studied experimentally and theoretically as an example of the application of chemical kinetics to a continuous-flow tubular reactor. Most experiments were isothermal; a few experiments were permitted to assume modest temperature variations. Experimental conditions were varied over the following ranges: H_2 concentration, 32.6–95.2%; temperature, 9°–79°; space velocity, 0.20×10^{-4}—32.0×10^{-4} total mol. per cc. sec.; catalyst particle size, 0.108–0.279 cm. diam. Kinetic equations for the flow system were developed and the experimental data were found to correspond to a first order reaction with respect to H_2. The precision of measurement of the rate constant is discussed. Because of small conversions, a high precision analysis for H_2 by means of thermal conductivity cells was developed. An effect of reversible poisoning of the catalyst by water vapor was encountered. Flow equations and precautions that must be used in their development are discussed. A mechanism for the hydrogenation reaction is proposed.

3750. WYSOCKI, J. [One-Step Conversion of Carbon Monoxide for Rendering Illuminating Gas Nonpoisonous.] Plyn, Voda zdravotni Technika, vol. 17, 1937, p. 184; Chem. Zentralb., 1937, II, p. 1487; Chem. Abs., vol. 33, 1939, p. 4763.

Furnace, constructed by Eskreis, is described; it is suitable for the conversion $CO+H_2O=CO_2+H_2$ as well as the 2-step conversion according to this reaction and the reaction $CO+3\ H_2=CH_4+H_2O$. It operates on the principle of the successive carrying off of the excess heat along the whole length of the furnace with the progress of the reaction so that the products of the reaction leave the furnace with a final temperature of 400°–350°.

Y

YANIMKIN, N. A. *See* abs. **3536.**

YAMADA, H. *See* abs. **1893.**

YAMADA, T. *See* abs. **1890, 1891, 1909.**

YAMAMOTO, K. *See* abs. **1801, 1802, 1803.**

3751. YAP, C. P. Influence of Dissolved Carbide on the Equilibria of the System: Iron–Carbon. Am. Inst. Min. and Met. Eng., Tech. Pub. 382, 1931, 19 pp.; Chem. Abs., vol. 25, 1931, p. 1148.

Previously published data on the Fe–C diagram are used to discuss the shape of the solidus. The straight solidus is obtained by cooling a sample from the melt, whereas the curved solidus is obtained by heating samples that have already reached room temperature. Fe_3C exists as a structurally stable phase that the austenite must redissolve. This leads to the conclusion that within a certain range of temperature the C in solution in austenite must be in the form of a carbide.

3752. ———. Thermodynamic Study of the Phasial Equilibria in the System: Iron–Carbon. Am. Inst. Min. and Met. Eng., Tech. Pub. 381, 1931, 26 pp.; Chem. Abs., vol. 25, 1931, p. 1148.

Previously published Fe–C diagrams are reviewed and the disagreements regarding the shapes of the liquidus and solidus are pointed out. The Fe–C diagrams were replotted and C was calculated as mol. % and as mol. % Fe–C. Thermodynamic laws of solutions that apply to a diagram of this type were calculated and values taken from the various Fe–C diagrams were substituted to determine which was the more nearly correct. The results indicated that in the liquid state C exists mainly as Fe_3C, but in the solid γ–Fe it is dissolved as C. The correct liquidus bounding the field Δ+melt is probably that of Ruer and Goerens (Chem. Abs., vol. 12, 1918, p. 2524), which is slightly convex. In the Δ-field, C is dissolved as such in the melt. Heat of transition of γ– to Δ–Fe is about 2.0 cal, per gm. and accordingly the heat of fusion of γ–Fe is about 64.4 cal. per gm.

3753. YAP, C. P., AND LIU, C. L. Free Energy, Entropy, and Heat of Formation of Fe_3C. Trans. Faraday Soc., vol. 28, 1932, pp. 788–797; Chem. Abs., vol. 27, 1933, p. 462.

Following values are calculated from existing equilibrium data on CH_4–H_2 and CO–CO_2 mixtures over austenite and Fe_3C: $3a$—$Fe+C=Fe_3C$: $\Delta F_{298}=9{,}300$ cal., ΔH_{298} 12,300 cal., $\Delta S_{298}=9.9$ cal., $S_{298}=3.8$ cal. per degree. From its free energy of formation, Fe_3C is stable above 750°. Austenite behaves as an ideal solution and follows Raoult's law.

YASHIRO, R. *See* abs. **1896.**

YASUDA, M. *See* abs. **1895, 1916, 1917, 2210.**

YATSKOVSKAYA, N. S. *See* abs. **281.**

3754. YENSEN, T. D. Evidence Obtained by X-Ray Analysis of Films of Iron in Magnetic Fields as to the Ultimate Nature of Magnetism. Phys. Rev., vol. 32, 1928, pp. 114–123; Chem. Abs., vol. 22, 1928, p. 3580.

Results of other workers showed that there is no change in crystal structure of single crystals of magnetite and hematite when placed in strong magnetic fields. In the present investigation, films of electrolytic Fe were analyzed by X-rays to determine whether there is any change in the random orientation of the minute crystals, of the order of 150 Å., found in these films when placed in strong magnetic fields up to 2,600 gausses. If so, the uniform circular diffraction patterns resulting from the randomly oriented crystals should, because of the preferred orientation, be changed to show greater or less density along a diameter parallel to the applied magnetic force than along the other perpendicular to it. The circles were analyzed microphotometrically and the results indicate no change in the orientation. The average of all the measurements is a ratio of the intensities along the 2 diagrams of 1.00 ± 0.08, the variation being attributed to incidental sources arising from the developing and handling of the film. Conclusion: The most minute crystal aggregates in Fe are not oriented in a magnetic field. This lends strength to the previous conclusion in regard to the ultimate nature of magnetism, namely, that the magneton is an atomic property.

YOHE, G. R. *See* abs. **930.**

YOKOMAKU, Y. *See* abs. **1918, 1919, 1920, 1921, 1922, 1923, 1924, 1925, 1926.**

3755. YOKOYAMA, T. [Gas-Producer Furnace With Oxygen Blast.] Jour. Fuel Soc. Japan, vol. 20, 1941, pp. 9–11; Chem. Zentralb., 1941, II, p. 294.

Discusses production of synthesis gas for NH_3 and motor-fuel catalysis, operating constants and gas prop-

erties, gasification process, and properties of coke used as raw material.

3756. YOSHIKAWA, K. [Oxidation of Methane to Carbon Monoxide and Hydrogen.] Bull. Chem. Soc. Japan, vol. 6, 1931, pp. 106–110; Sci. Papers Inst. Phys. Chem. Research, (Tokyo), vol. 25, 1934, pp. 295–301; Chem. Abs., vol. 25, 1931, p. 3956.

Experiments were made by a flow method at 800°–1,000° with and without catalysts on CH_4–air and CH_4–O_2 mixtures. Ni and Co were efficient catalysts and their activity was promoted by adding various oxides. The most efficient catalysts of those studied were Ni–ThO_2 and Ni–SiO_2. In the presence of these catalysts the reaction, $2\ CH_4+O_2=2\ CO+4\ H_2$, proceeds almost quantitatively at 850°–900°. Without catalysts most of the CH_4 remains unchanged at 1,000°.

YOSHIMORI, K. *See* abs. **2200, 2201, 2202, 2203, 2204, 2205.**

YOSHIOKA, Y. *See* abs. **1897, 1898, 1899.**

3757. YOSHISAKI, H. [Velocity of Decomposition of Cementite.] Sci. Repts. Tôhoku Imp. Univ., Ser. A, vol. 1, No. 1, 1949, pp. 63–70; Chem. Abs., vol. 44, 1950, p. 9887.

In the conversion of white cast Fe to gray, namely, decomposition of cementite to Fe and graphite, it is assumed that: (1) The reaction occurs selectively at the surfaces of a number of singular points, as reaction nuclei; (2) the number of reaction nuclei diminishes as the reaction continues; and (3) the velocity of movement of a reaction zone in a fixed direction in a homogeneous crystal grain of the reactant does not vary at constant temperature. On the basis of these assumptions, the following empirical equation was derived for the reaction velocity constant as a function of temperature, C, and Si contents: $K=5.8 \times 10^{20}\ C^{4.0}\ Si^{4.8-}\ T^{1/2}\ e^{-40000/T}$.

YOUNG, D. W. *See* abs. **3238.**

YUGUCHI, M. *See* abs. **1119, 1120.**

YUKIO, U. *See* abs. **2019.**

Z

ZABOLOTSKIĬ, T. V. *See* abs. **2913.**

3758. ZABOLOTSKIĬ, T. V., AND SNIGUROVSKA, Y. O. [Determination of the Surface of Iron Catalyst in Ammonia Synthesis.] Ber. Pissarjewsky Inst. physik. Chem., Akad. Wiss. Ukr. S. S. R., vol. 12, 1940, pp. 23–30 (in German, p. 31); Chem. Abs., vol. 35, 1941, p. 2685.

About 1 gm. of the Fe catalyst used in NH_3 synthesis was placed in a tube kept at 23° and containing a benzene solution of the dye. At definite time intervals, samples of solution were withdrawn and the dye concentration was determined with a photocolorimeter. The areas were calculated by the method of Emmett and Brunauer (abs. **822**). The areas also were determined by the method of Gaukhman and Roifer (abs. **1164**) with N_2 and A at temperatures close to their condensation points. Definite relationship was established between both methods.

ZAHNSTECHER, L. W. *See* abs. **1708.**

3758a. ZAĬDENMAN, I. A., AND KHOMYAKOV, K. G. [Initial Stages of the Interaction of Carbon Monoxide and Hydrogen With Nickel Catalyst at the Temperatures of Synthesis of Gasoline.] Doklady Akad. Nauk S. S. S. R., vol. 78, 1951, pp. 901–904; Chem. Abs., vol. 45, 1951, p. 8,336.

Heat evolved on contact between CO or a mixture $1CO:1H_2$ and a skeleton Ni catalyst, by leaching Ni–Al, reduced by H_2 2–4 hr. at 190°–200° was determined in an Al calorimeter with a Pt resistance thermometer, accuracy 0.0005°–0.001°, in experiments at 180°–185° in both flow and circulation systems. With the aid of simultaneous measurements of the change of pressure, the heat was referred to 1 mole gas disappeared. First contact of CO with a freshly prepared Ni catalyst evolved over 85 kcal. per mole gas disappeared. This is considerably higher than the heat effects, per 1 mole gas disappearing, of any of the 5 possible reactions (I) $2CO \rightarrow C+CO_2$, 42.9; (II) $2CO+3Ni \rightarrow Ni_3C+CO_2$, 31.7; (III) $2CO+2H_2 \rightarrow CH_4+CO_2$, 30.15; (IV) $CO+3H_2 \rightarrow CH_4+H_2O$, 16.9; (V) $3Ni+CO+H_2 \rightarrow Ni_3C+H_2O$, 11.1 kcal. The abnormally high initial heat effect of 85 kcal. can be attributed only to a change within the catalyst itself, specifically to partial recalescence. On consecutive admissions of CO, each time after reduction of the catalyst with H_2, the heat effect drops to and remains constant at about 34 kcal. per mole gas disappeared. This corresponds to the carbide-formation reaction (II); reaction (V) is excluded, as there is no H_2O formation with CO alone. The rate of reaction (II) passes through a maximum within the 1st few minutes. Its activation energy in the range 165°–195° is 15.8 kcal. per mole. The same heat effect, 34 kcal. per mole gas disappeared, is found in contact with a $1CO:1H_2$ mixture, on a catalyst previously exposed to CO. This again is evidence for the occurrence of reaction (II); reaction (III) is out of the question, as in this instance one does observe formation of H_2O; furthermore, subsequent admission of H_2 alone produces hydrocarbons, which is proof that Ni carbide has been formed. On more prolonged contact with the gas mixture, the heat effect decreases gradually, which indicates beginning occurrence of reaction (IV). However, in the initial stage, the preponderance reaction is (II).

ZAMRZLA, E. *See* abs. **3187.**

ZARAKOVSKAYA, A. I. *See* abs. **3763, 3764.**

3759. ZEITSCHRIFT DES VEREINS DEUTSCHER INGENIEURE. [Diesel Fuels From Coal.] Vol. 83, No. 47, 1939, pp. 1240–1241; Kohle u. Erz, vol. 36, 1939, p. 278; Coke Smokeless-Fuel Age, vol. 2, 1940, pp. 70–71.

H. Kölbel claims to have developed stable diesel fuels from coal-tar oil and Kogasin, utilizing the selective solvent action of the latter to remove constituents liable to cause coking. The process is said to be applicable also to low-temperature tar oils. The latter have inherently higher cetene nos. Synthetic hydrocarbons of the Kogasin type have a cetene no. of 120, and, when about 38% is mixed with tar oil of 20 cetene no., a diesel fuel of 60 cetene no. is obtained, which is equal in ignition qualities to commercial diesel oil of petroleum origin. A 45:55 Kogasin–coal-tar–oil mixture shows better properties than an unnamed petroleum fuel.

3760. ZELINSKIĬ, N. D. [New Syntheses of Hydrocarbons From Carbon Monoxide.] Doklady Akad. Nauk S. S. S. R., vol. 60, 1948, pp. 235–237; Chem. Abs., vol. 42, 1948, p. 6510.

Occurrence of free CH_2 radicals in the Fischer-Tropsch synthesis is considered demonstrated by the methylation of C_6H_6 introduced into the reaction mixture, to PhMe, and the proof that these radicals actually originate from $CO+H_2$. Comparative kinetic studies of the rates of formation of hydrocarbons from $CO+H_2$, of formation of carbide in the reaction between CO and the catalyst, and of the reduction of the carbides by H_2, have demonstrated that intermediate carbide formation plays a role only on Fe catalysts, not on Co and on Ni. The Fischer-Tropsch reaction proceeds by way of the intermediate radical CHOH and $CHOH+H_2 \rightarrow H_2O+CH_2$. Closely related to this mecha-

nism is the catalytic hydrocondensation of CO with olefins (C_2H_4, C_3H_6, C_4H_8, etc.) to saturated and unsaturated aliphatic hydrocarbons, and the catalytic hydropolymerization of olefins to saturated and unsaturated aliphatic hydrocarbons, occurring only in the presence of some (5–7%) CO. It is obvious that these reactions are determined by intermediate formation of CH_2 radicals. (*See* abs. **785, 792, 795,** and **3761.**)

———. *See* abs. **793, 794, 795, 796, 797, 798, 799, 800, 801, 802, 802b, 802c, 803, 1704, 1705, 2916, 3558.**

3761. ZELINSKIĬ, N. D., AND SHUĬKIN, N. I. [Peculiar Conversion of Cyclohexane in the Presence of a Nickel Catalyst.] Compt. rend. acad. sci. U. R. S. S., vol. 3, 1934, pp. 255–257 (in German, p. 258); Chem. Abs., vol. 28, 1934, p. 7252.

In the presence of a Ni catalyst precipitated on $Al(OH)_3$, cyclohexane (I) in H_2 atmosphere at 330°–350° undergoes a peculiar conversion with the formation of complex hydrocarbons. Along with a dehydrogenation of (I) to C_6H_6 a deep-seated cleavage takes place with the formation of free CH_2 radicals. These are, in part, reduced to CH_4 and in part combine with the C_6H_6 and the unaltered (I) to form toluene, xylene, methylcyclohexane, and dimethylcyclohexane.

ZELINSKIĬ, N. D., AND VERESHCHAGIN, L. F. [Chemical Reactions at Superhigh Pressures and High Temperatures. II. Reactions of Polymerization of Cyclohexene and Vinylcyclohexene.] *See* abs. **3559.**

ZELINSKIĬ, N. D., EĬDUS, Y. T., PUZITSKIĬ, K. V., AND BATUEV, M. I. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. V. Hydrocondensation of Carbon Monoxide and Propylene.] *See* abs **802a.**

ZELYAKOV, N. V. *See* abs. **3267.**

3762. ZERNER, E. [Catalytic Oxidation of Paraffin and Mineral Oil.] Chem.-Ztg., vol. 54, 1930, pp. 257–259, 279–281; Brennstoff-Chem., vol. 11, 1930, p. 291; Chem. Abs., vol. 24, 1930, p. 3635.

Experiments were made on the oxidation of paraffin and mineral oil in the presence of catalysts. Catalysts consisting of the stearates and oleates of Al, Ba, Cr, Pb, Fe, Mn, stearic, and oleic acids, as well as other organic substances such as fats, oils, turpentine oil, and sugar were used. A very efficient catalyst was Mn stearate; with this the reaction began at 110°–115°, whereas, without a catalyst, an induction period and heating to 160° were necessary. The reaction products obtained were a salve-like neutral portion (103%), an oily, acid distillate (2.5%), an aqueous distillate (5.5%), and a volatile material absorbable on activated C. CO_2 was only 2% of the raw material. The neutral portion can be bleached with H_2O_2 and can be saponified (saponification No. 175) and yields thereby: 40% unsaponifiable material, 20% H_2O soluble, and 40% H_2O insoluble acids. The recovered acids are dark and semisolid. The oily distillate consists of only ⅓ fatty acids; the rest is neutral substances. The aqueous distillate is 15–20% acetic acid contaminated with homologous substances. The volatile material yields up to 15% of a highly unsaturated oil. The oxidation of mineral oil in both an acid and alkaline medium was not satisfactory; the physical properties of the products were not nearly so good as with paraffin, and the odor was very unpleasant and persistent, making the products unsuitable for soap making.

ZETTLEMEYER, A. C. *See* abs. **1372.**

ZHABROVA, G. M. *See* abs. **814, 815.**

ZHEMOCHKIN, M. N. [Utilization of the Permanent Gases From the Dry Distillation of Wood for Organic Synthesis. III.] *See* abs. **3765.**

3763. ZHEMOCHKIN, M. N., LAPSHIN, S. I., AND ZARAKOVSKAYA, A. I. [Utilization of the Permanent Gases From the Dry Distillation of Wood for Organic Synthesis. I. Sulfur Compounds in the Products of Thermal Decomposition of Wood.] Lesokhim. Prom., No. 4, 1939, pp. 22–26; Khim. Referat. Zhur., No. 8, 1939, p. 117; Chem. Abs., vol. 34, 1940, p. 5272.

3764. ZHEMOCHKIN, M. N., LAPSHIN, S. I., TROITSKAYA, F. B., AND ZARAKOVSKAYA, A. I. [Utilization of the Permanent Gases From the Dry Distillation of Wood for Organic Synthesis. II. Composition and Yield of Permanent Gases Produced During Dry Distillation.] Lesokhim. Prom., No. 5, 1939, pp. 32–40; Khim. Referat. Zhur., No. 12, 1939, p. 103.; Chem. Abs., vol. 35, 1941, p. 878.

3765. ZHEMOCHKIN, M. N. [Utilization of the Permanent Gases From the Dry Distillation of Wood for Organic Synthesis. III.] Lesokhim. Prom., vol. 2, No. 9, 1939, pp. 12–14; Chem. Zentralb., 1940, I, p. 1106; Chem. Abs., vol. 35, 1941, p. 7152.

Permanent gases are now used for heating. This is uneconomical owing to the low heating value, 2,000–3,000 cal. per m.^{3}, and high CO_2 content, 50%. By passing the gases and steam over Ni catalysts at 800°, CH_4+CO_2 or H_2O giving CO and H_2, and 500°, $CO+H_2O=CO_2+H_2$, a gas is obtained, which, after cooling and removal of CO_2, can be used directly for MeOH synthesis.

3766. ZHEMOCHKIN, M. N., LAPSHIN, S. I., AND TROITSKAYA, F. B. [Utilization of the Permanent Gases From the Dry Distillation of Wood for Organic Synthesis. IV. Conversion of the Permanent Gases.] Lesokhim. Prom., vol. 2, No. 10, 1939, pp. 11–20; Chem. Zentralb., 1940, I, p. 1106; Chem. Abs., vol. 35, 1941, p. 7152.

Best conditions for the 1st conversion are: Ni catalyst, temperature of 800°, volume velocity of 200 and a H_2O content of 0.3 m.^{3} per m.^{3} The product contained CO_2, 27; CO, 35; H_2, 33; and N_2, 5%. For the 2d stage (formation of gas with a CO : H_2 ratio of ½), a volume velocity of 200, temperature of 500°, and a H_2O content of 0.6 m.^{3} per m.^{3} is used.

ZHEMOCHKIN, M. N., LAPSHIN, S. I., TROITSKAYA, F. B., AND ZARAKOVSKAYA, A. I. [Utilization of the Permanent Gases From the Dry Distillation of Wood for Organic Synthesis. II. Composition and Yield of Permanent Gases Produced During Dry Distillation.] *See* abs. **3764.**

ZIEGLER, —. *See* abs. **872.**

ZIESECKE, K. H. *See* abs. **2688, 2689, 2690, 2691, 2692, 2693.**

ZIMMERMANN, F. *See* abs. **3068.**

3767. ZIMMERSCHIED, W. J., DINERSTEIN, R. A., WEITKAMP, A. W., AND MARSCHNER, R. F. Complexes of Urea With Linear Aliphatic Compounds. Jour. Am. Chem. Soc., vol. 71, 1949, p. 2947; Chem. Abs., vol. 44, 1950, p. 1033.

Work confirms the observation of Bengen (German Patent Application O. Z. 12,438, Mar. 18, 1940) that $C_{16}H_{34}$ (0.1 mol.) in 9 vol. mixed decahydronaphthalenes, treated with 1.5 mol. $CO(NH_2)_2$ and 0.15 mol. MeOH and stirred 45 min. at 25°, gives a complex containing 11 mol. $CO(NH_2)_2$; the formation is accompanied by the evolution of 23 kcal. per mol. $C_{16}H_{34}$. Decomposition of the complex in 300 ml. H_2O gives 0.097 mol. $C_{16}H_{34}$. Halogen, S, and various O derivatives form entirely similar complexes if the linearity of the C skeleton is preserved. Compounds with a single Me branch form complexes when the linear chain approaches 20, the exact number depending upon the nature of the substituent and the position of the Me group.

3768. ———. Crystalline Adducts of Urea With Linear Aliphatic Compounds. A New Separation Process. Ind. Eng. Chem., vol. 42, 1950, pp. 1300–1306; Chem. Abs., vol. 44, 1950, p. 9356.

With *n*-alkanes and their linear derivatives, urea forms crystalline complexes; with most branched and cyclic hydrocarbons and their derivatives, it does not. The effects of time, concentration of urea, concentration of urea solvent, concentration of *n*-alkane, and volume of wash liquid were studied, and optimum conditions were applied in the separation of unbranched hydrocarbons from complex petroleum fractions. Compounds such as 2-bromoöctane, where substitution occurs at a point other than the end of a linear chain, often do not yield urea adducts. No simple molecular ratio of urea to C atoms was determined. An empirical value of 0.8 ± 0.1 for the ratio was found for chains 7–32 C atoms long. The heats of adduct formation were measured for straight chain paraffins, olefins, alcohols, bromides, mercaptans, and Me esters. From a comparison of this heat with the heats of crystal transition, fusion, vaporization, H bonding, adsorption, and gas hydrate formation, urea adduct formation resembles adsorption more closely than any other physical process. Petroleum fractions usually contain inhibitors to adduct formation. This was overcome by the use of an activator such as MeOH, or by seeding with freshly prepared adduct. Formation of the adduct at room temperature is reasonably rapid, and recovery of the components by heating or stirring with H_2O is virtually quantitative.

ZISSON, J. *See* abs. **3153a.**

ZOLOTOV, M. N. *See* abs. **1107.**

3769. ZOLOTOV, N. N., AND SHAPIRO, M. I. [Activity and Structure of Copper-Zinc Catalysts for the Decomposition of Methanol.] Jour. Gen. Chem. (U. S. S. R.), vol. 4, 1934, pp. 679–682; Chem. Abs., vol. 29, 1935, p. 2062.

ZnO–CuO catalyst used for the decomposition of MeOH undergoes reduction at not less than 220°, the CuO being reduced completely and the ZnO partly. In consequence, α-brass is formed, the Zn content of which increases with duration of contact.

3770. ZORN, H. [Carbon Monoxide-Hydrogen Synthesis at I. G. Farbenindustrie A.-G.] FIAT Final Rept. 1267, April 14, 1949, 173 pp; PB 97,368.

Part 1 of a 3-part report compiled by German technicians in the French occupation zone. It contains the following papers: (*A*) Researches on CO–H_2 Synthesis in the Badische Anilin und Soda Fabrik Laboratory in 1925–1945, Dr. F. Duftschmid; (1) Development of Fused Fe Catalysts According to Research by E. Linckh and R. Klemm; (2) Oil-Circulation Process, Dr. F. Duftschmid; (3) The High-Pressure Gas-Circulation Process for the Synthesis of EtOH From Waste Gases, E. Linckh and R. Klemm; (*B*) Hydrocarbon Synthesis From CO and H_2, Researches of the Ammonia Laboratory, 1935–1944, A. Scheuermann; (*C*) Hydrocarbon Synthesis From CO and H_2 With Fe Catalysts, Gas-Circulation Process, and Foam Process, W. Michael.

———. *See* abs. **3143.**

ZUEVA, V. P. *See* abs. **2754.**

3771. ZWERGAL, A. [Role of Hydrocarbons in the Production of Synthetic Fats by Oxidation in Germany.] Kolloid-Ztschr., vol. 112, 1949, pp. 168–182; Chem. Zentralb., 1950, I, p. 238.

Describes Fischer–Tropsch process and discusses Fe catalyst, its preparation and reduction, the synthesis gas, and the effect of certain variables, such as space velocity and heat of reaction upon the synthesis. Normal, medium, and high pressures and the Synol and Oxo processes are considered. The physiological effect of the isocompounds is explained. It is shown how the synthesis of fuels can be suppressed in favor of the synthesis of solid paraffins.

SUBJECT INDEX

A

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