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BIBLIOGRAPHY OF THE FISCHER-TROPSCH SYNTHESIS AND RELATED PROCESSES

II. PATENTS

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

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(In Two Parts)

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BUREAU OF MINES

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BIBLIOGRAPHY OF THE FISCHER-TROPSCH SYNTHESIS AND RELATED PROCESSES

(In Two Parts)

II. Patents[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 appears 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, formerly chief of the Fuels-Technology Division, Region VIII, and Dr. M. A. Elliott, former assistant chief, and Dr. R. B. Anderson, present assistant chief, of the Synthetic Fuels Research Branch, Fuels-Technology Division, Region VIII, Bureau of Mines, Bruceton, Pa. They wish to thank Helen C. Douglass and Myrtle R. Lee for their able assistance in preparing the manuscript and Edwin M. Murphy, Theodore E. Ross, Karl C. Stein, and John F. Shultz for aid in preparing the subject index.

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Foreword

Processes for the hydrogenation of carbon monoxide have had commercial importance since about 1920, when the commercial production of methanol and higher alcohols on oxide catalysts was begun. Basic discoveries on the hydrogenation of carbon monoxide to principally liquid hydrocarbons on cobalt, nickel, and iron were made by F. Fischer and H. Tropsch in 1925. Following extensive catalyst and engineering development, commercial production with cobalt catalysts was begun in Germany in 1935; and this process, together with coal hydrogenation, was a source of liquid fuels during World War II. Continued research and development in Germany have led to improved processes employing iron catalysts. Detailed studies of the synthesis have also been made in Great Britain and Japan.

Acceleration of the Bureau of Mines research program in 1944 led to a wealth of scientific and engineering data on the Fischer-Tropsch synthesis and carbon monoxide chemistry. Simultaneously, American industry began extensive development of the fluidized synthesis with iron catalysts, with special emphasis upon natural gas as a starting material.

There is still considerable interest in the Fischer-Tropsch synthesis as a source of fuels and chemicals, as indicated by the commercial synthesis plant at Brownsville, Tex., and the plant under construction in the Union of South Africa. The gasification of coal and gaseous hydrocarbons, methanation, and the production of chemicals by reactions involving carbon monoxide, such as the oxo process, are of great current interest. Although the staff of the Bureau of Mines has published a critical review of The Fischer-Tropsch and Related Syntheses (John Wiley & Sons, 1951), continued development of such synthetic liquid-fuel processes demanded an exhaustive bibliography of all relevant publications, patents, and captured documents. It is anticipated that this bibliography will serve the needs of all experimenters in carbon monoxide chemistry.

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PATENTS

A

ABRAMS, A. J. *See* abs. **826.**

1. ABRAMS, A. J., GORIN, M. H., AND BAKER, C. O. (Socony-Vacuum Oil Co., Inc.). Carbon Monoxide and Hydrogen From Methane. United States Patent 2,449,359, Sept. 14, 1948; appl. filed Jan. 25, 1945, Serial No. 574,612; 15 claims (*Cl. 48–196*). Chem. Abs., vol. 42, 1948, p. 9124.

CH_4 or natural gas is cracked to yield H_2 and C by passage up through a tower filled with refractory, such as CaO, heated by a countercurrent stream of melted Sn or Pb entering at around 2,150° F. (range 1,800°–2,400° F.). Part of the C deposited on the refractory is removed by reaction with CO_2 recovered in the process, and the rest of the C is removed by oxidation with air to form a producer gas, which is burned to supply part of the heat requirements for heating the molten metal. The combustion products from the metal-heating furnace are passed over CaO to absorb CO_2; this CO_2 is later desorbed by the hot metal from the reaction tower and the cooled but still fluid metal is then pumped to the heating furnace, where it is protected from oxidation during heating by a layer of Ca metaphosphate. The desorbed CO_2 is used as described above. The process is carried out in such a manner as to give a mixture of CO and H_2, 1 : 2.

ACKERMANN, P. *See* abs. **1904, 1905, 1906, 1907, 1908.**

ACKROYD, N. *See* abs. **3732.**

2. ADAMS, C. E., AND BURNEY, D. E. (Standard Oil Co. of Indiana). Oxo Process. United States Patent 2,464,916, Mar. 22, 1949; appl. filed Nov. 29, 1947, Serial No. 788,846; 10 claims (*Cl. 260–638*). Chem. Abs., vol. 43, 1949, p. 5032.

Single gas stream of CO and an excess of H_2 are supplied to the carbonylation reaction zone. The temperature is 200°–500° F., the pressure 50–300 atm., and the space velocity 0.05–10 vol. of liquid per vol. of catalyst per hr. The effluent gases containing unreacted H_2 are subsequently contacted with fresh olefin feed and metallic catalyst. Enough of the catalyst in the form of the metal carbonyl may be added to the olefin feed to make up for the quantity normally lost, and simultaneously, virtually all metal carbonyls and at least part of the CO in the H_2 stream are removed. The 2d zone has a temperature 125°–200° F. The H_2 stream, optionally after an additional purification step, may be used for the hydrogenation of the carbonylation product. 1 literature ref. and 5 United States patents cited.

3. ADAMS, C. E., AND DINERSTEIN, R. A. (Standard Oil Co. of Indiana). Urea Fractionation of Organic Compounds. United States Patent 2,588,602, Mar. 11, 1952. Chem. Abs., vol. 47, 1953, p. 1181.

Straight-chain organic compounds (hydrocarbons, alcohols, or aldehydes) of the highest molecular weight are separated from a mixture of straight-chain compounds of the same class by treating a solution of the mixture with urea (I) and a urea activator (H_2O, MeOH, EtOH, PrOH, or Me_2CO) to form a complex with the compound (II) of highest molecular weight and separating the complex from the reaction mixture. The molar ratio of (I) : (II) is around (n–2), where n is the number of C atoms in (II).

AGNEW, G. H. *See* abs. **2209.**

4. AHRENS, A. [Gas From Lignite.] French Patent 838,918, Mar. 20, 1939. Chem. Abs., vol. 33, 1939, p. 7082.

Gas for the manufacture of synthetic liquid fuel is made by passing lignite or like fuel in an exteriorly heated retort through a drying zone, a carbonizing zone, a degassing zone, a reduction zone, and then a zone for the production of water gas by steam introduced from below. The water gas produced in the last zone is introduced wholly or partly from above into the reduction zone of the retort.

5. ———. Synthesis Gas From Brown Coal. Australian Patent 105,659, Nov. 24, 1938; appl. filed June 7, 1938, in Germany June 7, 1937. Chem. Zentralb., 1939, I, p. 3997.

In a continuous retort for the production of water gas, between the water gas outlet and that for the synthesis gas ($CO : H_2 = 1 : 2$) an intermediate zone is provided through which a part of the water gas is passed to regulate the CO content.

6. AICHER, A. A. Catalytic Apparatus Suitable for Exothermic Reactions. United States Patent 2,240,481, May 6, 1941; appl. filed Nov. 17, 1938, Serial No. 240,992, in Great Britain Nov. 19, 1937; 1 claim (*Cl. 23–288*). Chem Abs., vol. 35, 1941, p. 5000.

Use is made of a plurality of reaction units. Each unit includes a catalyzer chamber containing a catalyst and having inlet and outlet openings for the passage of reaction gases therethrough; a casing enclosing the chamber and spaced therefrom to provide a liquid compartment containing a liquid in heat-exchange relationship with the catalyst; an outlet tube opening into a vapor space in the compartment above the liquid to remove vaporized liquid therefrom and an inlet tube connected to the compartment to return liquid thereto; a tubular element extending into the body of the liquid in heat-exchange relationship therewith, having its upper end opening into the vapor space and its lower end opening into a conduit for withdrawal of liquid condensed in the tube; and a conduit interconnecting the vapor space of each unit whereby vapor may flow from one space to the other upon temperature fluctuations in the several units.

——— *See* abs. **2456, 2457.**

7. AICHER, A. A., AND SYNTHETIC OILS, LTD. Catalytic Apparatus for Exothermic Reactions. British Patent 505,452, May 11, 1939. Chem. Abs., vol. 33, 1939, p. 9057.

The reaction chamber is formed of a number of tubes, which may be filled with catalytic material and are connected together at their ends by headers forming an inlet and outlet for the reaction materials. The tubes are surrounded by a common casing partly filled with a liquid that under the prevailing pressure conditions boils at the temperature at which the reaction chamber is to be maintained, the lower part of the casing being provided with an inlet for the liquid whereas the upper part contains vapor produced by

the boiling liquid and is provided with an outlet for the vapor, 1 or more additional tubes communicating at their upper ends with the vapor space and extending into, preferably through, the liquid space of the casing but not communicating therewith.

8. Air Reduction Co., Inc. Gas. British Patent 413,130, July 12, 1934. Chem. Abs., vol. 29, 1935, p. 582.

A gas consisting mainly of CO and H_2 is made by supplying a carbonaceous fuel, such as powdered coal, oil, together with O_2, to a heated reaction chamber to which superheated steam, with or without further fuel supply, is subsequently delivered. In an example, 12 lb. powdered coal per min. with 8.4 lb. O_2 are used for the initial reaction to produce CO, the O_2 being under about 5 lb. per in.^{2} pressure, and 6.5 lb. steam per min. is delivered to the reaction chamber to meet the CO, carrying fuel particles at 2,000°–3,000°. Describes apparatus.

9. ———. [Gas.] French Patent 759,246, Jan. 31, 1934. Chem. Abs., vol. 28, 1934, p. 4211.

Carbonaceous fuel and O_2 virtually free from N_2 are brought in a continuous manner into a heated reaction chamber, the amount of O_2 being limited so that only a part of the fuel reacts with it to form CO, and steam is introduced in limited amount to react with the rest of the fuel and produce CO and H_2.

Aktiokohle-Union-Verwaltungs-G. m. b. H. *See* abs. **210.**

10. Albert, W. (Mannesmannröhren-Werke). [High-Pressure Contact Furnaces for Benzine Synthesis.] German Patent 725,488, Aug. 6, 1942 (*Cl. 12 g–4.02*). Chem. Zentralb., 1943, I, p. 239; Chem. Abs., vol. 37, 1943, p. 6112.

Narrow, thin-walled tubes are arranged in bundles within the converter. They are held with solder until they can be welded in place.

11. Alberts, L. (Ruhrchemie A. G.). [Apparatus for Treating Hot Gases With Solid Purifying Materials or Catalysts Arranged in Superimposed Layers.] German Patent 677,111, June 20, 1939 (*Cl. 26 d–5*). Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 167; Chem. Abs., vol. 33, 1939, p. 6664.

12. ——— (Hydrocarbon Synthesis Corp.). Production of Hydrocarbons by Catalytic Hydrogenation of Carbon Monoxide. United States Patent 2,238,766, Apr. 15, 1941; appl. filed Apr. 13, 1938, Serial No. 201,807; in Germany Apr. 17, 1937; 3 claims (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 4777.

Describes arrangement of apparatus and a method of operation in which the temperature of the reaction zone is controlled by means of a boiling cooling medium, such as H_2O conducted in tubes across the reaction zone under a pressure corresponding to the temperature desired in the reaction zone.

13. Alberts, L., and Feisst, W. (Ruhrchemie A. G.). [Catalytic Hydrogenation of Carbon Monoxide Under Pressure.] German Patent 744,184, Nov. 18, 1943; appl. R 107,457 filed Apr. 30, 1940 (*Cl. 12 o–103*). FIAT Reel AA 88, frames 3,491–3,493. PB 70,273; FIAT Reel E 29, frames 876–877; PB 70,432; Chem. Zentralb., 1944, II, p. 93; Chem. Abs., vol. 39, 1945, p. 2861.

Pressure synthesis is conducted under such conditions that the CO : H_2 ratio in the converter remains constant. A synthesis gas is added, the CO : H_2 ratio of which agrees with that of the end gas. By this means a high yield of liquid hydrocarbons is obtained with a simultaneous reduction in the formation of CO_2 and CH_4.

Acock, E. H. *See* abs. **3748.**

14. Alexander, C., and Palmer, G. H. (M. W. Kellogg Co.). Manufacture of a Gaseous Mixture Rich in Hydrogen. United States Patent 2,618,542, Nov. 18, 1952; appl. filed Feb. 27, 1948, Serial No. 11,474; 7 claims (*Cl. 48–196*). Chem. Abs., vol. 47, 1953, p. 2964.

Hydrocarbon and steam and any available CO_2 are reacted at a temperature <1,300° F. in presence of a fluidized, highly active Ni catalyst with <50% supporting or diluting material such as alumina or silica. Co, Fe, or coal may be used in place of Ni. The mol ratio of steam : hydrocarbon charged is maintained at a low value whereby the conversion of hydrocarbon to CO_2 is minimized and the CO : CO_2 ratio in the product gas is relatively high. A portion of the hydrocarbon is converted to H_2 and C, and the C is deposited on the fluidized catalyst. The catalyst is separated from the product gas and sent to a 2d zone where it is contacted with O_2-containing gas at 1,200°–2,000° F. and in a C : O_2 ratio such that C is converted mainly to CO. The catalyst is then recycled to the 1st zone. 7 United States Patents cited.

15. Allgemeine Staubvergasungs-G. m. b. H. [Gas Mixtures Containing Hydrogen.] German Patent 616,466, July 29, 1935 (*24e–1.07*). Chem. Abs., vol. 29, 1935, p. 7622.

For the manufacture of mixtures of H_2 with oxides of C, with or without N_2, a mixture containing a gaseous hydrocarbon, steam, and fuel dust is preheated to 700°–1,000° and introduced continuously as a single stream into a reaction chamber, in which, at the point of entry, it is treated with air or O_2 or mixtures thereof. The initial mixture may contain coal gas or natural gas or may be generated in a water-gas generator fed with pulverulent fuel and operated with an excess of steam. Describes apparatus.

16. ———. [Gaseous Mixtures for Syntheses.] French Patent 731,052, Feb. 4, 1932. Chem. Abs., vol. 27, 1933, p. 354.

Gaseous mixture of water gas and N_2 or H_2 and CO is obtained by introducing and burning continuously in a reaction chamber a mixture of water gas, double gas, or lighting gas, and steam, as well as a powdered fuel with air and/or O_2. Describes apparatus.

Allied Chemical & Dye Corp. *See* abs. **163, 909, 2115.**

17. Allner, W. (Braunkohlen und Brikett-Industrie A. G.). [Water Gas and in Particular Synthesis Gas of Specific Composition From Solid Fuels.] German Patent 701,501, 1940 (*Cl. 26a–5*). Chem. Zentralb., 1941, I, p. 2759; Chem. Abs., vol. 35, 1941, p. 7689.

Coal distillation gases and tar vapors are instantaneously removed from the top of the reaction chamber whereby a considerable amount of heat is saved that would otherwise be consumed in cracking the removed gases. These gases, freed from their products difficult to crack, are reheated in a recuperator and then reintroduced into the cracking chamber. The gases having a high H_2 content have the effect of increasing the proportion of H_2 in the end gas.

18. Almquist, J. A. (E. I. duPont de Nemours & Co.). Apparatus for Effecting Exothermic Catalytic Gas Reactions Such as Ammonia Synthesis. United States Patent 1,855,040, Apr. 19, 1932. Chem. Abs., vol. 26, 1932, p. 3150.

A purifier catalyst chamber and a producer catalyst chamber are surrounded by separate pressure-resisting walls, the pressure-resisting wall around the producer catalyst chamber being spaced from the chamber to form an annular passage to which compressed gases are delivered and from which they are passed to the purifier catalyst chamber and then returned to the producer catalyst chamber.

See also British Patent 344,576 (abs. **19**).

19. ——— (DuPont Ammonia Corp.). Catalytic Exorthermic Gas Reactions. British Patent 344,576, Dec. 31, 1928. Chem. Abs., vol. 25, 1931, p. 4667.

In effecting reactions such as production of organic compounds such as MeOH from CO and steam or H_2, the gases are first warmed by passage in heat-exchange relation to, but out of direct contact with, the main catalyst and are then passed to the purifier catalyst in a vessel surrounded by separate pressure-sustaining walls, and, after removal of the products of the purification, the gases are passed to the main catalysts. For MeOH synthesis, the catalyst may be a mixture of Zn and Cr oxides with use of a mixture of Zn and Cu oxides to remove organic S compounds.

ALUMINUM CO. OF AMERICA. *See* abs. **1116.**

AMERICAN LURGI CORP. *See* abs. **507, 1007, 1012, 1021, 1022, 1023.**

20. AMMONIA CASALE S. A. [Catalysts.] French Patent 797,934, May 6, 1936. Chem. Abs., vol. 30, 1936, p. 7294.

One hundred parts, by weight, of catalytic substances or the corresponding amount of their constituents is intimately mixed with 10–50 parts, by weight, of a mixture of CuO and Cu_2O, and the mixture is heated to a temperature at which a commencement of fusion of the oxides takes place. The catalytic substance may be a mixture of MnO, ZnO, and Cr_2O_3.

21. ANDERSON, R. B., AND SHULTZ, J. F. Iron Nitride Catalysts in Carbon Oxide Hydrogenations. United States Patent 2,629,728, Feb. 24, 1953; appl. filed Aug. 22, 1949, Serial No. 111,755; 15 claims (*Cl. 260–449.6*).

The most practical method for formation of nitrided Fe catalysts has ben found to be treatment of reduced Fe catalyst in a relatively rapid stream of NH_3 gas at elevated temperature. The reaction is expressed as:

$$8\ Fe + NH_3 \rightleftharpoons 2\ Fe_4N + 3\ H_2,$$
$$6\ Fe_4N + 2\ NH_3 \rightleftharpoons 3\ Fe_3 + 3\ H_2.$$

The formation of the nitride depends upon the ratio of the concentration of $NH_3 : H_2$ at the surface of the Fe, or the formation of the nitride depends on the ratio of the square of the partial pressure of NH_3 to the cube of the partial pressure of H_2:

$$p\ NH_3^2 : p\ H_2^3.$$

For any given temperature, there is a ratio of concentration of $NH_3 : H_2$ below which it is thermodynamically impossible for either or both reactions to proceed at all. The concentration of NH_3 necessary to form a nitride decreases with increase in temperature. The practical temperature range is 200°–550° C. Increasing the flow of NH_3 over the catalyst being nitrided will improve the rate and completeness of nitriding by increasing the NH_3 concentration. Above 550° C. the rate of nitriding is not improved by increasing the velocity of flow, because above this temperature the rate of decomposition of NH_3 is very rapid. At temperatures below 200° C., although the rate of decomposition of NH_3 in the presence of Fe is virtually negligible, the rate of formation of the nitride is extremely slow. Substantially 100% NH_3 should be used. Nitriding an Fe catalyst markedly increases its activity, particularly in the case of the fused Fe catalyst. It gives the catalyst longer life and increases resistance to deposition of free C within the catalyst granules. The catalyst expands during nitriding and does not change in volume during use in the synthesis. It resists oxidation during use. Nitriding of the catalyst tends to shift the distribution of products toward those of lower molecular weight and to increase the fraction of oxygenated compounds. The higher the degree of nitriding, the greater the shift in distribution of products. 3 literature refs. and 3 United States patents cited.

ANDREWS, H. J., JR. *See* abs. **2762.**

ANDREW, T. *See* abs. **3938.**

22. ANDRY-BOURGEOIS, C. H. (Société anonyme le pétrole synthétique). Reactions of Hydrogen With Carbon Compounds Induced Electrically. British Patent 223,543, Dec. 10, 1924; appl. filed Oct. 10, 1923. Chem. Zentralb., 1926, I, p. 2837; Chem. Abs., vol. 19, 1925, p. 1101.

Mixtures of gaseous hydrocarbon compounds or CO with an excess of H_2 are passed consecutively through a series of electric arcs. There are formed CH_4, C_2H_4, C_3H_6, C_4H_{10}. If a mixture of benzol, CO, and H_2 are used, homologous aromatic hydrocarbons are formed. *See also* French Patent 574,173 (abs. **24**).

23. ——— (Société anonyme le pétrole synthétique). Synthesis of Hydrocarbons. Austrailian Patent 19,-926, May 21, 1925; appl. filed Oct. 6, 1924. Chem. Zentralb., 1926, II, p. 292.

See also French Patent 574,173 (abs. **24**), and British Patent 223,543, (abs. **22**).

24. ——— (Société anonyme le pétrole synthétique). [Synthesis of Hydrocarbons.] French Patent 574,-173, July 7, 1924; appl. filed Oct. 19, 1923. Chem. Zentralb., 1926, I, p. 2837.

See British Patent 223,543 (abs. **22**).

25. ANGLO-IRANIAN OIL CO., LTD. [Aldehydes and Alcohols From Carbon Monoxide, Hydrogen, and Olefins.] French Patent 969,735, Dec. 26, 1950; appl. filed July 28, 1948. Chem. Zentralb., 1951, I, p. 2220.

The synthesis is performed in presence of a Co catalyst at 100°–150° and at least 50 atm. pressure. Suitable olefins are ethylene, propylene, and butylene or mixtures of these. Aldehydes are first formed by the conversion and are then reduced to alcohols.

26. ———. Improvements Relating to the Preparation of Catalysts. British Patent 640,965, Aug. 2, 1950. Chem. Abs., vol. 45, 1951, p. 288.

Describes preparation of catalysts for use in hydrogenation reactions and more particularly for preparation of catalysts of the Co molybdate type. A Co molybdate catalyst is prepared by mixing an aqueous solution of a Co salt with an aqueous solution of a salt of molybdic acid in the presence of NH_3, thereby precipitating Co molybdate and adding more NH_3 to redissolve the precipitate. The resulting solution is mixed with a support selected from the class consisting of anhydrous porous γ-Al_2O_3 and mixtures of boehmite, so that the solution is absorbed wholly or in part by the porous Al_2O_3, evaporating to dryness, and heating the impregnated support above 1,000° F. to convert the complex into the desired catalytic form. The invention attempts to create a catalyst of high activity without using specially prepared Al_2O_3, so that any commercially available porous Al_2O_3 may be used in the preparation of the catalyst.

———. *See* abs. **188.**

APPLIED CHEMICALS, INC. *See* abs. **2038.**

ARMACOST, W. H. *See* abs. **2625.**

27. ARMIT, J. W., AND IMPERIAL CHEMICAL INDUSTRIES, LTD. Purifying Alcohols Such as Methanol. British Patent 346,658, Dec. 13, 1929. Chem. Abs., vol. 26, 1932, p. 1939.

Impure MeOH and other alcohols b. $< 100°$ are treated with a halogen such as Cl or Br in a quantity $<$ that required to satisfy the unsaturated value of the alcohol, and the material is distilled, treated with alkali to remove halogen acid, and then fractionated.

28. ARMIT, J. W., WAINWRIGHT, G. E., AND IMPERIAL CHEMICAL INDUSTRIES, LTD. Purification of Alcohols. British Patent 350,502, Dec. 1929. Chem. Abs., vol. 26, 1932, p. 5309.

Alcohols, such as those produced by catalytic hydrogenation of CO, are purified by preliminary distillation with caustic alkali (which may be mixed with brine) followed by the addition of small quantities of a primary amine (such as aniline or its homologs) having a boiling point above the distillation temperature of the alcoholic mixture. Sulfanilic acid and H_3PO_4 or H_2SO_4 may be added to the material also, and it may be refractionated.

ARNOLD, G. B. *See* abs. **264, 1043, 1044, 1045, 1046, 1047.**

29. ARNOLD, G. B., AND HESS, H. V. (The Texas Co.). Method for the Separation of a Heterogeneous Mixture of Compounds. United States Patent 2,539,393, Jan. 30, 1951; appl. filed Jan. 18, 1947, Serial No. 722,844; 2 claims (*Cl. 260–450*).

Integrated process is given for treating a heterogeneous mixture so as to isolate organic acids in 1 fraction, aldehydes in another, ketones in another, and all alcohols in another, leaving a H_2O phase and hydrocarbon phase, both substantially free from O-containing organic compounds. Isolation of individual constituents of each class is effected by close fractionation. 2 literature refs. and 1 foreign and 7 United States patents cited.

30. ——— (The Texas Co.). Method of Synthesizing Gasoline Hydrocarbons. United States Patent 2,568,841, Sept. 25, 1951; appl. filed Feb. 1, 1947, Serial No. 725,836; 11 claims (*Cl. 260–450*).

The product of synthesis gas conversion at about 500°–700° F., comprising mainly hydrocarbons, H_2O and, O_2-containing organic compounds consisting of alcohols, aldehydes, ketones, esters, and acids, is separated at elevated temperature 175°–300° F. and pressure 150–300 p. s. i. into a gas phase, a liquid hydrocarbon phase, and aqueous phase. The last 2 phases are treated to remove the O-containing organic compounds distilling<245° F., and these are recycled to the reaction zone where they are converted into liquid hydrocarbons in the gasoline range.

31. ——— (The Texas Co.). Process for Manufacturing Hydrocarbons and Alcohols. United States Patent 2,542,454, Feb. 20, 1951; appl. filed Aug. 31, 1946, Serial No. 694,320; 3 claims (*Cl. 260–450*).

Product mixture from the Fischer-Tropsch synthesis is separated into gas, hydrocarbon, and H_2O phases at 175°–350° F. and a pressure sufficient to maintain liquid-phase conditions. The O-containing organic compounds are removed from the hydrocarbon phase leaving a hydrocarbon fraction relatively free of O-containing organic compounds. The H_2O phase is subjected to a countercurrent contact with a portion of the oxygenate-free hydrocarbon fraction at 175°–350° F., 150–300 p. s. i. A hydrocarbon extract phase containing nonacidic oxygenates is formed and an aqueous raffinate of reduced nonacidic oxygenate content. The raffinate is discharged, and the hydrocarbon phases are combined. 1 literature ref. and 6 United States patents cited.

32. ARNOLD, G. B., HESS, H. V., AND STEWART, M. M. (The Texas Co.). Method for Treating Products of Synthesis Gas Conversion. United States Patent 2,516,940, Aug. 1, 1950; appl. filed Dec. 20, 1946, Serial No. 717,346; 3 claims (*Cl. 260–450*). Chem. Abs., vol. 44, 1950, p. 10302.

CO and H_2 in ratio 1:2 are converted at 200°–750° F. and 2,000 p. s. i. to a complex product mixture. The mixture is separated at 175°–300° F. and reaction pressure to aqueous phase, hydrocarbon phase, and gas phase. The aqueous phase is solvent extracted with a hydrocarbon fraction, and residual nonacidic oxygenated compounds are extracted. The elevated temperature and pressure makes this separation more efficient. The hydrocarbon-rich extract phase contains nonacidic, O-containing organic compounds and the H_2O-rich phase, organic acids. The hydrocarbon-rich phase is combined with the hydrocarbon phase originally separated and catalytically hydrogenated with a part of the initial gas to convert the aldehydes and ketones to alcohols. The alcohols are separated. 7 United States Patents cited.

33. ARNOLD, J. C. (Standard Oil Development Co.). Catalytic Apparatus. British Patent 589,342, Mar. 16, 1944. Chem. Abs., vol. 42, 1948, p. 356.

Aryl amines of benzene series are obtained by introducing a mixture of aryl nitro hydrocarbons, which may include polynitro compounds, H_2, and large quantities of liquid diluent into a reaction zone at a number of points in the presence of a hydrogenation catalyst at elevated temperature. The products are separated from the diluent, and the diluent is recycled as cooling medium. The diluent is present as 20–90% vol. of the total liquid feed mixture. Liquid products from hydrogenation of diisobutylene or by alkylation of olefins with isoparaffins or by hydrogenation of CO are mentioned as diluents.

34. ——— (Standard Oil Development Co.). Contacting Finely Divided Solids With Gases. British Patent 636,401, 1950. Fuel Abs., vol. 8, No. 1, 1950, abs. 380.

Process for synthesis of hydrocarbons from CO and H_2 in which finely divided solids are maintained in a fluidized state in a treating zone by an upflowing suspending gas and in which the buoyancy of the solids progressively changes within the treating zone, wherein there is maintained, in all or part of the zone, solid nonfluidized packing relatively larger than the finely divided solids and defining a plurality of passageways for the passage therethrough of the gas and suspended solids, finely divided solids, which have undergone a change of buoyancy within the treating zone being withdrawn therefrom, treated to restore at least partly their original buoyancy, and returned to the heating zone.

35. ——— (Standard Oil Development Co.). Improvements in the Production of Industrial Mixtures of Carbon Monoxide and Hydrogen. British Patent 635,909, Apr. 19, 1950; appl. filed Mar. 31, 1947; 19 claims. Chem. Abs., vol. 44, 1950, p. 7515.

Gaseous products from reaction of CH_4 and Fe oxide with enough hydrocarbons to react with the CO_2 and H_2O are passed over a reforming catalyst, such as Fe or Ni, at elevated temperature and pressure. The metal oxide is kept in a fluidized state. A pressure head for the parts of the process to be conducted under pressure is achieved by locating the vessel for the oxidation of the metal at a considerably higher level than the other vessels and connecting the former with the latter by a standpipe in which the metal oxide is kept in a fluidized state. The exothermic heat in the oxidation stage is carried directly into the reduction and reforming stages by a heat carrier. The carrier may be the metal used in the process in its free state. The period of contact for hydrocarbon and metal oxide is relatively long before the mixture enters the reforming stage. This lowers the C formation. The metal oxide may be on a light carrier such as MgO or Al_2O_3.

36. ARNOLD, J. H. (Hydrocarbon Research, Inc.). Hydrocarbon Synthesis. United States Patent 2,623,057, Dec. 23, 1952. Chem. Abs., vol. 47, 1953, p. 2462.

Hydrocarbons and oxygenated hydrocarbons are prepared from H_2 and CO in a molar ratio in the approximate range of 0.8:1 to 2.2:1, in the presence of an Fe-containing catalyst at superatmospheric pressure and 288°–399° with the formation of the liquid and gaseous organic compounds and byproduct CO_2 and

H_2O; the catalyst has a predetermined characteristic selectivity for the production of liquid organic compounds expressed as the ratio of the new production of hydrocarbons containing 3 or more C atoms plus all the oxygenated hydrocarbons to the total net production of hydrocarbons and oxygenated hydrocarbons. Production of the liquid organic compounds is brought to a maximum by maintaining the production of CO_2 at a predetermined rate, which, expressed as the percentage of CO consumed in the reaction, does not deviate from 91–33 R—0.2 S by more than about 9%, where R is the aforesaid molar ratio of H_2: CO in the synthesis gas and S is the selectivity of the catalyst. The extent of production of CO_2 is controlled somewhat by each of the factors catalyst selection, adjustment of recycle ratio, catalysts bed temperature, and the extent of conversion of CO feed.

37. ARNOLD, J. H., AND GROSSELFINGER, F. B. Synthesis of Liquid Hydrocarbons. United States Patent 2,628,970, Feb. 17, 1953; appl. filed July 7, 1950, Serial No. 172,478; 4 claims (*Cl. 260–449.6*).

Long catalyst life and high yield of liquid products is achieved by maintaining a high H_2 concentration during the course of the synthesis. Inlet concentration of H_2 is restricted to 40–50 vol. % and outlet concentration to 25–30 vol. %. The reaction gases must be withdrwan from the synthesis zone before the H_2 content has fallen $<$ 20 vol. % and when the CO content of the reaction stream is preferably 2–3 vol. %. Tail gas, substantially free of C_3 and higher hydrocarbons, is withdrawn and recycled to the gas-generation and to the synthesis zones. 1–15% by volume of the recycled tail gas is returned to the gas-generation zone and the remainder to the synthesis zone. 4 United States patents cited.

38. ARNOLD, M. H. M., PRYDE, D. R., MORLEY, R. J., AND IMPERIAL CHEMICAL INDUSTRIES, LTD. Producer Gas. British Patent 578,711, July 9, 1946. Chem. Abs., vol. 41, 1947, p. 1830.

Finely powdered noncaking coal, or caking coal blended with inert material, of a particle size of about 0.035–0.039 mm. is carbonized in a fluid or suspended state maintained by recirculation of the carbonization gases from top to bottom of the carbonizing chamber. The heat required for carbonization is secured by introducing a part of the residue from the gasification state at about 1,100° into the top of the carbonizing chamber, where it is mixed with the powdered coal. The carbonized residue is also kept in a fluid or suspended state during the gasification stage in a separate chamber by an air-steam mixture, which may or may not be preheated. In an example, the producer gas analyzed CO, 22; H_2, 24; and N_2, 44%, with small quantities of CO_2 and CH_4.

39. ARSEM, W. C. (Commercial Solvents Corp.). Formaldehyde. United States Patent 1,740,141, Dec. 17, 1929. Chem. Abs., vol. 24, 1930, p. 866.

In producing CH_2O and formic acid, a mixture of CO and H_2O vapor is passed over a catalyst comprising the oxide of a metal forming a weak base such as ZnO at a temperature of 150°–350° and a pressure of 10–500 atm. under conditions such that H_2O vapor is not appreciably condensed to liquid form. Oxides of Sn, Al, Zr, V, Mo, Th, and Cr also may be used.

40. ——— (Commercial Solvents Corp.). Formic Acid. United States Patent 1,740,140, Dec. 17, 1929; appl. filed Sept. 12, 1925, Serial No. 56,056. Chem. Abs., vol. 24, 1930, p. 863.

Cuprous halide catalyst, such as Cu_2Cl_2 is used for treating a gas mixture obtained by the partial conversion of a mixture of CO_2 and H_2 to CO and H_2O. Temperatures of 50°–150° and pressures of 20 atm. or higher may be used.

41. ARVESON, M. H. (Standard Oil Co. of Indiana). Catalytic Conversion Process. United States Patent 2,398,489, Apr. 16, 1946; appl. filed Nov. 24, 1941, Serial No. 420,204; 3 claims (Cl. 196–52). Chem. Abs., vol. 40, 1946, p. 4207.

Invention is concerned with catalytic conversion processes in which a powdered catalyst acts while suspended in gases or vapors. The catalyst is separated from the reaction products and regenerated while suspended in a regeneration gas. It is separated from the regeneration gas and returned to the converter as a slurry with fresh and recycle feed. The catalyst may be powdered solid as Mo, Cr, or V oxides on "activated alumina" base. In an example the following conditions are given:

Catalyst to naphtha-feed weight ratio	0.24
Molecules H_2 per molecule feed	3.0
Average reactor pressure p. s. i.	200
Temperature	960° F.
Weight space velocity	0.7 $hr.^{-1}$
Catalyst residence time	360 min.

Dehydrogenation and cyclization of paraffins and dehydrogenation of naphthenes are predominant reactions. East Texas heavy naphtha will be converted to a product of approximately 80 ASTM octane number with a yield of 80 vol. %. The product will contain 5–15% toluene, depending on the exact distillation of the feed. Both light and heavy naphtha prepared by hydrocarbon synthesis in the Fischer or Fischer-Tropsch process may also be converted to high octane number under these conditions.

42. ——— (Standard Oil Co. of Indiana). Conversion of Methane. United States Patent 2,360,463, Oct. 17, 1944; appl. filed Apr. 24, 1941, Serial No. 390,185: 7 claims (*Cl. 260–673.5*). Chem. Abs., vol. 39, 1945, p. 3900.

This process aims at the conversion of CH_4 into heavier hydrocarbons. CH_4 is decomposed into CO and H_2, and the gases are subjected to the Fischer process. The CH_4 may be derived from any source, but primarily the process is designed for CH_4 from distillate wells. CH_4-containing gases are freed of H_2S and are transferred to a reformer furnace into which steam is admitted. The mixture is heated to about 1,500° F. and then passed through catalyst tubes where CH_4 and steam react to produce approximately 1 CO and 3 H_2 mols. Since the optimum CO : H_2 ratio for synthesizing gas is 0.5 or slightly higher, additional S-free CO_2 is introduced into the reformer furnace. This purified CO_2 is derived from flue gas. From the reformer furnace the synthesis gas passes into a Fischer-reactor, where it is brought into contact with a catalyst at 400° F. and 2 p. s. i. A suitable catalyst is Co, ThO_2, and MgO deposited on kieselguhr. The Fischer synthesis products are then fractionated and further treated. The CH_4 treatment is an integral part of treating distillate-well hydrocarbons, of which a flowsheet is given.

43. ——— (Standard Oil Co. of Indiana). Multistage Hydrocarbon Conversion System. United States Patent 2,416,730, Mar. 4, 1947; appl. filed Feb. 27, 1942, Serial No. 432,548; 7 claims (*Cl. 196–52*). Chem. Abs., vol. 41, 1947, p. 4304.

Hydrocarbon stock, such as produced by coal hydrogenation or Fischer-Tropsch synthesis, may be converted into gasoline of low acid heat and low olefin content by a 2-stage operation. The catalyst from the primary zone with a temperature 750°–950° F. is passed to a regeneration zone and from there to a cooling zone. The cooled catalyst is used for increasing paraffinicity and quality of products from the primary stage in a secondary zone 500°–700° F. Heat from the regenerated catalyst is transferred to the catalyst leaving the secondary zone and the catalyst is returned

to the primary reaction zone. 8 United States Patents cited.

44. ASBOTH, K. [Pure Ethylene.] Austrian Patent 171,701, June 25, 1952. Chem. Abs., vol. 47, 1953, p. 2194.

C_2H_4 is obtained by catalytic hydrogenation of CO at 180°–265° under 0.05–1.0 atm. The CO : H_2 ratio is<1 : 1, preferably 1 : 1.5. Incompletely-reduced Fe catalysts, d. 1.1–1.3, containing 50–90% inert fillers are used.

45. ASBURY, W. C. (Standard Catalytic Co.). Motor Fuel From Carbon Monoxide and Hydrogen. United States Patent 2,264,427, Dec. 2, 1941; appl. filed May 20, 1938, Serial No. 208,989; 5 claims (*cl. 196–50*). Chem. Abs., vol. 36, 1942, p. 1759.

CO and H_2 are caused to react together at a temperature 475°–650° F. under a pressure of about 10–50 atm. in the presence of a catalyst containing Fe. A portion of the resulting product is treated at a temperature 700°–950° F. in the presence of an active siliceous catalyst to effect deoxidation and conversion into an improved motor fuel. Describes arrangement of apparatus.

ASINGER, F. *See* abs. **1036, 1041, 1042, 3354.**

46. ATKINSON, R. G. (Phillips Petroleum Co.). Coal Gasification Process and Apparatus. United States Patent 2,572,829, Oct. 30, 1951; appl. filed Dec. 28, 1948, Serial No. 67,735; 12 claims (*cl. 48–63*).

Mixture of powdered coal, O_2, and steam is gasified by being passed from end to end through the center of a reaction chamber maintained at a temperature> 750°. To protect the chamber walls from the intense heat radiations in the reaction zone, a gaseous suspension of powdered coal and steam is tangentially injected at high velocity over the whole inner surface of the sidewall thus preheating the coal-steam mixture, which is withdrawn, mixed with O_2, and recharged into the reaction chamber for conversion into gaseous products.

ATMOSPHERIC NITROGEN CORP. *See* abs. **474, 1113, 2710.**

47. ATWELL, H. V. (The Texas Co.). Catalytic Conversion. United States Patent 2,553,398, May 15, 1951; appl. filed Feb. 7, 1946, Serial No. 646,037; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 6824.

Hydrocarbons and oxygenated organic compounds are synthesized from a mixture of CO and H_2 in a modification of the Fischer-Tropsch process. These gaseous reactants containing suspended catalyst in powdered form or in the form of dust pass through a mass of fluidized, relatively coarse material confined within the reaction zone, the coarse material being relatively inert with respect to the reaction involved. Although the coarse particles are fluidized, there is substantially no entrainment in the gases leaving the reactor. The process provides greater turbulence in the reactor, and it also assures a uniformly high rate of heat transfer from the mass of fluid and solids to the adjacent cooling surfaces. Accordingly, a given weight of catalyst converts a much larger volume of synthesis gas/unit time than has been heretofore realized. The catalyst particles are preferably particles within the range of about 5–50μ, and the coarse particles are within the range of about 150–450μ. The catalyst powder may comprise about 0.1–1%, by weight, of solid particles in the system. A preferred catalyst is an Fe powder containing about 1–2% K_2O and 2–3% Al_2O_3.

48. ——— (The Texas Co.). Catalytic Conversion of Gaseous Reactants to Normally Liquid Carbonaceous Compounds. United States Patent 2,409,235, Oct. 15, 1946; appl. filed Dec. 18, 1943, Serial No. 514,768; 14 claims (*Cl. 260–676*). Chem. Abs., vol. 41, 1947, p. 1230.

Two steps of the conversion process are carried out in separate reaction zones. In the 1st step, CO is brought into contact with a solid Co, Fe, or Ni catalyst at 350°–425° F. and a carbide results: $2CO+2CO \rightarrow Co_2C+CO_2$. Then the catalyst is passed to a 2d zone where it is treated with H_2 at 200°–400° F. to decompose the carbide. The circulation of catalyst is continuous. CO_2 from the 1st stage is discharged and may be reduced to CO by contact with C or may be reacted with CH_4 to produce CO and H_2 to be reused in the process. The CH_4 used includes that obtained by separation from the hydrocarbon products. Instead of CH_4, a CH_4 fraction may be used. The gaseous hydrocarbons used for this purpose may be CH_4, C_2H_6, C_3H_8, C_4H_{10}, or a mixture. The use of such hydrocarbons is thought to involve adsorption of the hydrocarbons on the surface of the catalyst to form CH_2 groups. These groups are hydrogenated in the 2d stage. This adsorption of hydrocarbons on the surface of the catalyst may be carried out under relatively high pressure, 1,000–5,000 p. s. i., whereas the subsequent hydrogenation step may be carried out at relatively low pressure. A feature of the process is synthesis of hydrocarbons without the formation of H_2O.

49. ——— (The Texas Co.). Catalytic Synthesis of Hydrocarbons. United States Patent 2,583,134, Jan. 22, 1952; appl. filed June 22, 1948, Serial No. 34,533, 12 claims (*Cl. 260–449.6*).

Described process relates specifically to the conversion of hydrocarbon raw materials into desired liquid products by converting the raw material into synthesis gas by contact with reducible metal oxide, followed by subsequent catalytic conversion of the synthesis gas into the predetermined product hydrocarbons. Example: Finely divided MoO_3 is suspended in a stream of CH_4 at 1,500° F. and 200 p. s. i. g. After substantial time of contact the mixture is cooled to 650° F. and comprises essentially Mo in a lessor state of reduction suspended in a stream comprised essentially of H_2 and CO. The suspension is passed through a dense fluid phase of Fe synthesis catalyst of 100-mesh particle size at a velocity of about 1 ft. per sec. for 20 sec. at 650° F. and 250 p. s. i. The effluent gaseous products containing suspended particles of O_2 carrier are withdrawn from the upper surface of the dense fluid phase and the entrained solid particles separated and recycled into admixture with more feed gases. The product gas stream from the synthesis reaction zone under condensation yields a product oil layer boiling in the gasoline range and corresponding to about 70% of the CH_4 feed consumed on a weight basis.

50. ——— (The Texas Co.). Control of Catalytic Conversions. United States Patent 2,438,029, Mar. 16, 1948; appl. filed May 3, 1944, Serial No. 533,900; 3 claims (*Cl. 23–1*). Chem. Abs., vol. 42, 1948, p. 4334.

Reactions promoted by finely divided catalyst, specifically the hydrogenation of CO on Co, are controlled by recycling and heating or cooling the liquids in the reactor. Catalyst is retained in the reactor by settling out in an enlarged section at the top of the reactor. For example, a stream comprising 1 mol. CO : 2 mol. H_2 preheated to 365°–380° F. is brought into contact with catalyst suspended in a hydrocarbon fraction b. 450°–600° F. For the production of hydrocarbons, recycling is adjusted to maintain the reactor between 380° and 420° F.; for oxygenated products, a higher temperature is desirable.

51. ——— (Process Management Co.). Gasoline From Gaseous Hydrocarbons. United States Patent 2,178,824, Nov. 7, 1939; appl. filed Jan. 6, 1937, Serial No. 119,178; 7 claims (*Cl. 196–9*). Chem. Abs., vol. 34, 1940, p. 1474.

Describes arrangement of apparatus and a method of producing motor fuel of high antiknock value, which involves causing CO and H_2 to react over a catalyst such as Co and ThO_2 on kieselguhr at a temperature and pressure such that liquid hydrocarbons in the gasoline boiling range are formed, separating normally gaseous hydrocarbon constituents of the reaction products containing more than 1 C atom and heating them to effect substantial cracking, mixing with the resultant cracked product normally liquid constituents from the 1st-mentioned reaction mixture, and heating the resulting mixture to effect conjoint conversion of normally liquid and polymerization of normally gaseous hydrocarbons in it.

52. ——— (The Texas Co.). Method for Synthesizing Hydrocarbons and the Like. United States Patent 2,433,255, Dec. 23, 1947; appl. filed Sept. 26, 1946, Serial No. 699,439; 9 claims (*Cl. 260–449.6*). Chem. Abs., vol. 42, 1948, p. 1724.

Catalyst particles are distributed in a number of beds. A layer of noncatalytic packing material is superimposed on each catalyst bed. The temperature is controlled by direct contact of the catalyst in each stage with a cooling liquid. A substantial portion of the cooling liquid is vaporizable under the conversion conditions. Part of the nonvaporized cooling liquid is continuously withdrawn from the lower section of each stage. A fraction of this coolant is introduced into a separate unit for recovery of dissolved conversion products therefrom. Another portion is cooled and returned to the stage from which it was withdrawn at a point above the layer of noncatalytic packing material. The effluent from each catalyst bed is subjected to countercurrent contact with recycled cooled liquid in the layer of noncatalytic material. High-boiling components of the products and vaporized constituents of the cooling liquid in the effluent are condensed and flow back to the catalyst bed. In the example for conversion of CO and H_2 to liquid hydrocarbons, a gasoline-gas oil fraction derived from the products of conversion is used as liquid coolant. 5 United States patents cited.

53. ——— (The Texas Co.). Method of Carrying Out Exothermic Reactions. United States Patent 2,473,129, June 14, 1949; appl. filed Feb. 16, 1945, Serial No. 578,307; 13 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 1676.

In exothermic reactions such as Fischer-Tropsch synthesis using a fluidized Co or Fe catalyst, the temperature is controlled with a carrier powder suspended in the reactant gases. The carrier, such as powdered silica gel, is saturated with H_2O at 150°–250° F. before it enters the reaction zone. The heat of reaction vaporizes the fluid and expels it from the carrier. The carrier is separated from the effluent stream, saturated again with H_2O, and recycled. Owing to the fluidized condition of the catalyst, a uniform temperature level is maintained throughout the mass even though individual catalyst particles make frequent and repeated contact with relatively cool particles of carrier powder. The cooling fluid may be a fraction of the hydrocarbon products boiling either approximately at, or substantially below, the average reaction temperature, or in the lower range of temperature within the reactor. 9 United States patents cited.

54. ——— (The Texas Co.). Method of Effecting Catalytic Conversions. United States Patent 2,443,673, June 22, 1948; appl. filed May 3, 1944, Serial No. 533,901; 12 claims (*Cl. 196–52*). Chem. Abs., vol. 42, 1948, p. 9155.

This invention relates particularly to a method for effecting 2 separate catalytic reactions simultaneously in a common reaction space, such as the conversion of CO with H_2 to produce liquid hydrocarbons and the isomerization of unsaturated aliphatic hydrocarbons, particularly those formed in the synthesis reaction. The process is carried out in a reaction space filled with either a fixed or a fluid catalyst effective for isomerization through which is passed a stream of heated vaporized olefins and simultaneously a stream of CO and H_2, together with a suspension of a hydrogenation catalyst in a carrier fluid; thus effecting simultaneous isomerization of the olefins and conversion of CO and H_2 to normally liquid hydrocarbons. The hydrogenation catalyst may comprise either Co, Fe, or Ni promoted by the oxides of Th, Mg, U, V on a support of silica gel, and the carrier fluid may be the higher boiling fraction of the hydrocarbon products produced in the process. The isomerization catalyst may consist of precipitated hydrated silica and a hydrated oxide from the group consisting of precipitated Al_2O_3 or ZrO_2. The flow of vapors, gases, and suspended catalyst is downward, and the hydrocarbon products of reaction are drawn off in vapor phase from the bottom of the reactor.

55. ——— (The Texas Co.). Method of Producing Hydrocarbons and the Like. United States Patent 2,452,712, Nov. 2, 1948; appl. filed May 22, 1946, Serial No. 671,571; 10 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 1171.

In the synthesis of hydrocarbons from CO and H_2 the formation of CO_2 is minimized by removing H_2O as rapidly as it is formed by using a desiccant powder. CaO, $CaSO_4$, MgO, or BaO may be used. A stream of the desiccant is continuously removed from the synthesis zone to a regeneration zone where H_2O is removed. The regenerated desiccant is recycled. An inert gas, such as N_2, is used for the decomposition of a hydroxide or hydrate because the use of air or O_2 would result in oxidation of any conversion catalyst that may have been removed from the synthesis zone. The desiccant is cooled after its regeneration. The hot or partly cooled desiccant may be used to preheat the feed gas. 5 United States and 2 foreign patents cited.

56. ——— (The Texas Co.). Method of Synthesizing Gasoline and the Like. United States Patent 2,535,343, Dec. 26, 1950; appl. filed July 27, 1946, Serial No. 686,655; 10 claims (*Cl. 260–449.6*).

Temperature is controlled by direct contact evaporative cooling. Effluent is split into 2 streams. One is diverted to a product recovery system, the other is further divided into 2 portions. One is contacted with a cooling liquid that is a selective absorbent for H_2O or CO_2. The cooled uncondensed gas from this treatment is combined with the remaining portion to condense the higher boiling constituents in the form of a fog dispersed throughout the uncondensed gas. A stream of this mixture of gas and highly atomized liquid is recycled to the reaction zone where the atomized liquid components serve as evaporative coolant. Reduction of H_2O concentration in the recycle stream by using ethylene glycol as coolant reduces CO_2 formation. A CO_2 absorbent, such as monoethanolamine, may replace or be used in addition to the H_2O absorbent. Normally a recycle ratio, expressed as volume of recycle gas per volume fresh feed, of 1 : 1 or 2 : 1 is used. 1 foreign and 6 United States patents cited.

57. ——— (Process Management Co.). Motor Fuel From Reaction Products of Carbon Monoxide and Hydrogen. United States Patent 2,258,839, Oct. 14, 1941; appl. filed Oct. 30, 1937, Serial No. 171,919; 4 claims (*Cl. 196–9*). Chem. Abs., vol. 36, 1942, p. 640.

Describes arrangement of apparatus and a method for converting the normally liquid and normally gaseous hydrocarbon products of the reaction of CO and H_2, which comprises separating from the reaction products a fraction predominating in normally liquid constituents and including at most a minor proportion of hydrocarbons boiling above the gasoline boiling range; admixing with this fraction a substantial proportion of

normally gaseous hydrocarbons from a source set forth below; subjecting the resulting mixture to elevated temperature and pressure to convert normally liquid and normally gaseous constituents thereof to gasoline of high antiknock value, separating from the resulting conversion products gasoline constituents and a normally gaseous fraction predominating in C_3 and C_4 hydrocarbons, controlling the separation of the conversion products to include in such normally gaseous fraction a substantial proportion of the relatively low boiling normally liquid constituents of the conversion products; and admixing at least a portion of the gaseous fraction with the 1st-mentioned fraction, as described.

58. ——— (The Texas Co.). Process for the Production of Synthesis Gas. United States Patent 2,448,290, Aug. 31, 1948; appl. filed Dec. 18, 1943, Serial No. 514,769; 3 claims (*Cl. 23–212*). Chem. Abs., vol. 42, 1948, p. 9125.

CH_4, steam, and CO_2, in molecular ratio 4 : 3 : 1, are reacted in presence of powdered material, such as Al_2O_3, MgO, and diatomaceous earth, to form synthesis gas $CO : H_2$ (1 : 2). The heat carrier, 50–500 μ, impregnated or coated with a catalytic agent, such as Ni, is suspended in the reactants and supplies heat for the reaction. The carrier is removed continuously from the conversion zone, passed through a combustion zone wherein the heat content is restored, and returned to the converter. 7 United States patents cited.

59. ——— (The Texas Co.). Process for Upgrading Diesel Fuel. United States Patent 2,562,980, Aug. 7, 1951; appl. filed June 5, 1948, Serial No. 31,389; 7 claims (*Cl. 260–450*).

Olefin-containing diesel oil obtained by catalytic conversion of CO and H_2 at 550°–700° F. and 200–500 p. s. i. pressure is improved in quality by contacting it with CO and H_2 at 100°–350° F. and 100–5,000 p. s. i. in presence of an Fe-group catalyst, thus converting the olefinic constituents to oxygenated compounds. These are separated from the diesel fraction by solvent extraction with MeOH, extractive distillation, or adsorption on silica gel. Removal of the O_2-containing compounds produces a desel oil of high quality; a typical diesel fraction before treatment by the above method had a cetane number of 48, and after treatment 65.4. Hydrogenation of the O_2-containing compounds with tail gas from the synthesis operation as the source of H_2 and Cu chromite as the catalyst converts the O_2-containing compounds to high-molecular-weight alcohols, which are commercially valuable.

60. ——— (The Texas Co.). Production of Carbon Monoxide and Hydrogen From Hydrocarbons. United States Patent 2,632,690, Mar. 24, 1953; appl. filed Jan. 2, 1948, Serial No. 66; 2 claims (*Cl. 23–212*). Chem. Abs., vol. 47, 1953, p. 5667.

By using a continuous method of flow, heat liberated in the combustion zone is used for the endothermic reaction in the conversion zone. The catalyst is in a fluidized fixed bed. The powdered heat carrier passes through the fluidized catalyst effecting extremely rapid direct transfer of heat from the heat carrier to both the reactants and the catalyst. The gaseous hydrocarbon, such as CH_4, reacts with CO_2 and steam. The temperature is preferably 1,800°–2,000° F., and the reactants are charged in the proportion of 4 mols CH_4 : 3 mols steam : 1 mol CO_2. This gives a product gas of $CO : H_2 = 1 : 2$. The powdered heat carrier has an average particle size of $<50\mu$, or smaller than the average particle size of the catalyst.

See also United States Patents 2,443,673 (abs. **54**) and 2,448,290 (abs. **58**). 1 literature ref. and 5 patents cited.

61. ——— (The Texas Co.). Simultaneous Dehydrogenation and Hydrocarbon Synthesis With Fluidized Catalyst in a Single Reactor. United States Patent 2,486,243, Oct. 25, 1949; appl. filed Jan. 6, 1948, Serial No. 759; 8 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 1676.

Separate conversions are carried out simultaneously in a common reaction zone to produce a composite hydrocarbon product, certain constituents of which are formed from 1 conversion and cetrain of which are formed from the companion conversion. Naphthalene hydrocarbons are converted into aromatics by action of a dehydrogenating catalyst. H_2 so liberated is consumed, at least in part, in the synthesis of hydrocarbons from H_2 and CO. The endothermic dehydrogenation uses the exothermic heat of the hydrocarbon synthesis. Two catalysts may be used by confining a mass of 1 catalyst within the reaction zone while passing a suspension of the other catalyst in a suitable fluid, either gaseous or liquid, through the confined mass of catalyst. The suspended catalyst is removed with the products, separated, and recycled to the reaction zone. One foreign and 2 United States patents cited. Addition to United States Patent 2,443,673 (abs. **54**).

62. ——— (The Texas Co.). Synthesis of Hydrocarbons. United States Patent 2,534,395, Dec. 19, 1950; appl. filed June 12, 1948, Serial No. 32,731; 8 claims (*Cl. 260–449.6*).

Synthesis is effected by passing synthesis gas in contact with a typical hydrocarbon synthesis catalyst in the presence of, or in close proximity to, a 2d catalyst to polymerize gaseous olefins to motor gasoline, but free from any cracking activity under the conditions used. The 2 catalysts preferably are uniformly fluidized by upflowing reactants in good admixture. Both catalyst particles have approximately equivalent settling rates. The synthesis catalyst is preferably from the Fe group, the polymerization catalyst from the phosphoric acid type. The reaction temperature is preferably 600°–650°F., pressure 200–400 p. s. i. g. The synthesis catalyst is present usually in proportion 2–3 times the volume of the polymerization catalyst. 11 United States patents cited.

63. AUDIBERT, E. (Société nationale de recherches sur le traitment des combustibles). Apparatus for Effective Catalytic Reactions of Gases Such as Synthesis of Ammonia or Methanol. United States Patent 1,870,665, Aug. 9, 1932. Chem. Abs., vol. 26, 1932, p. 5457.

Describes various details of construction. The apparatus comprises a heat exchanger, a catalyzing tube, and a preheater, which can be placed in 1, 2, or 3 casings. Provision is made inside the reactor for heat exchange and for preheatings. A combination of valves is provided so that the temperature in the catalyst bed may be controlled by proportioning preheated and superheated feed.

64. ——— (Société nationale de recherches sur le traitment des combustibles). [Hydrocarbons and Oxygen Derivatives.] French Patent 639,441, Jan. 24, 1927. Chem. Abs., vol. 23, 1929, p. 604.

Hydrocarbons and their O_2 derivatives, such as alcohols, are prepared by circulating CO and steam over a catalyst with heat and pressure. A suitable catalyst is a mixture of oxides of Fe and Cu.

65. ——— Methanol. British Patent 271,538, Jan. 30, 1926. Chem. Abs., vol. 22, 1928, p. 1596.

CO and H_2 are passed under pressure and at an elevated temperature, suitably 100 atm. and not over 450° at any point in the reaction zone, over a Cu catalyst. To prepare the catalyst, a solution of Cu nitrate or an organic Cu salt is treated with alkali, the precipitate washed and dried in vacuo, mixed with a small proportion of violet-colored Cu, and then reduced at a temperature not exceeding 200° with H_2 or CO

under ordinary pressure with or without diluent gas such as N_2 or CH_4. The temperature of the CO and H_2 supplied to form MeOH does not exceed 180° before the reaction.

AUERHAHN, A. *See* abs. **605.**

66. AUREDEN, H. (F. Krupp A. G.). [Rectangular Heat Exchanger for Use in Synthesizing Benzine From Carbon Monoxide and Hydrogen.] German Patent 741,280, Nov. 8, 1943; appl. K 161,058 filed May 7, 1941 (*Cl. 12 o–1.03*). FIAT Reel AA 90, frames 1,429–1,432; PB 70,275; TOM Reel 36, bag 3,451, item 8; Chem. Zentralb., 1944, I, p. 841; Chem. Abs., vol. 40, 1946, p. 444.

———. *See* abs. **164.**

67. AVDEEVA, A. V. [Methane]. Russian Patent 53,249, May 31, 1938. Chem. Abs., vol. 34, 1940; p. 5276.

CO is hydrogenated in the presence of a magnetite catalyst prepared by fusing Fe in a stream of O_2 and containing 32–37% FeO and 63–68% Fe_2O_3.

AXE, W. N. *See* abs. **1784.**

AYTON, G. R. *See* abs. **2641, 2642.**

B

BADER, W. *See* abs. **564.**

68. BADER, W., AND GREEN, S. J. (Celanese Corp. of America). Zinc Oxide Catalysts for Methanol Synthesis. United States Patent 1,793,350, Feb. 17, 1931; appl. filed Sept. 15, 1927. Chem. Abs., vol. 25, 1931, p. 2155.

Catalyst suitable for use in producing MeOH from H_2 and C oxides is prepared by heating a $ZnCO_3$ gel at a temperature not exceeding that at which the catalyst is to be used.

69. BADER, W., AND THOMAS, E. B. (Celanese Corp. of America). Catalysts Such as Those Used for Synthesis of Methanol. United States Patent 1,999,388, Apr. 30, 1935; appl. filed Mar. 13, 1930, Serial No. 435,631 (*Cl. 260–166*). Chem. Abs., vol. 29, 1935, p. 4029.

Catalysts such as those comprising Cr and Zn oxides and which have been used for MeOH synthesis from gases containing traces of S are reactivated by the action of a gas rich in H_2 at temperatures not substantially exceeding those employed in the catalytic reaction.

70. ——— (Celanese Corp. of America). Oxygenated Organic Compounds From Hydrogen and Carbon Oxides. United States Patent 1,942,530, Jan. 9, 1934; appl. filed Feb. 10, 1930. Chem. Abs., vol. 28, 1934, p. 1713.

For the production of products such as MeOH, gaseous mixtures containing H_2 and oxides of C are subjected to the action of heat and pressure in the presence of a catalyst containing a catalytic metal such as Zn, Cu, Pb, and Cd solely in the form of its sulfide.

71. BADER, W., GREEN, S. J., AND BRITISH CELANESE, LTD. Catalyst for Methanol Synthesis. British Patent 300,142, May 2, 1927. Chem. Abs., vol. 23, 1929, p. 3479.

Catalysts for MeOH synthesis are prepared by precipitating $ZnCO_3$ in gelatinous form, washing and drying the precipitate so that it retains its colloidal state, and heating the gel at a temperature not exceeding that employed in the MeOH synthesis. Protective colloids also may be used. Gives various details and examples.

72. BADER, W., THOMAS, E. B., AND BRITISH CELANESE, LTD. Catalysts for Methanol Synthesis and Other Purposes. British Patent 345,649, Sept. 18, 1929. Chem. Abs., vol. 26, 1932, p. 37.

In catalytic reactions involving oxidation, reduction, hydrogenation, or dehydrogenation, especially synthesis of MeOH from CO and H_2 using as catalyst ZnO or a mixture of Zn and Cr oxides, the oxides or hydroxides used as catalysts are prepared by electrolysis of corresponding metal salts, such as the nitrates or formates. Describes numerous details of procedure.

73. ———. Methanol. British Patent 334,924, Apr. 12, 1929. Chem. Abs., vol. 25, 1931, p. 1265.

ZnS, alone or mixed with Cr oxide or other promoters, is used as catalyst in synthesizing MeOH from C oxides and H_2, suitably at 360°–400° and under 100 atm. pressure. Gives details for preparing the catalyst.

74. ——— Reactivating Catalysts Used in Methanol Synthesis. British Patent 334,251, May 31, 1929. Chem. Abs., vol. 25, 1931, p. 972.

Catalysts such as oxides, for example, ZnO alone or with metals such as Zn or Cu, employed in the synthesis of MeOH, from CO and H_2 or in like reactions, are reactivated by the action of H_2 or gas mixtures rich in H_2 at temperatures higher than those used for the reaction, suitably 370°, and suitably under high pressures such as those employed in the synthesizing reaction, for example, 100 atm.

75. BADISCHE ANILIN- UND SODA-FABRIK. Alcohol, Aldehydes From Carbon Oxides and Hydrogen. British Patent 238,319, Sept. 4, 1925; appl. filed May 24, 1924. Chem. Zentralb., 1926, I, p. 2150; Chem. Abs., vol. 20, 1926, p. 1995.

Oxygenated compounds of a higher order than MeOH are obtained by passing a mixture of CO or CO_2 with H_2 at an elevated temperature and pressure over a MeOH-forming catalyst but at a diminished speed as compared with that required for the formation of MeOH under otherwise similar conditions. Gives numerous examples and details.

76. ——— [Aldehydes Direct From the Corresponding Carboxylic Acids.] German Patent 185,932, Dec. 14, 1905. Chem. Abs., vol. 1, 1907, p. 3074.

Formaldehyde and acetaldehyde can be obtained from formic acid and acetic acid, respectively, by passing the acid vapors in admixture with H_2 at high temperatures over metals such as Fe, Zn, Sn, Pb, and S.

77. ——— (I. G. Farbenindustrie A. G. "In Auflösung"). Carbon Monoxide and Hydrogen Production in Runoff Gas Producers. British Patent 685,485, Jan. 7, 1953. Chem. Abs., vol. 47, 1953, p. 6636.

Gaseous mixtures containing CO and H_2 with essentially no hydrocarbon are made in runoff gas producers operated on coke. Finely divided gaseous liquid or solid carbonaceous materials are introduced through a burner with a gasifying agent containing O_2 and into a fuel bed of the gas producer. The O_2 content of the introduced gases is maintained at a level to hold temperature of 1,300°–1,800° in the fuel bed.

78. ———. Catalytic Production of Oxygenated Organic Compounds. British Patent 254,819, Mar. 9, 1925. Chem. Abs., vol. 21, 1927, p. 2703.

CO at high temperature and pressure is caused to react on a vaporized aliphatic alcohol or ester in the presence of hydrating or hydrating and hydrogenating catalysts. MeOH and CO are passed over a mixture of Fe and Mn oxides, forming a product containing butyric and valeric acids. MeOH vapor, CO, H_2, and N_2 are passed over a Co oxide–molybdic acid catalyst, forming O compounds and N compounds, such as methylamines; Ba uranate or Fe vanadate also can be used as catalyst. MeOH and CO passed over a K chromate–K molybdate catalyst yield higher alcohols, aldehydes,

and esters. EtOH and CO passed over a Cr oxide–Mn oxide catalyst give products boiling at 100°–250°, including aldehydes, acids, esters, and alcohols. MeOH, CO, H_2, and N_2, passed over a K_2Cr_2O—ZnO catalyst give a product containing isobutyl, *n*-proply-, amyl- and higher alcohols, and free or combined acids. Me formate, CO, H_2, and CH_4 passed over a catalyst prepared from $KMnO_4$, Zn chromate, and Cu chromate, give similar products. CO and H_2 are passed over a catalyst consisting of Cd and Cu oxides and vanadic acid, and the resulting MeOH-containing mixture is passed over a catalyst prepared from KOH, Tl oxide, and $KMnO_4$ to produce isobutyl alcohol and other products. Purified water gas and EtOH may be passed over K_2CO_3, Zn chromate, and Cu oxide to form liquid products insoluble in H_2O. Numerous catalysts listed for effecting hydrogenation, hydration, or both.

79. ———. [Hyrocarbons and Their Derivatives.] Austrian Patent 73,409, 1915.

See German Patents 293,787 (abs. **2360**), 295,202 (abs. **111**), and 295,203 (abs. **2359**).

80. ———. Hydrocarbons From Carbon Monoxide and Hydrogen. British Patent 20,488, June 10, 1915; appl. filed Sept. 10, 1913.

See German Patent 293,787 (abs. **2360**), French Patent 468,427 (abs. **2357**), and United States Patent 1,201,850 (abs. **2358**).

81. ———. Hydrogenation or Dehydrogenation of Compounds Containing Carbon. British Patent 2,306, Jan. 28, 1914. Chem. Abs., vol. 10, 1916, p. 287.

Process is effected in the presence of a catalyst consisting of Fe, Ni, Co, or Cu, intimately mixed with 1 or more of the following promoters: Oxides or O-containing salts of earth metals, rare-earth metals, Be, Mg, Mn, U, V, Nb, Ta, Cr, Ti, or B; difficultly soluble phosphates, molybdates, tungstates, or selenates, of the alkaline earths or of Li, or O-containing reduction products of these compunds. The proportion of the promoter in the catalytic mixture may be as small as 1% or less. The catalytic mixtures may be employed in the hydrogenation of fats or fatty acids, the conversion of phenol into cyclohexanol, the reduction of nitrobenzene to aniline, and the conversion of C oxides into hydrocarbons. These processes may be effected under ordinary or increased pressure. According to an example, a solution containing Ni and Be nitrates is precipitated with NaOH, the NiO is reduced with a mixture of CO and H_2 or H_2 alone, and the product is used to convert a mixture of CO and H_2 into CH_4.

82. ———. [Hydrogenation or Dehydrogenation of Hydrocarbons by the Aid of Catalysts.] German Patent 307,580, Sept. 3, 1918; appl. filed June 22, 1913. Chem. Zentralb., 1918, II, p. 573.

Organic compounds and CO can be converted into H-containing or H-rich compounds at relatively low temperatures by treatment with H_2 in the presence of catalysts. Ni, Fe, and Co are specifically mentioned.

83. ———. [Liquid Fuel.] French Patent 580,949, May 1, 1924.

See British Patent 215,776 (abs. **84**).

84. ———. Liquid Fuel for Internal-Combustion Engines. British Patent 215,776, July 9, 1924; appl. filed May 8, 1923. Chem. Zentralb., 1924, II, p. 1762; Chem. Abs., vol. 18, 1924, p. 3471.

Crude MeOH, obtained by the catalytic treatment of H_2 and CO, is used as motor fuel. If desired C_6H_6 or other fuels may be added.

85. ——— (I. G. Farbenindustrie A. G. "In Auflösung"). Making Magnetic Iron Oxides. British Patent 677,878, Aug. 20, 1952. Chem. Abs., vol. 47, 1953, p. 800.

Magnetic Fe oxides for magnetic sound recorders are produced directly from Fe carbonyl by burning it in an amount of O_2 producing an atom ratio of O : Fe substantially less than 3 : 2 by using a burner similar to those used for liquid fuel at 100°–1,500°. The nature of the Fe oxides formed is influenced by the combustion temperature and the cooling rate. Fe oxide obtained with a restricted supply of O_2 is oxidized to γ–Fe_2O_3 by introducing additional O_2 while still hot, preferably under 500°, because at a higher temperature γ–Fe_2O_3 is converted into the stable nonmagnetic α form. When Fe_3O_4 is oxidized to γ–Fe_2O_3, the permeability and remanence become functions of the oxidation temperature. The values of the permeability and remanence are 32, 35, 21, 8, and 64, 61, 56, 16, respectively, at 90°, 250°, 405° 585°.

86. ———. [Manufacture of Ammonia From Its Elements With the Aid of Catalyzers.] German Patent 249,447, Jan. 9, 1910. Chem. Abs., vol. 6, 1912, p. 3170.

See British Patent 19,249 (abs. **115**).

87. ———. [Methane From Carbon Monoxide and Hydrogen.] German Patent 390,861, Feb. 25, 1924; appl. filed Dec. 2, 1922. Chem. Zentralb., 1924, I, p. 2396.

Any H_2 or CO remaining after the conversion is removed by physical means such as deep cooling or absorption through porous bodies or by selective oxidation. This is an addition to German Patent 366,791 (abs. **2361**).

88. ———. [Methanol.] Austrian Patent 116,055, no date. Chem. Zentralb. 1930, I, p. 3628.

See British Patent 231,285 abs. **92**).

89. ———. Methanol. British Patent 227,147, Feb. 5, 1925; appl. filed Aug. 28, 1923. Chem. Abs., vol. 19, 1925, p. 2673.

MeOH and other O-containing organic compounds are prepared by the catalytic reduction of C oxides (preferably CO) with a mixture of oxides of metals of different groups as catalyst, such as ZnO with an oxide of Cr, U, V, or W; Mg and Mo oxides; Ce and Mn oxides, or Cd and Cr oxides. A Cu apparatus is used, and the catalysts should be free from Fe, Ni, and Co.

90. ———. Methanol. British Patent 228,959, Mar. 12, 1925; appl. filed Aug. 23, 1923. Chem. Zentralb., 1926, I, p. 2509; Chem. Abs., vol. 19, 1925, p. 2960.

In production of MeOH and O-containing organic compounds from C oxides and H_2 under pressure, catalytic agents being used, the gas mixture used is preliminarily subjected to an exhaustive purification treatment to remove organic S compounds and volatile Fe compounds. Describes various alternative procedures.

See British Patent 227,147 (abs. **89**).

91. ———. Methanol. British Patent 229,714, Mar. 26, 1925; appl. filed Aug. 23, 1923. Chem. Zentralb., 1926, I, p. 2508; Chem. Abs., vol. 19, 1925, p. 3093.

MeOH together with other oxygenated organic compounds is prepared by passing mixtures of CO or CO_2 (or both) with H_2 at increased temperature and pressure over a catalyst containing metal oxides or compounds that are not reduced by the reaction gases at temperatures up to 550° under pressure. Ni, Fe, and Co must be excluded from the catalytic material. Among the catalysts that it is stated may be employed are: Oxides, hydroxides or carbonates of the alkali, alkaline earth or "earth" and "rare-earth" metals, such as Al, Be, Zr, Th, or Ce; mixtures or compounds of MgO or Al_2O_3 with oxides of Pb, Bi, Tl, Zn, Cd, Cu, Sn, Sb, Si, B, and Ti; "potash-lime" or a mixture of KOH and Al_2O_3 or Mg chromate, a mixture of Pb chromate with Al_2O_3, together with a little KOH; MgO or ZnO mixed with KOH or RbOH or carbonates of K

or Rb; the product obtained by igniting in the air or in an inert gas a mixture of Cu oxide and powdered Al; mixtures of K, Cs, or Rb compounds with 1 or more of the oxides of U, Al, Cr, Mn or of rare earth metals such as Ce, La, Th, Zr, or Yt; mixtures or compounds of ZnO with oxides of Al, Ba, rare earth metals, Cr, Mg, Mn, Ta, Ti, W, or V; Sb oxide mixed with BeO; W threads containing Th; metallic Mo or Tl containing Al_2O_3; the product obtained by melting $K_2Cr_2O_7$ and adding ZnO or an oxide of Mn, Tl, Ce, U, Th, or Zr and breaking up the cooled mass, with or without subsequent leaching or reduction. The H_2 should exceed in volume the oxides of C employed; the pressure should preferably be higher than 50 atm. and temperatures of 300°–600° are used. The velocity of flow of the gases may vary between 5 and 200 m.^{3} (calculated on atmospheric pressure) per hr. for each kg. of contact mass.

See abs. **2667, 2668, 2669, 2670.**

92. ———. Methanol. British Patent 231,285, Apr. 23, 1925; appl. filed Feb. 8, 1924. Chem. Zentralb. 1926, I, p. 2149; Chem. Abs., vol. 19, 1925, p. 3490.

Apparatus for synthetic production of MeOH from CO and H_2 is made of or coated with a metal or alloy that does not form carbonyl compounds and is resistant to the temperatures used, such as Cu, Ag, Al, and their alloys, special steels containing substantial proportions of Cr, Mn, W, Mo, or V, such as "steel V2A" or the metals Cr, Mn, W, Mo, and V themselves, but Fe, Co, and Ni are excluded. To protect the reaction tube against the action of hot H_2, it may be formed with a steel mantle with an inner wall of Cu or other suitable metal.

See British Patents 229,714 (abs. **91**) and 229,715 (abs. **3289**).

93. ———. Methanol. British Patent 237,030, July 23, 1925; appl. filed Apr. 28, 1924. Chem. Zentralb., 1926, I, p. 2149; Chem. Abs., vol. 20, 1926, p. 1414.

Catalysts for producing MeOH and other products by reaction of C oxides with H_2 at elevated temperatures under pressure comprise a mixture of 2 or more metals, the oxides of which can be reduced to the metal by H_2 or CO at ordinary pressure and at <550°. Fe, Co, and Ni are excluded as are mixtures with metals of the 4th to 7th periodic groups or B. Cu, Ag, Pb, Zn, and Cd are suitable metals; carriers and additions such as K_2CO_3 may be present. MeOH may be formed under 150 atm. pressure.

94. ———. Methanol. British Patent 240,955, July 29, 1924. Chem. Abs., vol. 20, 1926, p. 2504.

Synthesis of MeOH by catalytic hydrogenation of CO under pressure is effected in absence of Fe from all materials and reaction apparatus used. Temperatures of 250°–600° and pressures of 50 atm. or more are used for production of MeOH either pure or mixed with high alcohols. A mixture of oxides of Cr and Mn may be used in a Cu-lined tube or a mixture of oxides of Cr and Zn in an Al-lined vessel. Other suitable contact substances specified are: Cu and Cr oxides; Cd and V oxides; alloys such as those of Cr and Mn or Cu and Zn; oxides of U and Al or other oxides nonreducible under the conditions of the reaction; and mixtures of such metals as Cu, Ag, Pb, and Zn with a metal oxide or salt acting as a promoter. A small quantity of K_2CO_3 is added to contact masses containing a difficultly reducible metallic oxide and preferably with a higher % of CO and a reduced velocity of the gas current there may be formed higher alcohols such as PrOH, BuOH, and AmOH in addition to MeOH. Ni and Co are excluded from the catalytic materials.

See abs. **93** *and* **2350.**

95. ———. Methanol. British Patent 266,405, Oct. 19, 1925. Chem. Abs., vol. 22, 1928, p. 597.

In the manufacture of MeOH and other oxygenated organic compounds by catalytic hydrogenation of C oxides, by using heat, pressure, and a catalyst, mixtures are used containing a high % of inert gases, or a large excess of 1 of the reacting gases that serves as a diluent, and the operation is conducted in a circulatory system with continuous removal of part of the mixture enriched in inert gases and replacement by fresh gas mixture.

See also British Patent 254,760 (abs. **114**).

96. ———. Methanol. British Patent 266,410, Oct. 19, 1925. Chem. Abs., vol. 22, 1928, p. 597.

Specifies partial oxidation of hydrocarbon-containing gases, such as coal gas, coke oven gas, natural gas, or cracking gases, to obtain a mixture containing CO and H_2, which are then used for producing MeOH and other compounds. Gives various details.

See also British Patents 254,760 (abs. **114**) and 266,405 (abs. **95**).

97. ———. [Methanol.] French Patent 31,551, Jan. 30, 1926. Chem. Zentralb., 1927, II, p. 1078.

This is an addition to French Patent 575,913 (abs. **99**).

See also British Patent 247,217 (abs. **1144**).

98. ———. [Methanol.] French Patent 32,175, Sept. 12, 1927; appl. filed Aug. 26, 1926. Chem. Zentralb., 1928, I, p. 584.

In the synthesis of MeOH and in all other processes for the production of O-containing organic compounds, free Fe, Ni, and Co are avoided in all places where the oxygenated compounds are subjected to raised temperatures.

See French Patent 585,169 (abs. **2356**).

99. ———. [Methanol.] French Patent 575,913, Aug. 8, 1924; appl. filed Jan. 17, 1924. Chem. Zentralb., 1926, I, p. 2148.

See German Patent 490,248 (abs. **2679**) and British Patent 231,285 (abs. **92**).

100. ———. [Methanol.] French Patent 580,905, Nov. 19, 1924; appl. filed Apr. 30, 1924. Chem. Zentralb., 1926, I, p. 2149.

See British Patent 237,030 (abs. **93**).

101. ———. [Methanol.] French Patent 581,816, Dec. 6, 1924; appl. filed May 19, 1924. Chem. Zentralb., 1926, I, p. 2150.

See British Patent 238,319 (abs. **75**).

102. ———. [Methanol.] Swedish Patent 58,458, Mar. 17, 1925; appl. filed Sept. 19, 1923.

See British Patent 229,714 (abs. **91**).

103. ———. [Methanol.] Swiss Patent 107,201, Oct. 16, 1924; appl. filed Oct. 8, 1923.

See United States Patent 1,558,559 (abs. **2366**).

104. ———. [Methanol.] Swiss Patent 108,071, Dec. 1, 1924; appl. filed Jan. 16, 1924. Chem. Zentralb., 1926, I, p. 2148.

See German Patent 490,248, British Patent 231-285, and French Patent 575,913 (abs. **92, 99, 2679**).

105. ———. [Methanol.] Swiss Patent 110,286, Aug. 17, 1925; appl. filed July 23, 1924.

See British Patent 237,030 and French Patent 580,905 (abs. **93,** and **100**).

106. ———. [Methanol.] Swiss Patent 110,746, July 1, 1925; appl. filed May 14, 1924. Chem. Zentralb., 1926, I, p. 2150.

See British Patent 238,319 (abs. **75**).

107. ———. [Methanol From Carbon Oxides.) Swiss Patent 107,391, Oct. 16, 1924; appl. filed Sept. 26, 1923.

See British Patent 228,959 and French Patent 571,285 (abs. **90, 2686**).

108. ——— (I. G. Farbenindustrie A. G. "In Auflösung"). [Oxo Carboxylic Acids.] German Patent 812,073, Aug. 27, 1951 (*Cl. 12 o.15*). Chem. Abs., vol. 47, 1953, p. 2769.

O_2-substituted hydroaromatic ketones or alcohols with O_2 or O_2-containing gases in the presence of O-transferring catalysts and organic acids give oxocarboxylic acids. The addition of ketones or aldehydes, such as AcH or EtCHO, is suitable to initiate the oxidation when *o*-substituted alcohols are used as the starting material. The reaction is preferably interrupted before all of the hydroaromatic alcohol or ketone is oxidized (at most up to 50–80%) to prevent a further oxidation. Bubbling air through adipic acid 20 and Mn nitrate (I) 1 in 2-methylcyclohexanone (II) 1,000 at 65° until 50% of the (II) is oxidized and fractionating the reaction mixture in vacuo gives unreacted (II) 500, an intermediate fraction 40, δ-acetylvaleric acid (III) 340, and a residue 270 parts consisting of a mixture of several acids. A further example describes the preparation of (III) by oxidizing a mixture of (II) and 2-methylcyclohexanol in the presence of AcOH and (I).

109. ———. [Process and Apparatus for Carrying Out Operations Employing Hydrogen Under Pressure and at High Temperature.] French Patent 441,695, Mar. 23, 1912. Jour. Soc. Chem. Ind., vol. 31, 1912, p. 922.

Such operations performed under pressure and at high temperatures, such as the synthesis of NH_3, can be carried out in vessels provided with special strengthening appliances, although the wall of the interior vessel in which reaction takes place is composed of some material, such as Fe, free from C, Ni, Ag, which is incapable of offering by itself sufficient mechanical resistance to the conditions imposed by the process but chemically is as resistant as possible to H_2. Means are also provided whereby the H_2 that diffuses through the wall of the vessel can escape without meeting with any great resistance.

110. ———. Process for Carrying Out Operations Employing Hydrogen or Gases Containing It. British Patent 1,490, Jan. 18, 1912. Jour. Soc. Chem. Ind., vol. 32, 1913, p. 234.

See French Patent 441,695 (abs. **109**).

111. ———. [Process for Producing Hydrocarbons and Their Derivatives.] German Patent 295,202, Nov. 8, 1916; appl. filed May 31, 1914. Chem. Zentralb., 1916, II, p. 1095.

The process of German Patent 293,787 is improved by the use of catalysts of higher heat conductivity such as Ni gage activated with alkali, ZnO, or Co_3O_4.

112. ———. Production of Fuel Gas in Particular Synthesis Gas in Gas Producers. British Patent 661,148, Nov. 14, 1951. Chem. Abs., vol. 46, 1952, p. 4203.

Powdered or granular coal or coke is gasified in a gasification chamber (which may be of the centrifugal type) with O_2 and steam, the amount of O_2 being limited so that CO is formed to a greater extent than CO_2. The hot gases from this step are then passed through a gas producer containing lump coke, so that CO_2 and H_2O vapor react to form additional gas. No additional air or O_2 is added before this step. In an example, 7.5 metric ton per hr. of dry brown-coal dust is gasified with 3,850 $m.^3$ per hr. of O_2 and 3.7 metric ton per hr. of steam in a centrifugal gasification chamber. The resulting gas then enters a runoff gas producer at about 1,700°. This producer is charged with 3 metric tons per hr. of bituminous coal coke. There are formed 20,000 $m.^3$ per hr. of synthesis gas having the following composition: CO_2 5.7; CO, 54.5; H_2, 38.4; and N_2, 1.4%. The CO_2 may be washed from this gas in the usual manner. Passage through the coke-gas producer removes tar and dust, making the gas especially suitable for synthesis purposes.

113. ———. [Production of Methane From Water Gas.] German Patent 396,115, June 3, 1924; appl. filed Mar. 24, 1923. Chem. Zentralb., 1924, II, p. 1269.

CH_4 is produced from water gas or the like by the catalytic conversion at 700°–800° of the CO by means of steam and by subsequent passing of the resulting gas mixture over catalysts such as Ni. The difficultly removable S in the initial gas mixture is completely or partly converted into H_2S and is then easily removed.

114. ———. Synthesis of Methanol. British Patent 254,760, Feb. 2, 1925. Chem. Abs., vol. 21, 1927, p. 2703.

Synthesis of MeOH and other oxygenated organic compounds is effected from oxides of C and H_2, with Fe, Ni, Co, or their oxides as catalysts, in the form of such chemical compounds, alloys, or solid solutions as are stable, contain no free Fe, Ni, or Co, and do not form such by reduction or decomposition by the hot reducing gases. Combinations of the metals with Cu or Ag or of Co with the metals specified in British Patent 229,715 (abs. **3289**) are excluded. Among the catalysts that are suitable are compounds or solid solutions of the metals specified with oxides of Cr, V, W, Zr, Al, and Ti; alloys of the metals with Mn, Cr, W, Sn or Zn, or silicides; borides; sulfides; and phosphides or arsenides of the metals; but not carbides. Alkali metal compounds may be added. Volatile compounds of Fe, Mi, or Co should be excluded from the gases, and the exposed surfaces of the apparatus should be free from such metals; it may be formed of or lined with Cu, Al, Ag, Mn, Cr, steel V2A or Fe sulfide, or arsenide. Gives numerous additional details.

115. ———. Synthetic Production of Ammonia. British Patent 19,249, Aug. 16, 1910. Chem. Abs., vol, 6, 1912, p. 1346.

Promoters are added to the Fe, Ni, or Co used as the catalytic agent. These substances are generally compounds of Mg, Be, Al, or of the alkali, alkaline earth, or rare earth metals, or of Zr, Va, Ta, Cr, Mn, Mo, or W. Addition of the oxide or other compound of Mg or Al is particularly favorable. Details specified.

———. *See* abs. **271, 351, 430, 743, 782, 2072, 2356, 2357, 2358, 2359, 2360, 2361, 2362, 2365, 2366, 2368, 2369, 2370, 2371, 2531, 2667, 2668, 2669, 2670, 2761, 3289, 3290, 3291, 3292, 3294, 3307, 3907, 3916.**

116. BÄHR, H. (I. G. Farbenindustrie A. G.). [Mixtures of Hydrogen With Oxides of Carbon.] German Patent 538,012, July 15, 1930. Chem. Abs., vol. 26, 1932, p. 1615.

Hydrocarbons and steam are led at a temperature of the order of 700° over a catalyst, for example, Ni, arranged in an indirectly heated space, the direction of flow of the mixture being periodically reversed. Gives example.

117. BÄHR, H., AND BRAUS, K. (I. G. Farbenindustrie A. G.). Hydrogen Sulfide Recovery From Gas Mixtures. United States Patent 2,083,213, June 8, 1937. Chem. Abs., vol. 31, 1937, p. 5522.

Gas, such as waste gas from coal hydrogenation, containing both H_2S and CO_2 is scrubbed in the cold with a solution having an alkaline reaction and capable of taking up both H_2S and CO_2 and of giving them off on heating, such as a solution of alanine Na salt, while the solution is used in sprayed form and a gas-contact period of <5 sec. is provided to effect recovery of a high proportion of H_2S on heating.

118. ——— (I. G. Farbenindustrie A. G.). [Recovering Hydrogen Sulfide From Gases.] German Patent

654,373, Dec. 22, 1937 (*Cl. 12 i–18*). Chem. Abs., vol. 32, 1938, p. 2718.

See United States Patent 2,083,213 (abs. **117**).

119 BÄHR, H., AND WENZEL, W. (I. G. Farbenindustrie A. G.). [Eliminating Organic Sulfur Compounds From Gases.] German Patent 678,191, July 15, 1939 (*Cl. 26 d–9.04*). Chem. Abs., vol. 33, 1939, p. 7998.

See British Patent 461,001 (abs. **120**).

120. ——— (I. G. Farbenindustrie A. G.). Removing Organically Combined Sulfur From Gases. British Patent 461,001, Feb. 2, 1937. Chem. Abs., vol. 31, 1937, p. 5545.

S combined with CS_2, COS, and others is removed by bringing the gas into contact, preferably in the presence of moisture, with strong bases or basic-reacting salts of strong inorganic or organic bases at such high temperatures that the combined S is converted into H_2S, which is led away together with the gas. No substantial absorption of weak gaseous acids by the purifying agent takes place. Suitable agents listed.

121. BAILEY, G. C., AND REID, J. A. (Phillips Petroleum Co.). Catalytic Polymerization of Olefins. United States Patent 2,606,940, Aug. 12, 1952. Chem. Abs., vol. 47, 1953, p. 5420.

Method described comprises essentially the polymerization of gaseous olefins with a Ni oxide catalyst on a silica-gel carrier with alumina as a catalyst promoter. Shows diagram of process.

BAKER, C. O. *See* abs. **1**.

122. BAKER, H. T. (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,560,325, July 10, 1951; appl. filed Nov. 16, 1948, Serial No. 60303; 2 claims (*Cl. 260–449.6*).

Process is disclosed for operating the hydrocarbon synthesis reaction under synthesis conditions of temperature and pressure and in the presence of a fluidized Fe catalyst promoted by an alkali metal salt. The main purpose of the present improvement to the process is to maintain a high carbide content of the powdered Fe catalyst to render it resistant to serious oxidation and disintegration and also to maintain the catalyst at a high level of activity and selectivity. This is accomplished by frequently interrupting the synthesis reaction between CO and H_2, about every 24 hr. for 15 min. to 2 hr., and treating with H_2 until the effluent gas from the reaction zone is at least 90% H_2 and then switching back to synthesis gas without discontinuing the production of synthesis products. Essentially no catalyst reduction occurs during these periods of H_2 introduction, which are conducted at frequent enough intervals so that the % of Fe as Fe_2C remains at a level greater than about 20% of the catalyst volume. During the periods of H_2 introduction, the temperature in the reaction zone is about 650° F. and the pressure 400 p. s. i. g. Diagram.

123. BALACHOWSKY, D. [Apparatus for Catalytic Processes.] French Patent 862,926, Mar. 19, 1941. Chem. Abs., vol. 42, 1948, p. 8541.

Apparatus described and illustrated may be used for such catalytic processes as polymerization, depolymerization, hydrogenation, oxidation, and isomerization.

BALFOUR, HENRY, & Co., LTD. *See* abs. **283**.

BALZ, O. *See* abs. **2361**.

BAMAG, LTD. *See* abs. **1985**.

124. BAN, Y., AND TUTUMI, S. (Nenryo Kenkyuzyotyo). [Synthesis of Hydrocarbons.] Japanese Patent 133,533, Nov. 29, 1939. Chem. Abs., vol. 35, 1941, p. 4183.

Mixture of CO and H_2 or of gases containing them is brought into contact with a catalyst of reduced NI or Co or a mixture of these at 3–50 atm. and below 250°, preferably 200°.

BANKS, R. L. *See* abs. **1078**.

125. BANNISTER, W. (Commercial Solvents Corp.). Purifying Gases Such as Those for Methanol Synthesis. United States Patent 1,757,826, May 6, 1930. Chem. Abs., vol. 24, 1930, p. 3292.

Gas mixture containing principally an oxide of C such as CO is passed over Fe oxide at 400°–850° to remove substantially all the S content of the gas.

———. *See* abs. **3984**.

126. BARBER, E. M. (The Texas Co.). Production of Synthesis Gas in an Internal-Combustion Engine. United States Patent 2,605,175, July 29, 1952. Chem. Abs., vol. 47, 1953, p. 849.

By utilizing an internal-combustion engine a hydrocarbon, such as CH_4, is treated with O_2 of 90–95% purity to produce a synthesis gas comprised of CO and H_2 with the continuous production of mechanical energy. The reaction is carried out in proportions that approximate the theoretical combining proportions of O_2 and CH_4, except that excess O_2 is injected into a localized zone within the combustion chamber. In 1 example, a 95% yield of CO on the basis of C in the feed was obtained. The H_2: CO ratio was approximately 2 : 1.

———. *See* abs. **594**.

127. BARKER, M. E. Catalysts Suitable for Various Purposes. United States Patent 1,936,563, Nov. 21, 1933. Chem. Abs., vol. 28, 1934, p. 867.

An alloy containing Cu, Fe, and Mn is treated with an acid such as HCl, and the substances formed by reaction of the acid on the surface of the alloy are calcined to produce mixed oxides.

128. ———. Catalysts Suitable for Various Purposes. United States Patent 1,936,564, Nov. 21, 1933. Chem. Abs., vol. 28, 1934, p. 867.

This relates to catalysts in which the oxides are reduced to spongy metal; similar to United States Patent 1,936,563 (abs. **127**).

129. ———. Catalysts Suitable for Various Purposes. United States Patent 1,936,565, Nov. 21, 1933. Chem. Abs., vol. 28, 1934, p. 867.

This relates to catalysts that may be formed from ground particles of Cu, Fe, and Mn alloys; generally similar to United States Patent 1,936,563 (abs. **127**).

BARKOW, —. *See* abs. **3896**.

130. BARR, F. T. (Standard Catalytic Co.). Cooling Catalysts Such as Finely Divided Metal Suspensions Used in Hydrogenation of Oxides of Carbon. United States Patent Reissue 22,415, Jan. 14, 1944. Chem. Abs., vol. 38, 1944, p. 3786.

Reissue of original United States Patent 2,309,034 (abs. **131**).

131. ——— (Standard Catalytic Co.). Cooling Fluid Catalysts Such as Finely Divided Metals in Suspension Used in Promoting Reactions Such as Hydrogenation of Oxides of Carbon. United States Patent 2,309,034, Jan. 19, 1943; appl. filed Mar. 1, 1941, Serial No. 381,229; 3 claims (*Cl. 260–449*). Chem. Abs., vol. 37, 1943, p. 3890.

Heat is removed from reaction chambers in which exothermic reactions are carried out and wherein the reaction temperature is materially above the boiling point of H_2O by introducing therein in direct contact with the reactants, a stream of finely divided heat absorptive solid material, the inlet temperature of which is below the reaction temperature continuously withdrawing it at the reaction temperature, cooling it with a water spray, and then returning it to the reaction chamber.

132. ——— (Standard Oil Development Co.). High-Temperature Stripper for Use in the Production of Synthesis Gas. United States Patent 2,629,653, Feb. 24, 1953. Chem. Abs., vol. 47, 1953, p. 4064.

133. ——— (Standard Oil Development Co.). Hydrocarbon Products by Hydrogenation of Oxides of Carbon. United States Patent 2,248,734, July 8, 1941; appl. filed June 12, 1940, Serial No. 340,061; 7 claims (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 6768.

Describes apparatus and a process for removing heat from an exothermic reaction conducted in the presence of a catalyst, which comprises passing the reacting gases through a plurality of alternate zones containing catalyst that promotes the reaction and noncatalytic material situated within a reaction chamber removing heat of reaction through the walls of the reaction chamber, whereby a temperature gradient across the path of the flowing gases is prevented.

134. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,467,802, Apr. 19, 1949; appl. filed Dec. 14, 1945, Serial No. 635,100; 11 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 6811.

Gives method for controlling activity of the fluid catalyst used in the Fischer-Tropsch synthesis by using a multistage series operation and charging each stage with catalyst withdrawn from a subsequent stage, in the order of flow of synthesis gas. For example: Fresh synthesis gas may be supplied to the 1st of a series of fluid catalyst zones and from the 1st zone to 1 or more subsequent zones. Fresh catalyst may be charged to a last zone while catalyst of average activity is withdrawn, preferably at the same rate, and charged to the next preceding zone, wherein it is further deactivated in contact with relatively fresh synthesis gas. The average catalyst activity in this latter zone will be lower than that in the 1st catalyst zone. This procedure may be repeated until catalyst of lowest average activity is maintained in, and may be withdrawn from, the 1st fluid catalyst zone that receives the fresh synthesis gas.

135. ——— (Standard Oil Development Co.) Hydrocarbon Synthesis. United States Patent 2,475,214, July 5, 1949; appl. filed Oct. 12, 1944, Serial No. 558,338; 1 Claim (Cl. *260–449.6*). Chem. Abs., vol. 43, 1949, p. 8120.

After formation by the usual methods, synthesis gas is cooled to 400°–600° F., the temperature of the synthesis reaction. The hot synthesis gas may be cooled by direct introduction of an H_2O spray, forming steam. The H_2O may be injected into the transfer line connecting the synthesis gas generator with the synthesis reactor. The total concentration of steam finally present in the gaseous mixture is 25%–100% by volume of the amount of CO plus H_2 present in the mixture. The gases are fed to a reactor containing powdered Co catalyst (200- to 400-mesh). The space velocity is 1.5–3 ft. per second, and a dense turbulent suspension of catalyst, having a density of 10–30 lb. per cu. ft., is maintained. Normally liquid hydrocarbons are formed. 1 foreign and 7 United States patents cited.

136. ——— (Standard Catalytic Co.). Internally Cooled Catalytic Converter for Exthermic Reactions. United States Patent 2,384,874, Sept. 18, 1945; appl. filed May 2, 1941, Serial No. 391,560; 4 claims (*Cl. 260–449.6*). Chem. Abs., vol. 40, 1946, p. 2361.

Makeup synthesis gas plus recycled process gas is fed in parallel through an array of annular cylindrical catalyst beds arranged 1 above the other in an external cylindrical housing. Gas flow is downward through each bed, and suitable baffles are provided to produce a relatively uniform flow pattern. The reacted gases are collected in the annular space between the catalyst beds and the shell and flow downward to the bottom of the unit where they are directed radially inward over an annular cooler or waste heat boiler. An internal blower circulates the gases from the cooler and the makeup feed through the catalyst beds, thus completing the flow circuit. Part of the reacted gas is bled out before reaching the cooler. By adjusting the relative ratio of product takeoff and makeup gas to the total internal circulation, the temperature rise in passing through the catalyst beds can be held to 5°–10° F. A particular advantage of this design is that only 1 high-pressure external shell is needed and power requirements for circulation are relatively low.

137. ——— (Standard Oil Development Co.). Method and Apparatus for Solvent Cleaning Finely Divided Solids. United States Patent 2,500,056, Mar. 7, 1950; appl. filed Dec. 20, 1945, Serial No. 636,246; 8 claims (*Cl. 252–412*). Chem. Abs., vol. 44, 1950, p. 4168.

Gives process for reactivating fluid catalyst used in catalytic synthesis of hydrocarbons and oxygenated organic compounds from CO and H_2. The powdered solids in a dry dense turbulent bed of fluid solids are subjected to the action of a continuous rotary filter. The solids are picked from the fluidized bed in the form of a filter cake. The cake is treated with solvents during the subsequent revolution of the filter. The extract penetrating the filter material is continuously removed from the filter with the fluidizing gas. Solids free of soluble deposit are taken off the filter surface by conventional means before the return of the filter surface to the fluidized bed on its circular path. Enough pressure differential is maintained across the filter material to permit ready formation of filter cake of desired thickness to allow the solvent to flow through the cake and filter at the desired speed and direction. Hydrocarbon fractions produced in the synthesis may be used as solvent in dewaxing synthesis catalysts.

Gas feed rate	2–10 cu. ft. per lb. of solids feed
Gas velocity	0.1–0.5 ft. per sec.
Particle size	15%–60% through 400-mesh
Solvent feed rate	10–30 lb. total, including recycle; 205 lb. fresh per lb. of solids feed
Pressure differential	2–10 p. s. i.
Drum rotation rate	0.1–1.0 r. p. m.

1 foreign and 13 United States patents cited.

138. ——— (Standard Oil Development Co.). Method for Gasifying Solid Fuels. United States Patent 2,622,973, Dec. 23, 1952; appl. filed Oct. 2, 1945, Serial No. 619,874; 9 claims (*Cl. 48–206*).

Solid carbonaceous material is converted to volatile fuels, synthesis gas, or water gas with heat generated by partial combustion of the carbonaceous material in a fluidized bed. The conversion takes place in at least 2 zones at 1,600°–2,500° F. Heat is supplied by circulating particles highly heated by heat generated by the combustion. Extraneous solid particles of incombustible material are added to maintain a concentration of C in the conversion zone at 0.1%–1% of the fluidized solids. The extraneous material may be catalytic, capable of increasing oxidation reaction rates. 1 literature ref., 1 foreign patent, and 10 United States patents cited.

139. ——— (Standard Oil Development Co.). Process for Producing Gas Mixtures. United States Patent 2,556,835, June 12, 1951; appl. filed Dec. 29, 1945, Serial No. 638,423; 4 claims (*Cl. 48–196*).

Process for the production of H_2 and CO mixtures from hydrocarbons by reforming them with agents such as steam and CO_2, wherein the reforming process is carried out under pressure, and consists of first heating the regenerator zone to the proper pressure-reforming temperature by burning fuel with compressed air. When the temperature is reached the combustion products are withdrawn and the hydrocarbons are entered into the heated zone together with the reforming agent at substantially the same pressure under which the combustion occurred. When the reforming reaction has proceeded long enough to cause the zone to fall below the reforming temperature, the flow of reactants is stopped, and the combustion procedure is resumed again. In this manner, a cyclic combustion and reforming process, under a more or less uniform pressure, is carried on. 8 United States patents and 1 foreign patent cited.

140. ——— (Standard Oil Development Co.). [Production of Liquid Hydrocarbons Consisting Mainly of Branched Paraffins From Carbon Monoxide and Hydrogen by the Fluidized Process.) French Patent 943,220, Sept. 18, 1946, Mar. 2, 1949, in United States, Oct. 12, 1944. Chem. Zentralb., 1950, I, p. 1173.

To attain and maintain a reasonably high catalyst concentration in the reaction zone, an easily condensable gas, such as steam, is used in addition to the synthesis gas. Example: The hot synthesis gas can be cooled by a water spray to the synthesis temperature (203°–315°). By such means steam is formed, which contributes to the formation of a dense catalyst zone.

See United States Patent 2,475,214 (abs. **135**).

141. ——— (Standard Oil Development Co.). Production of Sulfur-Free Water Gas. United States Patent 2,614,038, Oct. 14, 1952; appl. filed Dec. 28, 1945, Serial No. 637,615; 8 claims (*Cl. 48–204*).

Solid carbonaceous material is gasified at 1,400°–2,400° F. in admixture with 0.2–1% by weight, of catalyst useful in promoting cracking of organic S compounds. Re-formation of S compounds is prevented by rapid quenching of the gaseous products to 400°–600° F. Catalysts with suitable cracking activity include Ni, Cu, Ag, Au, Ca, Mg, Ti, Zn thiomolybdates, natural minerals, ores, earth or clays containing oxides or hydrated oxides of Fe, Al, or Si. Bauxite, either alone or in combination with Fe oxides, caustic alkalies, or alkaline earth, is particularly good. 3 literature refs., 1 foreign patent, and 5 United States patents cited.

142. ——— (Standard Oil Development Co.). [Regulating the Activity of Catalysts.] French Patent 930,214, Jan. 20, 1948; appl. filed July 4, 1946; in United States, Dec. 14, 1945. Chem. Zentralb., 1949, II, p. F–57.

Reactions with finely powdered catalysts are carried out in 2 steps in such a manner that the fresh catalysts are used in the 2d step and then, gradually, as their activity declines, moved little by little to the 1st step. The catalyst thus moves countercurrent to the reacting components and is freed from the reaction mixture between the 2 reaction steps. The flow of catalyst in the separate steps is greater, the weaker the catalyst is, with the condition, however, that the amount of catalyst present in the separate reaction chambers is kept constant. The catalyst is transported by being fluidized and elevated to such an extent that at times a certain amount of catalyst substance is carried over into the delivery pipe leading to the preceding zone. The process is applicable to the synthesis of hydrocarbons from CO and H_2. Example: A gas having a CO : H_2 ratio of 0.2 : 0.8 is caused to react at 190°–232° on a finely divided Co catalyst (15–60% passing through a 400-mesh sieve) under 5–10 atm. pressure and under a throughput of 200–500 cc. and a gas flow of 45 cm. per sec. The introduction of catalyst and its replacement are so regulated that a total replacement takes place in about 10–15 days. With Fe catalysts a complete replacement within 100–400 days was found necessary.

143. ——— (Standard Oil Development Co.). Temperature Control in the Catalytic Hydrogenation of Carbon Oxides. United States Patent 2,256,969, Sept. 23, 1941; appl. filed June 12, 1940, Serial No. 340,062; 5 claims (*Cl. 260–449*). Chem. Abs., vol. 36, 1942, pp. 249–250.

Describes apparatus, and a process employed for removing the heat of reaction and maintaining a relatively constant temperature in a reaction involving the hydrogenation of oxides of C for producing hydrocarbon constitutents containing more than 1 C atom in the molecule that comprises passing feed gases containing oxides of C and H_2 in contact with a suitable catalyst under conditions adapted to hydrogenate the oxides of C, whereby exothermic heat is evolved, removing the exothermic heat as it is evolved by utilizing a sufficient quantity of the catalyst and by absorbing the same as sensible heat of the catalyst, separating the heated catalyst from the reaction zone, removing the heat of reaction therefrom by cooling, and again utilizing the cooled catalyst in the reaction zone.

144. ——— (Standard Oil Development Co.). [Water Gas.] French Patent 970,040, Dec. 28, 1950; appl. filed Aug. 5, 1948. Chem. Zentralb., I, 1951, p. 1963.

Finely divided fuels, such as coal, coke, shale, etc., are gasified in a fluidized bed with superheated steam. The gases in the carbonaceous residues are blown out with CO and passed to the gasifier. The residues are passed first into a combustion chamber in which they are heated by circulating O_2-containing gases and then into the gasification chamber. Gases of high heating value and synthesis gases with CO : H_2 in the ratio of 1 : 0.5–5% are obtained.

———. *See* abs. **300, 301, 3252, 3253.**

145. BARR, F. T., AND MARTIN, H. Z. (Standard Oil Development Co.). Manufacture of Gas Mixtures Containing Carbon Monoxide and Hydrogen. United States Patent 2,592,377, Apr. 8, 1952; appl. filed Aug. 8, 1946, Serial No. 689,156; 14 claims (*Cl. 48–206*).

Steam, preheated to about 1,200°–1,600° F., is passed upward through a fluidized bed of finely divided coal in a gas generator where it reacts at 1,600°–1,800° F. to form water gas. About 0.5–3.0 lb. of steam per lb. of coal is sufficient. The gas generation zone also contains a fluidized, finely divided Fe oxide in sufficient amount (2–10 lb. per lb. of coal) to supply the O_2 necessary to support the reaction. Steam velocities of about 1–4 ft. per sec. are maintained, and under the conditions of particle sizes and gas flow the fluidized solids are classified ranging from a lower dense layer consisting substantially of reduced and unreduced Fe oxide to a middle layer of reacting coal and Fe oxide and an upper layer of coal undergoing gasification with steam. The spent oxide can thus be withdrawn from the bottom of the generator and passed to the reoxidizer and then returned to the generator. About 40–130 $ft.^3$ of air per lb. of coal and temperatures of 1,700°–1,900° F. are sufficient to promote reoxidation. The gasification zone is operated at pressures ranging from atmospheric to 400 p. s. i. g.

146. BARR, F. T., AND SCHARMANN, W. G. (Standard Oil Development Co.). Two Stage Synthesis of Hydrocarbons. United States Patent Reissue 23,145, Sept. 6, 1949; original United States Patent No. 2,434,537, Jan. 13, 1948, Serial No. 568,514, Dec. 16, 1944; appl. for reissue filed Jan. 12, 1949, Serial No. 70,566, 13 claims (*Cl. 260–449.6*). Chem. Abs., vol. 42, 1948, p. 2087.

See United States Patent 2,434,537 (abs. **147**).

147. ——— (Standard Oil Development Co.). Two-Stage Synthesis of Hydrocarbons. United States Patent 2,434,537, Jan. 13, 1948; appl. filed Dec. 16, 1944, Serial No. 568,514, 13 claims (*Cl. 260–449.6*). Chem. Abs., vol. 42, 1948, p. 2087.

Fluid catalyst reactor is used in the 1st stage, and a stationary bed reactor is used in the 2d stage. The fluid catalyst operation is used on the fresh synthesis gas under conditions such that only a portion of the gas is converted to hydrocarbons higher than methane. Conversion is limited so that products liquid under the conditions of operation are not formed. The tail gas from this stage is led to fixed catalyst reactors. The concentration of reactants is now low enough that satisfactory temperature control in fixed-bed operation is obtained, and liquid products such as may be formed drain from the catalyst without slowing the reaction. The tail gas from the 2d stage is led to a cooler-condenser and naphtha-recovery plant. Tail gas from the fluid catalyst section may be cooled if desired, but operation taking the gas directly from the separating system is simpler and ordinarily superior. 4 patents and 3 literature refs. cited.

148. Barrick, P. L. (E. I. du Pont de Nemours & Co.). Olefin Reactions. United States Patent 2,542,747, Feb. 20, 1951. Chem. Abs., vol. 45, 1951, p. 7584.

O-containing and N-containing saturated organic compounds are prepared by heating a mixture of an olefinic hydrocarbon, $Co(CO)_4(I)$, and H_2 or NH_3 at 25°–250° under superatmospheric pressure in the absence of CO. Thus, iso-AmOH is prepared in a Ag-lined, high-pressure reaction vessel from (I) 28, $Me_2CH : CH_2$ (II) 56, and cyclohexane (III) 70 parts as solvent, at 285 atm. H_2 pressure; iso-$AmNH_2$ 11+ 5(iso-Am)$_2$NH are prepared from CO 15, (III) 70, and (II) 56 parts at 950 atm. CO pressure at 135° for 15 hr., then, after bleeding off the CO, NH_3 38 and H_2 240 atm. are charged into the reactor and heated to 185°; following this same procedure but omitting the H_2 and heating at 225° gives isovaleramide; EtCHO is prepared from (I) 42, (III) 70 parts, C_2H_4 $2O_2$, and H 40 atm.

149. Barrick, P. L., and Pavlic, A. A. (E. I. du Pont de Nemours & Co.). Acetals. United States Patents 2,491,915, Dec. 20, 1949. Chem. Abs., vol. 44, 1950, p. 3008.

Iso-C_4H_8 28, MeOH 50, finely divided Co 5, and an equimolecular mixture of CO and H_2 heated in a Ag-lined autoclave for 2 hr. at 135°–140° and 800–1,400 p. s. i., followed by distillation, gave $Me_2CHCH_2CH(OMe)_2$ b_{48} 48°–50°, 12 parts; 2,4-dinitrophenylhydrazone, m. 123°–124°. Similarly, diisobutylene 84 yielded a di-Me acetal 80 parts, $C_{11}H_{24}O_2$, b_{50} 109°–111°, n_D^{25} 1.4181, d_4^{25} 0.8436; 2,4-dinitrophenylhydrazone, $C_{15}H_{22}N_4O_4$, m. 92.5°–95.0°.

150. ——— (E. I. du Pont de Nemours & Co.). 3,3-Dialkoxybutyronitriles. United States Patent 2,506,571, May 9, 1950. Chem. Abs., vol. 44, 1950, p. 7344.

Acetals of $NCCH_2CH_2CHO$ prepared by the reductive carbonylation of $CH_2 : CHCN$ (I) in the presence of saturated alcohols or glycols, are useful intermediates in the manufacture of dyes, pharmaceuticals, and pesticides. MeOH 120, (I) 75, tert-butylcatechol 1, reduced Co–thoria catalyst 10, H_2 230 atm., and CO 170 atm., shaken 1 hr. at 150° and 600–900 atm. CO pressure in a Ag-lined autoclave gave 59 gm. γ,γ-dimethoxybutyronitrile, b_{14} 90°–91°. $(CH_2OH)_2$ 110 gm gave 12 gm. 2-(2-cyanoethyl)dioxolane, b_6 71°–75°, n_D^{21} 1.4248. Derivatives of these compounds may be used in or as lubricating oils or as additives.

Bartholome, E. *See* abs. **3225.**

151. Baum, K. (Didier-Werke A. G.). [Continuously Operated Vertical Chamber Oven for the Production of Synthesis Gas by the Direct-Current Method.] German Patent 715,531, Nov. 27, 1941; appl. D. 74,918, filed March 1937 (*Cl. 26a–8.01*). Chem. Abs., vol. 38, 1944, p. 2189.

152. Baumann, W. [Removing the Catalyst Used for Synthesizing Benzine From the Contact Oven.] German Patent 715,759, Dec. 4, 1941; appl. B 180,408 filed Oct. 22, 1937 (*Cl. 12o–1.03*). FIAT Reel AA–90, frames 1,436–1,439; PB 70,275; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 6, chap. 172, 1949, p. 26; Chem. Abs., vol. 38, 1944, p. 2188.

The catalytic mass consists of metals of the 8th group, oxides of metals of the 4th group, and a filler. To remove this mass from the reaction chamber, the mass is broken up by the action of NaOH and steam, then it is carried out by the mechanical action of steam, compressed air, or hot H_2O.

153. Bayerische Stickstoff-Werke A. G. Improved Process for Making Carbon Black and Hydrogen or Hydrogen-Containing Gases. British Patent 493,929, Jan. 11, 1937.

C_2H_2 or waste gases, for example, from coal hydrogenation or benzine synthesis, are thermally cracked with or without additional substances, for example, $Fe(CO)_5$, and the cracking products chilled directly after their formation.

154. ———. [Methane From Carbon Oxides and Hydrogen.] German Patent Appl. B 203,626, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 16.

CH_4 is produced from H_2 and C oxides by using a catalyst arranged on a metal carrier in a thin layer.

Beati, E. *See* abs. 2523.

155. Beck, C., and Kremp, F. (I. G. Farbenindustrie A. G.). [Oxidation Products of Mixtures Rich in Solid, Crude Paraffins.] German Patent 716,506, Jan. 24, 1942; appl. I 54,189 filed Jan. 31, 1936 (*Cl. 12 o–11*). Chem. Abs., vol. 38, 1944, p. 2343.

Substances such as brown-coal tar, crude paraffin, coal- or tar-hydrogenation product, and others are freed of whole or most of their oily components with, for example, nitrobenzene. Then they are oxidized with HNO_3 or with nitrous gases. The oxidation products are finished in the usual way.

156. ——— (I. G. Farbenindustrie A. G.). Oxidation Products of Paraffin Hydrocarbons. United States Patent 2,158,650, May 16, 1939. Chem. Abs., vol. 33, 1939, p. 6873.

See British Patent 482,954 (abs. **155**) and German Patent 716,506 (asb. **1368**).

157. Beck, C., and Weissbach, H. (I. G. Farbenindustrie A. G.). [Soaps and High-Molecular Fatty Acids.] German Patent 695,647, Aug. 1, 1940 (*Cl. 23 e–1*). Chem. Abs. vol. 35, 1941, p. 5734.

High molecular fatty acids, derived from oxidation of paraffins, are saponified in stages. Only 10–30% of the acid value in saponifying agent is added at first. The H_2O-soluble part is separated and the residue saponified in the usual way. The soaps can then be decomposed with acids.

Beck, R. A. *See* abs. **3327, 3328, 3329, 3330, 3331, 3333.**

158. Beck, R. A., and Millendorf, A. J. (The Texas Co.). Process and Apparatus for Effecting Catalytic Reactions. United States Patent 2,540,706, Feb. 6, 1951; appl. filed May 22, 1947, Serial No. 749,848; 9 claims (*Cl. 260–449.6*).

The invention is an improvement of United States Patent 2,501,695 (abs. **3331**). Gives apparatus for agitating catalyst particles in Fischer-Tropsch synthesis.

The upright cylindrical reactor is fitted with a helical screwlike impeller rotatably supported to agitate catalyst particles furnished at its base, scooping and elevating them into the reaction zone. A 2d short, reversely directed, helical, screwlike impeller, progressing in the opposite rotational direction and preferably rotated with it, impinges catalyst particles lifted above the 1st helical screw and directs them downward or laterally. The surfaces of the 1st helical screw may occupy only a portion of the reaction zone, allowing gravity to take the catalyst down. Means may be provided for directing particles projected above the reaction zone to a stripping zone. 3 United States patents cited.

159. BECK, R. A., AND SENSEL, E. E. (The Texas Co.). Carrying Out Catalytic Reactions. United States Patent 2,492,349, Dec. 27, 1949; appl. filed Nov. 26, 1946, Serial No. 712,410; 6 claims (*Cl. 260–449.6.*). Chem. Abs., vol. 44, 1950, p. 2293.

Reaction zone has a series of scoop-or funnel-shaped baffles spaced vertically apart in the line of flow of the fluid reactants. The funnel shape tends to jet the flow as a relatively restricted stream at a relatively high rate of speed with substantial entrainment of the catalyst particles. The upper surface of each baffle is convex. About the lateral margins of the baffle where the upward rate of flow is less, the entrained catalyst is free to gravitate downward into the space below the baffle from which it was jetted. 2 foreign patents cited.

160. ——— (The Texas Co.). Hydrocarbon Synthesis. United States Patent 2,640,845, June 2, 1953; appl. filed May 1, 1947, Serial No. 745,358; 6 claims (*Cl. 260–449.6*) Chem. Abs. vol. 47, 1953, p. 7839.

The invention is particularly applicable to catalytic reduction of CO with H_2. Uniform contact and prevention of slugging are obtained by changing the direction of movement of the reactant stream with stationary baffles configurated to induce rotational or whirling motion. Vertical discontinuity of the baffle is essential. The flow of gases containing the fluid phase is repeatedly subjected to a whirling type of distribution in predetermined zones. In between these zones the mixed phase tends to readjust itself more or less to the general upflow of reactant gas. 3 foreign and 12 United States patents cited.

161. BECK, R. A., SENSEL, E. E., AND MILLENDORF, A. J. (The Texas Co.). Hydrocarbon Synthesis. United States Patent 2,464,480, Mar. 15, 1949; appl. filed Dec. 3, 1946, Serial No. 713,844; 7 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 4448.

Activity of a Co catalyst can be maintained at a high level of activity with relatively constant product distribution by periodically or progressively, as activity tends to diminish, incorporating an alkali metal compound, such as sodium, carbonates, bicarbonates, hydroxides. The proportion of alkali metal is thus increased over the maximum present in the catalyst during any previous period of operation. 3% of alkali metal, based on weight of Co, represents the upper limit to which the alkali metal can advantageously be raised. The operating temperature is raised to the new optimum level. With additions of 0.3–0.4% alkali metal to a typical Co catalyst, the increase in temperature is generally 9°–18° F. The addition may be made by spraying an aqueous solution of the alkali metal on the catalyst particles from numerous points and drying the catalyst before reuse. The method is applicable to fixed-bed, fluid, or foam-type reactions. 4 United States patents cited.

162. ——— (The Texas Co.). Preparation and Use of Synthesis Catalysts. United States Patent 2,550,442, Apr. 24, 1951; appl. filed Jan. 4, 1946, Serial No. 639,166; 2 claims (*Cl. 260–449.6*).

In preparing supported synthesis catalysts, such as Co or Ni, alkaline compounds of NH_3, such as $(NH_4)_2CO_3$ or NH_4OH, are used to precipitate these metals from the slurry of supporting material in which they are present in the form of their soluble salts. After precipitation, the catalyst is reduced with H_2 during which action the excess NH_3 compound precipitating agents are decomposed into gaseous components that are readily removed. By employing the alkaline NH_3 compounds, the use of alkali metal compound precipitating agents, such as Na or K carbonate, whose presence is claimed to have a deleterious effect on Co and Ni catalysts, is avoided. Also avoided is the plurality of washings needed to remove any excess of alkali metal compound that remains after precipitation. It is also claimed that a catalyst that is prepared by using $(NH_4)_2CO_3$ gives about 20% better yields of liquid hydrocarbons than does a catalyst prepared by using NA_2CO_3, even though adequate provision is made to remove thoroughly the excess alkali metal by repeated washings. 5 United States patents and 1 literature ref. cited.

BECKE, F. *See* abs. **3657.**

BECKER, S. B. *See* abs. **1777.**

163. BECKHAM, L. J. (Allied Chemical & Dye Corp.). Nitrosyl Chloride-Olefin Addition Products. United States Patent 2,435,570, Feb. 10, 1948. Chem. Abs., vol. 42, 1948, p. 2983.

Gaseous or liquid NOCl is added to an olefin containing 12–30 C atoms. Example: 100 parts of a mixture obtained from the dehydration of alcohols prepared by the hydrogenation of fatty acids from coconut oil and consisting largely of 1–$C_{12}H_{24}$ and 1–$C_{14}H_{28}$ with small amounts of other olefins are mixed at about 0° with 96 parts liquid NOCl. After 5 hr. excess NOCl is removed with a stream of dry air, leaving the green-colored adducts of the olefins. In like manner are prepared the adducts of 1–$C_{16}H_{32}$ obtained by cracking paraffin wax at 403°–425°, a fraction b. 200°–300° from the reaction of CO and H_2 at 185°–190° over Co on kieselguhr; and a fraction $b._{50}$ 131°–250° from the cracking of a wax by-product from the Fischer-Tropsch hydrogenation process.

164. BECKMANN, E., AND AUREDEN, H. (F. Krupp A. G.). [Heat Exchanger for Heat-Exchanging Mediums Working Under Pressure Suitable for Chemical Processes.]. German Patent 729,339, Nov. 19, 1942 (*Cl. 12 g–2.01*). Chem. Abs., vol. 38, 1944, p. 285.

165. BEDFORD, F., AND WILLIAMS, C. E. (Cedford Gas Process Co.). Catalytic Synthesis of Methane. United States Patent 983,199, Jan. 31, 1911; appl. filed Feb. 25, 1910, Serial No. 546,016. Chem. Abs., vol. 5, 1911, p. 1184.

Catalytic synthesis of CH_4 from a commercial gas containing H_2 and CO, comprising cooling the gas to about −190° to −180° to separate out in the solid form impurities having little or no vapor tension in such manner that the H_2 retains the requisite amount of CO, passing the mixture into contact with a heated catalytic substance, as Ni heated to 250°, in the presence of an excess of N_2, and separating the CH_4. The gas used is subjected to a preliminary treatment, as with Na_2CO_3 solution, to remove the CO_2. The cooling may be sufficient to condense substantially all the CO, which is then distilled and if desired may be further purified and separated from N_2 by absorption in Cu_2Cl_2 solution and distillation.

166. ——— (Cedford Gas Process Co.). Catalytic Synthesis of Methane. United States Patent 989,755, Apr. 18, 1911. Chem. Abs., vol. 5, 1911, p. 2172.

Catalytic synthesis of CH_4 from a commercial gas containing H_2 and CO—for example, Mond or Duff gas—by cooling, after removal of CO_2, to separate out

in the solid form at —190° impurities having little or no vapor tension; separating the purified gas into its constituents, such as by absorption of CO by Cu_2Cl_2 and subsequent heating to recover the CO; and mixing the CO thus obtained with H_2 in the required quantity and passing the mixture into contact with a heated catalyst such as Ni.

BEECK, O. A. *See* abs. **3355.**

167. BELCHETZ, A. (M. W. Kellogg Co.). Preparation of Hydrogen-Carbon Oxide Mixtures and Catalytic Reactions Thereof. United States Patent 2,577,563, Dec. 4, 1951. Chem. Abs., vol. 46, 1952, p. 2271.

CO and H_2 are produced by oxidation at 1,650° F. of CH_4 or other hydrocarbon gases over Fe, Cu, Co, or Ni oxides. The catalytic material serves as a heat-transfer agent and in the reduced form at 600° F. as the fluidized catalyst for the hydrogenation of CO. Spent catalyst from the oxidation of CH_4 and hydrogenation of CO is regenerated at 1,850° F. in a common catalyst oxidation zone. Montmorillonite-type clays, such as Ittawamba clay, containing 5% Fe_2O_3 and 1.3% TiO_2, are satisfactory as catalysts after activation with H_4S at room temperature followed by roasting at 1,000°–1,400° F., at which temperature the sulfide is converted to the oxide.

168. BENEDICT, M., FAATZ, A. C., JR., AND WOEBCKE, H. N. (Hydrocarbon Research, Inc.). Hydrocarbon Synthesis Process and the Production of Synthesis Gas. United States Patent 2,649,468, Aug. 18, 1953; appl. filed Nov. 12, 1947, Serial No. 785,552; 4 claims (*Cl. 260–449.6*).

Claim 1. In a process for the generation of CO and H from coal, wherein coal is reacted with O_2 and steam to produce a gas stream rich in CO and H_2 and containing CO_2 and hydrocarbons, the improvement comprises separating CO_2 from said gas stream and thereafter converting the hydrocarbons to additional CO and H_2 by reacting said hydrocarbons in admixture with said CO and H_2 in said gas stream with substantially pure O_2 in an amount sufficient only for reaction with said hydrocarbons at a temperature within the range of 2,000°–2,500° F. and a pressure above 20 atm. in an unpacked reaction zone and in the absence of a catalyst to produce CO and H_2 substantially free from hydrocarbons and CO_2.

169. BENNETCH, L. M. (Reconstruction Finance Corp.). Black Oxide of Iron. United States Patent 2,631,085, Mar. 10, 1953. Chem. Abs., vol. 47, 1953, p. 7172.

Yellow oxide of $Fe(Fe_2O_3 \cdot H_2O)$ is combined with $FeO \cdot H_2O$ in an aqueous slurry to yield black magnetic oxide of $Fe(Fe_3O_4)$. $FeSO_4$ solution is treated with just enough NaOH to precipitate approximately 65% of the Fe as $FeO \cdot H_2O$. The slurry is oxidized at room temperature with air to form $Fe_2O_3 \cdot H_2O$ from the precipitate, and the slurry is then made slightly alkaline by adding NaOH to precipitate the balance of the Fe in solution as $FeO \cdot H_2O$. The mixture of hydrates is filtered, washed, and heated for 2 hr. at 200° F. to produce the black oxide.

BENSON, H. E. *See* abs. **451.**

170. BERENBRUCH, A. (I. G. Farbenindustrie A. G.). Apparatus for Exothermic Catalytic Gas Reactions. United States Patent 1,869,736, Aug. 2, 1932. Chem. Abs., vol. 26, 1932, p. 5230.

Tubes containing the catalyst are closely packed together in a bundle in a reaction chamber. Describes various structural details.

171. BERG, C. H. O. (Union Oil Co. of California). Adsorption Process and Apparatus for Separating Gaseous Hydrocarbon Mixtures. United States Patent 2,609,887, Sept. 9, 1952. Chem. Abs., vol. 47, 1953, pp. 849–850.

Gaseous hydrocarbon mixtures are separated by passing a moving bed of solid granular absorbent through a vertical column consisting of a succession of individual adsorption and reflux zones; the rich absorbent thus formed is passed successively through a heating zone, a seal gas-removal zone, and a cooling zone immediately before being removed from the bottom of the column for reuse. An example of the column operation is the fractionation, by absorption, of a cracked petroleum hydrocarbon gas, which was fed at 150 p. s. i. into a 12-ft.-diameter column at the rate of 2,141 lb.-moles per hr. by using 330,000 lb. of activated vegetable charcoal per hr. The 4 fractions obtained consisted essentially of a H_2–CH_4 mixture, a pure C_2 fraction of ethane and ethylene, a pure C_3 fraction of propane and propylene, and a C_4-rich fraction containing also C_5 and higher hydrocarbons.

172. ——— (Union Oil Co. of California). Apparatus for Coal Gasification. United States Patent 2,627,455, Feb. 3, 1953. Chem. Abs., vol. 47, 1953, p. 4065.

———. *See* abs. **2752.**

173. BERGFELD, K. [Generating Water Gas.] German Patent 724,873, July 23, 1942 (*Cl. 24 e–1.07.*) Chem. Abs., vol. 37, 1943, p. 5850.

Oxyhydrogen gas is used in the combustion.

174. ———. [Generating Water Gas.] German Patent 730,968, Dec. 24, 1942 (*Cl. 24 e–1.07*). Chem. Abs., vol. 38, 1944, p. 634.

The process described in German Patent 724,873 (abs. **173**) is used for generating water gas.

175. BERGIUS, F. Gases for Hydrogenation. United States Patent 1,699,177, Jan. 15, 1929; appl. filed Nov. 30, 1925. Chem. Abs., vol. 23, 1929, p. 1252.

Waste hydrogenation gas, such as that from the hydrogenation of coal, is subjected to steam treatment in 2 successive stages at different temperatures; in the 1st stage the higher temperature is used (suitably about 1,100°), which is high enough to decompose CH_4 in the absence of a catalyzer and to cause formation of CO and H_2; the 2d stage may be effected at a temperature of about 300°–500° in the presence of a catalyzer such as Fe oxide adapted to enhance the reaction between CO and steam. Describes arrangement of apparatus.

176. ———. [Hydrogen and Carbon Dioxide From Carbon and Water.] German Patent 259,030, June 24, 1911. Chem. Abs., vol. 7, 1913, p. 2670.

The same volume of CO_2 and H_2 as of water gas may be obtained at a low temperature according to the equation: $C+2H_2O=CO_2+2H_2$. For the same amount of coal, double the amount of H_2 is obtainable as when CO is formed according to the equation: $C+H_2O=CO+H_2$. The process consists of reacting C with H_2O in the liquid state at a high temperature, not above the critical temperature. A catalyst such as a Th compound or Mn compounds may be employed. The operation must be conducted in a pressure vessel. Details specified.

177. BERGWERKSGESELLSCHAFT HIBERNIA. [Benzo l.] German Patent Appl. B 199,292, no date (*Cl IV d–12 o*). Auszüge deut. Patent Anmeldungen, vol. 6, p. 12. Obtaining pure benzol from CO and H_2 in presence of an Fe-Mn-K-Co catalyst.

178. ———. [Toluol.] German Patent Appl. B 199,586, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent Anmeldungen, vol. 6, p. 12.

Toluol is obtained by passing a gas mixture of benzol, CO, and H_2 at 400°–600° over a catalyst of ZnO or CdO and Al_2O_3 or ThO_2 and then over a cokelike substance.

179. BERLINER, J. F. T. (E. I. Du Pont de Nemours & Co.). Motor Fuel. United States Patent 2,010,005,

Aug. 6, 1935; appl. filed Apr. 6, 1932, Serial No. 603,679 (*Cl 44–9*).

Lubricated motor fuel comprising by volume 60–75% MeOH, 24–10% liquid byproducts of the catalytic hydrogenation of CO to MeOH boiling in the range 133°–200°, gasoline not exceeding ½ the volume of the liquid byproducts and not exceeding 15% of castor oil.

180. BERTSCH, H., AND SCHMITT, F. (Böhme Fettchemie G. m. b. H.). [Deliming Hides.] German Patent 716,747, Dec. 24, 1941 (*Cl. 28 a–2*). Chem. Abs., vol. 38, 1944, p. 2522.

Fatty acids, b. 140°–200°, obtained as first runnings from paraffin oxidation products, are used for deliming. The fatty acids are used as an aqueous emulsion.

See also German Patent 713,915 (abs. **1893**).

BETHEA, S. R. *See* abs. **3273.**

181. BEWLEY, T., AND BRAMWYCHE, P. L. (Distillers Co., Ltd.). Hydrogenation Catalysts by Reduction. British Patent 662,907, Dec. 12, 1951. Chem. Abs., vol. 46, 1952, p. 11513.

Improved hydrogenation catalysts are prepared by the H reduction of a kieselguhr-suported Cu or Ni compound suspended in a liquid containing an organic polysiloxane, preferably polydimethylsiloxane.

182. ——— (Distillers Co., Ltd.). Preparation of Hydrogenation Catalysts by Reduction. United States Patent 2,623,078, Dec. 23, 1952; appl. filed Aug. 8, 1950, Serial No. 178,360, in Great Britain Aug. 19, 1949; 15 claims (*Cl. 260–690*).

Active hydrogenation catalysts are prepared by treating a kieselguhr-supported Cu or Ni compound. which is reducible to the metal with H_2 while the compound is suspended in a liquid medium such as organic polysiloxane. The reduction may be a preliminary step or the material to be hydrogenated may be present. 2 United States patents cited.

183. BICHOWSKY, F. R. (Delco-Light Co.). Methyl Ether. British Patent 278,353, Sept. 28, 1926. Chem. Age, vol. 17, 1927, p. 515; Chem. Abs., vol. 22, 1928, p. 2573.

Mixture of Co and H_2 is passed at an elevated temperature and pressure, suitably 500° and 125 atm., over a hydrogenation catalyst, suitably ZnO and reduced Cu or Cr salts but excluding Fe, and then over a dehydration catalyst or over a mixture of both catalysts; or, MeOH may be passed over a dehydration catalyst. Alumina prepared by partly dehydrating $Al(OH)_3$ at 300°, partly dehydrated Ti hydroxide, Th hydroxide, or silica gel may be used as dehydration catalysts, Gives various details. Describes apparatus.

184. BIEDERBECK, H. (Ruhrchemie A. G.). [Sluice-like Device for Feeding Small-Lump Reagents Into Gas-Treating Installations.] German Patent 729,729, Nov. 26, 1942 (*Cl. 12 f–4*). Chem. Abs., vol. 38, 1944, p. 284.

See abs. **713.**

185. BILISOLY, J. P. (Standard Oil Development Co.). Catalytic Conversion. United States Patent 2,509,204, May 30, 1950; appl. filed Feb. 18, 1946, Serial No. 648,555; 4 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 8092.

Satisfactory yields of valuable motor fuels are obtained when CO and H_2 are reacted at 400°–450° F., preferably 415° F., and low pressure 1–10 atm., preferably atmospheric in presence of a catalyst containing Co, preferably with Fe on a magnesia base carrier. Other active components, such as Ni, Mo, or Th, may be used in combination with the Co and Fe. Preferred promoters are those obtained by adding K compounds, such as KOH, K_2CO_3, KNO_3, or KCl to the original composite. In general the catalysts contain 20–60 parts by weight of the active component, Fe+Co (calculated as metals), 40–80 Mg, 0.5–10 promoter and 1–20 stabilizer. 1 literature ref, and 10 United States patents cited.

186. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis Process. United States Patent 2,496,265, Feb. 7, 1950; appl. filed July 25, 1944, Serial No. 546,583; 12 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 3701.

Silica hydrogel is prepared by reaction of an aqueous sodium silicate solution with H_2SO_4, HCl, or HNO_3. After the mixture sets, it is washed to remove the water-soluble salts and is impregnated with a mixed solution of water-soluble salts of the hydrogenation type metals of the VIII group and the water-soluble sales of difficultly reducible metal oxides. The excess solutions are drained. The gel is dried and heated to the lowest temperature necessary to effect decomposition of the metal salts. The catalyst is ground to 20- to 200-micron size and reduced in a stream of H_2, temperature 600°–800° F., space velocity 4,000–6,000 vol. feed gas per volume catalyst per hr. for 1–4 hr. Before reduction the H_2O content may be reduced 6–10%. The gel carrier may be spherically shaped. 1 literature ref., 1 foreign patent, and 10 United States patents cited.

187. BINDLEY, W. T. R. Hydrocarbon Oils. British Patent 394,506, June 29, 1933. Chem. Abs., vol. 28, 1934, p. 308.

Hydrocarbon oils are produced by passing mixtures of CO and H_2 at atmospheric pressure and at 208°–230° over catalysts consisting of oxides of Co and Mn, with which may be mixed Cr as metal or oxide and Ce oxide. The powdered or granular catalysts are attached to supports by spraying or otherwise coating the support with a Si ester and sprinkling the catalyst onto it while it is still tacky.

188. BIRCH, S. F., AND HABESHAW, J. (Anglo-Iranian Oil Co.). Hydrocarbons From Carbon Monoxide and Hydrogen. British Patent 618,455, June 12, 1946, Feb. 22, 1949. Chem. Abs., vol. 43, 1949, p. 5573.

Fischer-Tropsch synthesis of hydrocarbons from CO and H_2 modified by adding at least 2–5 mol. % of C_2H_4 or C_3H_8 to the charge gave products with higher content of olefin and branched-chain hydrocarbons. Considerable quantities of oxygen-containing compounds were obtained. Operating temperatures were less critical, and the design of full-scale converters for the synthesis was thus simplified.

BIRCHER, J. .R *See* abs. **513.**

BIRIBAUER, F. A. *See* abs. **2406.**

189. BLACK, J. F. (Standard Oil Development Co.). Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,435,551, Feb. 3, 1948. Chem. Abs., vol. 42, 1948, p. 2419.

CO and H_2 are reacted at 300°–450° F. in the presence of a fluidized catalyst comprising Ni chromite prepared by combining at elevated temperature and under agitation an aqueous solution of a Ni salt with an ammoniacal solution of NH_4 chromate and separating, drying, and calcining the precipitate formed. The use of the novel catalyst makes unnecessary the otherwise required accurate temperature control of the Fischer-Tropsch process.

190. ——— (Standard Oil Development Co.). [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 915,586, Nov. 12, 1946; appl. filed Oct. 8, 1945; in United States, Apr. 20, 1944. Chem. Zentralb., 1949, II, p. E–145.

Catalyst for the process consists of Ni chromite or a mixture of reduced Ni and Cr oxides supported on kieselguhr or silica gel. It is preferably in the finely powdered and fluidized state. It is distinguished by a limited sensitivity to temperature changes so that a

close temperature control, as in previous catalysts, is unnecessary. The optimum reaction temperature is 177°–190°, with a throughput of about 100–150 vol. of gas per vol. of catalyst per hr. and atmospheric pressure.

191. ——— (Standard Oil Development Co.). Synthetic Adsorbent for Separating Hydrocarbons. United States Patent 2,442,191, May 25, 1948; appl. filed June 23, 1945, Serial No. 610,329 (*Cl. 252–270*). Chem. Abs., vol. 42, 1948, p. 5628.

Adsorbent for straight-chain hydrocarbons, particularly n-paraffins, consists of a mixture of hydrous oxides having the empirical formula $4CaO \cdot Al_2O_3 \cdot 4SiO_2$ and prepared by reacting a hydrous oxide of Al, a hydrous oxide of Si, and $Ca(OH)_2$ in the presence of a solution of 1–10% concentration of a salt of the group II element, such as $CaCl_2$ or Ca acetate, for 48–216 hr. at 220°–400°. After thus heating, the material is cooled to room temperature and dehydrated. Increasing the heating time increases the adsorptive capacity of the material. 1 literature ref. and 7 United States patents cited.

192. Black, J. F., and Kearby, K. K. (Standard Oil Development Co.). [Catalysts for the Conversion of Carbon Monoxide With Hydrogen.] French Patent 970,823, Jan. 9, 1951; appl. filed Apr. 28, 1948. Chem. Zentralb., 1952, I, p. 1269.

Catalysts comprise mainly Fe and a metal soluble in alkaline solutions such as Si or Al. The mixture is applied in the form of an alloy containing 85% Fe and 15% Si. The catalyst particles contain in their outer layers a larger % of Fe than do the inner layers. To accomplish this the catalyst particles are treated with NaOH or K_2CO_3 solution, which dissolves out a part (1.5–3%) of the Si in the outer layers. According to an example, aqueous solutions containing 15–20% of NaOH or a corresponding amount of K_2CO_3 are used.

193. ——— (Standard Oil Development Co.). Catalytic Conversion. United States Patent 2,542,464, Feb. 20, 1951; appl. filed Dec. 22, 1945, Serial No. 637,099; 3 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 4431.

Gives preparation for an Fe catalyst containing 0.1–10%, preferably 1%, of the Fe oxide as F compound of K as promoter. The Fe oxide is moistened with an aqueous solution of KF of suitable concentration and the catalyst is dried and pilled. It may be reduced in H_2 for 2–6 hr. at 600°–1,400° F. and sintered in non-oxidizing atmosphere at 1,000°–1,800° F. for several hours. Convention conditions for Fe catalyst are used in carrying out hydrocarbon synthesis with this catalyst. 3 United States patents cited.

194. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,593,250, Apr. 15, 1952; appl. filed July 30, 1947, Serial No. 764,928, 2 claims (*Cl. 260–449.6*).

Valuable conversion products are produced from CO and H_2 in the presence of Fe catalysts by contacting the CO and H_2 in synthesis proportions and under synthesis conditions with catalyst particles containing ferrosilicon from which about 1.5–3 wt. % of silicon based on the total catalyst has been removed by etching with a caustic alkali solution.

195. Blanchard, D. W., Lauer, G. G., and Pratt, R. S. (M. W. Kellogg Co.). Separations of Aldehydes and Ketones. United States Patent 2,552,513, May 15, 1951; appl. filed July 24, 1948, Serial No. 40,618; 11 claims (*Cl. 260–450*).

Substituted ammonias from the group consisting of hydroxylamine, hydrazine, and their salts are used to treat a hydrocarbon mixture containing nonacid oxygenated compounds produced by the hydrogenation of C oxides to selectively remove aldehydes from the mixture and thus facilitate subsequent separation of remaining ketones. This treatment converts the aldehydes and a minor portion of ketones to their corresponding oximes. The whole reaction mixture is then neutralized and subjected to a distillation procedure that separates the high-boiling oxime fraction from the rest of the hydrocarbons, which are relatively low-boiling. The oxime fraction is next acidified to convert the oximes to their corresponding pure aldehydes and ketones, which are then separated from the resulting reaction product by distillation. The low-boiling hydrocarbon mixture can be subjected to any known process, such as distillation or chromatographic absorption, to effect separation of pure ketones that have not entered into the previous oxime reaction. 2 United States patents and 1 literature ref. cited.

196. Blanding, F. H. (Standard Oil Development (Co.). Fluidized-Catalyst Regeneration. United States Patent 2,454,373, Nov. 23, 1948. Chem. Abs., vol. 43, 1949, p. 1956.

Spent or fouled catalyst particles (I) in the hydrocarbon conversion operation containing coke or carbonaceous material are sprayed into regeneration gases (II) containing only a small quantity of suspended (I). The injected (I) reduce the temperature in the (II) because of their high specific heat and their temperature, which is about 23°–38° lower than the regeneration temperature. Enough (I) is injected to reduce the O_2 concentration to 1.6%, or below, thus preventing afterburning. Includes drawing.

197. Blass, K., and Bruecke, O. [Separating Unsaponifiable Compounds From Oxidation Products of Higher Molecular Hydrocarbons.] German Patent Appl. —, filed Mar. 13, 1941; APC 383,242.

Paraffin gatsch, obtained by the Fischer-Tropsch synthesis from CO_2 and H_2, is oxidized to crude fatty acids containing as high as 60% unoxidized or partly oxidized products. Theoretical Na_2CO_3 or NaOH required for saponification of the fatty acids is added in an autoclave, heat applied, and saponification completed under a pressure of 7 atm. The mixture is dehydrogenated under pressure, transferred to a distillation vessel agitated, and treated with steam and heated in vacuo to 335° C. Hydroxy acids, lactones, etc. are converted to fatty acids. Half of the unsaponifiable materials are distilled off while the mixture remains thinly liquid. The steam is shut off and a high vacuum is gradually applied, and everything distillable is driven off. The temperature is held above 290° C. Treatment with H_2O in an autoclave yields a liquid soap, which on decomposition with H_2SO_4 gives fatty acid that may be further distilled in known manner.

198. Blondelle, R. (Société des mines de Dourges). Treating Blowoff Gas From Hydrogen Production by the Iron-Water-Vapor Reaction. United States Patent 2,018,118, Oct. 22, 1935; appl. filed Jan. 9, 1.931. Chem. Abs., vol. 30, 1936, p. 255.

Cyclic process for obtaining a mixture of H_2 with CO and a small proportion of N_2 and only traces of hydrocarbons involves first causing coke oven gases to pass over Fe oxides at about 750° in H_2-producing apparatus of the Fe–H_2O–steam type, then causing the resultant gases to pass continuously through a mass of coke externally heated to about 1,200°, and collecting the gaseous mixture passing from the mass of coke (the coke being particles small enough to offer high contact surface without causing excessive loss of pressure in the apparatus). Describes apparatus.

199. Bloomfield, G. Zinc Oxide Catalysts. United States Patent 1,668,838, May 8, 1928; appl. filed June 21, 1926. Chem. Abs., vol. 22, 1928, p. 2247.

In preparing a catalyst suitable for use in MeOH synthesis or other processes, ZnO is combined with a solution of NH_4NO_3, and the mass is ignited.

———. *See* abs. **3970, 3971, 3972, 3973, 3974, 3975, 3976, 3977, 3978, 3979, 3980, 3981, 3982, 3983, 3984.**

200. BLUDWORTH, J. E., AND KOTZEBUE, M. H. (Celanese Corp. of America). Cooling Reaction Gases. United States Patent 2,497,973, Feb. 21, 1950; appl. filed Nov. 11, 1944, Serial No. 563,054; 3 claims (*Cl. 260–451*). Chem. Abs., vol. 44, 1950, p. 4230.

Reaction gases are quenched with H_2O, then passed through a turbine where the pressure is allowed to drop. The temperature drops and power is developed. H_2O is condensed and collected in an accumulator or scrubber connected to the turbine. The gases go from the scrubber to a H_2O absorber, where the oxygenated compounds are removed. Heat of compression causes the temperature to rise, and this heat is removed by a cooler between the compressor and the absorber. Unreacted gases are recycled to the reaction zone. The centrifugal compressor may be placed on the discharge side of the H_2O absorber, which eliminates the necessity of having the compressor made of stainless steel. The process is applied to the partial oxidation of hydrocarbons to obtain organic oxygenated compounds. 8 United States patents cited.

BOEGEL, M. J. *See* abs. **1062.**

BÖHME FETTCHEMIE G. m. b. H. *See* abs. **180, 1893, 2094, 3297, 3298.**

BOLT, B. M. *See* abs. **2753.**

201. BOND, H. A. (Roessler & Hasslacher Chemical Co.). Temperature Control of Exothermic Reactions. United States Patent 1,888,066, Nov. 15, 1932; appl. filed Apr. 2, 1930. British Chem. Abs., 1933, B, p. 768.

Only the end of the catalyst body is cooled. This causes the heat to be removed in lines parallel to the gas flow rather than transversely.

202. BOOTH, N., AND JOLLEY, L. J. Purification of Gases. British Patent 572,471, July 9, 1941. British Abs., 1946, I, B, p. 54.

Catalyst suitable for reducing the organic S compounds to H_2S is prepared by depositing Fe, by thermal decomposition at 400°–450° of $Fe(CO)_5$, on porcelain rings, porous pot, glass beads, Cu gauze, or other support. The operating temperature is not less than 450°. Spent catalyst is reactivated by oxidation and subsequent reduction at not less than 450°. The degree of purification depends on the space velocity V (vol. per vol. per hr.). At V=400° and 500°, the organic S in coal gas previously freed from H_2S is reduced to <1 grain per 100 cu ft. By combining the process with a prior oil scrubbing to remove the more resistant S compounds, the residual organic S is brought to <0.1 grain per 100 cu. ft.

203. BOOTH, N., JOLLEY, L. J., AND TEBBOTH, J. A. Catalyst for Gas Reactions. British Patent 579,427, Nov. 30, 1943. British Abs., 1946, B, p. 369; Chem. Abs., vol. 41, 1947, p. 2228.

Catalyst for conversion of CO into other products, as in the water-gas shift reaction or synthesis of CH_4, comprises Ni, a support, for example kieselguhr, and a difficultly reducible metal oxide, such as ThO_2 or MgO, in which is incorporated a small amount of a phosphate, such as $NaPO_3$ or K_3PO_4.

204. BORDENCA, C. (Sloss-Sheffield Steel & Iron Co.). Conversion of Aromatic Hydrocarbons to Aldehydes and Alcohols. United States Patent 2,619,506, Nov. 25, 1952. Chem. Abs., vol. 47, 1953, p. 8091.

Useful saturated cyclic aldehydes and alcohols are prepared by bringing an active Co or Ni hydrogenation catalyst, such as thoria-promoted, freshly reduced Co–kieselguhr (I), at 150°–300° and at least 250 p. s. i. pressure into contact with a mixture of H_2, CO, and an unsubstituted or alkyl-substituted aromatic hydrocarbon, until the reaction pressure, which gradually falls during the process, ceases dropping. Thus, H is forced into a high-pressure reaction vessel containing a 175 gm. C_6H_6 and 2 gm. (I), until the pressure reaches 1,550 p. s. i. The vessel and its contents are heated to 169° until a reduction in pressure occurs, signifying that the reaction has begun, the pressure is raised to 2,380 p. s. i. with CO, the vessel heated at 230° until another pressure drop occurs, CO again added, and the vessel heated at 260° until the pressure drops; this process is continued 4 hr. until no further pressure drop is apparent, the reaction vessel is cooled, and the gas allowed to escape. Fractional distillation of the product yields cyclohexane and a higher-boiling fraction identified as hexahydrobenzaldehyde as its semicarbazone, m. 170°, and by oxidation with alkaline permanganate to cyclohexanecarboxylic acid.

205. BORDENCA, C., AND LAZIER, W. A. (Food Machinery & Chemical Corp.). Reaction of Limonene With Carbon Monoxide and Hydrogen. United States Patent 2,584,539, Feb. 5, 1952; appl. filed July 20, 1946, Serial No. 685,241; 3 claims (*Cl. 260–598*).

Original Roelen patent (United States Patent 2,327,066, abs. **2803**) for the production of oxygenated C compounds does not produce according to instructions any substantial amounts of aldehydes and ketones but rather an intractable tar as the principal product. It became obvious from experiments carried out to convert limonene, for example, to a carbonylic derivative by reaction with CO and H_2 that catalysts other than those mentioned in the original patent would be necessary. In accordance with the present invention, it was found that 2 pure β-substituted butyraldehydes (β–4–methyl–Δ^3–cyclohexanyl–butyraldehyde and β–4–methyl–cyclohexyl–butyraldehyde) can be produced by reacting limonene with CO and H_2 in the presence of Raney Co catalyst, prepared by extracting the Al from a powdered Co–Al alloy with aqueous alkali at a temperature of 130°–175°, and a pressure of 1,000–5,000 p. s. i. for 0.5–10 hr. The products have been found useful in manufacturing perfumes.

206. BOUDINEAU, L., AND NATIONAL INDUSTRIEL DE L'AZOTE. Production of Mixtures of Hydrogen and Carbon Monoxide. British Patent 655,869, 1951. Fuel Abs., 1951, abs. 4059.

Method of catalytically converting gaseous hydrocarbons, more particularly CH_4, or gases containing such hydrocarbons into H_2 and CO by controlled combustion with O_2 or air that may be enriched with O_2. Controlled flameless combustion is arranged to take place in contact with a conversion catalyst, preferably a Ni-base catalyst, in the form of particles of diameters not exceeding 1 cm., whereby formation of C black by combustion with flame in the interstices between adjacent particles is substantially prevented.

BOURSOIS, E. *See* abs. **457, 458.**

BOWEN, A. R. *See* abs. **2501.**

207. BOWMAN, N. J., AND WEITKAMP, A. W. (Standard Oil Co. of Indiana). Separation of Alcohols. United States Patent 2,594,481, Apr. 29, 1952. Chem. Abs., vol. 47, 1953, p. 1181.

Separation is based on the formation of adducts between urea and esters of mono-Me branched alcohols and acids of at least 5 C atoms, whereas esters of more highly branched alcohols do not form such adducts. Thus, crude C_{10} alcohol mixture (from the CO–H_2 reaction) acetylated with AcCl and the esters 23 stirred 1 hr. with urea 120, MeOH 4, and pentane 126 parts yields a solid adduct, which, washed with pentane, treated with H_2O, and extracted with Et_2O yields 15 parts decyl acetate. The wash liquor can be retreated, as above, to give smaller amounts of the same ester,

and the pure product is saponified to pure decyl alcohol. The adduct formed after the 3d treatment with urea on hydrolysis yields pure 2-undecanol, and the wash fluid from this adduct yields mixed branched-chain alcohols. Similarly, n-$C_8H_{17}OAc$ forms a urea adduct in MeOH–isooctane mixture, whereas CH_3-CHMeOAc does not form such an adduct. The heat of the reaction of urea with n-$C_8H_{17}OH$ is 8.5 kcal. per mol, that of $C_6H_{13}CHMeOAc$ only 1.3 kcal. per mol.

208. Boyd, G. A., and Seeley, C. H. (Standard Oil Co. of Indiana). Hydrocarbon Conversion Process. United States Patent 2,253,607, Aug. 26, 1941; appl. filed June 19, 1937, Serial No. 149,104; 2 claims (*Cl. 196–10*). Chem. Abs., vol. 35, 1941, p. 8259.

Describes an arrangement of apparatus and a method of preparing high-antiknock motor fuel. The method involves subjecting substantially S-free gaseous hydrocarbons such as a natural or refinery gas to a controlled oxidation by bringing into contact with steam and a catalyst comprising Ni at a temperature of about 1,200°–1,500° F. to produce CO and H_2; admixing the CO and H_2 with substantially unpolymerizable hydrocarbons; subjecting the mixture to a hydrocarbon synthesis step, including contacting with a catalyst comprising a metal of the 8th group at a temperature of about 400° F. to synthesize hydrocarbon gases; separating from such synthesized hydrocarbon gases a fraction containing substantially unpolymerizable fixed gases; recycling the recovered fixed gases to the first-mentioned high temperature; controlling oxidation to produce additional CO and H_2 separating from such synthesized hydrocarbon gases a second fraction containing polymerizable gaseous hydrocarbons; polymerizing at least a part of such synthesized hydrocarbon gases to form liquid hydrocarbons boiling within the motor-fuel boiling range; fractionating the polymerization product to recover at least 1 fraction comprising unpolymerized hydrocarbons; admixing the CO and H_2 from the oxidation step with the unpolymerized hydrocarbons from the polymerization step and passing the mixture to the hydrocarbon-synthesis step.

209. Bramwell, F. H., and Synthetic Ammonia & Nitrates, Ltd. [Catalytic Gas Reactions.] German Patent 502,768, July 10, 1926. Chem. Abs., vol. 24, 1930, p. 5395.

In a catalytic gas reaction especially suitable for NH_3 synthesis, the gases are forced through a mass of catalyzer in an apparatus including a heat exchanger.

Bramwyche, P. L. *See* abs. **181, 182.**

210. Bratzler, K. (Aktiokohle-Union Verwaltungs-G. m. b. H.). [Ethylene and Ethane From Gaseous Mixtures Containing Them and Carbon Dioxide.] German Patent 724,518, July 16, 1942 (*Cl. 26 d–13.20*). Chem. Abs., vol. 37, 1943, p. 5736.

C_2H_4, C_2H_6, and other gases are separated from CO_2 by adsorption, then desorption. The adsorption is conducted at a pressure inversely proportional to the CO_2 content of the gaseous mixture. The basis for this proportion is the following relation: For a CO_2 content of 5% by volume, a maximum pressure of 6 atm. is used.

211. Braune, A. (Gewerkschaft Victor, Stickstoffwerke). [Hydrocarbons.] German Patent 597,515, May 26, 1934; appl. G 78,657 filed Jan. 29, 1931 (*Cl 12 o–1.03*). FIAT Reel AA90, frames 1,354–1,355; PB 70,275; Chem. Abs., vol. 28, 1934, p. 5467.

Gases containing H_2 and CO are subjected to the action of catalysts of the 8th group, such as Fe, Ni, Co, and Pt, activated by a small addition of halide of alkaline earth metal. Thus, a catalyst consisting of Fe_3O_4 and $CaCl_2$ may be used to produce a mixture of hydrocarbons b. 100°–200° from a gas mixture of CO and H_2 containing small amounts of CO_2 and N_2.

212. Braune, W., and Schaefer, H. (Braunkohle-Benzin A. G.). [Synthesizing Hydrocarbons From Carbon Monoxide and Hydrogen.] German Patent 710,963, Aug. 21, 1941 (*Cl. 12 o–1.03*). Chem. Abs., vol. 37, 1943, p. 3911.

Co catalysts free of Ni are used for the synthesis. The catalyst is reduced and then treated with NH_3 at a temperature close to that of the synthesis.

213. Braunkohle-Benzin, A. G. [Antiknock Fuel.] German Patent Appl. B 200,039, no date (*Cl. IV d–23 b*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 742.

Hydrocarbon fractions b. 60°–100°, obtained by synthesis from CO and H_2, are converted by means of H halides into alkyl halogenides. These are subjected to a splitting off of H halide and then dehydrogenated if necessary.

214. ———. [Antiknock Fuel.] German Patent Appl. B 201,900, no date (*Cl. IV d–23 b.*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 744.

Antiknock motor fuel is made from the hydrocarbons b. 60°–100° obtained by synthesis from CO and H_2 by converting the hydrocarbons with H halide into halogenides, splitting off H halide, and dehydrogenating. This is an addition to German Patent Appl. B 200,039, (abs. **213**).

215. ——— [Antiknock Fuel.] German Patent Appl. B 201,901, no date (*Cl. IV d–23 b*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 744.

Antiknock fuel is made from the hydrocarbon mixtures from the hydrogenation of CO by adding H halide to the olefins present and splitting off H halide from the resulting nonhalogenides.

216. ———. [Antiknock Fuel.] German Patent appl. B 202,816, no date (*Cl. 12 o–1.01.*) Auszüge deut. Patent Anmeldungen, vol. 6, p. 15.

Highly antiknock fuels are made from isoparaffin and olefin hydrocarbons, which were obtained by the hydrogenation of CO and were isomerized before the transformation.

217. ———. [Catalyst Pretreatment.] German Patent Appl. B 182,020, filed Feb. 19, 1938 (*Cl. IV d–12 o*). PB Rept. 412, May 15, 1945.

Pretreating a synthesis catalyst with synthesis gas containing NH_3 for about 20 min. at 185° C. Longer catalyst life results.

218. ———. [Catalyst Removal.] German Patent Appl. B 184,450, filed Aug. 27, 1938 (*Cl. IV b–12 g*). PB Rept. 412, May 15, 1945.

Catalyst ovens or tubes are emptied of catalyst by suddenly applying a gas pressure of 5–20 atm., preferably after wetting the pressure side of the catalyst bed with a liquid.

219. ———. [Catalytic Cracking.] German Patent Appl. B 181,885, no date (*Cl. IV d–23 b*). PB Rept. 412, May 15, 1945.

Cracking heavy hydrocarbons over catalysts that serve at lower temperatures for the synthesis of hydrocarbons from CO and H_2. Such a catalyst, which is spent for synthesis, can be used for cracking. The oil to be cracked may be vaporized or atomized with H_2. A cracking temperature of 300°–350° C is suggested.

220. ———. [Gas Purification.] German Patent Appl. B 179,047, filed June 29, 1937 (*Cl. IV–26 d*). PB Rept. 412, May 15, 1945.

Catalytic removal of organic S compounds from gases is carried out by plural stage operation with a higher temperature in the last stage than in the 1st.

221. ———. [Heat Control.] German Patent Appl. B 178,964, filed June 24, 1937 (*Cl. IV c–12 o*). PB Rept. 412, May 15, 1945.

Operating conditions, particularly coolant supply, are adjusted by using the relative CO_2 content or density of end gas in comparison with charge gas as a guide.

222. ———. [Heat Control.] German Patent Appl. B 181,705, filed Jan. 31, 1938 (*Cl. IV d–12 o*). PB Rept. 412, May 15, 1945.

Exothermic reactions such as Fischer-Tropsch synthesis are carried out with such a large % of inert gas in the charge gas that the entire heat of reaction can be carried out as sensible heat of the effluent without harmful temperature rise. No data given. Addition to German Patent Appl. B 178,085 (abs. **3855**).

223. ———. [Hydrogenation of Carbon Monoxide.] German Patent Appl. B 208,194, no date (*Cl. IV d–12 o.*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 21.

Multistage CO hydrogenation over Co catalysts with introduction of the gas set free by cooling of condensable reaction products into the next stage after the gas has been so dried or preheated that no liquid H_2O separates out on the catalyst.

224. ———. [Improving the Effect of Cobalt Catalysts in Hydrocarbon Synthesis.] German Patent Appl. —, no date. German Patent Abridgments, vol. 64, 1943, p. 726; British Coal Utilization 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.

225. ———. [Oil Condensation.] German Patent Appl. B 182,662, filed June 25, 1938 (*Cl. IV d–23 b*). PB Rept. 412, May 15, 1945.

To avoid fog formation in condensing oil from synthesis oven effluent by spraying with H_2O, vapors of the oil condensate or of some oil miscible with the condensate are combined with the effluent ahead of the H_2O spray.

226. ———. [Oil Products.] German Patent Appl. B 179,862, filed Sept. 8, 1937. PB Rept. 412, May 15, 1945.

Fischer-Tropsch oil is neutralized by percolation through bleaching earth at about 150° C.

227. ———. [Shoe Polish.] German Patent Appl. B 186,214, no date (*Cl. 22 g–6.02*). Auszüge deut. Patent Anmeldungen, vol. 6, p. 593.

Waxlike hydrocarbons, b. 250°–345° at 15 mm. pressure are used to produce shoe polishes. They are obtained from the solid products occurring in the catalytic production of hydrocarbons from CO and H_2 by the Fischer-Tropsch process by distillation, crystallization, or solvent extraction.

228. ———. [Sulfur Removal.] German Patent Appl. B 178,627, filed May 29, 1937 (*Cl. IV–26 d*). PB Rept. 412, May 15, 1945.

Catalyst containing an oxidizing salt such as Na nitrate on active C is used for organic S removal, as covered by German Patent Appl. B 175,954, (abs. **230**). The spent catalyst is used to convert organic S to H_2S, which can be removed by well-known methods.

229. ———. [Synthesis Gas.] German Patent Appl. B 177,992, filed Apr. 6, 1937 (*Cl. IV c–12 o*). PB Rept. 412, May 15, 1945.

Using for the Fischer-Tropsch process a synthesis gas prepared from coal or coke and removing residual hydrocarbons from the synthesis gas by active charcoal or by contact with hot H_2SO_4 or by cooling enough to condense the hydrocarbons.

230. ———. [Synthesis-Gas Purification.] German Patent Appl. B 175,954, filed Oct. 23, 1936 (*Cl. IV b–12 e*). PB Rept. 412, May 15, 1945.

Desulfurizing synthesis gas by contact with an oxidizing agent, such as a nitrate, chlorate, or permanganate, on a support such as active C or silica gel at a temperature of about 80° C.

231. ———. [Synthesis-Gas Purification.] German Patent Appl. B 179,612, filed Aug. 14, 1937. PB Rept. 412, May 15, 1945.

Synthesis gas from brown coal is freed from resin-forming constituents, independent of desulfurizing, by cracking in a cowper stove or adsorbing on active C, brown coal, coke, or bleaching earth.

232. ———. [Synthesis of Antiknock Motor Fuel.] German Patent Appl. B 195,169, filed Aug. 2, 1941; PA 551,590 (*Cl. IV d–23* b). FIAT Reel B 196, frames 258–262; PB 83,253.

In the synthesis of antiknock motor fuel from CO and H_2 over Fe catalysts at high temperature and pressure, as soon as formed, the products are passed directly through a H_3PO_4 catalyst arranged in the same converter as the Fe catalyst, preferably in alternate layers having between them inert substances, such as kieselguhr, or isomerizing catalysts, such as bleaching earth. The Fe catalyst is present in the larger amount. In an example, the operation was carried out at 240° and 7.5 atm. with synthesis gas consisting of 55% CO, 34% H_2, 11% inerts. At an 80% CO conversion 120–130 gm. of liquid hydrocarbons and gasol per N $m.^3$ of synthesis gas were obtained. A larger % of antiknock gasoline and a lower % of gasol were obtained than with an Fe catalyst alone.

233. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] German Patent Appl. B 205,242, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 19.

The fresh gas is thoroughly purified in the activated C vessel. The fresh gas remaining in the adsorber at the reversal of an adsorber to residual gas is conducted to the suction side of the blower.

234. ———. [Temperature Control.] German Patent Appl. B 185,130, filed Nov. 3, 1938 (*Cl. IV d–12 o*). PB Rept. 412, May 15, 1945.

Controlling the temperature in the catalytic hydrogenation of CO by carrying out simultaneously over the same catalyst an endothermic reaction, specifically the catalytic cracking of alcohols and preferably of isobutyl alcohol.

235. ———. [Thermocouple.] German Patent Appl. B 184,414, filed Aug. 23, 1938 (*Cl. IX–42 i*). PB Rept. 412, May 15, 1945.

Thermocouple with the leads extending in opposite directions from the junction to avoid the problems of electrical insulation associated with parallel leads. For measuring the temperature along the center of a vertical reaction tube, the ends pass through stuffing boxes at the top and bottom of the tube so that the junction can be raised or lowered as desired.

236. ———. [Treatment of Catalysts for the Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen.] German Patent 759,366, Mar. 15, 1939; appl. B 186,669 (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 6; Chem-Ztg., vol. 69, No. 2, 1945, p. 39.

Catalysts used in the hydrogenation of CO and impregnated with solid paraffin are freed from this by means of easily boiling solvents.

237. ———. [Treatment of Solid Paraffins.] German Patent Appl. B 195,924, no date (*Cl. 23 b–1.04*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 743.

Solid paraffin hydrocarbons from CO hydrogenation is heat treated at cracking temperatures of 400°–450° until it is converted without the formation of essential

amounts of gases or low-boiling oils into products similar to vaseline.

238. ———. [Vaselinelike Products.] German Patent Appl. B 201,768, no date (*Cl. IV d–23 b*). Auszüge deut. Patent-Ammeldungen, vol. 6, p. 744.

Vaselinelike products from the paraffin hydrocarbons obtained by CO hydrogenation are made by mixing oils b. >250° from the CO hydrogenation and heating 400°–450° in presence of H_2 to a salvelike consistency. Addition to German Patent Appl. B 195,924 (abs. **237**).

239. ———. [Wax Removal.] German Patent Appl. B 182,389, filed Mar. 15, 1938 (*Cl. IV d–12 o*). PB Rept. 412, May 15, 1945.

Extracting paraffin from synthesis catalyst by supplying vapors of a solvent, preferably synthesis oil, of such a boiling point that condensate therefrom is formed and flows down through the catalyst to extract the wax at a temperature > its melting point.

240. ———. [Waxes From Fischer-Tropsch Paraffins.] German Patent Appl. B 194,988, no date (*Cl. 12 o–11*). Auszüge deut. Patent-Ammeldungen, vol. 6, p. 8.

Waxlike products easily emulsifiable with aqueous alkaline solutions and obtained by oxidation of the paraffins occurring in the catalytic synthesis of hydrocarbon from CO and H_2 (melting >90°) until a saponification number of about 45–60 is attained and in such a manner that the ratio of saponification to acid number lies 1.5 : 1–2 : 1.

———. *See* abs. **212, 1884, 1961, 2107, 2308, 2434, 2715, 3228, 3230, 3231, 3232, 3855, 3887.**

241. Braunkohlen- und Brikett-Industrie A. G. [Apparatus for Generating Water Gas.] German Patent 721,603, Apr. 30, 1942 (*Cl. 26 a–5*). Chem. Abs., vol. 37, 1943, p. 4884.

242. ———. [Apparatus for the Production of Gas and Coke From Solid Bituminous Fuel.] French Patent 815,894, July 24, 1937. Chem. Abs., vol. 32, 1938, p. 1909.

243. ———. Coke Ovens. British Patent 481,278, Mar. 8, 1938. Chem. Abs., vol. 32, 1938, p. 6446.

Continuously operating chamber oven is adapted for the production of town gas, synthesis gas, water gas, and coke from bituminous coal, the distillates formed in the upper part of the chamber passing downward with the coke, the water gas obtained by the admission of steam to the lower part of the chamber reacting if required with the distillates from the upper part. The composition of the gas is controlled by regulating the proportion of the heating surface of the upper part to that of the lower part by regulated gas withdrawal in combination with regulated heating of the predistillation zone, distillation zone, and gasification zone and steam introduction at various levels.

244. ———. [Production of Synthesis Gas From Solid Fuels.] German Patent 679,961, Aug. 18, 1939; appl. filed Apr. 19, 1935 (*Cl. 20 a–5.*). Chem. Zentralb., 1929, II, p. 3917.

Apparatus and method for producing water gas of determined composition in chamber ovens.

———. *See* abs. **17.**

Braus, K. *See* abs. **117, 118.**

245. Bredig, G., and Carter, S. R. Formic Acid. British Patent 9,762, July 5, 1915. Chem. Abs., vol. 11, 1917, p. 86.

Formic acid is obtained by interaction of H_2 and CO_2 at high pressures in the presence of catalytic agents and solvents. Metals of the Pt group, such as Pd black, are suitable catalysts and H_2O, ether, alcohol, esters, ketones, paraffin, or liquid acids are suitable solvents.

246. ———. [Formic Acid From Hydrogen and Carbon Dioxide Under High Pressure.] German Patent 337,503, May 30, 1921; appl. filed Feb. 3, 1914. Chem. Zentralb., 1921, IV, p. 421.

With Pd sponge and 5% borax solution under H_2 pressure of 30 atm. and 70° temperature, about 20% of the borax is converted to formic acid salts. This is an addition to German Patent 283,895 (abs. **248**).

247. ———. [Formic Acid From Hydrogen and Carbon Dioxide Under Pressure.] German Patent 339,946, Aug. 22, 1921; appl. filed Aug. 16, 1914. Chem. Zentralb., 1921, IV, p. 1221.

With a catalyst of Pd sponge and 110 atm. pressure and 20° temperature, about 1% formic acid is obtained from the reaction of H_2 and CO_2. This is an addition to German Patent 283,895 (abs. **248**).

248. ———. [Formic Acid Salts by Catalytic Reduction of Carbonates and Bicarbonates.] German Patent 283,895, Apr. 29, 1915; appl. filed Dec. 23, 1913. Chem. Zentralb., 1915, I, p. 1190.

Bicarbonate or a mixture of carbonates with CO_2 in the presence of catalysts such as Pt metal with or without a carrier substance is treated with H_2 under high pressure with active stirring. Salts of formic acid are obtained up to 75% yield.

249. Breywisch, — (I. G. Farbenindustrie A. G.). [Working-Up the Products of Carbon Monoxide-Hydrogen Conversion.] German Patent Appl. —, OZ 14,074, filed Mar. 16, 1943. TOM Reel 19, item 143, frames 1675–1679; Meyer Transl. PC-S-II, Fischer-Tropsch Process, vol. 3, chap. 117, 1948, p. 32.

Products are divided into 2 layers, 1 aqueous and 1 oily. The oily layer is treated with a part of the aqueous layer and with a neutralizing caustic soda wash. The treatment gives a clean separation without the disadvantage of emulsions forming.

———. *See* abs. **3903.**

250. Brill, J. L. Ammonia and Methanol Synthesis and Other Catalytic Gas Reactions. British Patent 342,854, Dec. 31, 1928. Chem. Abs., vol. 25, 1931, p. 4364.

Heat required for initiation of gaseous exothermic catalytic reactions carried out under pressure at high temperatures is supplied from an auxiliary catalytic exothermic reaction of like gases, to which other gases may be added temporarily if desired, which serves to heat initially the apparatus and catalyst used for the main reaction. Describes various details of apparatus and procedure. In the production of NH_3 from a N_2H_2 mixture derived from water gas, the amount of CO purification may be reduced and the gases passed over a low-temperature CH_4-forming catalyst to initiate the NH_3 synthesis. Describes production of homologs of MeOH from CO and H_2 also.

251. ——— (E. I. du Pont de Nemours & Co.). Exothermic Catalytic Gas Reactions Such as Ammonia Synthesis. United States Patent 1,893,492, Jan. 10, 1933; appl. filed Dec. 31, 1928. Chem. Zentralb., 1933, II, p. 3192; Chem. Abs., vol. 27, 1933, p. 2255.

Reactions under pressure and at an elevated temperature are initiated by passing the compressed gases, at a temperature lower than that at which the catalyst for the main reaction will function, into contact with a priming catalyst that is suitable for catalyzing an exothermic reaction at a lower temperature, and the heated gases are then passed into contact with the catalyst for the main reaction. Describes apparatus. The process is suitable for the synthetic production of MeOH or higher alcohols from CO and H_2.

British Celanese, Ltd. *See* abs. **71, 72, 73, 74, 519, 2570, 3748.**

252. Brooks, R. E. (E. I. du Pont de Nemours & Co.). Preparation of Alcohols. United States Patent

2,549,416, Apr. 17, 1951; appl. filed Feb. 4, 1948, Serial No. 6350; 9 claims (*Cl. 260–638*).

High yields of alcohols are obtained when aldehydes, which are preferably prepared by simultaneously reacting CO and H_2 with diisobutylene at elevated temperatures and pressures in the presence of a hydrogenation catalyst, are hydrogenated in the vapor phase by passing them together with H_2 over a catalyst comprising reduced Cu+ZnO. 6 United States patents, 4 foreign patents, and 1 literature ref. cited.

253. ——— (E. I. du Pont de Nemours & Co.). Process for Production of 5-Carbon Acyclic Aldehydes. United States Patent 2,517,383, Aug. 1, 1950; appl. filed Nov. 13, 1947, Serial No. 785,799; 2 claims (*Cl. 260–604*). Chem. Abs., vol. 45, 1951, p. 1158.

Mixture of Co hydrogenation catalyst, 1–9 molar equivalents of CO and 3 H_2 is heated to 75°–200° C. at 500–1,500 atm. Butadiene is injected into the heated mixture. The molar ratio of butadiene to unreacted H_2 is kept $<1:2$. 1 United States patent cited.

254. ——— (E. I. du Pont de Nemours & Co.). Synthesis of Esters. United States Patent 2,457,204, Dec. 28, 1948; appl. filed May 17, 1946, Serial No. 670,527; 5 claims (*Cl. 260–488*). Chem. Abs., vol. 43, 1949, p. 3443.

Esters are prepared by treating alcohols or ethers with CO under 200–1,500 atm. pressure preferably 400–1,000 atm. at 100°–325°, preferably 220°–240° in the presence of 2–10% based on the weight of alcohol originally present, of a catalyst such as Co or its oxide, carbonyl, or carbonyl hydride. For example: 192 gm. MeOH and 10 gm. finely divided, reduced sintered Co oxide catalyst are heated 1 hr. at 220° in a Ag-lined shaker tube with CO under 650–700 atm. pressure to yield 14.9% MeOAc. A similar experiment is described in which the effect of temperature on the reaction rate is studied by injecting H_2 and CO at different temperatures and pressures and detecting the rate of reaction by a pressure drop. It is concluded that the catalyst concentration is not so critical as the temperature, which must be below 300°, preferably 220°–440°, to obtain good yields of MeOAc. At temperatures above 300° AcH and EtCHO are formed with decreased yields of MeOAc.

———. *See* abs. **859, 860, 861, 862, 863, 864, 865, 866, 867, 868, 876, 877, 878, 879.**

255. Brooks, R. E., and E. I. du Pont de Nemours & Co. Improvements in and Relating to the Synthesis of Esters From Carbon Monoxide and Alcohols. British Patent 628,160, Aug. 23, 1949. Chem. Abs., vol. 44, 1950, p. 1526.

See United States Patent 2,457,204 (abs. **254**).

256. Brooks, R. E., and Schreyer, R. C. (E. I. du Pont de Nemours & Co.). Process of Preparing Alcohols From Olefins. United States Patent 2,644,844, July 7, 1953; appl. filed Jan. 25, 1950; Serial No. 140,556; 1 claim (*Cl. 260–638*).

Claim 1. A process for the synthesis of a branched-chain primary heptadecyl alcohol that comprises reacting CO and H_2 simultaneously with tetraisobutylene and methyl acetate at a temperature of 255°–275° C. in the presence of a catalytic quantity of Co acetate dissolved in the reaction mixture, under a pressure within the range of from 325–1,500 atm., the mol ratio of CO : H_2 being initially in the range of about 1 : 3 to 3 : 1, whereby a mixture containing MeOH and an acetic acid ester of branched chain primary heptadecyl alcohol is obtained, and thereafter recovering the said heptadecanol by methanolysis of the said ester.

257. Brown, B. K. (Commercial Solvents Corp.). Synthesis of Ketones and Hydrocarbons. United States Patent 1,757,830, May 6, 1930; appl. filed July 31, 1926, Serial No. 126,347. Chem. Abs., vol. 24, 1930, p. 3247.

In the synthesis of products such as propyl-methyl ketone, a mixture of olefin gas such as C_2H_4 and acetone, at a temperature of 250°–550° and under a pressure $>$ 50 atm., is passed over a catalyst comprising materials such as Zn and Cr oxides and $ZnCl_2$ which accelerate hydrogenating and dehydrogenating reactions.

———. *See* abs. **760, 761.**

Brown, C. S. *See* abs. **2388.**

258. Brown, R. L. (Solvay Process Co.). Methanol. United States Patent 2,281,228, Apr. 28, 1942; appl. filed Mar. 3, 1939, Serial No. 259,622; 10 claims (*Cl. 260–449*). Chem. Abs., vol. 36, 1942, p. 5483.

In a cyclic system for the catalytic synthesis of MeOH and H_2 and CO under high pressure, the gas, after contact with the catalyst, is treated to remove MeOH, and the residual gas from which the MeOH has been removed is recirculated into contact with the catalyst, with an equilibrium concentration of CO_2. The catalyst used is free from oxides and salts of the alkali and alkaline earth metals at a temperature of 300°–340° and at a space velocity of 10,000–20,000, and CO_2 is removed from the circulating gas so that the gas brought into contact with the catalyst contains materially less than the equilibrium concentration, thus preventing the substantial decrease in catalytic activity of the catalyst, which results when the gas introduced into contact with it contains the equilibrium concentration of CO_2. Describes arrangement of apparatus.

259. ——— (Solvay Process Co.). Regeneration of Catalysts Such as Zinc and Chromium Oxides Used for Methanol Synthesis. United States Patent 2,276,921, Mar. 17, 1942; appl. filed Sept. 26, 1939, Serial No. 296,625 (*Cl. 260–449*). Chem. Abs., vol. 36, 1942, p. 4521.

Process is employed for the catalysis of a gas to promote a chemical reaction therein by direct contact with a catalyst substantially free from metals of the Fe group and compounds of such metals, which are reducible by CO under the conditions of the catalysis of the gas, wherein contamination of the catalyst with material from the group consisting of the metals of the Fe group and compounds thereof reducible by CO and resulting loss of activity of the catalyst occurs during passage of the catalysis gas in contact with the catalyst, which comprises regenerating the activity of the catalyst thus contaminated by heating the contaminated catalyst at 100°–300° and flowing in direct contact with the thus heated catalyst a gas containing CO in which the CO partial pressure is at least 50 atm. and which contains an amount of carbonyl of a metal of the Fe group $<$ the equilibrium concentration of the metal carbonyl in said gas containing CO at the temperature at which the gas is flowed in contact with the contaminated catalyst, thereby removing from the catalyst the metal of the Fe group contaminating the catalyst.

260. Brubaker, M. M. (E. I. du Pont de Nemours & Co.). Interpolymers of Carbon Monoxide. United States Patent 2,495,286, Jan. 24, 1950. Chem. Abs., vol. 44, 1950, p. 4285.

Copolymers of CO with unsaturated organic compounds are prepared using peroxide catalysts and are useful as protective coatings, fibers, plasticizers, and adhesives. Thus, 125 parts H_2O and 0.5 part Bz_2O_2 under 325 atm. CO and enough C_2H_2 to give 500 atm. pressure give after 11 hr. at 115° a polymer, m. 200°–202°, containing keto groups and having $1.2:1 = C_2H_2$: CO ratio. It is soluble in Me_2NCHO, insoluble in toluene, MeOH, Me_2CO, and AcOH. A lower melting polymer forms if solvent is absent (73°–77° reaction tem-

perature at 1,000 atm.). Et_2O_2 catalyst gives a polymer infusible to 250°, whose molecular ratio is 1.3 : 1; use of 30 : 70 CO–C_2H_2 mixture in this case at 129° for 14 hr. gives an orientable polymer, m. above 250°. Mixtures of olefins and dienes may be used, as well as unsaturated esters, such as vinyl acetate, diallyl phthalate, di-Etmaleate, C_2F_4, and vinyl chloride. Various organic peroxides are the preferred catalysts.

BRUECKE, O. See abs. **197.**

261. BRUGGEMAN, E. (Metallgesellschaft A. G.). [Synthesis Gas.] German Patent 745,069, Nov. 25, 1943 (*Cl. 26 a–18.01*). Chem. Abs., vol. 40, 1946, p. 445. CH_4-rich, thermally treated, and purified gas produced by pressure gasification is used for synthesis.

262. BRUNER, F. H. (Texaco Development Corp.). Apparatus for Catalytic Conversion of Carbon Monoxide. British Patent 672,880, May 28, 1952. Chem. Abs., vol. 46, 1952, p. 8833.

See United States Patent 2,508,743 (abs. **263**).

263. ——— (The Texas Co.). Apparatus for Catalytic Conversion of Carbon Monoxide. United States Patent 2,508,743, May 23, 1950; appl. filed Sept. 13, 1947, Serial No. 773,884; 15 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 7515.

Volatile metal carbonyls formed in the conversion of CO at 150°–400° F. and 150–2,000 p. s. i. with catalysts containing metals of the Fe group are decomposed on a catalyst carrier or spent catalyst in a secondary reaction zone maintained at a temperature 50°–1,000° F. above the primary reaction zone and at atmospheric pressure. When a substantial amount of metal has accumulated in the decomposition zone, the flow of reactants is reversed and the secondary zone is used as the reaction zone, whereas the primary zone is used for the decomposition of the metal carbonyl.

264. BRUNER, F. H., HESS, H. V., AND ARNOLD, G. B. (The Texas Co.). Separation of Oxygen-Containing Organic Compounds From Aqueous Mixtures. United States Patent 2,605,276, July 29, 1952; appl. filed Aug. 31, 1946; Serial No. 694,408; 1 claim (*Cl. 260–450*).

Synthesis product obtained in the conversion of CO and H_2 by contact with a synthesis catalyst is separated into a liquid hydrocarbon phase and a liquid H_2O phase by cooling; the H_2O phase usually containing the oxygenated compounds ranging mainly 2–8 or more C atoms per molecule and occurring in both the nonacidic aliphatic H_2O-soluble form and the acidic aliphatic H_2O-soluble form. To separate these 2 forms, the aqueous solution containing them is extracted countercurrently with naphtha at about 175°–300° and under a pressure of about 150 p. s. i. or more, by which means a solvent-rich phase comprising aliphatic alcohols, aldehydes, and ketones, and a H_2O phase consisting essentially of H_2O and organic acids are obtained. The constituents may then be separated and the individual compounds recovered. For example, the solvent-rich phase may be treated with Na bisulfite solution to remove aldehydes and ketones. Thereafter the treated solvent-rich phase is extracted with a secondary solvent such as ethylene glycol to separate the alcohols, which are then distilled to recover the individual alcohols.

BRUNER, W. M. *See* abs. **876, 877.**

265. BRUNS, B. P., GERCHIKOVA, S. Y., GEĬMAN, I. B., AND CHURO, L. N. [Composite Catalysts for Methanol Synthesis.] Russian Patent 65,854, Feb. 28, 1946. Chem. Zentralb., I, 1948, p. 403; Chem. Abs., vol. 41, 1947, p. 5268.

Instead of starch or similar substances commonly used to hold together the oxides used as catalysts in the synthesis of CH_3OH, one of the oxides itself is used. It is added to the mixture as a gel and has the advantage that it does not decompose at the reaction temperature.

266. BRUTZKUS, M. [Catalyst Chamber.] Swiss Patent 118,972, no date. Das Kohlenoxyd, by J. Schmidt. Akad. Verlagsgesell., Leipzig, 1950, p. 161.

See United States Patent 1,832,762 (abs. **270**).

267. ———. Effecting Chemical Reactions. British Patent 155,776, Dec. 22, 1920. Chem. Abs., vol. 15, 1921, p. 1585.

Describes apparatus for carrying out chemical reactions in a compressor. One reaction that can be performed thus is the reduction of CO and CO_2 by H_2 to produce HCHO. The pressure and temperature are kept constant by injecting H_2O.

268. ———. Fuel for Internal-Combustion Engines. British Patent 252,786, Mar. 5, 1925. British Chem. Abs., B, 1926, p. 954; Chem. Abs., vol. 21, 1927, p. 2551.

Production of light oils from gases containing CO and H_2 is effected in the cylinder of a compressor; the reaction is carried out during the compression stroke in such a manner that as the pressure is increasing heat is abstracted, and, at the same time the concentrations of the gases are increased by injecting reacting gases into the reaction space. The compressor may be in the form of a diesel engine, and water gas, coke-oven gas, producer gas, illuminating gas, and blast-furnace gas may be used, with addition of H_2 if necessary. Catalysts may be used, and among the products obtained are: MeOH and higher alcohols, CH_2O, other aldehydes, ketones and HOAc, and other acids. The reactions are exothermic and may be utilized for heating or developing power.

269. ———. [Producing Fuel for Internal-Combustion Engines From Water Gas.] German Patent 520,222, Feb. 21, 1925. Chem. Abs., vol. 25, 1931, p. 2836.

See British Patent 252,786 (abs. **268**) and United States Patent 1,832,762 (abs. **270**).

270. ———. Synthetic Automobile-Engine Fuel From Water Gas. United States Patent 1,832,762, Nov. 17, 1931; appl. filed Mar. 20, 1925, Serial No. 17,078. Chem. Abs., vol. 26, 1932, p. 1100.

Gas containing CO and H_2 is compressed under heavy pressure, and water gas of higher pressure is introduced into the compressed gas during further compression to a still higher pressure (suitably about 140–200 atm.)., the pressure is released and liquefied organic compounds are recovered. Describes apparatus.

271. BÜCHE, W., EILBRACHT, H., AND SCHUSTER, C. (Badische Anilin- und Soda-Fabrik). [Oxygen-Containing Organic Compounds.] German Patent 803,-352, Apr. 2, 1951 (*Cl. 12 o–7.02*). Chem. Abs., vol. 45, 1951, p. 8030.

The known method of preparing O-containing compounds, such as aldehydes or ketones, by treating compounds containing olefinic double bonds with CO and H_2 at elevated temperatures and pressures in the presence of catalysts in the liquid phase is improved by using a recycled CO–H_2 mixture; the content of gaseous olefinic compounds to be treated with this mixture corresponds to the saturation pressure of the olefins under the particular reaction conditions. To regulate the olefin content of the recycled gas mixture, the gaseous reaction mixture may be introduced into a separator heated above the condensation point of the olefins to remove the O-containing products formed, the olefins remaining unchanged. Alternatively the gaseous reaction mixture may be introduced into several separators in series that have different cooling temperatures to remove first the O-containing products and thereupon the unreacted olefins. The necessary amount of olefins is added to the recycled gas mixture

before it enters the reaction zone. An olefin-paraffin mixture d. 0.752, b. 100°–150°, olefin content 67%, containing Co naphthenate (0.75 gm. Co per l.) is introduced, 200 l. per hr., into a high-pressure tube of 500 l. packed with pumice, 10–12 mm., together with a recycled CO–H_2 mixture (1:1) under 200 atm. pressure. A recycled gas feed of 20 $m.^3$ per hr. is enough to keep a temperature of 140°–160°. The reaction mixture is passed through a separator and cooled to 20° below the reaction temperature to separate the addition products formed; the unreacted olefin-paraffin portions are separated in a 2d appropriately cooled separator. The exit gas mixture after passing the circulation pumps is saturated with the necessary amount of olefin-paraffin in a saturator kept at the reaction temperature; 95% of the liquid olefin-paraffin mixture is thus treated, 80% being converted to aldehydes and the residual amount to higher boiling condensation products.

272. Buchmann, F. J. (Standard Oil Development Co.). Synthesis Catalyst. United States Patent 2,512,608, June 27, 1950; appl. filed Nov. 8, 1946, Serial No. 708,795; 1 claim (*Cl. 252–466*). Chem. Abs., vol. 44, 1950, p. 8094.

Hydrocarbon-synthesizing catalyst is formed by spraying molten Fe, Co, or Ni, containing a promotional amount of an activating material, on to spherical particles of Al in a reducing atmosphere. A thin coating is formed on the Al particles. Other suitable base materials are clays, silica gels and C. 1 literature ref. and 2 foreign and 6 United States patents cited.

Buchmann, F. J. *See* abs. **3712**, **3713**.

273. Buchmann, F. J., and Voorhies, A. (Standard Oil Development Co.). Low-Pressure Hydrocarbon Synthesis Process. United States Patent 2,552,308, May 8, 1951; appl. filed June 16, 1949, Serial No. 99,378; 6 claims (*Cl. 260–449.6*).

Fluidized Fe catalyst supported on an active C carrier and promoted with a critically small quantity of alkali metal salt promoter is used in a once-through synthesis operation for the production of liquid olefins, which is conducted at low pressures with a synthesis gas, which may or may not contain appreciable quantities of N_2. Critical factor in preparation of the catalyst is the ratio of the promoter content to the Fe surface. 6 United States patents cited.

274. Büchner, K. (Ruhrchemie A. G.) [Reclaiming Thorium From Spent Hydrogenation Catalysts.] German Patent 729,059, Nov. 12, 1942; appl. R 102,874, R 392, filed July 2, 1938 (*Cl. 12 m–9*). TOM Reel 37, bag 3,451, item 35, 3 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 4, chap. 132, 1949, p. 17; Chem. Abs., vol. 38, 1944, p. 462.

The Fe–Th mixture is dissolved in H_2SO_4. K_2SO_4 is added to this solution to precipitate $K_2Th(SO_4)_3$. The precipitate is filtered, washed, and then boiled with a concentrated solution of Na_2CO_3; this converts Th to Th bicarbonate. The trace of K remaining in the catalyst is said to have a beneficial influence.

275. ——— (Hydrocarbon Synthesis Corp.). Regeneration of Catalysts Containing Thorium. United States Patent 2,278,644, Apr. 7, 1942; appl. filed June 26, 1939, Serial No. 281,152; in Germany July 1, 1938; 6 claims (*Cl. 23–23*). Chem. Abs., vol. 36, 1942, p. 4982.

Process is employed for recovering Th values of high catalytic activity, virtually free from Fe, Ni, Co, Al_2O_3 and SiO_2, from spent Th catalysts containing substantial amounts of Fe, such as those used in the production of hydrocarbons from CO and H_2, which involves treating them at a moderately elevated temperature with an inorganic acid to extract the catalytically active constituents, adding to the resulting acid solution a soluble carbonate to produce a precipitate rich in Th, dissolving this precipitate in H_2SO_4, precipitating the Th from the H_2SO_4 solution as Th K sulfate, and converting the latter into insoluble Th hydrocarbonate.

276. Büchner, K., and Schwarz, H. (Ruhrchemie A. G.). [The Direct Conversion of Aldehydes, From the Oxo Synthesis, Into Esters.] German Patent 815,038, Sept. 27, 1951; appl. filed Oct. 2, 1948 (*Cl. 12 o*). Chem. Zentralb., 1952, I, p. 3733.

Conversion takes place through stepwise esterification by treatment with alkali. The operation is performed in step (1) at 100°–200°, preferably under reflux. The amount of alkali is 5–10 parts per 100 of aldehydes, the esterification taking 1–3 hr. Example.

Bucker, E. R. *See* abs. **3724**.

277. Buckley, G. D. (Imperial Chemical Industries, Ltd.). Olefin Oxidation. United States Patent 2,636,898, Apr. 28, 1953. Chem. Abs., vol. 47, 1953, p. 6973.

See British Patents 649,680 (abs. **278**) and 668,309 (abs. **2823**).

———. *See* abs. **2823**.

278. Buckley, G. D., Driver, A. P., Jones, F. S. B., and Imperial Chemical Industries, Ltd. Olefin Oxidation. British Patent 649,680, Jan. 31, 1951. Chem. Abs., vol. 45, 1951, p. 8548.

Compounds containing an olefinic bond react with N_2O at 200°–400° and >20, usually 100–500, atmosphere to form O-containing products. Reactant, product, and % yield in 1–4 hr.: Cyclohexene, cyclohexanone, 65; C_3H_6, EtCHO, substantial; iso-C_4H_8, 1,1-dimethylcyclopropane, 8; Me_3CCH_2CMe: CH_2, 1-methyl-1-neopentylcyclopropane, 50, and Me_3CCH_2COMe, 50; methylenecyclohexane, cyclohexanone, 17, and 2,5-spiroöctane, 17; MeCH: CHCl, $MeCOCH_2Cl$, 25; 2,3-dihydropyran, δ-valerolactone, 20; BuOCH: CH_2, BuO_2CH, 50, BuOAc, 10, Bu cyclopropyl ether, 23; acenaphthylene, acenaphthenone, 60; $(p\text{-}MeOC_6H_4)_2C$: CH_2, 1,1-bis(*p*-methoxyphenyl) cyclopropane, 50, and $(p\text{-}MeOC_6H_4)_2CO$, 50.

Buffleb, H. *See* abs. **710**.

279. Burk, R. E., and Hughes, E. C. (Standard Oil Co. of Ohio). Hydrocarbon Synthesis. United States Patent 2,284,468, May. 26, 1942; appl. filed Feb. 6, 1939 (*Cl. 260–668*). Chem. Abs., vol. 36, 1942, p. 6546.

Aliphatic naphtha b. 140°–420° F. is changed to aromatics and H_2 by heating in the presence of a catalyst containing Cr_2O_3 at temperatures of 700°–1,250° F. and in the same reaction chamber concurrently reacting the H_2 so formed with a C oxide in presence of a catalyst containing NiO.

280. Burke, S. P. Methanol. United States Patent 1,602,846, Oct. 12, 1926. Chem. Abs., vol. 20, 1926, p. 3698.

Direct hydrolysis of Me ether is effected by steam at a temperature of about 350°–375° and in the presence of Al_2O_3 or an equivalent hydrolyzing agent.

281. ——— (Combustion Utilities Corp.). Mixtures of Carbon Monoxide and Hydrogen in Controlled Proportions. United States Patent 1,843,063, Jan. 26, 1932; appl. filed Mar. 13, 1926. Chem. Abs., vol. 26, 1932, p. 1727.

In producing mixtures of CO and H_2, reaction is effected between O_2 and a hydrocarbon material such as CH_4 with the latter present in proportions >the flame-producing range at a controlled temperature (suitably about 1,000°), and the reaction temperature is maintained by supplying heat from an external source, while the reaction products are rapidly removed and cooled as they are formed. Describes apparatus.

Burney, D. E. *See* abs. **2**.

282. BURNEY, D. E., AND SHOEMAKER, B. H. (Standard Oil Co. of Indiana). Preparation of Improved Motor Fuel. United States Patent 2,628,981, Feb. 17, 1953; appl. filed Nov. 29, 1947, Serial No. 788,845; 9 claims (*Cl. 260–604*).

CO and H_2 react only partly under Oxo conditions with the gasoline-boiling-range olefinic products resulting from the copolymerization of secondary olefins with tertiary olefins. The unaffected olefin fraction is converted, by hydrogenation, to saturated hydrocarbons of high performance number and high sensitivity. The hydrogenation may be carried out in part during the carbonylation reaction if the carbonylation is carried out under severe conditions. The hydrogenation may then be completed using a hydrogenation catalyst, temperature 150°–700° F. and pressure >50 atm. It is best to remove first all CO from the carbonylation product by purging with H_2 or an inert gas or by washing the liquid successively with an acid and with H_2O. After hydrogenation, the gasoline and byproduct fractions may be separated by conventional means. 1 foreign and 6 United States patents cited.

283. BURNS, W. L., GIBSON, J. W., AND HENRY BALFOUR & Co., LTD. Water-Gas Plant. British Patent 581,447, Oct. 14, 1946. Chem. Abs., vol. 41, 1947, p. 849.

Describes apparatus for producing gas of constant quality.

284. BURTON, W. P. (M. W. Kellogg Co.). Separation of Organic Compounds. United States Patent 2,505,752, May 2, 1950; appl. filed June 19, 1947, Serial No. 755,654; 24 claims (*Cl. 260–450*). Chem. Abs., vol. 44, 1950, p. 7340.

Hydrocarbons and oxygenated organic compounds can be separated from the aqueous and oil phases of Fischer-Tropsch products by the suggested process. The uncondensed gases are scrubbed with a polar solvent for oxygenated organic compounds. The gas obtained is recycled to the synthesis feed, and the extract is used to scrub the oil phase to obtain a 2d extract of water-soluble oxygenated organic compounds. The 2d extract is combined with the aqueous phase and sent to an alcohol stripper. The organic acids and a major part of the H_2O present are separated from alcohols and nonacidic oxygenated organic compounds and are removed as bottoms. Aldehydes boiling not higher than propionaldehyde are next separated from nonacidic compounds in the overhead from the alcohol stripper. The raffinate from scrubbing the oil phase is solvent extracted with the nonacidic compounds free of aldehydes boiling not higher than propionaldehyde used as solvent to obtain oxygenated chemicals. This extraction with nonacidic compounds as solvent is an essential feature of the invention. The extract is given a wash-oil treatment to remove heavy hydrocarbons, and distilled methanol with any undissolved light hydrocarbons are taken overhead as azeotropes and recycled to the last extraction step. The hydrocarbon-free bottoms are treated with alkali to neutralize the acids and saponify the esters. Individual components are recovered by known means. 1 literature ref., 2 foreign patents, and 3 United States patents cited.

285. ——— (M. W. Kellogg Co.). Separation of Organic Compounds. United States Patent 2,647,139, July 28, 1953; appl. filed Mar. 31, 1948, Serial No. 18,202; 12 claims (*Cl. 260–450*).

Claim 1. A process for treating the reaction product obtained in the hydrogenation of oxides of C wherein said product comprises a mixture of hydrocarbons and oxygenated organic compounds comprising alcohols, acids, aldehydes, and ketones, which comprises: Cooling said product to effect substantial condensation of normally liquid components to form an oil product liquid phase and a H_2O product liquid phase, each of said phases containing at least a portion of said oxygenated compounds; separately scrubbing said oil product liquid phase with H_2O to obtain a H_2O layer comprising H_2O-soluble oxygenated compounds and an oil layer comprising oil-soluble oxygenated compounds and hydrocarbons; subjecting said oil layer to extraction treatment with an aqueous solution of a H_2O-soluble alcohol to obtain a raffinate containing hydrocarbons and an extract containing oil-soluble oxygenated compounds; subjecting said extract to selective hydrogenation to convert aldehydes present to their corresponding alcohols and to form a mixture comprising alcohols and ketones; separating alcohols from ketones in the mixture thus produced; combining said H_2O layer from H_2O-scrubbing of said oil product liquid phase with said H_2O product liquid phase; fractionating the combined mixture into a relatively high boiling fraction comprising organic acids and a relatively low boiling fraction comprising alcohols, aldehydes, and ketones; subjecting said relatively low boiling fraction to selective hydrogenation to convert aldehydes present to their corresponding alcohols and to form a mixture comprising alcohols and ketones; and separating alcohols from ketones in the mixture thus produced.

286. ——— (M. W. Kellogg Co.). Synthesis of Organic Compounds. United States Patent 2,598,503, May 27, 1952; appl. filed Mar. 29, 1947, Serial No. 738,237; 11 claims (*Cl. 260–449.6*).

In a process for the hydrogenation of CO to produce organic compounds, using a fluidized Fe catalyst containing a predetermined amount of 0.1–3% of alkali or earth alkali compound as promoter, the catalyst, after regeneration and before being returned to the reaction zone, is mixed with fresh promoter in an amount sufficient to compensate in part at least for the decrease of the catalyst in alkali content but insufficient to increase its alkali content over the initial predetermined amount.

BURTON, W. P. *See* abs. **2194, 2195.**

287. BURTON, W. P., AND MCGRATH, H. G. (M. W. Kellogg Co.). Separation of Organic Compounds. United States Patent 2,566,311, Sept. 4, 1951; appl. filed Sept. 26, 1947, Serial No. 776,366; 10 claims (*Cl. 260–450*).

In the catalytic hydrogenation of C oxides at elevated temperatures, a reaction product is obtained, which contains a mixture of organic acids with nonacid organic compounds comprising alcohols, ketones, esters, aldehydes, or hydrocarbons. To separate such a mixture comprising a saponifiable organic acid and at least 1 unsaponifiable nonacid compound selected from the above group, it is treated with an alkali to convert the acid compound to its corresponding alkali salt. The resulting salt is then separated from the mixture by subjecting the salt solution to evaporative distillation under subatmospheric pressure to evaporate the liquid portion of the solution without any decomposition and to deposit the salt as a solid residue. The distillation may be carried out under a combined vapor pressure of the solution and unsaponifiable nonacid organic compound of not more than 25 mm. Hg and at a temperature 200°–400° F. Diagram.

288. ——— (M. W. Kellogg Co.). Separation of Organic Compounds. United States Patent 2,568,717, Sept. 25, 1951; appl. filed Oct. 28, 1948, Serial No. 56,928; 5 claims (*Cl. 260–450*).

Detailed instructions are presented with flowsheets for the separation of the reaction products obtained in the hydrogenation of CO at elevated temperatures. A combination of steps is employed in which the synthesis reaction product is condensed and separated into oil and H_2O product and uncondensed gas phases, which are subsequently treated in a series of interrelated steps by which the separation between oxygenated organic compounds and hydrocarbons is obtained.

289. BURTON, W. P., AND SOLOMON, E. (M. W. Kellogg Co.). Recovery of Organic Acids. United States Patent 2,590,087, Mar. 25, 1952; appl. filed Nov. 14, 1946, Serial No. 709,882; 5 claims (*Cl. 260–450*).

Process refers specifically to the separation of organic acids from their aqueous salt solutions obtained as products in the reduction of CO with H_2 in the presence of a catalyst at elevated temperatures. The process comprises 3 steps: (1) An aqueous solution of alkali salts of acetic and higher boiling H_2O-soluble organic acids and H_2O-insoluble organic acids is mixed with an inorganic acid having a boiling point higher than that of H_2O (H_2SO_4) or with one which forms a maximum boiling azeotrope with H_2O (HCl); (2) this mixture is separated into an acid-rich phase comprising H_2O-insoluble organic acids and a portion of the H_2O-soluble organic acids and a H_2O-rich phase comprising inorganic salts and the remainder of the H_2O-soluble organic acids; (3) the 2 phases are separated, and the H_2O-rich phase is distilled to separate substantially all H_2O-soluble organic acids having at least 3 C atoms per molecule as their H_2O azeotropes from the remaining aqueous solution.

290. ——— (M. W. Kellogg Co.). Separation of Organic Compounds. United States Patent 2,595,223, May 6, 1952; appl. filed May 28, 1947, Serial No. 751,072; 8 claims (*Cl. 260–450*). Chem. Abs., vol. 47, 1953, p. 1183.

Total reaction products obtained in the hydrogenation of C oxides is scrubbed in the vapor state and without prior condensation with an alkali carbonate at a temperature within the range 300°–700° F. An extract comprising salts of fatty acids and an acid-free gas comprising the remainder of the reaction product are formed and the components separated.

291. BURTON, W. P., MCGRATH, H. G., AND RUBIN, L. C. (M. W. Kellogg Co.). Separation of Organic Acids From Alcohols. United States Patent 2,580,403, Jan. 1, 1952; appl. filed Apr. 30, 1947, Serial No. 745,004; 13 claims (*Cl. 260–450*).

Describes a process for separating H_2O-insoluble organic acids from their mixture with H_2O-insoluble alcohols and other oxygenated organic compounds present in the oil or nonaqueous liquid product obtained in the hydrogenation of CO at elevated temperatures. The process comprises the steps of neutralizing such mixtures with a strong alkaline solution to convert the organic acids to their corresponding organic salts, diluting the alkali to obtain desired concentrations, and separating these salts from other oxygenated organic compounds by extracting the latter with a H_2O-insoluble liquid organic or inorganic solvent. Such H_2O-insoluble liquid solvents may be used as SO_2, ethyl acetate, and diethyl ketone. The insolubility of the solvent in the aqueous salt solution and its mutual solubility with the layer of oxygenated organic compounds causes the phase separation to take place. The addition of pentane to the acid-oxygenated chemicals mixture enhances the phase separation.

BÜTTNER, A. *See* abs. **2326, 2327, 2328.**

BUYERS, T. B. *See* abs. **773.**

292. BYK-GULDENWERKE CHEMISCHE FABRIK A. G. [Emulsion Paste.] German Patent Appl. B 190,297, no date (*Cl. 22 g–6.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 593.

Clear, aqueous, nongranular emulsion pastes are made from high-melting, synthetic paraffin mixed with <15% of wool fat saponified in the presence of small amounts of ethanolamine and low-melting paraffin or mineral oil.

293. ———. [Emulsion Paste.]. German Patent Appl. B 198,331, no date (*Cl. 22 g–60.2*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 594.

Clear, aqueous emulsion pastes are made of high-melting synthetic paraffins, wool, fat, low-melting paraffin (mineral oil), ethanolamine, tripropanol-, di-, polyamines, morpholin.

294. ———. [Separation of Synthetic Paraffin From Hydrocarbon Mixtures.] German Patent Appl. B 190,143, no date (*Cl. 23 b–2.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 742.

High-melting synthetic paraffins from CO hydrogenation are separated into several fractions by treatment with organic solvents.

295. ———. [Synthetic Paraffins.] French Patent 892,152, no date. Kainer, p. 249.

Low-melting, 30°–40°, gatsch paraffins from the Fischer-Tropsch process are suitable as a base for hair-treating agents.

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296. CAIN, V. L., AND HEMMINGER, C. E. (Standard Oil Development Co.). [Catalytic Production of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 963,531, July 12, 1950; appl. filed Mar. 22, 1948, in United States May 9, 1947. Chem. Zentralb., 1950, II, p. 2271.

Operation is carried out with a Fe catalyst, such as is used for NH_3 synthesis, under a H_2 partial pressure of 10.5–19 atm. with a synthesis gas that contains H_2 and CO in proportions of 2:1. The temperature in the reaction zone is kept high enough to form essential amounts of olefins. The fluidized catalyst is pretreated before use with a CO-rich gas at temperatures about 55° below the synthesis temperature.

297. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,589,925, Mar. 18, 1952; appl. filed May 9, 1947, Serial No. 747,112; 3 claims (*Cl. 260–449.6*).

Fluidized bed of active powdered Fe catalyst having a total O content of about 5–10% is first treated with a CO-rich gas, in which the partial pressure of CO is about 25–75 p. s. i. abs. at 300°–400°, long enough to convert the Fe powder to Fe carbide containing 1.0–3.5 wt. % of carbide C, mostly in the form of Fe_2C. The catalyst is then contacted with synthesis gas at reaction-zone temperatures of 550°–700° F. and a H_2 partial pressure of 170 p. s. i., whereby the carbide C content of the catalyst in the reaction zone is maintained during the desired synthesis reaction, and effluent vapors containing normally liquid hydrocarbons are recovered.

298. CALDWELL, L. Gaseous Reduction of Iron Oxide in Suspension. United States Patent 2,399,984, May 7, 1946. Chem. Abs., vol. 40, 1946, p. 4340.

Finely divided Fe_2O_3 or Fe_3O_4 is brought into contact with vertically moving H_2, CO, hydrocarbon gas, or natural gas at 1,300°–1,700° F. in vertical tubes to provide more intimate contact between oxide and gas than is possible in horizontal equipment. Magnetic separation removes Fe from oxide.

CALIFORNIA RESEARCH CORP. *See* abs. **434, 435, 3442.**

299. CAMPARDOU, J., AND VERGUES, J. [Use of Wood Charcoal as Catalyst in Preparation of Methyl Alcohol From Carbon Monoxide and Hydrogen.] French Patent 613,470, Mar. 3, 1925. British Chem. Abs., 1928, B, p. 596.

Gases are heated in a closed vessel at 300°–400° in the presence of wood charcoal.

CAMPBELL, D. L. *See* abs. **2439.**

300. CAMPBELL, D. L., AND BARR, F. T. (Standard Oil Development Co.). [Reaction of Hydrogen With Carbon Oxides.] French Patent 915,583, Nov. 12, 1946, appl. filed Oct. 8, 1945, in United States Dec. 17, 1940. Chem. Zentralb., 1949, I, p. C 78.

Process is applicable to the production of MeOH and other alcohols, of liquid hydrocarbons and organic oxycompounds, in the presence of finely divided catalysts suspended in the gases in such a manner that the mixture of gas and catalyst is passed from bottom to top through comparatively narrow tubes (12.7–20.3 mm. diameter) cooled from without by means of liquids. By such means virtually the entire heat of reaction can be immediately removed.

301. ——— (Standard Oil Development Co.). Treating Hydrogen With Oxides of Carbon for the Production of Products Such as Methanol. United States Patent 2,266,161, Dec. 16, 1941; appl. filed Dec. 17, 1940, Serial No. 370,462; 5 claims (*Cl. 260–449*). Chem. Abs., vol. 36, 1942, p. 2272.

Describes arrangement of apparatus and a process, which involves passing synthesis gases comprising H_2 and oxides of C and containing suspended therein a powdered catalyst, through a reaction zone, under temperature and pressure conditions adapted to cause the oxides of C and H_2 to react, removing exothermic heat of reaction immediately as it is formed along the path of the flowing gases through the walls by circulating a cooling medium without the walls of the reaction zone.

CANADIAN INDUSTRIES, LTD. *See* abs. **323, 324, 325, 2026, 3311.**

302. CANON, F. A. Regulating Catalytic Reactions of Vapors and Gases. United States Patent 1,355,105, Oct. 5, 1920. Chem. Abs., vol. 15, 1921, p. 295.

Substances to be reacted are passed in the vapor state into contact with the catalyst, which is in the form of small particles, at such a velocity that the catalyst is picked up and swept along with the substance. The catalyst may be recovered by various means and returned to the reaction zone.

CARBIDE & CARBON CHEMICALS CORP. *See* abs. **629, 630.**

303. CARBO-NORIT-UNION VERWALTUNGS-G. M. B. H. [Discharging and Regenerating Solid Adsorbents.] French Patent 824,135, Feb. 1, 1938. Chem. Abs., vol. 32, 1938, p. 5592.

Useful substances are obtained from solid adsorbents used in gas synthesis by purging the adsorbent by steam, collecting the substances driven out, and cooling and drying the adsorbent by the initial synthesis agents.

304. ———. [Purifying Gaseous Mixtures.] French Patent 849,527, Nov. 25, 1939. Chem. Abs., vol. 35, 1941, p. 7073.

Method for preparing gaseous mixtures destined to be used for the catalytic synthesis of organic compounds or NH_3 consists in subjecting the mixtures 1st to a treatment with active C at ordinary temperature and then to a treatment at a temperature above 200° with substances acting catalytically such as the composition "Luata" (containing Fe oxide).

305. ———. [Rejuvenating Adsorption Agents.] German Patent 710,677, Sept. 19, 1941; appl. C 51,809, filed July 11, 1936 (*Cl. 12 o–1.03*). Chem. Abs., vol. 37, 1943, p. 3890.

Spent adsorption agents, for example, activated C, used for separating hydrocarbons from gases in benzine synthesis are treated consecutively with a heavy benzine, b. 120°–250°, and a light benzine, b. 30°–120°. The benzine treatments are at the boiling point or close to the boiling temperature of the respective benzine. Following the benzine adsorption the agent is treated with steam.

306. ———. Separating Gaseous Mixtures. British Patent 481,850, Mar. 18, 1938. Chem. Abs., vol. 32, 1938, p. 6510.

In the use of solid adsorbents for separating the products of synthesis from H_2–CO mixtures, the unsynthesized gas mixture is passed through the regenerated adsorbent to dry and cool the latter. A further advantage is that the final traces of impurities are thereby removed from the crude gas mixture. When the original water gas has been enriched in H_2 by catalytic treatment of a portion thereof with steam, this converted portion is preferably used for the drying and cooling, its CO_2 content being thereby reduced.

307. ———. Synthesis Oils. British Patent 482,093, Mar. 23, 1938. Chem. Abs., vol. 32, 1938, p. 6851.

This corresponds to French Patent 824,002 (abs. **309**).

308. ———. [Synthesis Products.] German Patent 710,766, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell. Leipzig, 1950, p. 184.

Extraction of the used adsorption C with solvent agents for the purpose of regeneration and then treatment with steam.

309. ———. [Synthetic Oils.] French Patent 824,002, Jan. 31, 1938. Chem. Abs., vol. 32, 1938, p. 4324.

Describes improvement in the synthesis of hydrocarbon oils from gaseous agents, such as CO and H_2, by processes in which the crude reaction products are brought into contact with a solid adsorbent, from which the adsorbed products are afterward recovered with steam. The improvement consists in fractionally condensing the mixture of steam and vaporized products in a rectifying column so as to recover separately a low-boiling oil useful as a motor fuel and a residual oil of higher boiling point. The mixture of steam and vaporized products may first be washed to eliminate acids and other oxygenated organic compounds that may be present.

310. ———. [Treatment of Synthesis Gases.] Belgian Patent 433,955, Nov. 21, 1939; appl. filed Apr. 22, 1939, in Germany Dec. 5, 1938. Chem. Zentralb., 1940, I, p. 2752.

Organic S compounds and resin formers are removed from synthesis gases by passing them through active C at temperatures > at least 100°.

———. *See* abs. **1013, 1015, 1029.**

311. CARBURETTED GAS, INC. Oil Gas. British Patent 416,957, Sept. 25, 1934. Chem. Abs., vol. 29, 1935, p. 1613.

In the continuous production of a CO–H_2 gas mixture from the combustion of oil and O_2 in a generating chamber, the temperature of the gas mixture is controlled by introducing steam and additional oil into the generator to react in a secondary zone, the quantities of oil-O_2 and steam-oil being regulated to produce only CO and H_2 in each case. Describes apparatus.

312. ———. British Patent 417,734. Oct. 11, 1934. Chem. Abs., vol. 29, 1935, p. 1613.

In the continuous production of a CO–H_2 mixture by the passage of steam and oil separately or together through a preheated porous bed of refractory material in a generator, the steam reacts with C deposited on the bed from the passage of oil in a preparatory step and the oil is cracked so that only CO and H_2 are produced. Describes appartus.

313. CARKEEK, C. R. (The Texas Co.). Cascade Catalyst System. United States Patent 2,534,853, Dec. 19, 1950; appl. filed Nov. 29, 1947, Serial No. 788,887; 8 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 2182.

Powdered catalyst, in several ranges of particle size, are distributed in a number of reaction zones, each operating under a predetermined linear velocity of reactant upflow such as will fluidize a specific range of particle sizes and carry overhead finer particles. Each successive zone has reactant flow suitable for a successively lower range of particle size. The finer particles below each range are carried out of the reaction zone by the upflowing reactants and deposited in the succeeding zone operating at a relatively lower rate of reactant upflow. The process is particularly applicable to Fischer-Tropsch synthesis using Fe or Ru catalyst, because under conditions giving high liquid-product yield, progressive disintegration of catalyst powder into particles of decreasing size occurs. 5 United States patents cited.

CARLSON, C. S. *See* abs. **814, 2406, 2407, 2408, 2409, 2410.**

314. CARLSON, C. S., CATTERALL, W. E., AND STAIB, J. H. (Standard Oil Development Co.). Treatment of Oxo Alcohols by Caustic and Air. United States Patent 2,595,763, May 6, 1952; appl. filed Dec. 21, 1949, Serial No. 136,282; 3 claims (*Cl. 260–638*). Chem. Abs., vol. 46, 1952, p. 6814.

Alcohols produced by the oxo reaction are purified from S impurities and are aerated with air while being simultaneously washed with a 10–50 wt. % NaOH solution, the volume of aqueous caustic being in the range of 0.5–50 vol. % based on the alcohol being treated. The treatment is carried out at temperatures of 30°–100° for 1–24 hr. The mixture stratifies into a lower aqueous layer containing the S impurities and an upper alcohol layer, which are separated.

315. CARLSON, C. S., MORRELL, C. E., AND SMITH, P. V. (Standard Oil Development Co.). Extractive Distillation of Normal Primary Alcohols. United States Patent 2,551,584, May 8, 1951; appl. filed June 24, 1948, Serial No. 34,896; 16 claims (*Cl. 202–39.5*). Chem. Abs., vol. 46, 1952, p. 521.

Normal primary alcohols are separated from mixtures also containing secondary, tertiary, and branched-chain primary alcohols by using an internal reflux containing 83–93.5 mol. % of H_2O. Tables and graphs.

316. CARLSON, C. S., ROBERTSON, N. C., AND PORTER, C. E. (Standard Oil Development Co.). Recovery of Normal Propyl Alcohol From Oxygenated Compounds. United States Patent 2,489,619, Nov. 29, 1949; appl. filed Aug. 23, 1948, Serial No. 45,724; 17 claims (*Cl. 202–42*). Chem. Abs., vol. 44, 1950, p. 1526.

PrOH is recovered from mixtures with H_2O, aldehydes, esters, and ketones by taking the propyl cut from the Fischer synthesis, oxo process, etc. and subjecting it to azeotropic fractionation with an aliphatic ether. Use of an ether b. 55°–70° results in no loss of PrOH, whereas ethers that b. 70°–110° may be used to form an azeotrope with PrOH; if the R_2O is used in limited amounts in such cases, it is possible to remove the contaminants with very little loss of PrOH when a continuous still is used. Low-boiling R_2O is preferred for batch distillations in which the impurities are removed and PrOH remains as still residue. If paraldehyde is present, a pH of 3 should be maintained in the fractionation zone. Specific claims of iso-Pr_2O and *tert*–BuOEt are made. Gives a diagrammatic flowsheet of distillation system.

CARMODY, D. R. *See* abs. **3339.**

317. CARPENTER, C. L. R. (Standard Oil Development (Co.). Catalytic Reforming Process. United States Patent 2,585,737, Feb. 12, 1952; appl. filed Oct. 21, 1948, Serial No. 55,674; 10 claims (*Cl. 252–373*).

In preparing synthesis gas by the re-forming of CH_4 or natural gas, the reaction is usually conducted by passing CH_4 and steam over a catalyst comprising Ni on kieselguhr within a preferred temperature range 1,500°–1,800° F. and a pressure 0–150 p. s. i. g. One serious problem met with in such an operation is the formation of coke on the catalyst necessitating frequent regeneration of the same. The object of the present invention is to reduce this formation of coke on the catalyst and permit its use on stream for a longer period of time before requiring regeneration. This is accomplished by splitting the hydrocarbon stream and introducing 1 part into the reactor with the oxidizing stream and at least 1 other portion, comprising about 10%–50% of the feed, further down stream at a point where the temperature is above the reactor inlet temperature. By these means, the ratio of steam to CH_4 in the upper zone of the reactor is increased, thus minimizing the danger of coking there, and in the lower zone the excess of oxidizing gas in the feed stream over that required for conversion to CO and H_2 tends to repress the deposition of carbonaceous material on the catalyst.

318. CARPENTER, G. B. (E. I. du Pont de Nemours & (Co.). Aliphatic Carboxylic Acids. United States Patent 1,924,763, Aug. 29, 1933; appl. filed June 28, 1932, Serial No. 619,737; 18 claims (*Cl. 260–116*). Chem. Abs., vol. 27, 1933, p. 5340.

Volatile halide such as HCl is employed as a catalyst in the production of acids, such as propionic acid, from steam, CO, and an olefinic hydrocarbon such as C_2H_4.

319. ——— (E. I. du Pont de Nemours & Co.). Aliphatic Carboxylic Acids. United States Patent 1,924,766, Aug. 29, 1933, appl. filed Aug. 24, 1931, Serial No. 559,130; 27 claims (*Cl. 260–116*). Chem. Abs., vol. 27, 1933, p. 5340.

General claim is made to the production of propionic acid or other aliphatic carboxylic acids from steam, CO, and an olefinic hydrocarbon such as C_2H_4 in accord with the reaction expressed by the equation $RR'C{:}CR''R''' + H_2O + CO = CHRR'.CR''R'''COOH$ in which R, R', R'' and R''' represent H or an alkyl radical.

320. ——— (E. I. du Pont de Nemours & Co.). Aliphatic Carboxylic Acids. United States Patent 1,924,767, Aug. 29, 1933; appl. filed Aug. 24, 1931, Serial No. 559,123; 13 claims (*Cl. 260–116*). Chem. Abs., vol. 27, 1933, p. 5340.

In the production of an acid such as propionic acid from steam, CO, and an olefinic hydrocarbon such as C_2H_4, a metal halide such as NaBr or $ZnCl_2$ is used as a catalyst.

321. ——— (E. I. du Pont de Nemours & Co.). Aliphatic Carboxylic Acids. United States Patent 1,924,768, Aug. 29, 1933; appl. filed Aug. 24, 1931, Serial No. 559,125; 7 claims (*Cl. 260–116*). Chem. Abs., vol. 27, 1933, p. 5340.

This patent is similar to United States Patent 1,924,767 (abs. **320**) but uses a catalyst containing at least 2 chemically combined elements the oxides of which are acidic, such as a phosphotungstic acid.

322. ——— (E. I. du Pont de Nemours & Co.). Aliphatic Carboxylic Acids. United States Patent 1,924,769, Aug. 29, 1933. Chem. Abs., vol. 27, 1933, p. 5340.

This relates to the production of acids such as formic acid from a gaseous mixture containing CO and steam by using catalysts comprising halides, such as those of Ca, Ba, Sr, Mg, Na, K, Cs, Rb, Li, Sn, Fe, Co, Ni, Bi, Mn, Pb, Ti, Zn, and Cd.

323. ——— (Canadian Industries, Ltd.). Formic Acid. Canadian Patent 343,563, July 31, 1934. Chem. Abs., vol. 28, 1934, p. 7265.

CO and steam are brought into contact with a H halide and a halide of an alkali or an alkaline earth

metal or of Sn, Fe, Co, Ni, Bi, Mn, Pb, Te, Zn, or Cd. The metallic halides may be used alone or admixed with one or more dissimilar metallic halides. The reaction may be conducted at pressures over atmospheric (25–900 atm.) at 200°–300°.

324. ——— (Canadian Industries, Ltd.). Formic Acid. Canadian Patent 343,564, July 31, 1934. Chem. Abs., vol. 28, 1934, p. 7265.

Mixture of CO and steam is passed over a catalyst that comprises a compound containing at least 2 substantially nonvolatile acidic elements, especially the acidic elements of groups III, IV, V, and VI of the periodic table. Typical compounds formed from 2 of the above nonvolatile acidic elements are phosphomolybdic acid, phosphotungstic acid, phosphosilicic acid, chromium vandate, vanadium molybdate and silicotungstic, and silicomolybdic acids. The reaction is conducted at pressures of 25–900 atm. at 200°–300°.

325. ——— (Canadian Industries, Ltd.). Formic Acid. Canadian Patent 343,740, Aug. 7, 1934. Chem. Abs., vol. 28, 1934, p. 7266.

Mixture of CO and steam is passed over a catalyst that comprises an acid salt of acidic oxides such as primary and secondary phosphates of Zn, Ca, Mg, Na, K, Cu, Ce, or Th, and the acid salts formed between these metals and the oxides of W and Mo. Inert gases, such as N_2 or CO_2, may be included with the reactants to control the temperature. The reaction is conducted at a pressure of 25–900 atm. and a temperature of 200°–300°.

326. ——— (E. I. du Pont de Nemours & Co.). Formic Acid. United States Patent 1,949,825, Mar. 6, 1934. Chem. Abs., vol. 28, 1934, p. 3082.

Gaseous mixture of CO and steam is passed over a catalyst, such as a silicotungstic, silicomolybdic, or phosphomolybdic acid catalyst, suitably at a temperature of about 325°.

327. ——— (E. I. du Pont de Nemours Co.). Formic Acid. United States Patent 1,991,732, Feb. 19, 1935. Chem. Abs., vol. 29, 1935, p. 2179.

See Canadian Patent 343,563 (abs. **323**).

328. ——— (E. I. du Pont de Nemours & Co.). Formic Acid. United States Patent 2,023,003, Dec. 3, 1935. Chem. Abs., vol. 30, 1936, p. 736.

Gaseous mixture of CO and steam (suitably at a temperature of about 325°) is passed over a catalyst containing primary Ca phosphate or other suitable acid salt of the acidic oxides of P, As, W, Mo, U, Cr, V, B, Si, or Zr. Pressures of 25–900 atm. may be used.

See also United States Patent 2,001,659 (abs. **3965**).

329. CARPENTER, M. T. (Standard Oil Co. of Indiana). Hydrocarbon Synthesis. United States Patent 2,500,516, Mar. 14, 1950; appl. filed Dec. 21, 1944, Serial No. 569,237; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 6106.

Natural gas is first freed from H_2S and organic S compounds by scrubbing with solvent such as mono- or triethanolamine, followed, if necessary, by scrubbing with a strong caustic solution. The gas is then mixed with CO_2 and steam to give a mixture of atomic H:C:O::4:1:1. The mixture is re-formed to H_2:CO::2:1. Heat for the re-forming is supplied by burning part of the desulfurized gas with recycle gas. Heat from the flue gas may be used for preheating air to be charged to the burner. The reactor is a vertical tower filled with vertical tubes 2–12 in. in diameter. The tubes are surrounded by a heat exchange fluid such as H_2O. Since each particle of catalyst is enveloped by gas and is in rapid motion, no hot spots develop. The time of contact between catalyst and synthesis gas is 20–25 sec. For light liquid products the pressure is 10–15 p. s. i., for heavier hydrocarbons and waxes lower temperature and higher pressure are used. All of the products are valuable for chemical synthesis as they are aliphatic. 9 United States patents cited.

330. CARRIER, E. W., AND NEIMAN, P. E. (Standard Oil Development Co.). [Dewatering Mixtures of Aqueous Alcohols.] French Patent 954,313; appl. filed Oct. 16, 1947, issued Dec. 22, 1949, in United States Mar. 15, 1947. Chem. Zentralb., 1950, II, p. 340.

Mixtures of aqueous alcohols, particularly of *n*-butyl-, *n*-amyl- and *n*-propyl alcohols, are dewatered by fractional distillation. The alcohol mixture is allowed to settle in a decanter, and the H_2O and alcohol phases are separated. By fractional distillation the 1st phase yields almost pure H_2O and the 2d phase almost H_2O-free alcohol mixture. The forerunnings of both distillations are combined and returned to the decanter. The alcohols are separated from the H_2O-free mixture by fractionation. Butylalcohol goes over at 117.7° and amylalcohol at 138°.

CARTER, S. R. *See* abs. **245, 246, 247, 248.**

331. CASALE, L. [Apparatus for Catalytic Production of Alcohols From Carbon Monoxide and Hydrogen.] French Patent 605,670, no date. Chem. Zentralb., II, 1927, p. 635.

See British Patent 252,713 (abs. **336**).

332. ———. Apparatus for Effecting Gas Reactions Such as Catalytic Production of Sulfuric Acid, Ammonia or Methanol. United States Patent 1,790,853, Feb. 3, 1931. Chem. Abs., vol. 25, 1931, p. 1642.

Describes various details of an apparatus with baffle plates and partitions arranged for heat exchange between products of reaction and gases supplied for the reaction.

333. ———. Carbon Monoxide and Hydrogen From Hydrocarbons. British Patent 274,610, June 2, 1926. Chem. Abs., vol. 22, 1928, p. 2246.

Reaction is effected at about 1,000° in an excess of steam and at a pressure <atmospheric pressure. H_2 and CO free from CH_4 are obtained and if air is used, a gas may be produced suitable for use in NH_3 synthesis.

334. ———. [Catalyst Chamber.] Swiss Patent 127,251, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 214.

See British Patent 252,713 (abs. **336**).

335. ———. [Catalytic Apparatus.] Austrian Patent 119,475, no date. Chem. Zentralb., II, 1930, p. 4337.

See British Patent 252,713 (abs. **336**).

336. ———. Catalytic Apparatus for Hydrogenation of Carbon Oxides to Produce Alcohols. British Patent 252,713, May 28, 1925. Chem. Abs., vol. 21, 1927, p. 2274.

Concentric tubes are arranged so that the reaction gases are heated by the hot reaction products; an electric heater in the inner tube supplies any deficiency of heat and catalytic material is placed in annular spaces between inner and outer tubular partitions. It is stated that by varying the conditions products are obtainable that contain alcohols, aldehydes, ketones, and organic acids, while if N_2 is present amines may be formed.

337. ———. Methanol and Ethanol. Canadian Patent 267,008, Dec. 28, 1926. Chem. Abs., vol. 21, 1927, p. 916.

MeOH and EtOH either isolated or mixed with other oxygenated organic compounds are produced by means of catalytic action between CO and H_2, the reacting gases being caused to flow through a closed circuit by

means of an apparatus having no moving parts and utilizing therein the kinetic energy obtained by transformation of part of the potential energy of the mixture admitted into the circuit under higher pressure than the pressure of the circuit.

338. ———. Methanol and Higher Alcohols. British Patent 252,573, July 27, 1925. Chem. Abs., vol. 21, 1927, p. 2274.

In the catalytic interaction of oxides of C with H_2 or gaseous hydrocarbons, the circulation of the reacting gases in the circuit of the apparatus used is effected by pressure of fresh gases introduced into the circuit, for example, through an injector nozzle. Aldehydes, ketones, and organic acids as well as alcohols are produced.

See also Canadian Patent 267,008 (abs. **337**).

339. ———. [Production of Methanol, Higher Alcohols or Other Oxygen-Containing Compounds.] French Patent 602,467, no date. Chem. Zentralb., II, 1927, p. 635.

See British Patent 252,573 (abs. **338**).

———. *See* abs. **345.**

CASALE, R. *See* abs. **345.**

340. CASALE-SACCHI, M. Apparatus for Heat Interchange and Catalytic Reactions Between Gases Under Pressure at High Temperatures. British Patent 328,139, May 22, 1929. Chem. Abs., vol. 24, 1930, p. 4965.

Describes various structural details.

341. ———. [Catalytic Apparatus.] Austrian Patent 121,245, 1925. Chem. Zentralb., 1931, I, p. 3421.

See British Patent 328,139 (abs. **340**).

342. ———. [Hydrogen and Carbon Monoxide.] French Patent 632,660, Apr. 12, 1927. Chem. Abs., vol. 22, 1928, p. 3497.

In a process for preparing a mixture of H_2 and CO free from CH_4 from hydrocarbons or gaseous mixtures containing hydrocarbons, O_2, and H_2O, the reaction is carried out at a temperature $>1{,}000°$, with excess of H_2O, and at a reduced pressure.

343. ———. [Methanol Synthesis.] Swiss Patent 125,971, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 215.

See British Patent 328,139 (abs. **340**).

344. ———. [Mixtures of Hydrogen and Carbon Monoxide.] Austrian Patent 121,228, Sept. 15, 1930. Chem. Abs., vol. 25, 1931, p. 2436.

Hydrocarbons are treated with O_2 and an excess of steam at a temperature above 1,000° under reduced pressure.

345. CASALE-SACCHI, M., CASALE, R., AND CASALE, L. [Production of Hydrogen, Hydrogen-Nitrogen, and Hydrogen-Carbon Monoxide Mixtures.] Polish Patent 10,649, Oct. 25, 1929; appl. filed July 29, 1927. Chem. Zentralb., 1930, II, p. 2172.

Reaction $C+H_2O=CO+H_2$ is carried out with H_2O in the liquid state, thus $<$ the critical temperature, and at a pressure $>$ the vapor tension at this temperature. The reaction is performed in the presence of finely divided metals and metal oxides. The conversion is complete, and the process is well suited for NH_3 synthesis.

346. CATTERALL, W. E. (Standard Oil Development Co.). Dehydration of Alcohols by Gasoline Extractive Distillation. United States Patent 2,591,672, Apr. 8, 1952. Chem. Abs., vol. 46, 1952, p. 11225.

Alcohols are dehydrated by extractive distillation using, as the solvent, all, or a fraction of the gasoline into which it is desired to blend the alcohol. Mixtures of hydrocarbons and oxygenated compounds are produced by a variety of reactions, such as low-temperature carbonization of coal or peat; destructive hydrogenation of coals, wood, and shales; the MeOH synthesis; the Oxo process in which olefins are caused to react in the presence of CO and H_2; oxidation processes, such as oxidation of propane and other petroleum fractions; and the hydrocarbon synthesis operation. The gasoline used may be gasoline made in the hydrocarbon synthesis, the polymer gasoline recovered from the polymerization process, benzene, or any gasoline or gasoline fraction produced extraneously by catalytic cracking, thermal cracking, and alkylation. The hydrocarbon extractive-distillation solvent added to the top of the tower and descending as reflux has very little capacity to absorb either H_2O or lighter alcohol from the ascending vapor and, therefore, to avoid excessive carryover of alcohol into the overhead, the amount of vapor ascending the tower should be held close to the minimum necessary to assure complete removal of H_2O from the bottoms.

———. *See* abs. **314, 2213.**

347. CATTERALL, W. E., AND OHSOL, E. O. (Standard Oil Development Co.). Multistage Process for Condensing Hydrocarbon Synthesis Products. United States Patent 2,614,115, Oct. 14, 1952; appl. filed Sept. 22, 1948, Serial No. 50,647; 1 claim (*Cl. 260–450*).

Claim 1. A process for separating and recovering neutral low molecular weight oxygenated products, which are more volatile than H_2O, in the presence of H_2O present in a gaseous mixture of uncondensible gases, hydrocarbons, fatty acids, H_2O, and the like in an effluent from an organic synthesis reaction, wherein H_2 and CO are the reactants, which comprises the steps of cooling and condensing the gaseous mixture in a 1st cooling step at a temperature above the dew point of H_2O to condense higher molecular weight hydrocarbons; cooling and condensing a residual uncondensed gaseous mixture from the 1st cooling step in at least 1 stage in a 2d cooling step at a temperature at which a major proportion of the H_2O and fatty acids are condensed but only a minor proportion of the neutral low molecular weight oxygenated products are condensed; cooling and condensing a residual uncondensed gaseous mixture from the 2d cooling step in a 3d cooling step at a temperature $<$in the 2d cooling step at which lower temperature the remaining H_2O is condensed; scrubbing countercurrently residual uncondensed gaseous mixture from the 3d cooling step with the predominantly H_2O and fatty acids condensate from the 2d cooling step as a scrubbing medium in a scrubbing zone to recover a substantial proportion of the neutral low molecular weight oxygenated products contained in this gaseous mixture; discharging liquid bottoms containing the neutral low melecular weight oxygenated products from the scrubbing step to a distillation zone; discharging the resulting condensate from the 3d cooling and condensing step to the distillation zone and distilling the neutral low molecular weight oxygenated products from a resulting mixture in the distillation zone; and recycling a residual liquid bottoms mixture containing fatty acids from the distillation step to an upper portion of the scrubbing zone.

348. CAZES, E., AND CHEFFER, P. [Catalytic Reactor.] French Patent 893,155, June 1, 1944. Chem. Abs., vol. 47, 1953, p. 7840.

Describes reactor that is useful, especially for hydrogenation of C_2H_2 and production of synthetic hydrocarbons. After initial heating by electric coils, gases rise in a vertical, perforated tube, and flow out to baskets filled with catalyst. The baskets can be easily disassembled. A H_2O or an oil jacket keeps the exothermic reaction under control.

349. CEDFORD GAS PROCESS CO., LTD. [Methane From Carbon Monoxide and Hydrogen.] German Patent

237,499, July 20, 1910. Chem. Abs., vol. 6, 1912, p. 1669.

In the catalytic manufacture of CH_4 from commercial gas, which after separation from the CO_2, is condensed to separate the impurities, the cooling is carried to such an extent that the condensed impurities solidify and, consequently, have little or no expansibility.

———. *See* abs. **165, 166.**

350. CELANESE CORP. OF AMERICA. Recovery of Oxygenated Compounds. British Patent 659,727, Oct. 24, 1951.

See United States Patent 2,545,889 (abs. **2095**).

———. *See* abs. **68, 69, 70, 200, 530, 535, 564, 890, 893, 2095, 2349, 2568, 2569.**

351. CENTRE D'ÉTUDES ET DE RECHERCHES TECHNIQUES DU PÉTROLE, DES CARBURANTS ET DES LUBRIFIANTS, AND BADISCHE ANALIN- UND SODA-FABRIK (I. G. Farbenindustrie A. G. "In Auflösung"). [Cracking of Hydrocarbons.] French Patent 976,166, Mar. 14, 1951. Chem. Abs., vol. 47, 1953, p. 2475.

Aliphatic hydrocarbons containing >5 C atoms in the molecule are passed at >450° over a catalyst consisting of an active Al_2O_3 prepared by precipitation from an aluminate with acid and peptizing the precipitate by HNO_3, or by precipitation by alkali from an Al salt at >80°. The product of cracking is a mixture of aromatic hydrocarbons, C_2H_4, C_2H_6, and coke. As aliphatic compounds petroleum products obtained by hydrogenation or cracking of mineral oils or by reaction of CO and H may be used. The catalyst may be supported in SiO_2 gel or on Al silicate. The aliphatic vapors are passed at a rate of 0.1–2 l. per hr. per l. of catalyst. The products may be separated by a selective solvent, for example, SO_2 alone or mixed with propane, phenol, a ketonic acid, or furfuryl alcohol, while unconverted hydrocarbons may be recycled.

352. CENTRE NATIONALE DE LA RECHERCHE SCIENTIFIQUE. [Reacting Carbon Monoxide and Hydrogen.] French Patent 973,289, Feb. 9, 1951. Chem. Abs., vol. 46, 1952, p. 9287.

Mixture of CO and H_2 is passed over a Ni catalyst at 300° and atmospheric pressure to remove substantially all the CO. Steam may be mixed with the gases before the reaction. A mixture of equal volumes of CO and H_2 and 15% steam is passed over a catalyst consisting of kaolin 30%, NiO 45%, sand 15%, K_2CO_3 3%, and Na_2CO_3 7% at the rate of 100 vol. per hr. The resulting gas which is 66.7% of the original volume consists of CO, 0.7%; CO_2, 41%; CH_4, 31.7%; and H_2, 26.6%. If steam is added to the extent of 30% the gas obtained, 91.6% of the original volume consists of CO, 0.5%; CO_2, 29%; CH_4, 29%; and H_2, 41%.

353. CHAFFETTE, M. [Decomposition of Methane.] French Patent 733,248, Mar. 14, 1932. Chem. Abs., vol. 27, 1933, p. 813.

CH_4 is submitted to partial combustion in a mixture containing O_2 and steam at a high temperature, such as 1,300°, to transform the greater part of the CH_4 into C_2H_2 and other unsaturated hydrocarbons, CO and H_2. Steam is added to the gas obtained, and the mixture is passed over a Ni catalyst at about 800°. The resulting gas contains a smaller amount of hydrocarbons and may be used for the synthesis of NH_3 or MeOH.

354. ———. [Decomposition of Methane.] French Patent 734,032, Mar. 23, 1932. Chem. Abs., vol. 27, 1933, p. 1111.

CH_4 is decomposed by steam to a mixture of H_2, CO, and CO_2 at 500° or more and in the presence of a catalyst composed of mixtures having a base of Ni and metals of the group of rare earths, particularly of the group of ceric earths.

See French Patent 733,248 (abs. **353**).

355. ———. [Gas Mixtures Rich in Hydrogen, Carbon Monoxide, and Carbon Dioxide.] Belgian Patent 387,296, Apr. 30, 1932. Chem. Abs., vol. 27, 1933, p. 1463.

CH_4, or gases containing it, are decomposed at a temperature of at least 500° in presence of a catalyst consisting of a mixture of salts of Ni and of rare-earth metals, particularly those belonging to the Ce group.

356. ———. [Production of Gas Mixtures Suitable for Various Syntheses.] Belgian Patent 387,055, Apr. 30, 1932. Chem. Abs., vol. 27, 1933, p. 1463.

Mixture of H_2, CO, and CO_2 is obtained from CH_4, H_2O, and O_2 by effecting incomplete combustion of CH_4 at high temperature and passing the resultant gas mixture, after addition of H_2O vapor, over a catalyzer at a temperature not less than 500°.

357. CHAKRAVARTY, K. M. Catalytic Masses for Hydrocarbon Synthesis. British Patent 580,612, Sept. 13, 1946, appl. filed July 7, 1944. Chem. Abs., vol. 41, 1947, p. 2218.

Catalytic masses, especially those containing Ni for promoting the reaction of CO and H_2 for the synthesis of hydrocarbons by the Fischer-Tropsch process can be improved in their capacity to form higher hydrocarbons, and their period of activity can be prolonged by reducing the metal carbonate (used in their preparation) in presence of residual alkali and removing the alkali after or during the reduction. In example (I) kieselguhr, is suspended in a solution containing pure salts of Ni and Th, preferably $Ni(NO_3)_2$ and $Th(NO_3)_4$, the quantities being such that the ratio by weight of $Ni : ThO_2$: kieselguhr in the final catalytic mass is 100 : 18 : 100. A solution of K_2CO_3 or Na_2CO_3 is then added to the mixture to precipitate the Ni and Th completely as their carbonates. The insoluble material is separated and washed with distilled H_2O until the washings have a pH of about 10. The material is then dried and heated at 400° in a current of H_2 to reduce the $NiCO_3$ to Ni, the Th being converted to ThO_2. The slight amount of alkali, necessary during reduction, is then removed by washing with distillated H_2O, while boiling, until the washings have pH of about 7. The mass is then dried by heating in a current of H_2. In example (II), the $NiCO_3$ and $Th(CO_3)_2$ are precipitated on kieselguhr, and the insoluble material is separated, washed, and dried, as in example (I); a powdered catalytic mass (0.5%–5.0% of the weight of the final catalytic mass) previously prepared and reduced as described in example (I), is added; the mixture is reduced by heating at 350° in a current of H_2; and the alkali is completely removed by washing and the mass dried as in example (I). This results in a further improved catalytic mass. For preparation of catalytic masses useful at higher temperature, the presence of Ce (1% of Ce_2O_3 based on combined weights of Ce_2O_3 and ThO_2) in the catalytic mass containing Ni and Th is beneficial. Substitution of $(NH_4)_2CO_3$ for K_2CO_3 or Na_2CO_3 above is permissible, and results in volatilization of the alkali during reduction.

CHEFFER, P. *See* abs. **348.**

CHEMICAL CONSTRUCTION CORP. *See* abs. **2782.**

CHEMICAL FOUNDATION, INC. *See* abs. **368.**

358. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON. Methane. British Patent 244,076, Dec. 3, 1924. Chem. Abs., vol. 21, 1927, p. 104.

CH_4 is prepared by interaction of CO and H_2-containing gases in the presence of a Ni catalyst at temperatures of 400° or higher. The gas flow is adjusted to insure rapid removal of the product from the reaction zone.

359. CHEMISCHE FABRIK VON HEYDEN A. G. [Thorium Oxide.] French Patent 828,334, May 16, 1938. Chem. Abs., vol. 33, 1939, p. 330.

Th oxide having particularly good reactional properties is made by heating complex salts containing Th oxalate to 285°–450°. The heating is continued until the oxide dissolves in some hours in 3–4 times the amount of boiling concentrated HNO_3.

———. *See* abs. **2432.**

360. CHEMISCHE WERKE ESSENER STEINKOHLE A. G. [Process for Obtaining a High-Grade Fuel Gas From the Catalytic Hydrogenation of Carbon Monoxide.] German Patent Appl. C 56,916, Nov. 25, 1941 (*Cl. IV d–12 o*). TOM Reel 177, frames 1,666–1,669; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 46, 1948, p. 110.

Before the synthesis gas centers the reaction space, CH_4 is added in such an amount that, after the termination of the reaction and separation of the nongaseous products, a high-grade fuel gas of normal heating value remains as residual gas. Coke-oven gas may be decomposed by steam and the products mixed with water gas to make a synthesis gas of composition $CO : H_2 = 1 : 2$ and 4–4.5% of CH_4.

361. ———. [Process for Producing Higher Hydrocarbons by the Catalytic Hydrogenation of the Oxides of Carbon.] German Patent Appl. C 57,060, filed Jan. 26, 1942 (*Cl. IV d–12 o*). TOM Reel 177, frames 1,653–1,654; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 42, 1948, p. 103.

Method described in German Patent Appl. C 56,917 (abs. **362**), in which the hydrogenation is accomplished in several steps in such a manner that the fresh synthesis gas is contacted in the 1st step with the least active catalyst, the activity of which increases progressively from the 1st to the last step and is improved by diluting the synthesis gas added in the last step with end gas. In such a manner overheating of the catalyst and a possible run-away reaction is avoided, prolonging the useful life of the catalyst and increasing the yield of desired products.

362. ———. [Process for the Production of Higher Hydrocarbons by the Catalytic Hydrogenation of the Oxides of Carbon.] German Patent Appl. C 56,917, filed Nov. 27, 1941 (*Cl. IV d–12 o*). TOM Reel 177, frames 1,663–1,665; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 45, 1948, p. 108.

Hydrogenation takes place in several stages, at least 2, and in such a manner that the activity of the catalyst increases in the direction of the gas flow, that is the fresh or regenerated catalyst is introduced into the last stage of the process and the exhausted catalyst withdrawn from the 1st stage.

363. ———. [Revivification of Catalysts Used in Benzine Synthesis.] German Patent 749,391, Feb. 17, 1942; appl. C 57,121 (*Cl. 12 o–1.03*). TOM Reel 177, frames 1,655–1,658; Auszüge deut. Patent-Anmeldungen, vol. 6, p. 30; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 43, 1948, p. 105.

Catalysts that have lost their operating efficiency are 1st revivified by extraction with benzine or other suitable solvent and then, after another operating period, by treatment at increased temperature (about 200°) with H_2, this rotation being repeated until the catalyst is exhausted. Several extractions may alternate with operating periods until further extractions are not worth while, then rotation of H_2 treatments with extractions may be used. This rotation method is preferred to the combination of the 2 kinds of treatment in that the valuable paraffin deposited on the catalyst can be saved, the life of the catalyst is further prolonged, and the quality of the hydrocarbon products is improved. Gives definitions of what differentiates revivification and regeneration.

364. CHEMISCHE WERKE HUELS G. M. B. H. (I. G. Farbenindustrie A. G.). [Oxygenated Compounds.] German Patent Appl. I 78,908, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 248.

Oxidation products, which are obtained by oxidation in the liquid phase with O_2 or gases containing it of the hydrocarbon fractions b. 200°–350° and produced by the conversion of CO or CO_2 with H_2, are catalytically hydrogenated under pressure in such a way that the product possesses virtually no acid number but still contains some O_2.

365. CHEMISCHES WERK SCHOLLENE G. M. B. H. [Cumarone Resins.] German Patent Appl. C57,983, no date (*Cl. IV c.–22* h.). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 654.

Indene-like resins are obtained from cumarone resins by dissolving them in benzol hydrocarbons and treating with Fischer-Tropsch benzine of highly unsaturated character, 3–4 C atoms.

366. ———. [Refined Cumarone Resins.] German Patent Appl. C 57,593, no date (*Cl. IV c–22 h*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 654.

Selective processing of cumarone resins by dissolving 2 parts of cumarone resin in 1 part benzol and then precipitating the dark constituents by means of Fischer-Tropsch benzine.

367. CHRIST, R. E. (General Aniline & Film Corp.). Stabilized Iron Carbonyl. United States Patent 2,514,312, July 4, 1950; appl. filed Dec. 30, 1947, Serial No. 794,785; 7 claims (*Cl. 44–67*). Chem. Abs., vol. 44, 1950, p. 9644.

Fe carbonyl's stability to light is improved by blending it through an organic solvent with at least 5% of its volume of tall oil soap composition. The tall oil is partly saponified in a liquid diluent aliphatic alcohol of at least 3 C atoms with an alkylene polyamine from the group of polyalkylene polyamines and hydroxyalkyl alkylene polyamines. The saponification is completed with K hydroxide. 2 United States patents cited.

368. CHRISTENSEN, L. M. (Chemical Foundation, Inc.). Power Alcohol. United States Patent 2,194,496, Mar. 26, 1940; appl. filed Feb. 17, 1938, Serial No. 191,116 (*Cl. 44–9*). Chem. Abs., vol. 34, 1940, p. 4,889.

Motor fuel consisting of a gasoline-alcohol blend, crude synthetic MeOH or the higher fractions of it containing 9–11 C atoms, may be used as the denaturant.

369. CHRISTESCU, J. Alcohol Production. British Patent 427,221, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 216.

$CO + H_2$ is passed at about 100° through a catalyst suspended in H_2O.

CHRISTMANN, F. *See* abs. **2651, 2652, 2653, 2654, 2655, 2656, 2657.**

370. CHURCH, H. [Formaldehyde From Carbon Monoxide and Hydrogen.] French Patent 519,649, 1919. Chem. Zentralb., 1921, IV, p. 653.

CH_2O is obtained by passing a mixture of molecular amounts of dry HCl, CO, and H_2 at 200°–300° over a mixture of Cu chloride with Cu, Fe, or Ni. Formic chloride is formed as the intermediate product, which is then decomposed by the H_2 to CH_2O and HCl. The reaction takes place at relatively low velocity at 200° and $< 300°$ quantitatively.

CHURO, L. N. *See* abs. **265.**

CIAMPI, C. *See* abs. **3990.**

371. C. I. B. A., Ltd. (formerly Société pour l'industrie chimique á Bâle.) [Catalytic Hydrogenation of Carbon Monoxide to Hydrocarbons.] Swiss Patent 273,952, June 1, 1951 (*Cl. 360*). Chem. Abs., vol. 46, 1952, p. 710.

Catalysts containing SiO_2 8–15; MgO 15–25 per 100 parts of total Co gave improved conversion to higher hydrocarbons and smaller amounts of CH_4. Na_2CO_3 solution, 140 gm. per 1.5 l., was added to 1.5 l. boiling Co salt solution containing 42.4 gm. Co per l., the precipitate was washed, stirred with 20 cc. water glass, filtered and washed, stirred with a paste made from 14 gm. calcined MgO, filtered, dried, and hydrogenated 2 hr. 400° to give 74 gm. catalyst with 233 gm. per l. total Co content, 38% metallic Co. The hydrocarbons obtained at atmospheric pressure from CO 39, H_2 59, inert gases 2% were 15.2% C_{1-2}, 25.7 C_{3-4}, 9.8 paraffin and heavy oil, and 45 benzine (C_{5-12}). The benzine contained olefin in the C_{5-8} fraction 55–70, and in the C_{9-12} fraction 40–50%.

CIE DES PRODUITS CHIMIQUES ET ÉLECTROMÉTALLURGIQUES. *See* abs. **744.**

372. CIER, H. E. (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,615,910, Oct. 28, 1952. Chem. Abs., vol. 47, 1953, p. 1359.

Hydrocarbons and oxygenated organic compounds are produced by treating an oxidized Fe-type catalyst free from carbonaceous material with a gaseous mixture of CO and H_2 at 343°–399° and 0–450 p. s. i. g. for 30 min. to 12 hr., and then reducing the temperature 10°–93° to form a substantial amount of the products. In an example, Fe oxide catalyst, to which has been added 2% by weight K_2CO_3, based on the catalyst weight, was divided into 2 portions. One part was pretreated by passing a mixture consisting of equal parts of H_2 and CO into contact with it at 343°–399° and 0 lb. pressure for 1 hr. The other part was treated in a conventional manner with H_2 at 482° for 4 hr. Each portion was then used to synthesize hydrocarbons by contact with a gaseous mixture of equal parts of CO and H_2 at the rate of 200 vol. feed gas per vol. catalyst per hr., 288°, and 150 p. s. i. g. In the case of the 1st portion, 172 cc. C_4 and heavier hydrocarbons per $m.^3$ H_2 and CO consumed were produced. With the 2d portion only 120 cc. of the hydrocarbons were formed.

CITIES SERVICE OIL CO. *See* abs. **755, 966, 967, 1111, 2106, 2574.**

373. CLAR, C., GEISER, N., AND KÜHNEL, P. (Ruhrchemie A. G.). Lubricating Oils. United States Patent 2,238,846, Apr. 15, 1941; appl. filed Aug. 2, 1938, Serial No. 222,680; in Germany Aug. 9, 1937; 4 claims (*Cl. 196–78*). Chem. Abs., vol. 35, 1941, p. 5303.

In the production of lubricating oils by catalytically hydrogenating CO, cracking the nongaseous hydrocarbons thus obtained, and converting the cracking products into lubricating oils with use of a polymerizing agent comprising $AlCl_3$, the oil is heated in the presence of the polymerizing agent to about 140°–240° C. without additions of halogenated hydrocarbons.

374. CLARK, A. (Phillips Petroleum Co.). Aliphatic Amines. United States Patent 2,518,754, Aug. 15, 1950. Chem. Abs., vol. 44, 1950, p. 10729.

Mixture of NH_3 15.6, H_2 52.4, CO 25.6, and N_2 2.5 mol.-% and CO_2, CH_4, and O_2, passed over a catalyst containing Co 100, ThO_2 18, and kieselguhr, 100 parts at a space velocity of 70–140 vol. per vol. catalyst per hr., 150 p. s. i. g., and 182°–221° formed a mixture of primary aliphatic amines containing 1–12 C atoms. Describes apparatus.

375. ——— (Phillips Petroleum Co.). Control of Catalyst Concentration. United States Patent 2,583,255, Jan. 22, 1952; appl. filed May 24, 1948, Serial No. 28,779; 9 claims (*Cl. 260–449.6*). Chem. Abs., vol. 46, 1952, p. 4203.

When synthesizing hydrocarbons in contact with a fluidized catalyst suspended in an upward flowing stream of synthesis gas comprising H_2 and CO in the molal ratio of 1:1 to 3:1, the concentration of the catalyst in the reaction zone is controlled by recycling thereto in the influent gas a portion of the effluent products containing <4 C atoms per molecule while maintaining a substantially constant pressure differential between the top and bottom of the reaction zone by varying the velocity of the recycled effluent gas so as to compensate for any variations in the pressure differential and thereby maintain substantially constant the density of the suspended catalyst and the pressure in the reaction zone. The volume ratio of recycled effluent gas to fresh synthesis gas varies between 1:1 and 8:1. The catalyst is powdered metallic Fe of 65- to 100-mesh size. The minimum velocity of the influent gas to maintain the catalyst bed in a fluid state is 0.6 ft. per sec. The preferred reaction temperature varies 500°–750° F., the pressure 50–500 p. s. i., and the space velocity 500–5,000 vol. fresh gas per vol. catalyst per hr.

376. ——— (Phillips Petroleum Co.). Conversion of Hydrocarbons. United States Patent 2,467,966, Apr. 19, 1949; appl. filed Jan. 2, 1948, Serial No. 238; 5 claims (*Cl. 260–450*). Chem. Zentralb, 1950, I, p. 1935; Chem. Abs., vol. 43, 1949, p. 4834.

Fischer-Tropsch process and a hydrogenolysis process are used simultaneously and in conjunction with one another to produce premium quality gasoline and diesel fuel. A minimum of light gases and virtually no heavy residue boiling above the diesel fuel range are formed. 5 United States patents cited.

377. ——— (Phillips Petroleum Co.). Fischer-Tropsch Catalyst Preparation and Regeneration. United States Patent 2,636,011, Apr. 21, 1953; appl. filed Feb. 2, 1948, Serial No. 5,909; 14 claims (*Cl. 252–411*). Chem. Abs., vol. 47, 1953, p. 6637.

Reduced Fe oxide catalyst for synthesis of hydrocarbons from CO and H_2, promoted with K oxide is improved by treatment with CO_2 for 5 hr. at 250°–350° C., pressure 5–30 atm. Wax formation is reduced. 1 literature ref. and 14 United States patents cited.

378. ——— (Phillips Petroleum Co.). Fischer-Tropsch Process for the Synthesis of Hydrocarbons. United States Patent 2,564,958, Aug. 21, 1951; appl. filed June 21, 1948, Serial No. 34,212; 3 claims (*Cl. 260–449.6*).

Object of the invention is to provide for the synthesis reaction and the catalyst regeneration to be carried out simultaneously in the same reactor. The reactor comprises 2 zones in free communication with each other, that portion above the synthesis gas inlet being the synthesis zone and that below being the catalyst regeneration zone, the former having 5–10 times the volume of the latter. The reactor is filled with fluidized catalyst, which is maintained at 295°–325° and 5–30 atm. pressure, the fresh synthesis gas being introduced at a space velocity of 1,500–3,000 vol. per vol. per hr. into the bottom of the synthesis reaction zone. The gaseous portion of the effluent from the synthesis zone rich in H_2 and CO_2 is recycled to the bottom of the regeneration zone at a space velocity 2–4 times that of the synthesis gas. The volume ratio of recycle to fresh synthesis gas is about 3:1. The fluidized catalyst particles are thus passed back and forth through the synthesis and regeneration zones and are reactivated. At the end of about 300 hr. continuous operation, CO conversion is 97%, as compared with 91% for systems not employing continuous regeneration. Diagram.

379. ——— (Phillips Petroleum Co.). Fischer-Tropsch Synthesis Gas From Oil Shale. United

States Patent 2,452,634, Nov. 2, 1948; appl. filed Aug. 25, 1947, Serial No. 770,534; 10 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 1170.

Oil shale and O_2 or a gas containing free O_2, such as air, are charged to the top of a reaction zone operated at a temperature 1,500°–2,000° F. The pressure may be atmospheric or as high as 500 p. s. i. Stripped shale is removed at the bottom of the reactor, and a gas mixture of CH_4, CO_2, and/or steam in ratio 3 : 1 : 2 is introduced. From an intermediate point in the reactor, synthesis gas is withdrawn. In the upper section, the exothermic reaction between the organic matter liberated from the shale and O_2 heats the shale and produces CO_2 and H_2. In the lower section heat for the endothermic reaction of CH_4 with steam and/or CO_2 to form H_2 and CO is furnished by the heat carried by the shale from the upper zone. The particle size of the oil shale may vary considerably, but 8- to 16-mesh has been found desirable.

380. ——— (Phillips Petroleum Co.). Hydrocarbon Synthesis Catalyst. United States Patent 2,583,254, Jan. 22, 1952; appl. filed Dec. 5, 1947, Serial No. 790,-017; 5 claims (*Cl. 260–449.6*).

Catalyst for the synthesis of hydrocarbons by the reduction of CO with H_2 comprises promoted metallic Fe formed by reduction of a comminuted fused mixture of Fe_3O_4, 0.05–1.0 wt. % of K_2O based on the Fe_3O_4, Al_2O_3 in a molecular equivalent proportion to the K_2O plus an excess of 1–2 wt. % based on the Fe_3O_4, and CaO in the proportion of 1–10 wt. % of the Fe_3O_4. Describes preparation and reduction of the catalyst.

381. ——— (Phillips Petroleum Co.). Process and Apparatus for Synthesis of Hydrocarbons. United States Patent 2,500,519, Mar. 14, 1950; appl. filed Oct. 14, 1947, Serial No. 779,673; 10 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 4656.

Process is illustrated by the following example: A gas mixture 30 wt. % H_2 : 15 CO : 55 N_2, CH_4 and other inerts are passed through a Fischer-Tropsch reactor containing 60 to 100 mesh reduced Fe catalyst. The vertical steel reactor is provided internally with vertical cylindrical cooling tubes through which oil is circulated to remove heat of reaction. The temperature is 320° C., pressure 200 p. s. i., space velocity 2,500 gas vol. (STP) per vol. catalyst per hr. The catalyst near the inlet is satisfactorily fluidized, but further downstream it is not. This is due to normal contraction of the gas during reaction. Large amounts of CH_4, CO_2 and C are formed. The cooling tubes are replaced with cylindrical tubes, each of which has 4 expanded sections equidistantly spaced along the tube axis and at points adjacent to those on the other tubes. The maximum cross-sectional diameter of the expanded sections is 4 times the diameter of the cylindrical part of the tubes. The increased cooling surface and the improved fluidization improves the cooling and increases the efficiency of the reaction. 8 United States patents cited.

382. ——— (Phillips Petroleum Co.). Production of Diolefins and Motor Fuel From Carbon Monoxide and Hydrogen. United States Patent 2,506,065, May 2, 1950; appl. filed Jan. 2, 1948, Serial No. 239; 7 claims (*Cl. 260–450*). Chem. Abs., vol. 44, 1950, p. 6605.

Effluent from Fischer-Tropsch process is separated into a hydrocarbon phase and an aqueous phase containing H_2O-soluble,, O-containing compounds. These compounds are recovered to the extent of 10–25% of the CO converted. The aqueous phase is then separated into 2 fractions at a distillation cut point of 100 C. The fraction boiling below 100° C is an azeotropic mixture containing 6–25% H_2O and is suitable charge stock without further refining for production of diolefins, particularly butadiene. Zn oxide–alumina or Mg oxide-silica as catalyst, temperature 380°–450° C, and pressures not greater than 20 lb. absolute are conditions for the butadiene production. With Ta oxide as catalyst the temperature is 300°–375° C. Yields of 27–40 lb. butadiene per 100 lb. anhydrous ethyl alcohol may be expected. C_5 and C_6 diolefins as well as some polymers and aldehyde condensation products are obtained. The last 2 materials are separated and refined along with the hydrocarbon phase from the Fischer-Tropsch synthesis. The method converts what was a waste product or material difficul to refine to a useful product. 1 foreign and 4 United States patents cited.

383. ——— (Phillips Petroleum Co.). Regeneration of Catalysts Used in the Production of Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,479,999, Aug. 23, 1949; appl. filed May 28, 1945, Serial No. 596,407; 7 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 9420.

Fischer-Tropsch reaction is carried out under known conditions until the activity of the catalyst declines owing to waxy deposit. Then the temperature of the catalyst bed is raised by cutting down the flow of cooling fluid or by introducing heating fluid into the heat exchanger until CH_4 and steam are the predominant reaction products formed. The actual minimum temperature to accomplish this result will depend on the catalyst used. For a Co : Th : kieselguhr catalyst 100 : 18 : 100, this temperature is approximately 270° C. For an ordinary Fe catalyst it will be 300° C. or higher, whereas for a sintered Fe catalyst it will be 340° C. In an example using a Co : Th : kieselguhr catalyst 100 : 18 : 100, the temperature was allowed to rise to 308° C. and maintained until analysis of the effluent showed essentially CH_4 and C_2H_6. The treatment was continued for 5 hr. The effluent was O_2, 6.1%; CO_2, 13%; olefins, 0.4%; H_2, 9.4%; CO, 1.1%; CH_4, 62%; and C_2H_6, 6.9%. At this point the catalyst was free from waxy deposit. The temperature was dropped to 246° C., and the synthesis continued. The reaction products with both fresh and reactivated catalyst in ml. per $m.^3$ of synthesis gas was as follows:

Solid and liquid hydrocarbon	90
Oil b. above 200° C	20
Gasoline b. below 200° C	41
Gaseous hydrocarbons (including O_3 and C_4)	5
Paraffin wax	25

2 literature refs. and 5 United States patents cited.

384. ——— (Phillips Petroleum Co.). Removal of Exothermic Heat of Reaction. United States Patent 2,526,934, Oct. 24, 1950; appl. filed Jan. 20, 1947, Serial No. 723,195; 3 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 1752.

Boiling point of coolant is coordinated with reaction temperature and pressure so that the coolant is introduced at its boiling point under such conditions that a substantial part is in the liquid phase. Maximum cooling effect is realized by adsorption as latent heat of vaporization of the liquid, preferably H_2 and CO are introduced countercurrent with the coolant. At no point should the coolant establish a level. When it is necessary, as in Fischer-Tropsch reaction to increase reaction temperature to maintain conversion level, the reaction pressure is correspondingly increased to keep the coolant under boiling conditions. Fischer-Tropsch products, 295°–305° F. fraction, may be used at 30–40 p. s. i. and 392° F. with Co–Th catalyst. With hydrocarbon coolant, ratio of coolant to product will be 40–100, with H_2O a ratio as low as 15 may be used. Reaction temperatures for Co–Th catalyst will be 180°–220° C., for Ni–Th, 170°–200° and for Fe, 220°–280° C. Space velocities for Co–Th and Ni–Th will be 100 vol. synthesis gas per vol. catalyst per hr.; for Fe it may be as high as 150 or 300. Pressure may be atmospheric—500 p. s. i. Synthesis gas composition for Co

and Ni catalysts may be H_2 : CO=2 : 1 ; for Fe, H_2 : CO= 1–2 : 1. 2 foreign and 4 United States patents cited.

385. ——— (Phillips Petroleum Co.). Synthesis of Hydrocarbons. United States Patent Appl. 684,143, no date. Official Gaz., vol. 628, 1949, p. 1531 ; Chem. Abs., vol. 44, 1950, p. 11067.

After pyrolysis of CH_4 and removal of aromatic hydrocarbons formed thereby, the residual gas is reformed in presence of O_2 and/or CO and then passed through a hydrocarbon-synthesis reactor. The products so obtained, either with or without preliminary separation of gaseous components, are mixed with the aromatic hydrocarbons from the pyrolysis step, and the mixture is fractionated to produce high-octane gasoline.

386. ——— (Phillips Petroleum Co.). Synthesis of Hydrocarbons. United States Patent 2,450,500, Oct. 5, 1948; appl. filed Sept. 5, 1945, Serial No. 614,578; 7 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 839.

Synthesis gas H_2 : CO=3 : 2 at a pressure of 200 p. s. i. is preheated to 180° C., then made to flow downward through tubes, 3 in. inside diameter, 10 ft. long, connected in parallel. Each tube is packed with 3 different layers of catalyst. The progressive order upward is sintered Fe, 4 ft.; Fe, 3 ft.; Co–Th, 3 ft. The space velocity is maintained at 150 vol. per vol. of catalyst per hr. The reactants and products become hotter as they flow downward. The temperature at the Co–Th and Fe junction is 205° C. and at the Fe-sintered Fe junction 260° C. The effluent gas is 320° C. A liquid mineral seal oil flows upward outside of the tubes countercurrent to the gas flow. The rate of flow is adjusted to maintain the catalyst junction temperatures. 70% conversion takes place representing a light hydrocarbon fraction, 86 wt. %, heavier fraction, 14 wt. %. Various combinations of catalysts may be used. 1 literature ref. and 3 United States patents cited.

387. ——— (Phillips Petroleum Co.). Synthesis of Hydrocarbons. United States Patent 2,486,633, Nov. 1, 1949; appl. filed Sept. 10, 1945, Serial No. 615,349; 4 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 1674.

Alcohol, preferably methyl or ethyl, is used for thermal control in hydrocarbon synthesis. The alcohol enters the reaction zone adjacent to the synthesis gas and at points in the direction of flow through the reaction zone. The vaporization of the alcohol absorbs heat evolved during the synthesis. The alcohol is used in combination with external cooling means. With methyl alcohol 0.002–0.003 lb. alcohol per B. t. u. of heat to be removed is used and with ethyl alcohol 0.0025–0.0035 lb. is used. The reaction chambers are considerably larger in diameter than those normally used in hydrogenation of CO. Example: CO : H : : 1 : 2 at 225° C. and 100 p. s. i. is reacted using Co–Th catalyst. Approximately ½ of the heat of reaction is removed by passing mineral seal oil around the reaction chamber. 6.5 lb. methyl alcohol per lb. of normally liquid hydrocarbon formed is introduced into the reaction chamber adjacent to the entering gas to hold the temperature at 225°. The effluent is condensed and the products separated. The alcohol is recycled. The hydrocarbon fraction analyzed about 75% or more normally liquid hydrocarbons. 1 literature ref. and 7 United States patents cited.

388. ——— (Phillips Petroleum Co.). Synthesis of Hydrocarbons. United States Patent 2,497,761, Feb. 14, 1950; appl. filed Sept. 10, 1945, Serial No. 615,348; 9 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 4655.

Hydrocarbons are synthesized by reacting H_2 and an oxide of C in presence of suitable catalyst and simultaneously contacting the products of reaction with excess vaporous hydrocarbons over and above those formed by the reaction. The hydrocarbon, preferably an unsaturated, aliphatic hydrocarbon, introduced into the reaction zone has 5–12 C atoms per mol. A hydrocarbon mixture such as 25°–200° C. fraction from a cracking process or from the reaction itself may be used. The hydrocarbon is volatilized and passes through the reaction zone as a vapor. The reaction may be alkylation or polymerization. Consumption of H_2 is not increased. An example in which a fraction is recycled shows an increase of normally liquid hydrocarbons of 66% or more. 8 United States patents cited.

389. ——— (Phillips Petroleum Co.). Synthesis of Hydrocarbons. United States Patent 2,567,596, Sept. 11, 1951 ; appl. filed Mar. 25, 1946, Serial No. 656,965 ; 4 claims (*Cl. 260–449.6*).

In performing the synthesis of hydrocarbons from CO and H_2, it is highly desirable to prevent the accumulation of liquid hydrocarbons in the reaction zone since they cover the catalyst and prevent intimate contact between catalyst and reaction gas, thus decreasing catalyst activity. Such liquid hydrocarbons comprise a mixture of C_{16}–C_{150} hydrocarbons of an average molecular weight of about 750. The removal of accumulated liquid hydrocarbons is effected by conducting the hydrogenation of CO in a horizontal elongated reaction chamber, the reactants entering 1 end and the reaction effluents draining from the bottom of the other by gravity. The reaction chamber also may be placed in a slanting position. The temperature range for the synthesis operation and for the various catalysts that may be used is 150°–400°, pressure 100–125 p. s. i., space velocity 80 for Co catalysts and up to 400 for sintered Fe catalysts. Composition of the feed is normally in a molar ratio of CO : H_2=1 : 2–2 : 3. The yield of liquid hydrocarbons is about 100 gm. per standard $m.^3$ and the conversion of CO in a single pass is about 70%. The condensed product at the outlets is about 20–25% of the total product and contains less wax than that obtained by conventional operation.

390. ——— (Phillips Petroleum Co.). Synthesis of Hydrocarbons. United States Patent 2,610,200, Sept. 9, 1952; appl. filed May 15, 1946, Serial No. 669,792; 4 claims (*Cl. 260–449.6*). Chem. Abs., vol. 47, 1953, p. 1359.

Synthesis of hydrocarbons from CO and H_2 in the presence of a Co catalyst is carried out in 2 stages. In the 1st stage the proportion of H_2 : CO=1 : 3 by volume and conversion of the CO amounts to not more than 70%. The C_{3+} products of reaction are separated from the effluent, and a residual gas is recovered containing unreacted CO and H_2 together with gases inert in the synthesis reaction, the vol. % CO and the H_2 : CO ratio being < that in the feed gas to the 1st conversion stage. Additional CO is added to the residual gas to raise the vol. % of CO to that present in the feed gas to the 1st conversion stage without increasing the H_2 concentration therein. The resulting gas mixture is introduced into a 2d stage conversion zone under the same conditions as in the 1st stage. The yields of additional hydrocarbons thus synthesized are equal to those of the 1st stage. The reaction temperatures in each stage are within the range of 175°–225° and the pressures 5–50 atm.

———. *See* abs. **2181.**

CLARK, E. L. *See* abs. **611.**

391. CLAUSSEN, W. F. (The Texas Co.). Manufacture of Gasoline Hydrocarbons. United States Patent 2,400,075, Aug. 14, 1946; appl. filed Apr. 14, 1943, Serial No. 482,975; 3 claims (*Cl. 196–52*). Chem. Abs., vol. 40, 1946, p. 4511.

Hydrocarbon oil is catalytically cracked to produce gasoline hydrocarbons and also gaseous materials including H_2 and normally gaseous hydrocarbons such

as CH_4. The catalyst is regenerated by treating with CO_2 under conditions such that CO_2 is converted to CO and the carbonaceous material is burned from the catalyst. The catalyst is used again in cracking fresh feed oil, and the CO produced in the regeneration is used for reactions with H_2 to form synthetic hydrocarbons by the Fischer-Tropsch process.

COAL & CHEMICALS, LTD. *See* abs. **2738, 2739.**

COAST REDUCTION, INC. *See* abs. **887.**

392. COGHLAN, C. A. (The Texas Co.). Conversion of Heavy Carbonaceous Oils to Motor Fuels, Fuel Gas, and Synthesis Gas. United States Patent 2,605,-215, July 29, 1952; appl. filed Jan. 15, 1949, Serial No. 71,088; 3 claims (*Cl. 196–62*).

Hydrocarbon oil is fed into a cracking zone as a spray and into direct contact with an upward flowing stream of hot gases comprising CO and H_2. The droplets of oil descend through the cracking zone, maintained at about 800°–1,500° F., and are gasified and cracked leaving a free-flowing and highly reactive granular coke residue, which is fed directly into a gasification zone of the fluid-bed type and there reacted with steam and O_2 at about 1,800°–3,000° F. to form a gas consisting essentially of CO and H_2. The cracking and gasification zones may be operated under pressures from atm. to 1,000 p. s. i.

393. COHN, H., AND NON-POISONOUS GAS HOLDING CO., LTD. Catalysts. British Patent 424,478, Feb. 21, 1935. Chem. Abs., vol. 20, 1935, p. 5254.

A catalyst for the water-gas reaction consists of an Fe compound, such as $Fe(OH)_3$, an activating alkali metal compound, for example K_2CO_3, and a H_2O-eliminating binder, such as cement. The Fe compound and the binder are loosely mixed and shaped into spheres without pressure, for example in a revolving drum. The activator may be mixed with the other ingredients but preferably part of it is applied in solution as an impregnating agent after the shaping.

394. COLE, R. M. (Shell Development Co.). Solvent Extraction of Olefins. United States Patent 2,523,-681, Sept. 26, 1950. Chem. Abs., vol. 45, 1951, p. 341.

Olefins of 2–8 C atoms are extracted from hydrocarbons in the gasoline boiling range using an aqueous solution of $AgNO_3$ and PhOH composed of 10%–22% by weight of H_2O and $AgNO_3$ and PhOH in the ratio 1:2. About 10%–20% by volume of olefins of 5 C atoms are absorbed by this solution, and a $AgNO_3$ solution solutized with ethylene glycol absorbs 4%, and straight $AgNO_3$ solution 1–2%. Since absorption increases only slightly with decreasing temperature, the process is carried out at room temperature. The high solubility of olefins in the solution can be utilized for storing and transporting olefins that are normally gaseous. Gives examples for extraction of various olefins under different conditions.

395. COLEY, J. R. (The Texas Co.). Method of Producing Ketones. United States Patent 2,516,958, Aug. 1, 1950; appl. filed May 23, 1946, Serial No. 671,685; 7 claims (*Cl. 260–595*). Chem. Abs., vol. 45, 1951, p. 1159.

CO and H_2 are converted into primarily oxygenated products by using temperatures below those normally used with particular catalyst and pressures 270–450 p. s. i., preferably 375 p. s. i. With unsupported fused Fe catalyst of 95–97% Fe, 2–3% alumina, and 1% alkali metal oxide such as K oxide, temperatures are 350°–395° F. and pressure 350–375 p. s. i. Synthesis gas composition range is H_2: CO=1:1—3:1. The total effluent, including water vapor, temperature 395°, is passed to a heater and the temperature raised to 660°–830° F. At this temperature the product mixture contacts Cr oxide catalyst, and the alcohols and acids are converted to aliphatic ketones of varying molecular weights.

$$RCH_2CH_2OH + RCH_2CH_2OH \rightarrow RCH_2COCH_2R + CO + 3H_2,$$
$$RCH_2COOH + RCH_2COOH \rightarrow RCH_2COCH_2R + CO_2 + H_2O.$$

The effluent from the ketone formation step is cooled to condense the normally liquid constituents containing a large % of H_2O. The uncondensed normally gaseous constituents H_2, CO, and CO_2 are recycled to the hydrogenation of CO. The ratio H_2: CO is about 3:1. 5 United States patents cited.

396. COLLIER, R. T. Method for Making Oil Gas and Water Gas. United States Patent 2,634,197, Apr. 7, 1953; appl. filed Oct. 9, 1944, Serial No. 557,818; 4 claims (*Cl. 48–197*). Chem. Abs., vol. 47, 1953, p. 6123.

Water gas is formed as a byproduct. Steam is blown over the heated refractory material as it passes between the reaction zone and the heating zone. The steam reacts with the carbonaceous material adhering to the refractory material as a result of pyrolysis. Water-gas formation should be intermittent, whereas oil-gas formation is continuous to permit heating the refractory material alternative to the formation of water gas. 3 foreign and 7 United States patents cited.

COLUMBIA ENGINEERING & MANAGEMENT CORP. *See* abs. **2541, 2542, 2543, 2544, 2546.**

COMBUSTION ENGINEERING-SUPERHEATER, INC. *See* abs. **2624 2625.**

COMBUSTION PROCESSES CO. *See* abs. **3786.**

COMBUSTION UTILITIES CORP. *See* abs. **281.**

397. COMMERCIAL MINERA S. A. [Active Iron Oxide Catalysts.] Spanish Patent 192,978, Apr. 26, 1951. Chem. Abs., vol. 47, 1953, p. 1309.

Oligiste (Fe_2O_3), in the form of scales, is mechanically broken up until the black original material acquires a dark-brown color. The material in this form is a much more active catalyst. Other agents may be added, and heat treatment may be used to improve the catalytic action.

398. COMMERCIAL SOLVENTS CORP. [Catalysts for the Production of Methanol.] French Patent 636,337, May 12, 1927. Chem. Abs., vol. 23, 1929, p. 155.

Catalyst for producing MeOH is made by reducing a Ni compound, for example, $Ni(NO_3)_2$, with H_2 at a temperature 300°–950°, preferably 500°–600°.

399. ———. [Methanol.] French Patent 34,361, June 21, 1927. Chem. Abs., vol. 23, 1929, p. 4484.

Catalyst for the synthesis of MeOH from CO and H_2 is prepared by combining ZnO, $Cr(NO_3)_3$ $Fe(NO_3)_3$ and $ZnCl_2$ in aqueous mixture and transforming the nitrates into oxides. *See also* French Patents 635,023 (abs. **402**) and 644,525 (abs. **400**).

400. ———. [Methanol.] French Patent 644,525, June 20, 1927. Chem. Abs., vol. 23, 1929, p. 1910.

Catalyst composed of 1 or more difficultly reducible oxides and a metallic halide is used in the production of CH_3OH from H_2 and CO. In examples a mixture of (1) Cr_2O_3 and $ZnCl_2$ or $MgCl_2$; (2) Cr_2O_3, ZnO, or MgO and $ZnCl_2$; (3) WO_3, ZnO, and $ZnBr_2$; and (4) oxide of U and $ZnCl_2$ are used.

401. ———. [Production of Oxygenated Organic Compounds.] French Patent 774,157, Dec. 3, 1934; appl. filed June 5, 1934. Chem. Zentralb., 1935, II, p. 593.

Higher alcohols are obtained from C oxides and H_2 in presence of hydrogenating catalysts such as metal oxides of groups 2 and 6 activated by means of the alkali salt of an organic acid. The reduction of CO takes place under the following conditions: Temperature 250°–650°, pressure > 140 atm., gas flow 10,000–70,000

cc. per cc. catalyst per hr. The higher temperatures give increased yields of higher alcohols.

402. ———. [Synthetic Methanol.] French Patent 635,023, May 25, 1927. Chem. Abs., vol. 22, 1928, p. 3893.

Catalyst for the preparation of MeOH from H_2 and oxides of C comprises 1 or more difficultly reducible metallic oxides, such as the oxides of Zn, Mg, Cd, Cr, V, W, with 1 or more easily reducible metallic oxides, such as the oxides of Fe, Ni, Co, Cu, and a metallic halide such as $ZnCl_2$, $MgCl_3$, $CrCl_3$, $MgBr_2$, $ZnBr_2$. The oxides difficult to reduce are preferably predominant.

———. *See* abs. **39, 40, 125, 257, 596, 597, 598, 599, 600, 601, 602, 603, 761, 3635, 3636, 3637, 3969, 3982, 3984.**

403. COMPAGNIE DE BÉTHUNE. [Ammonia and Methanol.] French Patent 670,878, June 27, 1928. Chem. Zentralb., 1930, I, p. 1348; Chem. Abs., vol. 24, 1930, p. 1942.

Residual gases from the manufacture of H_2 from coke-oven gases are partly burnt by passing them with insufficient air through a gas producer filled with refractory material at a high temperature. The mixture obtained is purified to remove traces of saturated hydrocarbons by catalytic destruction in the presence of Fe, Ni, or Cr and CO_2 by washing with NH_3. The purified gases are used to produce MeOH and NH_3.

404. ———. [Catalytic Processes.] French Patent 639,058, Jan. 11, 1927. Chem. Abs., vol. 23, 1929, p. 456.

In exothermic synthesis such as MeOH from CO and H_2, a liquid is added to the reaction gases to control the temperature of the reaction. With MeOH, H_2O is a suitable liquid.

405. ———. Gases for Ammonia Synthesis. British Patent 314,432, June 27, 1928. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 212; Chem. Abs., vol. 24, 1930, p. 1472.

Mixture of H_2, N_2, and CO, which is suitable after further treatment for the synthesis of NH_3, is produced from the residual gases obtained after H_2 has been separated from coke-oven gas by subjecting these residual gases, in admixture with air, to a flameless incomplete combustion in a tower filled with refractory material kept at a high temperature. Traces of unsaturated hydrocarbons such as those of the C_2H_2 series, detrimental to catalysts used for NH_3 synthesis, are removed by catalytic destruction in the presence of Fe, Ni, Cr or an alloy of these 3 metals. Describes various other details of procedure and of apparatus.

See also French Patent 670,878 (abs. **403**).

406. ———. [Higher Hydrocarbons From Methane.] French Patent 613,542, July 27, 1925. British Chem. Abs., 1928, B, p. 116.

CH_4 or a gas containing it is heated at 200°–600° C. under pressure with a catalyst such as ferric oxide, mixtures of metallic oxides, or the corresponding metals obtained by reduction of the oxides. Liquid hydrocarbons are obtained, the greater part of the product distilling 38°–100° C. Butane and ethane also are produced. The CH_4 used need not be pure, the presence of H_2, O_2 or other gases appearing favorable to the reaction.

407. ———. Hydrocarbons and Alcohols. British Patent 255,828, July 27, 1925. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 173; Chem. Abs., vol. 21, 1927, p. 2978.

Coal-distillation gases, which may be partly dehydrogenated, are passed under high temperature and pressure over a metallic oxide catalyst, for example, over Fe_2O_3 at 300°–600° under 400 atm. pressure, and then, after cooling and removal of condensed products, are passed over a catalyst having a polymerizing and condensing action at normal or increased pressure, for example, over activated C at 100°–400°. Alcohols are obtained in the first stage and hydrocarbons in the second.

See also French Patent 613,541 (abs. **410**).

408. ———. Hydrocarbons and Alcohols. British Patent 255,829, July 27, 1925. Chem. Abs., vol. 21, 1927, p. 2978.

Specifies producing hydrocarbon oils resembling petroleum by heating CH_4 or a gas containing CH_4 to 200°–600° under pressure in the presence of a catalyst such as Fe_2O_3 or a suitable mixture of metal oxides or metals. H_2 or some O_2 promotes the reaction.

409. ———. [Hydrocarbons From Methane.] French Patent 615,972, 1925.

It is necessary to have O present to produce petroleum hydrocarbons from CH_4. This O may be in the form of oxide catalysts.

410. ———. [Manufacture of Alcohols and Liquid Hydrocarbons.] French Patent 613,541, July 27, 1925. British Chem. Abs., 1928, B, p. 885.

Coal gas, or a suitable mixture of H_2, CH_4, and CO, is passed at 400°–600° and 400 atm. over magnetic Fe oxide, and the gaseous products, after condensation of alcohols, are converted into oily hydrocarbons, b. <100°, by passage over active C at 100°–400°.

411. ———. [Methanol.] French Patent 632,259, July 17, 1926. Chem. Abs., vol. 22, 1928, p. 3418.

See British Patent 274,492 (abs. **414**).

412. ———. [Methanol.] French Patent 633,139, Aug. 6, 1926. Chem. Abs., vol. 22, 1928, p. 3418.

See British Patent 275,600 (abs. **415**).

413. ———. [Methanol.] German Patent 534,551, June 5, 1927. Chem. Abs., vol. 26, 1932, p. 999.

MeOH is formed by subjecting CO and H_2 mixtures to high temperatures and pressures in the presence of catalyzers consisting of formates of Zn or Cr, or a mixture of these; wood charcoal or active C is also present to act as a carrier. Gives example.

414. ———. Methanol Synthesis. British Patent 274,492, July 17, 1926. Chem. Age, vol. 17, 1927, p. 291; Chem. Abs., vol. 22, 1928, p. 2171.

Catalysts for synthesis of alcohols, especially of MeOH, by reaction of CO and H_2 under the influence of heat and pressure, are prepared by depositing soluble salts such as formates of U, W, V, Zn, Be, Cr, or Ti upon a porous support such as pumice, asbestos, charcoal, or activated C.

415. ———. Methanol Synthesis. British Patent 275,600, August 6, 1926. Chem. Abs., vol. 22, 1928, p. 2171.

Catalysts suitable for use in hydrogenation of CO comprise irreducible oxides to which 2–10% of Ni, Ni oxide, or a Ni salt has been added; for example, a catalyst may be prepared by immersing heated active C in a solution of Zn and Cr formates containing a small quantity of Ni formate, and evaporating to dryness; this catalyst may be used for producing MeOH from a mixture containing CO, H_2, N_2, and CH_4 at 800 atm. pressure and a temperature of 300°.

416. ———. Methanol Synthesis. British Patent 283,499, January 11, 1927. Chem. Age, vol. 18, 1928, p. 248; Chem. Abs., vol. 22, 1928, p. 4133.

In making MeOH by oxidizing CH_4 or from CO and H_2 or in other exothermic reactions under pressure, H_2O or other suitable liquid is mixed with the reaction gases and utilized to control the temperature of the reaction by the abstraction of heat for its vaporization. Describes apparatus.

417. ———. [Methyl Formate.] French Patent 673,337, July 30, 1928. Chem. Abs., vol. 24, 1930, p. 2474.

Vapors of MeOH are passed over dehydrogenating catalysts, particularly Cu at 150°–250°.

———. *See* abs. **2348.**

418. COMPAGNIE DE PRODUITS CHIMIQUES ET ÉLECTRO-METALLURIGIQUES ALAIS, FROGES ET CAMARGUE. Antiknock Fuel. British Patent 542,836, Jan. 29, 1942. Chem. Abs., vol. 36, 1942, p. 4318.

CO is hydrogenated under pressures higher than 10 atm. using catalysts of the type having oxides and suboxides not reducible under the working conditions. Hydrocarbons and higher alcohols having branched chains are obtained. The speed of passage of the gases and the temperature are so regulated that the products condensed on leaving the catalyst separate into 2 layers; the proportion of MeOH formed is very low. The light-weight layer is separated by distillation into 2 fractions. The fraction b. below 115° is treated on Al_2O_3 at a temperature of about 420° in a tube lined internally with Cu. Isoolefins and olefins are obtained. The 2d fraction, which distills above 115°, is treated at a temperature of about 400° in the presence of H_2 and under a total pressure of 150 atms. on a catalyst constituted by Mo oxide deposited on activated C.

419. ———. [Antiknock Fuels.] French Patent 843,370, July 3, 1939. Chem. Abs., vol. 34, 1940, p. 7102.

Antiknock fuels of high quality are obtained by subjecting mixtures of CO of H_2 under various pressures and temperatures, to the action of catalysts of the type used in the synthesis of higher alcohols having a branched chain, adjusting the pressure, temperature, and the passing speed so as to obtain a mixture of alcohols and hydrocarbons in the greater part unsaturated without the formation of MeOH, transforming the alcohols into hydrocarbons, separating the liquid hydrocarbons from the gaseous ones, converting the latter into liquid hydrocarbons by polymerization, and converting the unsaturated liquid hydrocarbons into saturated ones by catalytic hydrogenation. The catalyst should contain at least 1 element of group 1 of the periodic table, such as Li, Na, K, Rb, and Cs, and 1 or more elements of groups 2, 6, and 7 of the periodic table, such as Zn, Cd, Hg, Cr, Mo, W, and Mn. The addition of small quantities of metals of the group Fe, Ni, Co or of the group Cu, Ag, Au or of the group V, Nb, Ta increases the yield.

420. ———. [Hydrocarbon Synthesis.] Netherlands Patent 52,832, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 173.

See French Patent 855,049 (abs. **421**).

421. ———. [Motor Fuel.] French Patent 855,049, Apr. 30, 1940. Chem. Abs., vol. 42, 1948, p. 2419.

CO and S-free H_2(2:1 vols.) are passed over an oxide catalyst at 1 $m.^3$ per hr. for each l. of catalyst at a temperature of 470°–475° and a pressure of 150 atm. The products form 2 layers, the lower being aqueous, which gives MeOH, acetone, etc., on distilling, and the upper is separated into 2 fractions. That below 115° is heated over an Al catalyst at 420°, and the resulting olefins are polymerized and then hydrogenated in the presence of Ni. The other fraction is hydrogenated at 400° under 150 atm. over MoO and active C as catalysts. H_2O is removed after this treatment and the fuel added to that obtained from the 1st fraction.

422. COMPAGNIE GÉNÉRALE DES PRODUITS DE SYNTHÈSE. [Fuel.] French Patent 658,643, Aug. 6, 1928. Chem. Zentralb. 1929, II, p. 3090; Chem. Abs., vol. 23, 1929, p. 5305.

Hydrocarbons corresponding to the general formula $C_2H_2+CH_4$ coming from the combustion and distillation in a gas producer or like apparatus are polymerized for the production of a fuel by heating to about 80° in the presence of a catalyst having a basis of $CeSO_4$. The catalyst is prepared by roasting monazite, treating with acid, neutralizing, taking up several times with acid, and evaporating, after which the residue added to a solution of $CoSO_4$ is electrolyzed.

423. ———. [Synthetic Fuel.] French Patent 38,825, July 22, 1930. Chem. Zentralb., 1931, II, p. 3066; Chem. Abs., vol. 26, 1932, p. 1756.

Mixture of carbonaceous gases and H_2 is passed at about 80° and under pressure of about 2 kg. per $cm.^2$ over a catalyst composed of a mixture of oxides or salts of metals of the rare earth series and of metals of the Fe group (Co, Ni).

See also French Patent 658,643 (abs. **422**).

424. ———. Synthetic Production of Hydrocarbons and Ketones. British Patent 316,945, Aug. 6, 1928. Chem. Abs., vol. 24, 1930, p. 1866.

Gases containing C oxides and H_2, produced by treating solid fuels in a producer with air and steam, to which hydrocarbons such as CH_4 and C_2H_2 may be added, are treated at 80° and at about atmospheric pressure with a catalyst formed mainly of the sulfates of Ce and Co, details of the preparation of which are given. The product comprises about 90% hydrocarbons and the remainder is chiefly ketones; it may be used as liquid fuel or as a solvent for fatty materials, rubber, cellulose, acetate, or other substances.

425. COMPAGNIE INTERNATIONALE POUR LA FABRICATION DES ESSENCES ET PÉTROLES. Hydrogenation of Fuel Gases. British Patent 302,683, Feb. 13, 1929; appl. filed Dec. 5, 1928. Chem. Zentralb., 1929, II, p. 519.

Coke oven gas is treated with gases containing H_2 in the presence of catalysts such as Ni. The hydrogenation is performed between 2 purifying operations.

See Austrian Patent 117,870 (abs. **426**).

426. ———. [Hydrogenation of the Gasification Products of Fuels.] Austrian Patent 117,870, Jan. 15, 1930; May 15, 1930.

Coke-oven gas is treated with H_2-containing gases in the presence of catalysts. The hydrogenation should take place between 2 purifying operations. Ni is a good hydrogenation catalyst.

See also British Patent 302,683 (abs. **425**).

427. COMPAGNIE PAN-EUROPÉENNÉ D'INSTALLATIONS ET D'EQUIPMENT INDUSTRIELS. Gas for the Synthesis of Ammonia. British Patent 677,643, Aug. 20, 1952. Chem. Abs., vol. 47, 1953, p. 277.

Gas containing CO, 32.4%; H_2, 34.1%; CO_2, 11.3%; and N_2 22.2% is produced in a multiple-stage process in which pulverized carbonaceous material, such as lignite or coal, is mixed in a 2-stage reaction chamber with air and steam at a temperature of 800°–1,000°; the product is passed through a dust separator and wash towers. Part of the gases produced in the 1st stage can be diverted to heat the unused reaction chamber for alternate operation. S-bearing gases are removed by distillation at 300°–500°. Gases for CH_3OH synthesis and for Fischer-Tropsch synthesis containing CO and H_2 can be prepared by passing O_2 and steam into the generator chambers at a temperature of 1,000°–1,300°. In this application, recirculation of a portion of the gases is not feasible.

428. COMSTOCK, J. A. (Surface Combustion Corp.). Gas. British Patent 534,517, Mar. 7, 1941. Chem. Abs., vol. 36, 1942, p. 1469.

Method of utilizing charcoal or coke to produce a gas of high CO content and controlled H_2 content comprises feeding the charcoal into 1 end of an externally heated retort continuously to maintain in the retort a column of incandescent C, continuously causing a stream of gas to flow out of the retort countercurrent to the incoming C to expel from the retort those volatile substances that are given off by the C when it is first heated. An oxidizing gas is then caused to flow into

the retort at a point where the C is substantially devoid of the volatile, and the resulting reaction products are withdrawn from the retort at another point where the C is substantially devoid of the volatile substances. The H content of the reaction products is controlled by controlling the composition of the oxidizing gas.

429. CONRAD, R. Olefins. United States Patent 2,619,511, Nov. 25, 1952. Chem. Abs., vol. 47, 1953, p. 6434.

See German Patent 808,936 (abs. **430**).

430. CONRAD, R., AND BADISCHE ANILIN- UND SODA-FABRIK. (I. G. Farbenindustrie A. G. "In Auflösung"). [Olefins.] German Patent 808,836, July 19, 1951 (*Cl. 12 o–19*$_{01}$). Chem. Abs., vol. 47, 1953, p. 3327.

Olefins or alcohols with aliphatic ethers at 200°–500° in the presence of dehydrating catalysts, such as difficultly reducible metal oxides, for example, Al, Mg, Cr, Th, W, or Ti, and also phosphates, silicates, china clay, graphite, or kieselguhr, give olefins of a higher molecular weight than that of the initial olefins. Suitable initial materials are C_2H_2, $MeCH:CH_2$, or butylene or the alcohols with the same number of C atoms or olefin-paraffin mixtures resulting from the catalytic dehydrogenation of gaseous hydrocarbons, or olefin-rich gaseous reaction products from the CO hydrogenation, and on the other hand Et_2O, MeOEt, $(iso\text{-}Pr)_2O$, or $CH_2:CHOMe$. Thus, leading Me_2O 19 and *n*-butylene (I) 132 l. per hr. through a quartz tube heated at 350°–360° and packed with activated alumina and cooling the reaction vapors with solid CO_2 gives a condensate from which unreacted Me_2O and (I) are removed by distillation. The liquid reaction product 1,700 gm. (within 70 hr.) consists of pentene 25 (containing diolefins 16), hexenes 12.7 (containing diolefins 16), heptenes 8 (containing diolefins 37), octenes 8 (containing diolefins 71), and higher molecular hydrocarbons 44%; I number 215–367, solid residue 2%; 6.4% of the Me_2O used is decomposed to CO and CH_4

431. CONSALVO, A. (Société internationale des carburants et des industries chimiques "Brevets Consalvo".) [Hydrocarbon Synthesis.] French Patent 869,341, Jan. 29, 1942; appl. filed Jan. 17, 1941. Chem. Zentralb., 1942, II, p. 244.

Synthesis gas is contacted with a suspended catalyst, which is circulated through the reaction zone. The catalyst consists of metals of the 4th group with Fe and Cu on carriers of kieselguhr or bleaching earths mixed with oxides of Al or Zn. The reaction products are cooled, the condensate separated, and the CO_2 washed out of the residual gas, which is used for making synthesis gas.

432. ———. [Liquid Hydrocarbons From Carbon Monoxide.] Italian Patent 341,317, Apr. 28, 1936. Chem. Zentralb., 1938, I, p. 727.

In the presence of powdered Zn or Zn vapor CO_2 is changed to CO. By adding H_2O, H_2 is produced in the gas mixture.

433. COOPER, C., HENSHAW, D. M., AND W. C. HOLMES & CO., LTD. Purification of Gases Containing Hydrogen Sulfide. British Patent 551,652, Mar. 4, 1943. Chem. Abs., vol. 38, 1944, p. 3114.

Describes process for treating coal gas and other gases containing H_2S with a dilute solution of NH_4OH. The time of contact of the gases with the liquid is so short that H_2S is selectively absorbed.

434. COPE, J. Q. (California Research Corp.). Adsorption Separation of Hydrocarbons and Oxygenated Organic Compounds. United States Patent 2,621,203, Dec. 9, 1952. Chem. Abs., vol. 47, 1953, p. 2473.

Crude reaction products obtained from the catalytic hydrogenation of CO may be separated by preferential adsorption on solid absorbents, such as silica gel. Generally the crude reaction product is fractionated into cuts of 100°–200° F. boiling range. Each cut is charged in liquid phase to the adsorption column. A desorbing liquid (light alcohol) is then passed through the column, and the effluent is collected in 3 cuts; the 1st consists essentially of paraffinic and olefinic hydrocarbons, the 2d consists essentially of aromatic hydrocarbons, and the 3d consists essentially of oxygenated organic compounds.

435. COPE, J. Q., AND SCOTT, J. W., JR. (California Research Corp.). Preparation of Alkylated Aromatic Hyrocarbons and Sulfonation Thereof. United States Patent 2,531,324, Nov. 21, 1950; appl. filed Oct. 18, 1947, Serial No. 780,758; 6 claims (*Cl. 260–450*).

Alkyl aryl sulfonates useful as detergents or wetting or emulsifying agents are produced from olefinic materials from the Fischer-Tropsch synthesis. The fraction boiling 300°–600° F., is passed through a silica gel column at a temperature below cracking. The fraction of the percolate that has flowed from the adsorbent mass, when the bromine number of the effluent percolate is at its maximum value, is separated. A mononuclear aromatic hydrocarbon is alkylated with at least a portion of the segregated fraction. 6 literature refs. and 7 United States patents cited.

436. CORNELL, P. W. (Gulf Oil Corp.). Method of Starting a Unit for High-Temperature Reactions. United States Patent 2,569,846, Oct. 2, 1951; appl. filed Dec. 30, 1948, Serial No. 68,271; 8 claims (*Cl. 48–196*).

Method is described for starting up units employed in carrying out high-temperature and high-pressure exorthermic reactions, especially those reactions concerned with forming a synthesis gas from natural gas and O_2 adapted to be used in the Fischer-Tropsch synthesis of hydrocarbons.

437. ——— (Gulf Oil Corp.). Process and Apparatus for Concentrating Dilute Solutions. United States Patent 2,509,136, May 23, 1950; appl. filed June 17, 1949, Serial No. 99,788; 14 claims (*Cl. 202–40*). Chem. Abs., vol. 44, 1950, p. 7100.

Dilute aqueous solutions of oxygenated organic compounds produced as secondary products in the Fischer-Tropsch process are concentrated by fractional distillation in 2 stages. The 1st fractionating column contains a relatively small number of plates and is operated so as to produce a bottoms fraction consisting essentially of H_2O. The enriched overhead fraction is compressed in a compressor driven by a steam turbine. The compressed vapors enter a heat exchanger, where they are condensed, supplying their heat of vaporization to the reboiler of the column. Part of the resulting liquefied overhead is returned to the column as reflux, and the remainder is fed to a 2d column containing a relatively large number of plates. This column produces an overhead fraction of the desired final concentration, the bottoms being essentially H_2O. The entire process is controlled by varying the degree of compression in accordance with the composition of the liquid on an intermediate tray in the 2d column, the degree of compression decreasing as the concentration of oxygenated compounds increases. Thus, the 2d column is operated to produce the desired separation between H_2O and oxygenated products, while the 1st column is automatically controlled to supply the maximum quantity of oxygenated products that the 2d column is capable of concentrating. The exhaust steam from the turbine is used to preheat the feed to the system and to supply heat to the reboiler of the 2d column. Thus, all the necessary heat is supplied in the steam to the turbine.

438. CORNELL, P. W., AND COTTON, E. (Gulf Oil Corp.). Catalytic Reactor. United States Patent 2,585,441, Feb. 12, 1952; appl. filed Dec. 22, 1947, Serial No. 793,306; 9 claims (*Cl. 23–288*).

Presents various structural and operative details. The reactor is specifically adapted for use in any chemical reaction employing a solid catalyst and involving the removal or supply of exothermic or endothermic heat from or to the reaction zone. The use of this reactor materially reduces the equipment necessary for a process, wherein large amounts of fluid reactants are recirculated for temperature control, and minimizes the amount of energy required for circulating the fluids.

439. CORNER, E. S., AND LYNCH, C. S. (Standard Oil Development Co.). Olefin Polymerization Catalyst. United States Patent 2,642,402, June 16, 1953. Chem. Abs., vol. 47, 1953, p. 8999.

An olefin polymerization catalyst having high activity and structural strength is prepared by heating-treating a silica-gel base at 400°–1,250° F., admixing the heat-treated silica gel and H_3PO_4, drying the mixture at 375°–425° F., and calcining the dried mixture at 600°–1,000° F.

440. ——— (Standard Oil Development Co.). Production of Industrial Gases Containing Carbon Monoxide and Hydrogen. United States Patent 2,607,669, Aug. 19, 1952; original appl. filed Aug. 12, 1947, divided and this appl. Feb. 4, 1948, Serial No. 6,227; 11 claims (*Cl. 48–196*).

Synthesis gas is produced by contacting a gaseous hydrocarbon at about 1,600° F. with an O carrier comprising an intimate mixture of Fe_2O_3 and MnO_2, the latter being present 10–70 wt. %. MgO and Cr_2O_3 may be included. Example: Operation with Fe_2O_3 alone gave a CH_4 conversion of 56% with a selectivity to CO of 22%. 10% of MnO_2 increased the conversion to 70% and the selectivity to 70%. Maximum conversion was obtained with a 50-50 mixture of Fe_2O_3 and MnO_2 with a selectivity to CO of 75%. As the Fe_2O_3 decreased, <50% the selectivity tended to rise, but conversion fell off rapidly. MnO_2 alone gave a conversion of only 22%. Operation is preferably performed at 1,600°–2,000°, 600 p. s. i., feed rates higher the higher the operating temperature and pressure, residence time of the O carrier in the hydrocarbon oxidation zone 10–15 minutes.

441. CORNER, E. S., MCGEE, R. V. J., AND LYNCH, C. S. (Standard Oil Development Co.). Oxygen Carrier for the Oxidation of Gaseous Hydrocarbons. United States Patent 2,507,502, May 16, 1950. Chem. Abs., vol. 44, 1950, p. 7046.

Oxidation of gaseous hydrocarbons to CO and H_2 through reaction with metal oxides at 1,600°–2,000° F. is carried out by using an O_2 carrier containing TiO_2 94–97% by weight and 3–6% of a blend of Fe_2O_3, 80%; NiO, 10%; and Cr_2O_3, 10%. For oxidation of CH_4 the carrier should contain 90% TiO_2 with the remainder composed as before. The process is best carried out by fluidized technique, and the composition of the carrier is selected according to its suitability for fluidized operation.

442. ——— (Standard Oil Development Co.). Production of Industrial Gases Containing Carbon Monoxide and Hydrogen. United States Patent 2,607,668, Aug. 19, 1952; original appl. filed Aug. 12, 1947, divided and this appl. filed Feb. 4, 1948, Serial No. 6,226; 11 claims (*Cl. 48–196*).

Gaseous hydrocarbons can be converted into synthesis gas by contacting them at about 1,600° F. with an O carrier consisting essentially of a major proportion (90 wt. %) of titania mixed with a minor proportion of an oxide of Fe, Ni, Co, Mn, Cr, and W. Example: Various runs were made using TiO_2 and an addition agent composed of Fe_2O_3, 80; Cr_2O_3, 10; and NiO, 10 wt. %. When using 6 wt. % of this composite agent the CH_4 conversion was almost 80%, and the selectivity to CO was nearly 100% without C formation. When used alone TiO_2 caused only 9.6% conversion. This particular addition agent was most effective when used in amounts 3–7%. Other examples presented.

443. CORNIC, Y. [Petroleum.] French Patent 696,163, Oct. 30, 1930. Chem. Abs., vol. 25, 1931, p. 2843.

Petroleum is obtained by treating CH_4 with nascent CO_2; the O of the CO_2 burns a part of the H of the CH_4, which then condenses to petroleum. The CO_2 is obtained from carbonates dissociated by heat, with or without the addition of substances favoring dissociation and with or without pressure.

444. ———. [Synthetic Fuel.] French Patent 705,845, Nov. 18, 1930. Chem. Abs., vol. 26, 1932, p. 283.

Industrial gases are oxidized to CO_2 and steam on metallic oxides, and the metals thus obtained are used to decompose the CO_2 and steam to CO and H_2, which in the nascent state are transformed to a synthetic hydrocarbon fuel.

COTTON, E. *See* abs. **438.**

445. COUPARD, C. [Synthesis of Liquid Hydrocarbons.] French Patent 877,010, July 10, 1941. SCHMIDT, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 173; Chem. Zentralb., 1943, II, p. 1167.

CH_4+CO are conducted at 700°–800° over Al–Cr–carbide. Benzol and homologs are the products.

446. CRAWFORD, C. L. (Gulf Research & Development Co.). Apparatus for Producing Synthesis Gas. United States Patent 2,613,145, Oct. 7, 1952; appl. filed Dec. 30, 1948, Serial No. 68,280; 1 claim (*Cl. 48–196*).

Describes apparatus for producing Fischer-Tropsch synthesis gas by introducing a mixture of natural gas and O_2 into a conversion zone maintained at 1,800°–2,300° F. and 150–650 p. s. i.

CRAWFORD, V. L. *See* abs. **1093.**

447. CROMEANS, J. S. (Phillips Petroleum Co.). Formation of Acetals to Separate Oxygenated Compounds From Fischer-Tropsch Products. United States Patent Appl. 43,202, filed Aug. 9, 1948 (*Cl. 260–450*). Official Gaz., vol. 652, Nov. 20, 1951, p. 891; Chem. Abs., vol. 47, 1953, p. 1728.

Narrow-boiling aldehyde-alcohol-ketone fraction, obtained from the aqueous layer of the product of the catalytic hydrogenation of CO, particularly a propionaldehyde-acetone-methanol fraction b. 45°–58°, is resolved by forming an acetal from a constituent alcohol and aldehyde, separating the ketone from the resulting acetal-containing mixture by ordinary fractionation methods, hydrolyzing the residual acetal to regenerate the original alcohol and aldehyde, and recovering the regenerated alcohol and aldehyde by ordinary fractionation.

448. ——— (Phillips Petroleum Co.). Recovery of Organic Compounds From Aqueous Carbon Oxide Hydrogenation Product. United States Patent 2,555,185, May 29, 1951; appl. filed Dec. 19, 1949, Serial No. 133,905; 7 claims (*Cl. 202–57*).

Process for recovering oxygenated organic compounds from the aqueous phase resulting from the catalytic hydrogenation of CO, which comprises distilling this aqueous phase at a temperature below the boiling point of H_2O to obtain an overhead fraction containing alcohols, aldehydes, ketones, 0.1–2.0 wt. % organic acids and 10–15 vol. % H_2O. The overhead product is then charged to a 2d fractionation column and distilled in such a manner that the aldehydes, ketones, MeOH

and EtOH pass overhead and organic acids, propyl-, butyl-, and amyl-alcohol are in the lower part of the distillation zone. At a point sufficiently below the feed point that aldehydes are not present, NaOH in an aqueous solution is introduced into the column to neutralize all the acids in the feed. Thus the products are recovered substantially free of organic acids.

449. ——— (Phillips Petroleum Co). Separation of Oxygen-Containing Compounds. United States Patent 2,573,185, Oct. 30, 1951; appl. filed Dec. 20, 1948, Serial No. 66,353; 11 claims (*Cl. 260–488*). Chem. Abs., vol. 46, 1952, p. 5294.

Describes process for resolving an aqueous solution containing as the chief organic components, acetaldehyde, acetone, methanol, ethanol, propanol, butanol, pentanol, acetic acid, propionic acid, and butyric acid, which is obtained from the catalytic hydrogenation of CO. The mixture is first charged to a fractionating column and topped at 85°. Acetaldehyde, acetone, methanol, ethanol, and H_2O are separated. The aqueous residual product from the topping step is then extracted with diethyl ether to separate the dissolved organic oxygenated compounds from the H_2O. The diethyl ether is distilled from the resulting extract and H_2SO_4 is added, also benzene. Esterification is next carried out and H_2O of esterification is removed as an azeotrope with benzene. The H_2O-free mixture is then fractionated to produce propyl acetate and acetic acid, after which butyric acid is added to displace propionic acid from the propionates in the residual product. Continued fractionation then yields propionic acid, butyl butyrate, and amyl butyrate.

———. *See* abs. **717.**

450. Cross, W. M. Water Gas. United States Patent 1,860,138, May 24, 1932. Chem. Abs., vol. 26, 1932, p. 3906.

In a continuous process, solid pulverized carbonaceous material is charged to a stage of reaction with steam suitably heated to a temperature that effects the formation of a hot gas containing CO and H_2, and the hot gas is passed into contact with a Ni catalyzer so that CH_4 is formed from CO and H_2. Describes apparatus, and the temperature of the gas entering the catalyzer is automatically controlled.

451. Crowell, J. H., and Benson, H. E. (The United States of America as Represented by the Secretary of the Interior). Catalytic Conversion of Carbon Monoxide and Hydrogen to Hydrocarbons and Oxygenated Organic Compounds. United States Patent 2,617,816, Nov. 11, 1952; appl. filed Oct. 11, 1950, Serial No. 189,639; 16 claims (*Cl. 260–449.6*). Chem. Abs., vol. 47, 1953, p. 1360.

Gives means for improving the usage ratio and allowing operation at lower temperature in catalytic conversion of CO and H_2 to hydrocarbons and oxygenated organic compounds. The catalyst is immersed directly in a cooling liquid. A stream of the cooling liquid is withdrawn from the reaction zone. Synthesis feed gas, both fresh and recycle gas, is passed in countercurrent contact with the liquid coolant treated for the removal of H_2O and other normally liquid products stripped from the cooling liquid and then conducted to the reaction zone to provide the major portion of the synthesis-gas feed. 3 United States patents cited.

Cunningham, F. C. *See* abs. 2782.

452. Currie, W. E. (Standard-I. G. Farbenindustrie A. G.). Forming Hydrocarbons by Hydrogenation of Carbon Oxides. United States Patent 2,209,190, July 23, 1940; appl. filed Jan. 11, 1936, Serial No. 58,772; 3 claims (*Cl. 260–449*). Chem. Abs. vol. 35, 1941, p. 304.

For producing hydrocarbons such as those in the gasoline range a mixture of a C oxide and H_2 such as water gas is subjected to the action of a Fischer-Tropsch catalyst at about 380°–450° and under a total pressure of 10–20 atm. but in the presence of a sufficient volume of a diluting gas such as N_2 to insure partial pressure of the combined reactants below 5 atm.

———. *See* abs. **806, 1804, 1805, 2052, 2055, 2317, 2331, 2332, 2333, 2360, 2661, 3437, 3834, 3951.**

453. Currie, W. E., Vogt, E., and Smeykal, K. (I. G. Farbenindustrie A. G.). [Synthesis Products.] Netherlands Patent 49,782, no date. Kainer, p. 272.

Sulfonated products of polymerized olefins with branched chains, obtained by the dehydrogenation and polymerization of the oxygenated product of the hydrogenation of CO b. 145°–165° or 165°–170°, are used as mineral oil emulsion breakers.

See United States Patent 2,216,257 (abs. **3834**).

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454. Dahm, F., and Tramm, H. (Ruhrchemie A. G.). [Catalyst for Cracking Hydrocarbons.] German Patent 716,239, Dec. 18, 1941 (*Cl. 23 b–1.04*). Chem. Abs., vol. 38, 1944, p. 3122.

The hydrocarbons are cracked to low-boiling olefins, which are suitable for polymerizing to yield antiknock gasoline. Acid-activated bleaching earth is used as catalyst, which is saturated with a H_3BO_3–H_3PO_4 mixture or only with H_3PO_4 and is activated with Co salts or similar salts. During the cracking the hydrocarbons are kept at a partial pressure of 1/10–1/40 kg. per cm.^{2}.

455. Daimler, K. (I. G. Farbenindustrie A. G.). [Aqueous Lubricant and Cooling Liquid for Working Metals.] German Patent 738,461, July 15, 1943 (*Cl. 23 c–1.04*). Chem. Abs., vol. 38, 1944, p. 4794.

For this purpose are used NH_4 or NH_4 alkali soaps of fatty acids with 5–11 C atoms. These fatty acids are a product of paraffin oxidation or oxidized byproducts of BuOH synthesis.

456. ——— (I. G. Farbenindustrie A. G.). [Lacquers and Paints.] German Patent 737,351, June 3, 1943 (*Cl. 22h–3*). Chem. Abs., vol. 38, 1944, p. 3860.

Naphthol pitch and pitch residue from the distillation of fatty acids, especially synthetic fatty acids, are heated together with a small quantity of a solvent. The hot mixture is emulsified with H_2O and NH_3.

Dally, M. *See* abs. **802, 803, 804.**

457. Dambly, E., and Boursois, E. [Hydrocarbons From Water Gas.] Belgian Patent 383,951, Dec. 31, 1931. Chem. Abs., vol. 26, 1932, p. 4823.

See French Patent 726,045 (abs. **458**).

458. ———. [Manufacture of Hydrocarbons and Their Derivatives From Water Gas.] French Patent 726,045, May 21, 1932; appl. filed Nov. 9, 1931. Chem. Abs., vol. 26, 1932, p. 4823.

Hydrocarbons and their derivatives, such as C_2H_4, EtOH, CH_4, CCl_4, and $CHCl_3$, are prepared by mixing water gas with H_2, coming from the bicarbonation of Na_2CO_3, K_2CO_3, or $CaCO_3$ by means of water gas, and passing the mixture over heated catalysts having an oxidizing, dehydrating, and/or halogenating action. All the residues of the reaction from the water gas that has been used for the bicarbonation are used in the manufacture of byproducts.

459. Danulat, F. (Metallgesellschaft A. G.). [Synthesis Gas.] German Patent 700,940, Dec. 5, 1940 (*Cl. 24 e–1.07*). Chem. Abs., vol. 35, 1941, p. 7689.

Coal is distilled under pressure of several atm. of O_2 and H_2O vapor and temperature, which leads to the formation of CH_4. To the gaseous mixture of O_2 and H_2O is added CO_2 0.5–3 fold the volume of O_2. This impedes the formation of CH_4, and the end product has a $CO:H_2$ ratio of 1:2 or more. The CO_2 is separated from the end product and reused. Before entering the generator the CO_2 is doused with hot H_2O (from the cooler) and is thereby saturated with H_2O vapor. The CO_2 itself or mixed with the H_2O vapor is preheated before entering the generator.

460. DART, J. C. (Standard Oil Development Co.). [Catalytic Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen.] French Patent 963,448, July 10, 1950; appl. filed Mar. 17, 1948, in United States June 18, 1947. Chem. Zentralb., 1950, II, p. 2270.

Fluidized catalyst consists of Fe, Co, or Ni and a carrier material, such as kieselguhr, pumice, silica gel, and alumina gel. The added activating agent is the carbonate, halogenide, or oxide of K, Cr, Zn, Al, Mg, or the rare earths. The partial pressure of H_2 lies above 10.5 atm. and the temperature above 315°. The total pressure in the reaction zone is above 24.6 atm. In general, propane, butane, and higher hydrocarbons are produced.

461. ——— (Standard Oil Development Co.). [Catalytic Production of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 964,636, Aug. 21, 1950; appl. filed Apr. 13, 1948. Chem. Zentralb., 1951, I, p. 280.

Synthesis is performed on a powdered Fe catalyst in suspended state at temperatures 329°–413°. The catalyst bed is connected with a liquid heat exchanger, the exchange temperature of which falls at least 83° below the temperature of the catalyst.

462. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis Operation. United States Patent 2,497,932, Feb. 21, 1950; appl. filed May 2, 1946, Serial No. 666,760; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 5568.

Reaction gases are withdrawn from the reaction zone and cooled to condense out H_2O and condensable hydrocarbons. The uncondensed gases are freed of oxygenated compounds and returned to the reaction zone. The solvent in the absorption zone may be polyethylene glycol. 5 United States patents cited.

463. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis Process. United States Patent 2,586,618, Feb. 19, 1952; appl. filed Nov. 8, 1946, Serial No. 708,627; 3 claims (*Cl. 260–449.6*).

Hydrocarbons are synthesized from CO and H_2 in the presence of an Fe catalyst, the temperature in the reaction zone being 350°–750° F. and the pressure 50–700 p. s. i. The particles of catalyst are of a size 0–200 microns and higher and are maintained in a fluidized state by means of upflowing suspending gases having a velocity of 0.1–5 ft. per sec. In operations of this character, the disadvantage is that the products of reaction are, for example, H_2O and CO_2. As the H_2 and CO of the synthesis gas charge are consumed and H_2O and CO_2 are produced, the gas atmosphere changes from reducing to oxidizing, and the catalyst deteriorates. It is now found that substantial improvements in the reaction are secured by withdrawing a vaporous stream from the reaction zone at a point between the point of introduction of the feed gases and the point of withdrawal of the synthesized hydrocarbons, removing both the H_2O and the CO_2 therefrom and recycling the treated gas stream to the reaction zone.

464. DART, J. C., AND SMITH, L. B. (Standard Oil Development Co.). Hydrocarbon Synthesis Process. United States Patent 2,489,451, Nov. 29, 1949; appl. filed June 20, 1946, Serial No. 678,168; 8 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 1676.

In conducting the Fischer-Tropsch synthesis the initial stage is run at pressure below 350 p. s. i., preferably 200–300 p. s. i., until C formation on the catalyst is 30–55%, based on weight of C-free catalyst. The pressure is then raised to above 350 p. s. i. for the 2d stage, preferably 400–800 p. s. i. 4 United States patents cited.

465. DAVIDSON, D. D. (Shell Development Co.). Production of Synthesis Gas. United States Patent 2,513,994, July 4, 1950; appl. filed Dec. 31, 1946, Serial No. 719,614; 7 claims (*Cl. 48–196*). Chem. Abs., vol. 44, 1950, p. 8625.

Gives cyclic process for production of synthesis gas by reaction of CH_4 with solid reducible metal oxide in absence of steam. The reaction is periodically discontinued and the reduced metal oxide reoxidized. Alkali metal catalyst 1–30% based on reducible metal oxide increases the yield of synthesis gas and decreases the formation of carbon black. Suitable metal oxides are of Fe, Co, Cr, Ni, Mn, V, or Ti, either alone or in various combinations. Using Fe_3O_4, temperature 2,200° F. and a flow rate of 2.4 cu. ft. CH_4 per hr. per lb. Fe oxide, 88% of the CH_4 was reacted. The synthesis gas was CO, 26%; CO_2, 6.5%; H_2, 62%; CH_4, 4%; and undetermined, 1.5%. Oxides of Mo, Mn, V, and Ti require somewhat higher temperatures than Fe oxide for optimum results. A 2d metal oxide known to retard reduction of Fe oxide to metallic Fe, such as Al, Mg, Si, Cr, W, Mo, or Mn may advantageously be combined with the Fe oxide. The amount is not critical. 5% allows the process period to be lengthened. Any desired pressure may be used, temperature 1,850°–2,300°. 7 United States patents cited.

466. DAVIS, W. G., AND IMPERIAL CHEMICAL INDUSTRIES, LTD. Higher Aliphatic Alcohols. British Patent 310,623, Mar. 21, 1928. Chem. Abs., vol. 24, 1930, p. 626.

Alcohols such as iso-Bu alcohol are separated from the crude product of the catalytic hydrogenation of oxides of C by distilling to remove most of the MeOH and treating the residue with a salting-out solution. Gives various details.

467. DE BARTHOLOMAEIS, E., AND DE NORA, V. Process for Reducing Organic Compounds by Hydrogenation. United States Patent 2,597,074, May 20, 1952; appl. filed May 22, 1948, Serial No. 28,604; 11 claims (*Cl. 260–638*). Chem Abs., vol. 47, 1953, p. 2199.

Describes improved operating method for producing higher molecular alcohols and the other hydrogenation products by the reaction of H_2 or gases containing H_2 with fatty or other organic materials under high pressures and temperatures in presence of a catalyst. The process is applicable to the reduction of Fischer-Tropsch fatty acids or esters to alcohols. With this improved process, it is possible to operate continuously instead of by batch hydrogenation and also to permit a more rapid and uniform reaction. This advantage has been accomplished by maintaining the reaction autoclave always under operating conditions of H_2 pressure and temperature and by charging the raw material and discharging the products without changing appreciably the pressure of temperature in the autoclave. Provision also is made for continuously circulating H_2 through the reaction autoclave during the hydrogenation process. This step not only stirs and mixes the substances involved in the reaction but also permits elimination of H_2O and also reduction products volatile at the temperature of the autoclave.

DEGER, T. E. *See* abs. **2556, 2557.**

468. DE JAHN, F. W. Production of a Gas Mixture for Synthetic Methanol. United States Patent 2,383,-

715, Aug. 28, 1945; appl. filed Apr. 17, 1943, Serial No. 483,534; 3 claims (*Cl. 252–373*). Chem. Abs., vol. 40, 1946, p. 5757.

Describes process for the catalytic gasification of C_3H_8 to a mixture of H_2, CO, and CO_2 in which the ultimate ratio of desired H_2 and CO end products can be accurately adjusted in a water-gas generator after the gasification step.

469. DE LACOTTE, A. H. [Catalytic Hydrogenation of Oxides of Carbon.] French Patent 835,899, Jan. 5, 1939. Chem. Abs., vol. 33, 1939, p. 5002.

In the hydrogenation of oxides of C to form MeOH, in addition to the ordinary catalysts, for example, having a basis of Cu or Zn, an intimate mixture of at least 2 oxides of the 3d and 4th group are used, a mixture in which the constituents of acid character are in preponderance over those of more basic character. An example of a catalyst contains Cu, 60; MnO_2 55; cerite 55, and SiO_2, 240 parts. The formation of secondary products is thereby reduced.

470. DELCO-LIGHT Co. [Methyl Ether.] French Patent 641,580, Sept. 27, 1927. Chem. Abs., vol. 23, 1929, p. 1142.

See British Patent 278,353 (abs. **183**).

———. *See* abs. **183.**

471. DEMAG, A.-G. [Catalyst Chamber.] German Patent 685,319, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 161.

DE MARCHI, V. S. *See* abs. **1794.**

472. DEMING, P. H. (Shell Development Co.). Production of Hydrocarbon-Oxygen Mixtures. United States Patent 2,519,955, Aug. 22, 1950; appl. filed Sept. 3, 1946, Serial No. 694,529; 12 claims (*Cl. 62–175.5*). Chem. Abs., vol. 44, 1950, p. 10,302.

Mixtures of CH_4 and O_2 suitable for preparation of Fischer-Tropsch synthesis gas are produced in a 2-stage process. (1) A stream of precooled air is passed upward through a rectifying absorption vessel, and a stream of liquefied portion of natural gas, principally CH_4, is passed downward in countercurrent flow to produce a separated stream of N_2 substantially free from O_2 and hydrocarbons and liquefied phase of natural-gas hydrocarbons and O_2. (2) The liquefied phase is stripped with CH_4 at a low temperature to produce a CH_4–O_2 mixture. A liquefied natural-gas residue containing a low concentration of O_2 remains. 2 United States patents cited.

DENKER, H. *See* abs. **3231.**

DE NORA, V. *See* abs. **467.**

473. DEPPE SÖHNE, A., AND ZEITSCHEL, F. Separation of Alcohols and Phenols From Mixtures. British Patent 252,570, July 21, 1925. Chem. Abs., vol. 21, 1927, p. 2274.

Alcohols and phenols are separated from mixtures in which they occur by treating the mixtures with H_3BO_3, arsenious acid, antimonious acid or phosphorous acid, or an anhydride of these acids or with a double anhydride of 1 of these acids and an organic acid such as HOAc, propionic, butyric, valeric, benzoic, or phthalic acid. An ester is obtained by the treatment, which on further treatment with a diluted alkali yields the alcohol or phenol. The process may be applied to obtain menthol from peppermint oil, geraniol from citronella oil, linaloöl from Shiu oil, benzyl alcohol from a mixture with benzyl acetate, terpineol and borneol from a camphor-oil fraction, and to various similar separations.

474. DE REWAL, F. J. (Atmospheric Nitrogen Corp.). Catalyst for Promoting Reaction of Methane With Steam to Produce Hydrogen and Carbon Oxides. United States Patent 2,030,283, Feb. 11, 1936; appl. filed Apr. 13, 1931. Chem. Abs., vol. 30, 1936, p. 2199.

Pd, MgO, and Ce oxide are used together. Cr_2O_3 and ThO_2 also may be used together.

DESCHAMPS, P. E. L. J. *See* abs. **3335.**

475. DE SIMÓ, M. (Shell Development Co.). Hydrogen and Carbon Monoxide. Canadian Patent 319,121, Jan. 19, 1932. Chem. Abs., vol. 26, 1932, p. 2023.

Paraffin hydrocarbons are oxidized substantially to H_2 and CO by reaction with ZnO at 950°–1,000°. The ZnO is regenerated and recycled, this forming a continuous process.

476. ——— (Shell Development Co.). Hydrogen and Carbon Monoxide From Natural Gas and Zinc Oxide. United States Patent 1,899,184, Feb. 28, 1933; appl. filed Mar. 24, 1930, Serial No. 438,633. Chem. Abs., vol. 27, 1933, p. 3063.

See Canadian Patent 319,121 (abs. **475**).

477. DEUTSCHE ERDOEL A. G. [Ceresinlike Products.] French Patent 874,918, Aug. 28, 1941. Oel u. Kohle, vol. 39, 1943, Sch. 193.

Paraffin obtained as a product of the Fischer-Tropsch process is dissolved in chlorinated hydrocarbons, and the various fractions are separated by cooling. From one of these fractions, a hard paraffin fraction, a fraction m. p. 55°–65° is separated and worked up into a vaselinelike product. A soft paraffin fraction is also obtained m. p. 40°–60°. These are either worked up into an impregnation agent or oxidized to fatty acids.

DEUTSCHE GLÜHFADENFABRIK. *See* abs. **3309.**

478. DEUTSCHE GOLD- UND SILBER SCHEIDEANSTALT VORMALS ROESSLER. [Process for Carrying Out Catalytic Reactions With Carbon Monoxide and Hydrogen.] Swiss Patent 204,840, Aug. 1, 1939; appl. filed March 3, 1938. Chem. Zentralb., 1940, I, p. 628.

MeOH synthesis is carried out by the use of neutral Zn carbonate, which has been obtained by precipitation from a Zn salt solution with a soluble (alkali) carbonate at low temperature in amorphous form and has been changed in the mother liquor at low temperature until the precipitate has assumed a crystalline structure as catalyst.

479. ———. [Production of Methanol From a Mixture of Carbon Monoxide and Hydrogen.] French Patent 996,442, Dec. 19, 1951; appl. filed Sept. 30, 1949. Chem. Zentralb., vol. 123, 1952, p. 4529.

MeOH is made from CO and H_2 with formation of methyl formate as byproduct and reduction of the same to MeOH at <200° (preferably 80°–170°) and at pressure 100 atm. (preferably 30–60 atm.). The proportions of H_2 : CO in the gas mixture are 2 : 1. The reaction is best performed in the liquid phase, for example, in a solution of alkali methylate in MeOH, in which the hydrogenation catalyst is suspended.

———. *See* abs. **2516.**

480. DEUTSCHE HYDRIERWERKE A. G. [Agent for Washing, Scouring, Wetting-Out, and Emulsifying.] German Patent 535,853, Mar. 28, 1929. Chem. Abs., vol. 26, 1932, p. 1078.

Mixture of high molecular alcohols obtained by the catalytic hydrogenation of oxides of C under pressure, in the synthesis of MeOH, is converted into the H_2SO_4 esters or their salts, to form such an agent. Thus, the alcohol mixture from a MeOH synthesis containing alcohols b. 170°–200° is treated with H_2SO_4 and oleum.

481. ———. Carboxylic Acids. British Patent 492,595, Sept. 22, 1938. Chem. Abs., vol. 33, 1939, p. 1762.

Soap-forming carboxylic acids or their salts are made by fusing with alkali-metal or alkaline-earth-metal bases the mixtures of glycols or products containing oxide groups obtained by oxidation of technical mixtures of aliphatic, aliphatic-alicyclic, or aliphatic-aromatic hydrocarbons, containing, besides 1 or more

unsaturated linkages in an aliphatic chain, at least 1 saturated aliphatic chain of at least 6 C atoms. Suitable hydrocarbon mixtures are unsaturated tar oils b. 200°–350° obtained by distilling lignite or cracking gas oil fractions b. 200°–325° and containing 70%–75% of olefins having 12–18 C atoms and olefinic products of the hydrogenation of CO. The unsaturated linkages may be oxidized with permanganates, persulfates, hypochlorites, H_2O_2, Cl, O_2, or air, preferably in the presence of solvents or diluents such as AcOH or Ac_2O, dioxane, Me_2CO, mineral oils, or saturated hydrocarbons present in the initial mixtures. The hydrocarbons may 1st be converted into aqueous emulsions with soaps, fatty alcohol sulfonates. Among examples, a benzine obtained by hydrogenation of CO, containing about 50% of higher olefins, is emulsified with soap and oxidized with H_2O_2 at 90°. The dried product is melted with caustic alkali at 250°–280° and the melt decomposed with mineral acid.

482. ———. [Liquid Soaps.] French Patent 902,029, Aug. 16, 1945; appl. filed Feb. 17, 1944, in Germany Feb. 20, 1943. Chem. Zentralb., 1949, I, p. E 13.

Liquid soaps are made by adding 5%–25% of hexahydrobenzyl alcohol to soaps or soap substitutes obtained by the sulfochlorination of Fischer-Tropsch paraffins with SO_2 and Cl_2 and neutralization of the sulfonates.

483. ———. [Plastic Softeners From Synthetic Fatty Acids.] French Patent 874,890, no date. Kainer, p. 286.

First running fatty acids from the paraffin oxidation are used as starting material in the production of softeners by the esterification of the fatty acids with alcohols. The resulting esters have softening properties similar to phthalic acid esters.

484. ———. [Softening and Solvent Agents for High-Polymer Substances.] French Patent 884,257, Aug. 9, 1943; appl. filed July 16, 1942. Chem. Zentralb., 1944, I, p. 605.

Agents are produced by the oxidation of paraffin gatch obtained by the hydrogenation of CO by the Fischer-Tropsch method.

485. ———. [Surface Active Substance.] French Patent 900,832, July 10, 1945; appl. filed Dec. 28, 1943, in Germany Sept. 26, 1941. Chem. Zentralb., 1948, II, p. 942.

Olefinic hydrocarbon mixture containing at least 6 C atoms, b. 100°–130° obtained by the hydrogenation of CO, is condensed in the presence of agents such as $AlCl_3$ or $HClO_4$ with aromatic oxycompounds (phenol, *o*-cresol, naphthol, etc.). The condensation product is sulfonated and converted with mineral or organic bases into its water-soluble salts. The reaction products are useful as detergents or emulsifiers.

486. DICKINSON, N. L. (M. W. Kellogg Co.). Process and Apparatus for the Synthesis of Organic Compounds. United States Patent 2,481,089, Sept. 6, 1949; appl. filed Mar. 6, 1947, Serial No. 732,846; 15 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 1673.

As a modification of United States Patent Application 726,620, filed February 5, 1947, by L. R. Hill and H. G. McGrath, a multiple-stage process for the synthesis of organic compounds is given. 2 steps (namely the sorption of CO on the catalyst and the hydrogenation of the sorbed CO and the growth of C–C chains), take place in the 1st reaction zone. The stabilization and desorption of the resulting synthesized organic molecules from the catalyst takes place in the 2d zone. The linear velocity of the gas passing through the 1st zone is at least 6 ft. per sec., preferably 8–40 ft. per sec. The temperature is 300°–600° F. The gaseous effluent from the 1st zone passes to a 2d zone where the average temperature is raised at least 25° F. to at least 100° F. above the outlet temperature of the 1st zone. Generally the pressure in the 1st stage is less than 500 p. s. i., preferably 80–400 p. s. i. for the Fe catalyst. The catalyst concentration is usually 1–18 lb. per ft.^{3} of gas. Usually less than 5–7 sec. contact per pass of the gases with the catalyst in the 1st zone is enough to produce the desired organic product. The cross-sectional area of any individual tube in the reactor is less than 2.5 in. in diameter and may be less than 1 in. Partial pressures in the 2d zone are usually lower than in the 1st. The gas velocity is equivalent or lower than in the 1st. The entrained catalyst is a finely powdered metal or metal oxide. The catalyst is separated from the gaseous effluent from the 2d zone. The gases are cooled and condensed for recovery of the organic compounds. 6 United States patents cited.

487. ——— (M. W. Kellogg Co.). Treatment of Solid Carbonaceous Materials to Produce Carbon Monoxide for the Synthesis of Organic Compounds. United States Patent 2,602,809, July 8, 1952; appl. filed July 10, 1948, Serial No. 38,134; 18 claims (*Cl. 260–449*). Chem. Abs., vol. 46, 1952, p. 8352.

In this 4-stage process, the gasification of carbonaceous solids with the aid of metallic oxides leads to the independent production of CO and H_2. In the gasification stage CO is produced by fluidization at 1,300°–1,650° F. of coal and hot Fe oxide with an O_2-free gas. The reduced metal oxide is transferred to the oxidation stage where H_2 is produced by fluidization with steam. In a 2d oxidizer reduced metal oxides are heated by fluidization with air. H_2 and CO are transported to a reactor for synthesis of organic compounds.

———. *See* abs. **1857**.

488. DICKINSON, N. L., EVERETT, E. F., AND HILL, L. R. (M. W. Kellogg Co.). Process for the Synthesis of Organic Compounds. United States Patent 2,568,953, Sept. 25, 1951; appl. filed Oct. 31, 1947, Serial No. 783,282; 13 claims (*Cl. 260–449.6*).

Invention relates to an integrated process involving the production of H_2 and CO in the ratio of 2 : 1 and their subsequent interaction in the presence of a hydrogenation catalyst under conditions of temperature 300°–700° F. and of pressure 500 p. s. i. g. to produce organic compounds as products.

489. DIDIER-WERKE A. G. Coking Process; Gas Producers. British Patent 461,402, Feb. 16, 1937. Chem. Abs., vol. 31, 1937, p. 5548.

Gas of stoichiometric composition is obtained from fuels, for example, brown coal, lignite, flame coal, by preheating the fuel by external heating and removing the products, carbonizing the fuel in an externally heated chamber, and leading the high-temperature gas with steam through a body of incandescent coke resulting from the carbonization to effect the substantial conversion of the gases into the desired mixture of H_2 and CO. For the treatment of brown coal, the preheating, carbonizing, reaction, and water gas chambers may be of Fe, SiC material, SiO_2 material, and fire clay, respectively.

490. ———. Coking Process; Retort Furnaces. British Patent 470,275, Aug. 12, 1937. Chem. Abs., vol. 32, 1938, p. 1080.

Gas mixtures containing H_2 and CO in proportions suitable for use in chemical processes such as destructive hydrogenation, are obtained in continuously operating, externally heated vertical retorts in which the time of contact of the reacting gases with the fuel is controlled by varying the position at which the gases are withdrawn.

491. ———. Distilling or Gasifying Fuels. British Patent 499,018, Jan. 17, 1939. Chem. Abs., vol. 33, 1939, p. 5161.

In the continuous distillation and gasification in a retort of fuels of different sizes, especially for obtaining a mixture of H_2 and CO for the synthesis of hydrocarbons, the distillates from a column of small-sized fuel together with steam are passed into an adjacent column of large-size fuel from which they are withdrawn. Describes apparatus.

492. ———. [Gas Mixtures Containing Carbon Monoxide and Hydrogen.] German Patent 669,434, Dec. 24, 1938 (*Cl. 24 e–1.01*). Chem. Abs., vol. 33, 1939, p. 2685.

A solid fuel, preferably coal or brown coal, is degasified and coked, and the coke is partly converted into water gas in the same apparatus. The residual coke is passed to a generator in which it is gasified, and the generator gas is mixed with the water gas to yield a mixture containing CO and H_2 but of low CH_4 content. The mixture may be used, for example, for producing N_2–H_2 mixture for use in the synthesis of NH_3. The gases evolved during the coking of the fuel are used to heat the plant.

493. ———. Generation of Synthesis Gas With Recovery of Aromatic Hydrocarbons. British Patent 531,288, Jan. 1, 1941; appl. filed July 17, 1939. Chem. Abs., vol. 35, 1941, p. 8262.

Solid fuels are carbonized by external heating in continuously operating vertical carbonizing retorts. That part of the gases and vapors that is generated between the commencement of the heating and a fuel temperature of 500°–600° is led away from the region of generation in the direction of increasing temperature through the fuel as far as a fuel temperature zone of 500°–600°. A mild cracking of these gases and vapor is thereby effected. The gas is drawn off from the retort, the benzene and light oil are removed, then it is mixed with the CO- and H_2-containing gas subsequently produced from the partly carbonized fuel.

See abs. **151, 3302.**

494. Dietrich, W., and Luther, M. (I. G. Farbenindustrie A. G.) [Alcohols.] German Patent 564,208, Oct. 16, 1929. Chem. Abs., vol. 27, 1933, p. 992.

Products obtained by the liquid-phase oxidation of higher aliphatic or naphthenic hydrocarbons are subjected to catalytic hydrogenation under pressure. A product in which alcohols predominate is obtained.

Dinerstein, R. A. *See* abs. **3.**

495. Dinwiddie, J. A. (Standard Oil Development Co.). Olefins From Oxides. United States Patent 2,542,487, Feb. 20, 1951; appl. filed Oct. 17, 1947, Serial No. 780,387; 3 claims (*Cl. 260–682*). Chem. Abs., vol. 45, 1951, p. 4431.

Olefins are prepared from monoolefin oxides, such as those obtained as byproducts in the Fischer-Tropsch synthesis, by passing the oxide vapors at 450°–650° F. and 50–300 p. s. i. pressure over a catalyst composed of Fe, Ni, or Co oxides promoted by 1%–8% K_2CO_3. C_3H_6 was prepared by passing $(CH_2)_3O$ over Fe_3O_4 containing 3% K_2CO_3 at 575° F. and 150 p. s. i. at a rate of 0.3 vol. per vol. of catalyst per hr. to yield a product containing 35.6% by vol. of C_3H_6.

496. ——— (Standard Oil Development Co.). Olefins From Oxides. United States Patent 2,542,488, Feb. 20, 1951; appl. filed Oct. 17, 1947, Serial No. 780,388; 4 claims (*Cl. 260–682*). Chem. Abs., vol. 45, 1951, p. 4431.

Process of United States Patent 2,542,487 (abs. **495**) also can be used for conversion of glycol derivatives of monoolefins to the corresponding olefins.

497. Directie van de Staatsmijnen in Limburg. [Conversion of Carbon Monoxide With Iron Oxide Catalysts.] Netherlands Patent 70,261, June 16, 1952. Chem. Abs., vol. 47, 1953, p. 296.

Suitable catalyst for the conversion of CO with steam is γ–Fe_2O_3 or a lower oxide obtained by the reduction of this oxide. The catalyst may be prepared by precipitated Fe_3O_4 from an equimolecular mixture of a ferrous and a ferric salt; this precipitate is converted to γ–Fe_2O_3 by O from the air. Preferably the precipitate is heated gradually not $> 330°$. A solution of a Cr salt, chromic acid, a chromate, or a bichromate may be added before heating; the catalyst then contains Cr_2O_3. If α–Fe_2O_3 is used as the starting material, this at 1st must be heated in a reducing atmosphere to form Fe_3O_4. If a ferrous salt is used, this is partly converted to the ferric form with the aid of $K_2Cr_2O_7$. In an example, a solution containing 20% of equimolecular quantities of ferrous and ferric salts is added to a strong solution of $NaHCO_3$ while stirring until pH is 7.5. After precipitation the clear liquid is removed by suction, the precipitate is washed, filtered, and dried at 110°; by this method Fe_3O_4 is converted to γ–Fe_2O_3. Then Cr nitrate is added so that the resulting product contains 8% Cr. The mixture is kneaded, dried, and made into tablets, which are roasted at 350°–375° for 3 hr. while air is passed through them. Over this catalyst a mixture of 1 part of CO and 5 parts of steam is passed at 350° and normal pressure. If the velocity of the gas is 1,200 normal cc. per hr. per cc. catalyst, a conversion is obtained amounting to 95.4%.

498. ———. Gasifying Carbonaceous Material. British Patent 690,214, Apr. 15, 1953. Chem. Abs., vol. 47, 1953, p. 7762.

See Netherlands Patent 68,486 (abs. **499**).

499. ———. [Gasifying Carbonaceous Material.] Netherlands Patent 68,486, Aug. 15, 1951. Chem. Abs., vol. 46, 1952, p. 5824.

Powdered coal or other carbonaceous material is gasified in two reactors in series, a smaller one being a cyclone or the like, in which the exothermic combustion reactions occur at a temperature above the melting point of the slag, and a bigger one, which may contain filling material and in which chiefly the endothermic reactions are effected at a lower temperature. Gives structural and operative details.

500. ———. [Gasifying Carbonaceous Material.] Netherlands Patent 68,491, Aug. 15, 1951. Chem. Abs., vol. 46, 1952, p. 5824.

In gasifying powdered coal in a gas generator, combustion gases are used as a gasifying medium for the material, which is preheated in a separate combustion chamber; the gases are fed to the generator in an upward stream at a temperature above the gasifying temperature and at a velocity somewhat above the suspension velocity of the bigger coal particles, whereas within the generator the velocity is somewhat below the suspension velocity. The generator may be of inverted conical form or it may have restricted passages with horizontal baffle plates between. Parallel or countercurrent flow may be applied. Gives structural and operative details.

Distillers Co., Ltd. *See* abs. **181, 182, 725, 729.**

501. Dodge, B. F. (S. Karpen & Bros.). Catalysts for Methanol Manufacture. United States Patent 1,908,696, May 16, 1933; appl. filed Jan. 16, 1930. Chem. Abs., vol. 27, 1933, p. 3724.

Stable highly active catalyst is prepared by reducing Cu carbonate admixed with Zn carbonate in the proportions of at least 2 atoms of Zn to 1 atom of Cu, producing a product containing ZnO and a stable purplish free Cu.

502. ——— (S. Karpen & Bros.). Catalytic Methanol Synthesis. United States Patent 2,014,883, Sept. 17, 1935; appl. filed Oct. 23, 1931. Chem. Abs., vol. 29, 1935, p. 7345.

Mixture of H_2 and a C oxide is passed, under superatmospheric pressure and at a temperature >200° (suitably under a pressure of about 2,600 lb. per sq. in. over a catalyst comprising an intimate mixture of Zn and Cr oxides and finely divided free Cu, the ratio of Zn to Cu being of the order of 2.0–4.5 atoms of Zn per atom of Cu.

503. Dolgov, B. N., and Osherova, M. M. [Catalyst for Synthesis of Gasoline.] Russian Patent 52,888, Mar. 31, 1938. Chem. Abs., vol. 34, 1940, p. 5632.

Solution of Al, Mn, and Cr nitrates is treated with K_2CO_3, the precipitate boiled, washed, heated to 450°, suspended in a solution of K_2CO_3, the product treated with a solution of $Ni(NO_3)_2$, and the precipitate formed again, boiled, washed, dried, and reduced at 180°–200°.

Dolph, R. N. *See* abs. **1052.**

504. Domann, F. (J. Pintsch Kom.-Ges.). [Gas Generator for Lumpy and Powdered Coal.] German Patent 744,970, Nov. 25, 1943 (*Cl. 26 a.–5*). Chem. Abs., vol. 39, 1945, p. 2862.

Donath, B. *See* abs. **660, 661.**

Donath, E. *See* abs. **2658, 2659, 2676.**

505. Dorndorf, H., Kelting, M., and Tramm, H. Apparatus Suitable for Catalytic Synthesis of Hydrocarbons From Hydrogen and Carbon Monoxide. United States Patent 2,148,545, Feb. 28, 1939; appl. filed June 17, 1936. Chem. Abs., vol. 33, 1939, p. 3809.

Gas-reaction apparatus, adapted for precise temperature control as required for the synthetic production of benzine hydrocarbons from H_2 and a C oxide, comprises a gastight casing having opposed end walls defining a catalytic chamber; a plurality of superposed rows of cooling tubes extending substantially horizontally through the casing and through the end walls thereof, the outer ends of several pluralities of adjoining tubes being connected to form several coils; thin heat conductive plates extending in closely spaced juxtaposition through the whole length of the catalytic chamber in the direction of flow of the reaction gas and substantially throughout the entire width of the chamber substantially at right angles to and traversed by the cooling tubes, the plates forming heat-abducting elements and defining narrow shafts; thin layers of a catalyst arranged within the shafts intermediate to the plates; and means for passing the gas to be reacted through the apparatus in the direction of the plates.

506. Dornte, R. W. (Standard Oil Development Co.). Recovery of Fatty Acids From Dilute Aqueous Solutions. United States Patent 2,537,658, Jan. 9, 1951; appl. filed Aug. 16, 1948, Serial No. 44,454; 2 claims (*Cl. 260–450*). Chem. Abs., vol. 45, 1951, p. 3581.

2-stage solvent extraction process uses a high-boiling hydrocarbon (b. above 205° C.) to extract the C_4–C_6 in the 1st stage and a high-b. (160° C. or higher) polar organic solvent to remove the remaining lower acids in the 2d stage. Symmetrical triethyl benzene, napthalene, methyl naphthalene, diphenyl, diphenyl methane, acenaphthene, dibenzyl, tetrahydronaphthalene, and hexahydronaphthalene are examples of suitable hydrocarbons. Methyl cyclohexanone, furfural, isophorone, and the cresols are suitable polar solvents. The process may be carried out in a standard apparatus. Fresh extractant may be added as needed to the recycled and recovered extractant. 4 United States patents cited.

507. Dorschner, O. (American Lurgi Corp.). Recovery and Detoxication of Illuminating Gas Containing Carbon Monoxide and Hydrogen. United States Patent 2,301,687, Nov. 10, 1942; appl. filed Sept. 5, 1939, Serial No. 293,487, in Germany Sept. 13, 1938; 7 claims (*Cl. 260–449*). Chem. Abs., vol. 37, 1943, p. 2164.

Process is employed that involves passing the gas at 150°–400° in contact with a catalyst containing as its chief active ingredient metallic Fe and capable at such temperature of causing H_2 and CO to react in a ratio of less than 2 vol. H_2: 1 vol. CO and of forming by such reaction liquid hydrocarbons and organic compounds which contain O and removing at least a portion of such substances from the gas.

508. d'Ouville, E. L. (Coppers Co., Inc.). Manufacture of Hydrocarbons. United States Patent 2,499,372, Mar. 7, 1950; appl. filed Mar. 9, 1946, Serial No. 653,406; 7 claims (*Cl. 260–449.6*).

CO and H_2 are passed into contact with a sintered Fe catalyst at 300°–350° C. at a pressure 10–50 atm. and a space velocity 300–5,000 vol. synthesis gas per vol. catalyst per hr. The synthesis gas is $CO : H_2 :: 4 : 3$ or $2 : 1$ or $1 : 1$. A final synthesis gas containing CO and H_2 in a ratio not greater than $1 : 0.65$ nor less than $1 : 1$ will produce a residue gas having a CO_2 content useful for production of 2 synthesis gases, 1 by reaction of residue with CH_4 and steam and the other by reaction of the residue gas with coke. The 2 synthesis gases are mixed. 1 foreign and 8 United States patents cited.

509. ——— (Standard Oil Co. of Indiana). Manufacture of Hydrogen-Carbon Monoxide Mixture. United States Patent 2,635,952, Apr. 21, 1953; appl. filed July 5, 1946, Serial No. 681,479; 1 claim (*Cl. 48–196*). Chem. Abs., vol. 47, 1953, p. 6636.

The process involves multiple-zone operation. The reactions for the 1st zone are:

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 + 67{,}960 \text{ cal.}$$
$$2\,H_2 + O_2 \rightarrow 2\,H_2O + 136{,}830 \text{ cal.}$$

For the 2d zone:

$$2\,CH_4 + 2\,H_2O \rightarrow 2\,CO + 6\,H_2 - 122{,}220 \text{ cal.}$$
$$CH_4 + CO_2 \rightarrow 2\,CO + 2\,H_2 - 61{,}016 \text{ cal.}$$

The net reaction is:

$$3\,CH_4 + 1\tfrac{1}{2}O_2 \rightarrow 3\,CO + 6\,H_2 + 11{,}554 \text{ cal.}$$

The oxidants and energy required for the conversion of CH_4 in the 2d zone are generated in the 1st zone. CH_4 is introduced into the 2d zone and is thus contacted only with the products of the 1st zone and not directly with O_2. The invention may be practiced with or without catalyst in various types of equipment. A Ni catalyst is preferred. Heat may be transferred in any of 3 ways. The preferred method depends on the size of operation and the purity of the product required. O_2 is introduced into the system in such a manner that it initially contacts CO and H_2 substantially free from CH_4, and CH_4 is introduced so that it initially contacts CO_2 and steam substantially free from O_2. Appreciable amounts of C or other undesirable products are not produced. 11 United States patents cited.

510. ——— (Koppers Co., Inc.). Reactivation of Catalysts in Hydrocarbon Synthesis. United States Patent 2,478,899, Aug. 16, 1949; appl. filed Apr. 27, 1945, Serial No. 590,566; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 9420.

Deactivated catalyst is treated with H_2 at a relatively low temperature, 50° C. for 0.5–5.0 hr. or 25° C. for 8–50 hr. to regenerate the activity of the catalyst without destruction of the carbide layer. The method is especially well adapted for fluid catalyst in cyclic process. 6 United States patents cited.

511. ——— (Koppers Co., Inc.). Synthetic Hydrocarbons. British Patent 631,325, Nov. 1, 1949. Chem. Abs., vol. 44, 1950, p. 3701.

In the Fischer-Tropsch synthesis of hydrocarbons, the exit gases, mainly CO_2 and CH_4 with some H_2 and CO, are reformed to CO and H_2 and used again in synthesis. Part of the exit gas reacts with added CH_4 and H_2O over a Ni catalyst at 1,000° to give CO and H_2 and some CH_4. The remainder is passed over coke at 1,000°–1,400°, forming mostly CO. The re-formed gases are blended and used for hydrocarbon synthesis.

DRABKIN, M. L. *See* abs. **1045, 1046, 1047.**

512. DRAWE, R. [Carbon Monoxide; Hydrogen.] German Patent 540,316, June 14, 1927. Chem. Abs., vol. 26, 1932, p. 1727.

Fuel is gasified with a highly saturated mixture of O_2 and steam to yield a gas rich in H_2 and CO_2. The CO_2 is washed out or otherwise separated and then mixed with O_2 and used for the gasification of fuel in a 2d generator, yielding a gas rich in CO.

513. DRESSLER, R. G., AND BIRCHER, J. R. (The United States of America, as represented by the Secretary of the Interior). Utilizing the Aqueous, Organic Chemical Wastes From the Fischer-Tropsch Process. United States Patent 2,574,469, Nov. 13, 1951. Chem. Abs., vol. 46, 1952, p. 2271.

Aqueous solution of the oxygenated organic compounds obtained as byproducts of the Fischer-Tropsch process is fractionated to yield an overhead product (I) containing the alcohols, aldehydes, and ketones in a fairly concentrated aqueous solution, and a bottoms product, which contains most of the organic acids in a dilute aqueous solution and which is evaporated and fed to a gasifier where the organic acids are converted to CO and steam for recycle to the process. (I) is treated to recover its organic content in a valuable form.

514. DREYFUS, H. Acetic Acid. British Patent 262,832, June 13, 1925. British Chem. Abs., 1927, B, p. 125. Chem. Abs., vol. 21, 1927, p. 3906.

Equimolecular proportions of CO and H_2 are passed under pressures of 50–200 atm. and at temperatures of 200°–300° or somewhat higher, but under 450°, over substances such as Cu oxide, Sn oxide, Pb oxide, Cu acetate, Al methylate, Sn methylate, or their mixtures.

515. ———. Acetic Acid. United States Patent 1,896,224, Feb. 7, 1933; appl. filed May 27, 1926, Serial No. 112,166. Chem. Abs., vol. 27, 1933, p. 2458.

Mixture of about equimolecular proportions of H_2 and CO is heated under pressure to 100°–450° in the presence of a contact mass containing a metal acetate or a metal compound capable of forming an acetate decomposable at temperatures <450°.

516. ———. Acetic Acid From Methanol and Carbon Monoxide. United States Patent 1,784,583, Dec. 9, 1930; appl. filed Oct. 22, 1926, Serial No. 143,516, in Great Britain Nov. 7, 1925. Chem. Abs., vol. 25, 1931, p. 304.

MeOH and CO are heated together under substantially atmospheric pressure to 100°–500° (generally 200°–350°) in the presence of a catalyst comprising a metal the acetate of which decomposes with formation of HOAc at temperatures such as are employed. Catalysts may be oxides, acetates, methylates, or other suitable compounds of Cu, Sn, Pb, Zn or finely divided metals such as Zn, Al, or Cu.

517. ———. [Aliphatic Compounds.] French Patent 692,736, Mar. 25, 1930. Chem. Abs., vol. 25, 1931, p. 1536.

Organic O compounds are synthesized by passing the reaction gases through a number of reaction vessels in series in an open circuit. Gives example of preparation of MeOH from water gas.

See also French Patent 691,209.

518. ———. Aliphatic Dialdehydes From Olefins and Aldehydes. United States Patent 2,434,313, Jan. 13, 1948. Chem. Abs., vol. 42, 1948, p. 2986.

Aldehydes and olefins are caused to react in the liquid phase. At low temperature the use of acids, organic peroxides, or alkalies as catalysts is beneficial. Formalin (I) (1 mol.) and 1, 5-hexadiene less than 0.5 mol. are caused to react in a stirred autoclave at 50°–80°. Suberaldehyde is isolated from the reaction mixture by extraction with $HCCl_3$ or Et_2O. Butadiene and (I) react similarly to give adipaldehyde.

519. ——— (British Celanese, Ltd.). [Catalyst for Methanol Synthesis.] French Patent 713,707, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 205.

Colloidal $Zn(OH)_2$.

520. ———. [Catalytic Materials.] French Patent 691,210, Mar. 5, 1930. Chem. Abs., vol. 25, 1931, p. 1045.

Catalytic materials, which are exhausted or poisoned in gas reactions such as the synthesis of MeOH, are reactivated or regenerated by submitting them to the action of gases rich in H_2 at temperatures not appreciably above those used in the catalytic operation.

See also British Patent 334,251 (abs. **74**) and United States Patent 1,999,388 (abs. **169**).

521. ———. [Catalytic Production of Aliphatic Compounds, Especially Methyl Alcohol.] French Patent 617,426, Feb. 19, 1927; appl. filed June 11, 1926. Chem. Zentralb., 1927, I, p. 2685.

Water gas or other gas mixtures, such as H_2 and CO in proportions of 1 : 1, is treated at 350°–450°, preferably 200°–300°, under pressures of 200 atm., preferably 50–150 atm., in an apparatus of Cu, Al, or similar catalytic metal. Suitable catalysts are ZnO, CuO, Cu, or Zn chromate and Zn aluminate. At temperatures of 450° and less velocity of gas flow, higher alcohols and oily substances are obtained.

522. ———. Catalytic Production of Hydrocarbons From Hydrogen and Carbon Monoxide. United States Patent 2,231,990, Feb. 18, 1941; appl. filed July 20, 1938, Serial No. 220,345, in Great Britain Aug. 5, 1937; 6 claims (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 3418.

Reaction is effected in the presence of a hydrogenating catalyst such as Co activated with ThO_2, at a pressure normally maintained above 0.5 atm. but periodically reduced below 0.5 atm. without interrupting the flow of reactant gases whenever the activity of the catalyst falls considerably to restore its activity.

523. ———. [Catalytic Production of Ketene.] French Patent 617,428, Feb. 19, 1927; appl. filed June 11, 1926. Chem. Zentralb., 1927, I, p. 2686.

Mixtures of CO and H_2 in proportions of about 3 : 1 are passed at 200°–300° and 50–150 atm. over catalysts of CuO and Cu and Zn chromate.

524. ———. [Catalytic Production of Oxygen-Containing Organic Compounds.] French Patent 617,433, Feb. 19, 1927; appl. filed June 11, 1926. Chem. Zentralb., 1927, I, p. 2686.

Gas mixtures containing H_2 and CO are passed at raised temperature and a pressure of about 5 atm., or at normal or reduced pressure over catalysts effecting the combination of CO with H_2, except those favoring the formation of CH_4 such as Ni, Fe, or Co. The gas mixture must be free from impurities such as S and volatile Fe compounds. The products are MeOH, acetic acid, acetone, and other aliphatic or cyclic compounds such as liquid hydrocarbons, higher alcohols, acids, and ketones.

525. ———. [Catalytic Reactions.] French Patent 742,760, Mar. 16, 1933. Chem. Abs., vol. 27, 1933, p. 3362.

Describes apparatus for carrying out exothermic catalytic reactions, a cooling fluid passing up vertical tubes in the reaction chamber and down tubes inside the first-mentioned tubes.

526. ———. [Formaldehyde.] French Patent 617,431, Feb. 19, 1927; appl. filed June 11, 1926. Chem. Zentralb., 1927, I, p. 2686.

Gas mixtures containing CO and H_2 in nearly equimolecular amounts are passed at 200°–300°, at most 450°, and at 50–150 atm., at most 200 atm., over catalysts consisting of Zn, Cu, Al, Zn salts of these metals, as chromates or vanadates or products arising from the reduction of the corresponding metal oxides with H_2 or gases containing it. Catalysts favoring the formation of CH_4 even in traces should be avoided. By slow passage of the gas mixture through the reaction chamber considerable amounts of hydrocarbons and higher alcohols arise as byproducts.

527. ———. [Formaldehyde and Methanol.] French Patent 22,293, May 25, 1921; appl. filed Mar. 22, 1917. Chem. Zentralb., 1921, IV, p. 708.

See British Patent 157,047 (abs. **528**).

528. ———. Formaldehyde; Methanol. British Patent 157,047, Feb. 10, 1921; appl. filed Aug. 25, 1917. Chem. Zentralb., 1921, II, p. 1061; Chem. Abs., vol. 15, 1921, p. 1725.

Pt black or Ni is used as catalyst, and it can be deposited on pumice. Hydrogenation takes place in Fe cylinders filled with the catalyst.

529. ———. Formaldehyde; Methyl Alcohol. British Patent 108,855, July 23, 1917. Chem. Abs., vol. 12, 1918, p. 155.

HCHO and MeOH, or mixtures thereof, are obtained by the reaction of H_2 on CO or CO_2 in the presence or absence of catalysts. Suitable catalysts are Pt, platinized asbestos, Cu, Fe, Cr, Ni, Ce, U, V, or their oxides, etc. The process is carried out by passing the mixture of gases through reaction vessels or tubes at 100°–400° and condensing the products. The mixture of gases is preferably preheated. The process may be effected in contact apparatus similar to that used in the manufacture of SO_3 or, when catalysts are not used, in metal or other apparatus containing glass scrap, glass wool, etc. to provide an extensive surface.

530. ——— (Celanese Corp. of America). Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen. United States Patent 2,338,805, Jan. 11, 1944; appl. filed Mar. 1, 1941, Serial No. 381,414, in Great Britain Mar. 16, 1940; 1 claim (*Cl. 260–449.6*). Chem. Abs., vol. 38, 1944, p. 3801.

Production of hydrocarbons is effected by a process that involves subjecting CO and H_2 in a proportion of 1:2 vol., respectively, to reaction in the presence of a catalyst comprising Co together with minor proportions of ThO_2 and Cu, supported on a carrier of kieselguhr, under a pressure not substantially above atmospheric and at 195°, the amount of kieselguhr used being 20–30 times that of the active catalytic material that is carried on it.

531. ———. Hydrocarbons. British Patent 496,292, Nov. 29, 1938. Chem. Abs., vol. 33, 1939, p. 2902.

Hydrocarbons are made by catalytic reaction of CO and H_2 while under a pressure of at most 0.5 atm., preferably 0.25–0.1 atm. Diluent gases, for example, steam, CO_2, N_2, and hydrocarbons, if desired reaction products of CO and H_2 may be present, for example, in amounts up to 10 or more times the volume of CO. Co and Fe catalysts may be used when liquid hydrocarbons are desired and Ni for CH_4 synthesis. They may be activated with Al_2O_3, ThO_2, MgO, or ZnO and deposited on carriers. In an example, CO is passed with 2 times its volume of H_2 at 0.1 atm. over a Co–ThO_2 catalyst at 180°, the greater part of the hydrocarbons are condensed and the residual vapors mixed with fresh gases and recycled.

532. ———. Hydrocarbons. British Patent 500,264, Feb. 6, 1939; appl. filed Aug. 5, 1937. Chem. Abs., vol. 33, 1939, p. 5410.

Hydrocarbons are produced by the catalytic reaction of CO and H_2, the absolute pressure in the reaction zone being normally above 0.5 atm. but periodically reduced to below 0.5 atm. The catalysts, apparatus, temperatures, and other conditions of working are those described in British Patent 496,292 (abs. **531**). As an example, CO with 2 times its vol. of H_2 and with or without 3 times its vol. of steam or CO_2 is passed at 1 atm. over a Co–ThO_2 catalyst at 180°; when, after some hours, the proportion of the hydrocarbons in the exit gases falls appreciably, the pressure is reduced to 0.1 atm., usually for a relatively short time, to reactivate the catalyst; most of the hydrocarbons are condensed from the exit gases, which are recycled with fresh reactants.

533. ———. Hydrocarbons and Oxygenated Derivatives. British Patent 505,121, May 5, 1939; appl. filed Nov. 6, 1937. Chem. Abs., vol. 33, 1939, p. 7814.

In the synthesis of these from CO and H_2, the catalyst is submerged in a liquid that boils completely within the permissible range of reaction temperatures under the pressure employed or partly within this range and for the rest above it. Hydrocarbons, such as a purified petroleum fraction or an oil obtained by reduction of CO, may be employed as the liquid medium. Part of the liquid vaporizes, the vapors being condensed and returned to the reaction zone.

534. ———. Hydrocarbons From Carbon Monoxide and Steam. United States Patent 2,257,293, Sept. 30, 1941; appl. filed Feb. 1, 1938, Serial No. 188,063, in Great Britain Feb. 19, 1937; 3 claims (*Cl. 260–449*). Chem. Abs., vol. 36, 1942, p. 250.

Process is employed for the production of hydrocarbons, which involves passing a mixture of CO and steam over a catalytic mass such as a Ni catalyst, which is adapted to produce CO_2 and H_2 from the mixture and to catalyze the reduction of CO with H_2, the gas mixture first coming into contact with the catalytic mass at 400°–500° to convert part of the CO to CO_2 and then, while the steam content of the gas mixture formed at such temperature is maintained, into contact with the catalytic mass at 150°–250°.

535. ——— (Celanese Corp. of America). Hydrogenation of Carbon Monoxide. United States Patent 2,361,997, Nov. 7, 1944; appl. filed Oct. 1, 1941, Serial No. 413,195, in Great Britain Aug. 22, 1940; 4 claims (*Cl. 260–449.6.*) Chem. Abs., vol. 39, 1945, p. 2394.

Reacting gases are fed into a reaction medium prepared by dissolving a catalytically active Ni, Co, or Fe salt in a hydrocarbon fraction boiling above the reaction temperature. The reaction products sought are distilled off as they are formed.

See also British Patent 564,730 (abs. **537**).

536. ——— (C. Bonard, administrator of the estate of H. Dreyfus). Improvements in Exothermic Chemical Reactions. United States Patent 2,393,240, Jan. 22, 1946; appl. filed June 27, 1942, Serial No. 448,837, in Great Britain May 15, 1941; 4 claims (*Cl. 260–524*). Chem. Abs., vol. 40, 1946, p. 2164.

Chemical reactions, especially strongly exothermic ones, are carried out in the presence of a solid catalytic material mixed with a material of little or no catalytic activity, both materials being in the form of granules with their surfaces exposed to the sub-

stances taking part in the chemical reaction. The 2 materials may be arranged in layers varying in number and thickness. For instance, at the beginning of the reaction zone there may be more or thicker layers of material of little or no catalytic activity than catalyst, farther along the 2 materials may be in layers of equal number and thickness, whereas still farther along the number or thickness of the catalyst layers may be greater or only catalyst may be present. The invention is not limited to oxidation reactions but may be used in the synthesis of hydrocarbons from oxides of C and H_2 whether an Fe-, Ni-, or Co-type of catalyst is used.

537. ———. Improvements Relating to the Production of Hydrocarbons. British Patent 564,730, Oct. 11, 1944; appl. filed Aug. 22, 1940. Chem. Abs., vol. 40, 1946, p. 3588.

Production of hydrocarbons from CO and H_2 is effected by introducing the reactant gases in an organic liquid containing the catalyst. Such an organic liquid may be anthracene oil; the catalysts being the fatty acid salts of high molecular weight of Ni or Co used in conjunction with Cu and Th.

See also United States Patent 2,361,997 (abs. **535**).

538. ———. Ketene. British Patent 262,364, June 13, 1925. British Chem. Abs., 1927, B, p. 125. Chem. Abs., vol. 21, 1927, p. 3626.

Mixture of CO and H_2 in the proportions of 3:1, respectively, is passed over a MeOH-forming catalyst, such as ZnO, Cu oxide, Cu chromate, Zn chromate, Zn aluminates, K zincate, or various specified mixtures, which may contain KOAc or K_2CO_3 or similar compounds. Pressures of about 50–150 atm. and temperatures of 200°–300° are preferred.

539. ———. Ketene. United States Patent 1,773,970, Aug. 26, 1930; appl. filed May 27, 1926, Serial No. 112,164, in Great Britain June 13, 1925. Chem. Abs., vol. 24, 1930, p. 5046.

Gaseous mixture containing H_2 and CO in the relative proportions of about 1 and 3 mols. respectively, is subjected to the action of heat and pressure in the presence of a catalyst such as ZnO, Cu oxide, Cu chromate, Zn chromate or aluminate or K zincate. A temperature of about 200°–300° and a pressure of about 50–150 atm. are suitable for the reaction.

540. ———. Methanol. British Patent 262,494, June 13, 1925. Chem. Abs., vol. 21, 1927, p. 3626.

Water gas or other suitable gas mixture containing CO and H_2 in equimolecular proportions is passed at high temperature and pressure over ZnO without addition of other MeOH-forming catalysts. A pressure of 50–150 atm. is preferred and a temperature of 200°–300°, but the pressure and temperature may rise as high as 200 atm. and 450°. A Cu-lined or Al apparatus is preferably used. If the gases are passed through the apparatus at too low a speed, hydrocarbons and higher alcohols predominate in the product.

541. ———. Methanol. British Patent 335,962, June 5, 1929. Chem. Abs., vol. 25, 1931, p. 1843.

In synthesizing MeOH from CO and H_2, the reaction gases are passed 1st over 1 or more masses of ZnO with or without Cr oxide and then over 1 or more MeOH catalysts, which are sensitive to S poisoning, such as catalysts containing Cu or Mn or their compounds. Describes various details of procedure. Water gas may be used as an initial material.

542. ———. Methanol. United States Patent 1,738,989, Dec. 10, 1929; appl. filed May 27, 1926. Chem. Abs., vol. 24, 1930, p. 865.

A gaseous mixture containing H_2 and CO in about equimolecular proportions is subjected to the action of heat and pressure in the presence of ZnO as sole catalyst.

543. ———. Methanol. United States Patent 1,868,096, July 19, 1932; appl. filed May 27, 1930, Serial No. 455,989, in Great Britain June 5, 1929. Chem. Abs., vol. 26, 1932, p. 5106.

See British Patent 335,962 (abs. **541**).

544. ———. [Methanol Synthesis.] French Patent 345,649, no date. Schmidt, J., Das Kohenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 205.

Catalysts are oxides that were precipitated electrolytically as hydroxides.

545. ———. [Methanol Synthesis.] French Patent 653,554, Apr. 28, 1928. Chem. Abs., vol. 23, 1929, p. 3716.

Catalysts for the synthesis of MeOH are prepared by precipitating $ZnCO_3$ in a gelatinous form, washing by decantation and drying the product under reduced pressure so as to retain the colloidal state, and heating the gel to a temperature not > that to be used in the synthesis, for example, 400°. The $ZnCO_3$ gel may be produced by precipitation in a very dilute solution, or by incorporating during or after precipitation with a protective colloid such as starch, pectin, saponin, or hydrated SiO_2. The catalyst may be used in conjunction with a promoter such as 5–10% of Cr_2O_3 or other catalyst.

546. ———. [Organic Oxygen Compounds.] French Patent 689,342, Feb. 3, 1930. Chem. Abs., vol. 25, 1931, p. 963.

Organic O compounds, particularly MeOH are obtained by heating mixtures of H_2 and CO or CO_2 under pressure in the presence of a catalytic mass in which the catalytic metal is present as the sulfide, such as sulfides of Zn, Cu, Pb, or Cd, which may be mixed with Cr_2O_3.

See also French Patent 669,370.

547. ———. [Organic Oxygen Compounds.] French Patent 697,726, June 20, 1930. Chem. Abs., vol. 25, 1931, p. 3011.

O compounds of C are hydrogenated in the presence of catalysts composed of or containing Fe or Co in the form of compounds having the metals in the acid radical; for example, ferrites, ferrates, cobaltites, or cobaltates of alkali or alkaline earth metals. Gives examples of the preparation of EtOH and higher alcohols along with aliphatic acids and aldehydes from CO and H_2 and from a mixture of MeOH, CO, CO_2 and H_2.

See also abs. **546** and **549**.

548. ———. [Organic Oxygen Compounds.] French Patent 697,727, June 20, 1930. Chem. Abs., vol. 25, 1931, p. 3011.

Describes the preparation of compounds similar to those prepared in French Patent 697,726 (abs. **547**). Catalysts composed of or containing compounds of metals of groups 1 and 2 are used with oxy acids of elements of groups 2, 3, 4, and 5 such as borates, aluminates, zincates, silicates or phosphates of alkali, or alkaline earth metals or Cu.

See also abs. **546**, **549**, and **550**.

549. ———. [Organic Oxygen Compounds.] French Patent 697,896, June 25, 1930. Chem. Abs., vol. 25, 1931, p. 3011.

EtOH and higher aliphatic alcohols are obtained from mixtures of H and O compounds of C in the presence of a catalyst composed of or containing Fe, Ni, or Co in the form of oxy acids of groups 2, 3, 4, or 5, or as free metals, or their compounds, in intimate association with other compounds of oxy acids. The metals may be used in the form of borates, aluminates, zincates, silicates, phosphates, or other salts of oxy acids of P.

550. ———. [Organic Oxygen Compounds.] French Patent 698,094, June 26, 1930. Chem. Abs., vol. 25, 1931, p. 3011.

Organic O compounds are prepared by the reaction of steam with aliphatic hydrocarbons such as CH_4, C_2H_6, C_2H_4, or C_2H_2. Alkaline earth metals or metals of groups 4, 5, 6, 7, and 8, Al, Mg, or Zn or their compounds may be used as catalysts. The reaction is carried out under pressure and preferably at 250°–500°. Examples are given of the preparation of MeOH and higher alcohols along with aldehydes, acids, and ketones.

551. ———. Oxygenated Organic Compounds by Catalytic Reactions. British Patent 263,503, July 1, 1925. British Chem. Abs., 1927, B, p. 237; Chem. Abs., vol. 22, 1928, p. 92.

Catalytic interaction of CO and H_2 is effected at approximately atmospheric pressure for the production of MeOH, CH_2O, HOAc, acetone, and higher alcohols, acids, ketones, and hydrocarbons. Catalysts may be used such as are specified in abs. **89, 91, 514, 538, 540,** and **3289**; CH_4-forming catalysts are excluded.

552. ———. Oxygenated Organic Compounds by Synthesis From Hydrogen and Oxides of Carbon. British Patent 337,409, July 24, 1929. Chem. Abs., vol. 25, 1931, p. 2152.

Compounds such as EtOH, acetaldehyde, HOAc, and their homologs and esters are prepared from H_2 and C oxides or from compounds such as MeOH synthesized from them (with or without presence also of H_2 and C oxides) by use of catalysts such as Fe, Ni, or Co borates, silicates, phosphates, or salts of other oxyacids of P. Various details and examples are given, and apparatus may be used having Cu or Cu-lined chambers or formed of steel containing Mo, Mn, Co, or Ni. Temperatures up to 600° and pressures up to 500 atm. are mentioned as suitable.

553. ———. Oxygenated Organic Compounds From Carbon Oxides and Hydrogen. British Patent 338,854, July 24, 1929. Chem. Abs., vol. 25, 1931, p. 2435.

Products such as EtOH, PrOH, acetaldehyde, HOAc, MeOAc, and their higher homologs and ketones are formed from mixtures containing C oxides and H_2 such as water gas, coke-oven gas, or producer gas, in the presence of catalysts consisting of alkali or alkaline earth or Cu silicates, borates or phosphates of salts of other oxyacids of P. Temperatures of 200°–600° and pressures of 50–500 atm. may be used, CH_4 or inert gases such as N_2 may be present and reaction chambers of Cu or steel lined with Cu or of steel containing Mo, W, Mn, Co, or Ni may be used.

554. ———. Oxygenated Organic Compounds From Carbon Oxides and Hydrogen by Catalytic Reactions. British Patent 337,014, July 24, 1929. Chem. Abs., vol. 25, 1931, p. 1839.

Compounds such as EtOH, HOAc, acetaldehyde, MeOAc, and higher homologs are made using catalysts comprising ferrites, ferrates, cobaltites, or cobaltates, such as those of alkali or alkaline earth metals or of Al, preferably at 200°–600° (suitably 250°–350°) under 50–500 atm. or higher pressure. Coke-oven gases may be used, producer or water gas, which may be preliminarily treated if desired to form synthetic products such as MeOH or EtOH in the presence of a catalyst such as ZnO or a basic chromate. The catalysts may be used in connection with Zn, Mg, Ca, Al, Cr, Mo, V, W, or U or their oxides or other compounds. Cu may be present, and the apparatus used may be of Cu or steel lined with Cu or of steel containing Mo, W, Co, or Ni.

See also United States Patent 1,996,101 (abs. **555**).

555. ———. Oxygenated Organic Compounds From Carbon Oxides and Hydrogen by Catalytic Reaction. United States Patent 1,996,101, Apr. 2, 1935; appl. filed July 21, 1930, Serial No. 469,648 (*Cl. 260–156*). Chem. Abs., vol. 29, 1935, p. 3349.

Production of products such as acetaldehyde, EtOH, PrOH, and acetone by the interaction of oxides of C, H_2, and substances produced by the catalytic hydrogenation of oxides of C is effected in the presence of ferrites, ferrates, cobaltites, or cobaltates such as those of alkali or alkaline earth metals.

556. ———. Oxygenated Organic Compounds From Methane and Steam. British Patent 337,410, July 24, 1929. Chem. Abs., vol. 25, 1931, p. 2152.

Compounds such as EtOH, HOAc, AcH, and their homologs and ketones are formed from CH_4 and steam at 200°–500° and pressures up to 500 atm. or more, and the products may be varied by adding to the reaction mixture C oxides, H_2 or O_2 and inert gases such as N_2 also may be present. Among the catalysts that may be used are Zn, Mg, Ca, Al, Cr, Mn, V, Mo, Ti, Fe, Co, Ni, and rare earths, or their compounds, such as oxides, As or S compounds, phosphates, silicates, or borates. Also these may be used mixed with alkali or alkaline earth compounds, with each other, with Cu, Ag or Au, with compounds, such as Zn vanadate, Zn chromate, Mn chromate, Zn tungstate or molybdate, or with the corresponding salts or Mg, Ca, or Al. Apparatus of Cu or lined with Cu or of steel containing V, Mn, Ni, or Co is suitable.

557. ———. [Production of Formaldehyde and Methanol From Carbon Monoxide or Carbon Dioxide by Catalytic Hydrogenation.] French Patent 492,154, Aug. 12, 1916.

See British Patent 157,047 (abs. **528**) and French Patent 22,293, (abs. **527**).

558. ———. [Production of Oxygenated Organic Compounds.] French Patent 722,850, Mar. 26, 1932; appl. filed Sept. 12, 1931. Chem. Zentralb., 1932, II, p. 923; Chem. Abs., vol. 26, 1932, p. 4061.

Oxides of C mixed with H_2 are passed at 300°–400° and 50–200 atm. over catalysts consisting of ZnO and Cr_2O_3, the latter being about 42% of the mixture. They are made by simultaneously precipitating the carbonates of Zn and Cr from aqueous solutions of suitable salts of the same, such as the nitrates.

See also abs. **547, 549,** and **550.**

559. ———. Synthesis of Compounds Such as Ethanol, by Reduction of Carbon Monoxide. Canadian Patent 343,080, no date.

See United States Patent 1,977,718 (abs. **560**).

560. ———. Synthesis of Compounds Such as Ethanol, By Reduction of Carbon Monoxide. United States Patent 1,977,718, Oct. 23, 1934; appl. filed July 21, 1930, Serial No. 469,651 (*Cl. 260–156*). Chem. Abs., vol. 29, 1935, p. 180.

Reaction of CO with H_2 is effected in the presence of a catalyst comprising a phosphate of a metal of groups 1 or 2 of the periodic system, such as Cu metaphosphate and Na phosphate, suitably at 250°–350° under 50–150 atm. pressure. Cu metaborate also may be used.

561. ———. Synthesis of Higher Alcohols. Canadian Patent 333,861, no date.

See United States Patent 1,996,101 (abs. **555**).

562. ———. Synthesis of Hydrocarbons. British Patent 476,292, no date. Schmidt, J., Das Kohlen-Oxyd. Akad. Verlagsgesell., Leipzig, 1950, p. 173.

Partial pressure of CO and H_2 is maintained <0.5 atm., preferably at 0.25–0.1 atm., and the temperature at 150°–300°.

563. ———. Synthesis of Oxygenated Organic Compounds From Oxides of Carbon and Hydrogen.

United States Patent 1,963,119, June 19, 1934; appl. filed July 21, 1930, Serial No. 469,649 (*Cl. 260–156*). Chem. Abs., vol. 28, 1934, p. 4743.

Gases containing CO and H_2, which also may contain MeOH, are heated to 250°–400° under 100–200 atm. pressure in the presence of a catalyst such as Co or Ni octaborate, Co Mg borate, ferric metaphosphate, or ferric silicate for the production of EtOH and higher alcohols together with aldehyde and acids. Describes various details and modifications of procedure.

———. *See* abs. **536.**

564. DREYFUS, H., AND BADER, W. (Celanese Corp. of America). Acetic Acid. United States Patent 1,864,-531, June 28, 1932; appl. filed Mar. 15, 1929, Serial No. 347,448. Chem. Abs., vol. 26, 1932, p. 4346.

Gaseous mixture containing CO and H_2 is subjected to the action of a phosphoric acid catalyst or the like, forming MeAc, and the MeOAc may be converted into free HOAc by saponification in the presence of substantially the quantity of H_2O necessary for producing glacial HOAc.

DRIVER, A. P. *See* abs. **278.**

565. DU CHAFFAUT, R. (E. I. du Pont de Nemours & Co.). Apparatus for Effecting Catalytic Exothermic Gas Reactions Such as Synthesis of Ammonia or Methanol. United States Patent 1,942,021, Jan. 2, 1934. Chem. Abs., vol. 28, 1934, p. 1581.

Catalyst container provided at 1 end with a gas outlet and having a helically grooved exterior is closely and removably fitted within a shell so as to form a helical gas passage communicating at the end of the catalyst container first named with a gas inlet and at the other end with the interior of the catalyst container.

———. *See* abs. **627.**

566. DUFFIELD, F. L. Producing a Gas Suitable for the Manufacture of Methyl Alcohol. British Patent 516,546, Jan. 4, 1940; appl. filed June 28, 1938. Chem. Zentralb., 1941, I, p. 319. Chem. Abs., vol. 35, 1941, p. 6424.

Steam is passed through a column of incandescent C to form water gas, and more steam is introduced to react with part of the CO of the water gas to form CO_2 and H_2. The additional steam is regulated in such a manner that in the product there are 2 parts H_2 to 1 part CO. Describes apparatus.

567. ———. Production of Water Gas. British Patent 570,007, June 19, 1945; appl. filed Sept. 20, 1943. British Chem. Abs., 1945, B, I, p. 354; Chem. Abs., vol. 40, 1946, p. 4498.

In the production of water gas low in CO and of necessity high in CO_2 (eliminated later by scrubbing), the reaction of $C+H_2O=CO+H_2-28{,}900$ gm. cal. takes place at above 1,000°, with 99% decomposition of the H_2O, whereas $C+2\ H_2O=CO_2+2\ H_2-18{,}900$ gm. cal. occurs at about 600°, and only 5% of the H_2O is decomposed. The % decomposition of H_2O is increased (in the latter reaction) by raising the pressure of operation and superheating the steam so that it supplies nearly all the endothermic heat, and the steam flow can continue for a long period. An example of running conditions is: 4 units of steam at 20 atm. and 1,160° provide enough heat to decompose 1 unit of steam at the coke-bed temperature of 760°; the resulting gas comprises H_2, 65%, CO, 8%, and CO_2, 27% and is already at a pressure at which elimination of CO_2 is simple. The coke is raised to the necessary temperature by a producer gas run, and that gas is burned in regenerators, which superheat the steam. The excessive superheat at the beginning of a steam flow is reduced by admixture of saturated steam in reduced proportion as the flow proceeds.

568. DUFTSCHMID, F. (I. G. Farbenindustrie A. G.). [Iron Catalysts for the Conversion of Carbon Monoxide With Hydrogen.] German Patent Appl. I 74,468, OZ 14,034, filed Mar. 2, 1943 (*Cl. IV d–12 o*). FIAT Reel 170, frames 9,195–9,199; PB 64,183; FIAT Reel 172, frames 365–366; PB 25,616.

Fe catalysts are made from natural Fe ore of predominantly oxide character or from Fe ore that, by roasting or heating with reducing gases at >300°–350°, is converted into the oxide. Example: A magnetic Fe ore is treated with H_2 (0.2 *N* m.^{3} per kg. of ore). Through the catalyst thus formed is passed a synthesis gas ($CO:H_2=55:45$) together with recycled products of a previous operation in the liquid phase at 260°–280° and about 25 atm. About 50% of the synthesis gas is converted, with a yield of 120 gm. of multibranched hydrocarbons per *N* m.^{3} of converted synthesis gas, of which about 60% is in the boiling range of gasoline and 30–35% of hydrocarbons with 3 and 4 C atoms.

569. DUFTSCHMID, F., LINCKH, E., AND WINKLER, F. (I. G. Farbenindustrie A. G.). Catalytic Hydrogenation of Carbon Monoxide to Form Hydrocarbons. United States Patent 2,207,581, July 9, 1940; appl. filed Nov. 4, 1937, Serial No. 172,738, in Germany Nov. 4, 1936; 4 claims (*Cl. 260–449*). Chem. Abs., vol. 34, 1940, p. 8225.

Hydrocarbons containing more than 2 C atoms in the molecule are produced from a mixture of H_2 with a greater volume of CO by use of an Fe catalyst at 200°–420° in a liquid medium consisting of hydrocarbon oils produced in a preceding operation of the same type.

570. ——— (I. G. Farbenindustrie A. G.). Catalytic Production of Hydrocarbons and Oxygen Derivatives From Carbon Monoxide and Hydrogen. United States Patent 2,159,077, May 23, 1939; appl. filed Nov. 17, 1936. Chem. Abs., vol. 33, 1939, p. 6872.

Process for the catalytic conversion of mixtures comprising 1–8 parts of CO and 9–2 parts of H_2 in each 10 parts of the sum of these gases at an elevated temperature 200°–420° into substances selected from the group consisting of hydrocarbons and their O derivatives in the presence of a catalyst promoting this conversion comprises carrying out this conversion in a liquid medium consisting of the oils obtained by a previous conversion of an amount of the same kind of initial materials under the same or similar conditions and which contains substantial amounts of constituents, the boiling point of which is within the boiling range of benzines, and applying a pressure under which the said liquid medium is established. An Fe-containing material may be used as the catalyst.

See also abs. **1285.**

571. ——— (I. G. Farbenindustrie A. G.). [Conversion of Carbon Monoxide With Hydrogen.] German Patent Appl. I 64,241, OZ 11,661, filed Mar. 31, 1939 (*Cl. IV d–12 o*); APC TC 1,225. TOM Reel 134, frames 495–497; Bureau of Mines Transl. T–433, January 1948.

In the hydrogenation of CO to hydrocarbons with recycling of liquid hydrocarbons through the catalyst bed, the relatively high boiling hydrocarbon products are withdrawn from the system instead of being recycled, preferably by separation from the hot gases directly at the outlet of the reaction zone.

572. ——— (Standard Catalytic Co.). Hydrocarbon Synthesis From Hydrogen and Carbon Monoxide. United States Patent 2,287,092, June 23, 1942; appl. filed May 20, 1939, Serial No. 274,736, in Germany May 27, 1938; 4 claims (*Cl. 260–449*). Chem. Abs., vol. 37, 1943, p. 250.

Process is employed for the catalytic conversion of CO and H_2 into hydrocarbons containing more than 1

C atom in the molecule while contained in a hydrocarbon oil, which involves passing the oil along the catalyst chamber in indirect heat-exchange relation with the reaction participants introduced into and passing through the catalyst chamber, and thereupon passing the oil through the catalyst chamber in the same direction as the reaction participants.

573. ——— (I. G. Farbenindustrie A. G.). [Liquid-Phase Process.] German Patent Appl. I 56,290, OZ 9,635, filed Nov. 3, 1936 (*Cl. IV d–12 o*). TOM Reel 134, frames 495–497; Auszüge deut. Patent-Anmeldungen, vol. 6, p. 93.

Use of a mixture of CO and H_2 containing over 50% and preferably 55–70% by volume of CO. Appears to correspond to United States Patent 2,207,581 (abs. **569**). Addition to German Patent Appl. I 53,688 (abs. **574**).

574. ——— (I. G. Farbenindustrie A. G.). [Synthesis in the Liquid Phase.] German Patent Appl. I 53,688, OZ 9,104, filed Nov. 18, 1935. TOM Reel 134, frames 495–497.

Process for synthesis in the liquid phase with the products of the synthesis used as the liquid medium, appreciable amounts of which evaporate under the conditions of the synthesis, and the products of the synthesis recovered by condensation of the gases and vapors are given. Appears to correspond to United States Patent 2,159,077 (abs. **570**).

575. ——— (Standard Catalytic Co.). Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,318,602, May 11, 1943; appl. filed June 1, 1939, Serial No. 276,856, in Germany June 2, 1938; 1 claim (*Cl. 260–449*). Chem. Abs., vol. 37, 1943, p. 6111.

Describes arrangement of apparatus, and a process is employed for the catalytic conversion of CO and H_2 into hydrocarbons with more than 1 C atom in the molecule, which involves continuously circulating through the reaction space, concurrently with the reaction gas, a liquid medium, such as a "proper oil," preheated to about the desired reaction temperature, injecting into the reaction zone at spaced points along the passage of the gases additional regulated amounts of the same liquid medium at temperatures substantially below the reaction temperature so as to maintain the temperature throughout the reaction space within the desired limits, and employing as the liquid medium mentioned an oil obtained by a previous conversion and containing a considerable amount of constituents, which are gaseous or vaporous under the reaction conditions.

DU PONT AMMONIA CORP. *See* abs. **19, 2600, 3941, 3942, 3943.**

576. DU PONT DE NEMOURS, E. I., & Co. Alcohol Synthesis. British Patent 323,240, June 22, 1928. Chem. Abs., vol. 24, 1930, p. 3022.

Alcohols, other than MeOH, are synthesized from CO and H_2 in the presence of a MeOH catalyst to which an alkali metal has been added, with a space velocity of the reacting gases that is more than 5 times the space velocity at which a MeOH synthesis employing only the MeOH catalyst would reach equilibrium under the same temperature and pressure conditions. Describes various details and examples.

577. ———. Aldehydes and Other Organic Oxygen-Containing Compounds. British Patent 631,316, Nov. 1, 1949. Chem. Abs., vol. 44, 1950, p. 4023.

Saturated aldehydes and ketones are prepared from olefins, CO, and H_2 in presence of a hydrogenation catalyst at 125°–350° and pressures > 300 atm. The catalyst, a soluble salt of Co or Cu ($CoCl_2.6\ H_2O$, Co(OAc).4 H_2O, Co naphtherate, etc.) used in amounts of 0.1–3% of the total reaction mixture, is recycled as a distillation residue from the distillation of the reaction product.

See also United States Patent 2,437,600 (abs. **877**), and British Patent 614,010 (abs. **585**).

578. ———. [Aliphatic Alcohol.] French Patent 657,124, July 6, 1928. Chem. Abs., vol. 23, 1929, p. 4229.

In the catalytic production of alcohols from CO and H_2 the yield of higher alcohols per unit of volume and time is increased by increasing the flow of gases to more than 5 times the flow used for the production of MeOH and by using catalysts favoring the formation of higher alcohols, such as basic Zn-NH chromate containing 15% K_2CrO_4 or Zn chromite or ZnO containing K_2SO_4.

579. ———. Catalyst for Methanol Synthesis. British Patent 301,109, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 205.

Double chromate of NH_4 with Zn (Cd, Cu, Mg, Mn, Ag, Fe) after decomposition by heating and pretreating by washing with 10% acetic acid.

580. ———. [Catalysts for Organic Synthesis.] French Patent 635,777, June 10, 1927. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 205; Chem. Abs., vol. 22, 1928, p. 4535.

Catalysts for the synthesis of organic compounds are made by heating to redness mixtures or compounds containing sexivalent Cr and 1 or more of the metals, Zn, Cu, Cd, Mg, Mn, Ag, and Fe to form Cr salts containing tervalent Cr. *See also* British Patent 301,806 (abs. **2029**) and United States Patent 1,746,783 (abs. **2025**).

581. ———. Catalytic Production of Formic Acid. British Patent 406,344, Feb. 26, 1934. Chem. Abs., vol. 28, 1934, p. 4746.

Catalysts for the production of HCOOH from CO and steam comprise the halides (preferably iodides) of a large number of metals. The halides may be made by adding a hydrohalogen acid to the gases and using an oxide, hydroxide, carbonate, or acetate. Carriers may be used. Gives examples.

582. ———. Catalytic Production of Formic Acid. British Patent 406,345, Feb. 26, 1934. Chem. Abs., vol. 28, 1934, p. 4747.

The catalysts comprise a nonvolatile acidic oxide not combined with a base or an acid salt derived from an acidic oxide. The oxide may be one of P, As, W, Mo, U, Cr, V, Ti, B, Si, or Zr, and the salts may be primary or secondary phosphates, tungstates, or molybdates of Zn, Ca, Mg, Na, K, Cu, Ce, or Th. Mutually combined acid oxides may be used, for example, phosphotungstic, phosphosilicic, silicotungstic, or silcomolybdic acid or Cr or V molybdate. *See also* United States Patent 1,949,825 (abs. **326**). Apparatus similar to that of British Patent 406,344 (abs. **581**), may be used.

583. ———. One-Step Nonyl Alcohol Process. British Patent 662,706, July 6, 1949; British Abs., 1952, B, II, p. 219.

3 : 5 : 5–trimethylhexan–1–ol is made by passing a mixture of diisobutene, CO, and H_2 in presence of >0.25 mol. H_2O (per mol. of diisobutene) and of a Co salt (acetate or naphthenate; 0.001–5 wt. % of diisobutene) dissolved in 1 ingredient through a 1st reaction zone at 175°–225° and 350–2,000 atm. and a 2d zone at 240°–300° and 350–2,000 atm. The 2-phase product is continuously removed, the aqueous phase separated, and the product distilled.

584. ———. Preparation of Organic Oxygen-Containing Compounds, Including Glycol Ethers and Alcohols. British Patent 665,698, June 7, 1949. British Abs., 1952, B, II, p. 447.

Glycol ethers and alcohols are synthesized by interaction in a pressure-resistant vessel of a OH-compound (preferably a C_{1-9} saturated aliphatic alcohol) with CO and H_2 ($CO:H_2$ is preferably 3:1–1:3) at 1,000–5,000 atm. in presence of a Co-containing catalyst at 100°–350°. Solid or dissolved catalysts may be used, those particularly effective being the acetate, stearate, naphthenate, and isobutyrate of Co employed in amounts of not less than 0.001% based on the weight of alcohol. Reaction times are 5–15 min., and products are separated by known means.

585. ———. Synthesis of Organic Oxygen-Containing Compounds. British Patent 614,010, Dec. 8, 1948; appl. filed June 5, 1946. British Abs., 1949, B, II, p. 711; Chem. Zentralb., 1950, I, p. 228; Chem. Abs., vol. 43, 1949, p. 4685.

Olefinic compound is treated with CO and H_2 (1:2–4) at 75°–250° and >300 atm. in presence of a reducing catalyst (0.1–10% by weight of the reaction mixture), for example, Ni, Co, Fe, Cu, Ru, promoted with ThO_2 or Mn, in an inert solvent, such as cyclohexane, xylene, HCO_2Me, Et_2O, or an inert gas, or with an excess of 1 reactant as diluent, to give O-containing compounds with a preponderance of aldehydes. Ketone formation is virtually completely avoided above 300 atm. In presence of H_2O unsaturated aldehydes are formed. The products may be treated further in situ to give cyclic trimers or hydrogenated further to give alcohols. Above 180° interaction between alcohol and aldehyde may give acetals. Example: A mixture of C_2H_4, CO, and H_2 (1:1:4) is passed at 140°–150° at 500 atm. over reduced fused Co, and the liquid product is fractionated to give EtCHO (95.5%). Various olefins may be used for the reaction.

586. ———. Synthesis of Primary Alcohols. British Patent 665,705, July 7, 1949. Ind. Chemist, vol. 28, 1952, pp. 132–133; Chem. Abs., vol. 46, 1952, p. 10,190.

Primary alcohols are prepared by reacting an olefinic hydrocarbon (propylene, butenes, butadiene, vinyl acetylene, cyclohexene, and hexenes) having 2–30 C atoms per molecule with CO and H_2 at 250°–400° and 325–1,500 atm. The initial mol ratio of $CO:H_2$ should lie 2:1–1:2. For maximum production of alcohol and efficient absorption of exothermic heat, the amount of H_2O present should be controlled 0.1–1.5 parts, by weight, per part of olefin. A Co salt (chloride, sulfate, nitrate, acetate, propionate, and naphthenate) preferentially soluble in the olefinic reactant is present as the catalyst. The amount of catalyst per unit weight of olefin should be as low as 0.005–2.0%. Use of the catalyst in solution suppresses the hydrogenation of olefin hydrocarbons to alkanes and the formation of other byproducts.

———. *See* abs. **18, 148, 149, 150, 179, 251, 252, 253, 254, 255, 256, 260, 318, 319, 320, 321, 322, 326, 327, 328, 565, 627, 641, 723, 847, 848, 849, 850, 851, 852, 853, 854, 855, 856, 857, 858, 859, 860, 861, 862, 863, 864, 865, 866, 867, 868, 869, 870, 871, 872, 873, 874, 875, 876, 877, 878, 879, 1102, 1103, 1740, 1741, 1885, 1997, 1998, 2001, 2002, 2003, 2004, 2006, 2007, 2008, 2009, 2010, 2023, 2024, 2025, 2028, 2030, 2031, 2032, 2033, 2063, 2066, 2067, 2068, 2069, 2070, 2411, 3304, 3310, 3312, 3647, 3788, 3789, 3790, 3791, 3913, 3961, 3962, 3963, 3964, 3965, 3966, 3967, 3968, 3991.**

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587. EASLEY, J. C., AND KELLNER, H. L. (Gulf Research & Development Co.). Regeneration of a Fixed-Bed Fischer-Tropsch Catalyst. United States Patent 2,609,345, Sept. 2, 1952. Chem. Abs., vol. 47, 1953, p. 8995.

An Fe synthesis catalyst is regenerated with a mixture of air and an inert gas, whereby the maximum temperature difference in the catalyst bed is <300° F., with little increase in pressure drop across the bed. The regeneration gas mixture is preheated to 700°–800° F., and the component and rate of flow of gas are regulated so that the maximum temperature at any point in the catalyst bed does not exceed 1,000° F. In practice the regeneration is begun by flowing over the catalyst 100% inert gas preheated to 700°–800° F., to which air is then added. After 25 hr. the coke is burnt off, and the catalyst is ready for partial reduction. The total on-stream time for a catalyst treated in this manner was increased from 765 hr. to approximately 1,300 hr.

588. EASTMAN, D. (The Texas Co.). Catalytic Synthesis of Hydrocarbons With Controlled Recycle of Carbon Dioxide. United States Patent 2,436,957, Mar. 2, 1948; appl. filed Dec. 20, 1945, Serial No. 636,226; 8 claims (*Cl. 260–449.6*). Chem. Abs., vol. 42, 1948, p. 3932.

Effluent from the catalytic conversion of CO and H_2 into hydrocarbons consisting of normally gaseous and liquid constituents is separated into a liquid and a gaseous portion. The gases themselves are next divided into a major and a minor stream, the former consisting essentially of gaseous paraffinic and olefinic hydrocarbons, N_2 and CO_2 and unreacted CO and H_2, and the latter of almost pure CO_2. The former is entirely recycled to the process together with enough CO_2 from the latter to maintain the CO_2 in the reactor feed within the limits of about 15–30%. There should be 1–4 vol. of recycled material comprising both the major gaseous stream and the CO_2 from the minor stream per vol. fresh feed.

589. ——— (The Texas Co.). Method of Manufacturing Hydrogen and Carbon Monoxide. United States Patent 2,523,284, Sept. 26, 1950; appl. filed Aug. 17, 1945, Serial No. 611,173; 8 claims (*Cl. 23–212*).

Two separate reaction zones, 1 exothermic and the other endothermic, are used. The exothermic oxidation of gaseous hydrocarbons takes place in the presence of a solid heat carrier, which contains a catalyst for the endothermic conversion of hydrocarbon gas, CO_2 and steam into synthesis gas. The catalyst bearing carrier acquires its heat in the oxidation zone, 2,000°–2,500° F., and gives it up in the production of synthesis gas, 1,500°–2,000° F., then is returned to the exothermic zone. 8 United States patents cited.

590. ——— (The Texas Co.). Treatment of Naphtha Containing Oxygenated Compounds. United States Patent 2,569,463, Oct. 2, 1951; appl. filed Nov. 26, 1947, Serial No. 788,329; 3 claims (*Cl. 260–450*).

Process for the synthesis of motor fuel hydrocarbons by the interaction of CO and H_2 in presence of an Fe group catalyst may be improved by separating from the synthesis products a hydrocarbon fraction b. 100°–400° F. containing oxygenated compounds produced by the reaction and passing it in the vapor phase in admixture with 5–50 wt. % of stream into contact with fuller's earth or the like at 700°–900° F. and 15–25 p. s. i. g. for a sufficient time to substantially improve the octane value, usually to about 12 octane numbers.

591. EASTMAN, D., AND GAUCHER, L. P. (The Texas Co.). Catalytic Reduction of Carbon Monoxide With Hydrogen. United States Patent 2,594,301, Apr. 29, 1952; appl. filed June 17, 1947, Serial No. 755,234; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 46, 1952, p. 6811.

In the catalytic synthesis of hydrocarbons, H_2 and CO together with enough H_2O vapor to suppress the formation of light paraffinic hydrocarbons are continuously passed through a reaction zone in contact with the catalyst. After an appropriate contact time gaseous reaction products are withdrawn, the liquid products condensed and separated, and the normally gaseous residue recycled in admixture with the fresh feed gas. The recycle ratio is maintained within such a calculated range that the inclusion of H_2O vapor suppresses net formation of paraffin gases with an increased yield of liquid product. Example: Synthesis gas (64 vol. % H_2, 32 CO, 1.5 CH_4, 1 CO_2) is passed upward at space velocity 1,000 vol. per vol. per hr. through a fluidized Fe catalyst finer than 200-mesh promoted by 1% Al_2O_3 and 0.5% Na_2O. Temperature is maintained at about 625° and pressure 200 p. s. i. g. The effluent products are withdrawn, condensed, and separated at about 70° F. and the liquid normally gaseous products recycled to the fresh feed at the rate of about 1.5 : 1. Simultaneously, dry steam is mixed with the recycle stream at a pressure of about 200 p. s. i. g. at a rate equal to about 0.5 mol. H_2O per mol. CO in the fresh feed. After 48 hr. operation, products withdrawn show a 99.4% conversion of the CO, about 80% of the products being normally liquid hydrocarbons in the gasoline boiling range and about 8% oxygenated hydrocarbons. The net formation of gaseous paraffins, mainly CH_4, is about 1% based on the CO converted, and that of CO_2 9%.

592. ——— (The Texas Co.). Catalytic Synthesis of Hydrocarbons. United States Patent 2,632,017, Mar. 17, 1953; appl. filed June 17, 1947, Serial No. 755,236; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 47, 1953, p. 5666.

In catalytic synthesis of hydrocarbons and oxygenated compounds from CO and H_2, low net CH_4 and CO_2 formation is obtained by operating at a recycle rate particularly favorable to minimum net CH_4 formation while carrying the degree of conversion, and accordingly CO_2 suppression, materially beyond that which would be characteristic of such recycle by fortifying the fresh feed with CH_4 or other light saturated hydrocarbon gas. In addition, the added CH_4 by itself appears to suppress net CH_4 formation. The CH_4 added to the feed passes through the reactor essentially unchanged and, after separation of the desired reaction products, can be conveyed directly to the power plant for recovery of the required thermal energy. 1 literature ref. and 10 United States patents cited.

593. ——— (The Texas Co.). Manufacture of Synthesis Gas. United States Patent 2,582,938, Jan. 15, 1952; appl. filed Oct. 21, 1950, Serial No. 191,446; 11 claims (*Cl. 48–196*). Chem. Abs., vol. 46, 1952, p. 3244.

Synthesis gas consisting essentially of CO and H_2 and substantially free from solid C is produced by reacting a hydrocarbon (natural or coke oven gas, liquid hydrocarbon) with a gas containing at least 40 vol. % O_2. The reactants are continuously passed into a closed reaction zone free from packing and catalyst and having an internal surface area no >about 1.5 times the area of a sphere of equal volume. The ratio of total O_2 : C in the feed gas is about 1.0–1.5. The hydrocarbon gas is charged at a rate of about 1,000–3,000 cu. ft. per hr. per cu. ft. of reaction space, the temperature in the reaction zone being maintained at about 2,300°–3,000° F. and the pressure, 200–500 p. s. i. g. It is desirable to reduce the temperature of the effluent stream of gas from the reaction zone from about 2,600° F. to 1,000°–1,500° F. in not >1 sec. so as to avoid undesired side reactions. The effluent gas consists essentially of CO and H_2 substantially free from uncombined O_2 and C and with a CH_4 content of 0.0–0.5 mol. %.

594. EASTMAN, D., BARBER, E. M., AND REYNOLDS, B. (The Texas Co.). Process for the Manufacture of Synthesis Gas. United States Patent 2,591,687, Apr. 8, 1952; appl. filed Jan. 17, 1947, Serial No. 722,742; 5 claims (*Cl. 48–196*).

Mixture of CO and H_2 is produced by partial combustion of a hydrocarbon fuel, such as CH_4, with substantially pure O_2 in a cylinder of an internal combustion engine. The fuel and the O_2 are charged at a pressure of 50–100 p. s. i. g. in sufficient amount to fill the cylinder, the ratio of O_2 : C being within the range 1.0 : 1.4. The charge is then compressed to $\frac{1}{3}$–$\frac{1}{5}$ the volume of the cylinder and ignited, the products of the partial combustion being withdrawn at a pressure of at least 50 p. s. i. g. The gaseous hydrocarbon fuel may be preheated before being introduced into the cylinder to above 1,000° F., the fuel and the O_2 then being separately charged into the combustion zone.

EASTMAN KODAK CO. *See* abs. **919, 920, 921, 955.**

595. ECKELL, J., AND RITTER, G. Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,159,140, May 23, 1939; appl. filed Mar. 5, 1936. Chem. Abs., vol. 33, 1939, p. 6872.

Process for the production of normally solid hydrocarbons of the paraffin series by thermal conversion of CO and H_2 in the gaseous phase in the presence of a solid catalyst and under a pressure ranging from atmospheric pressure to 50 atm. involves continuously passing the catalyst through the reaction space, then freeing it at least partly from solid paraffin hydrocarbons deposited on it, and then supplying it again to the reaction space.

596. EDMONDS, W. J. (Commercial Solvents Corp.). Catalytic Apparatus. Canadian Patent 300,962, June 10, 1930. Chem. Abs., vol. 24, 1930, p. 3678.

Apparatus for carrying out the catalytic synthesis of materials through high pressure catalytic reaction is disclosed, particularly the manufacture of MeOH from CO and H_2 or the production of synthetic NH_3.

See also Canadian Patent 300,963 (abs. **597**).

597. ——— (Commercial Solvents Corp.). Catalytic Apparatus. Canadian Patent 300,963, June 10, 1930. Chem. Abs., vol. 24, 1930, p. 3403.

Apparatus for carrying out chemical reactions, particularly the production of MeOH by the high-pressure catalytic reactions of H_2 and C oxides, is disclosed.

598. ——— (Commercial Solvents Corp.). Catalytic Apparatus for Exothermic Reactions Such as Methanol Synthesis. United States Patent 1,980,718, Nov. 13, 1934. Chem. Abs., vol. 29, 1935, p. 383.

Describes various details of a heat-interchange system.

599. ——— (Commercial Solvents Corp.). Catalytic Apparatus Suitable for Effecting Reactions Under Pressure Such as Methanol Synthesis. United States Patent 1,848,466, Mar. 8, 1932. Chem. Abs., vol. 26, 1932, p. 2752.

Describes various structural details.

600. ——— (Commercial Solvents Corp.). Methanol Synthesis. United States Patent 1,875,714, Sept. 6, 1932; appl. filed Dec. 13, 1926. Chem. Abs., vol. 27, 1933, p. 103.

Gas containing CO_2, 1–5%, and H_2, 99–95% is passed over any suitable catalyst to produce MeOH, and H_2 and CO_2 are added to the circulating gas to replenish that consumed (the CO_2 being maintained at 5% or less).

601. ——— (Commercial Solvents Corp.). Synthesis of Methanol. Canadian Patent 286,289, Jan. 8, 1929. Chem. Abs., vol. 23, 1929, p. 1420.

In the manufacture of MeOH by the interaction of H_2 and CO_2 in the presence of a catalyst and under elevated pressure and temperature, the concentration of CO_2 in the gas in contact with the catalyst is maintained $< 11\%$.

602. EDMONDS, W. J., AND STENGEL, L. A. (Commercial Solvents Corp.). Methanol Synthesis. United States Patent 1,797,569, Mar. 24, 1931; appl. filed Dec. 13, 1926. Chem. Abs., vol. 25, 1931, p. 2739.

In effecting catalytic reaction of H_2 with C oxides, substantially pure H_2 is first circulated over a catalyst such as oxides of Zn and Cr. Then a mixture of H_2 and C oxides is added to the circulating gas in proportions required to produce MeOH and effect continuance of the reaction under suitable pressure.

603. ——— (Commercial Solvents Corp.). Synthesis of Methanol. Canadian Patent 286,290, Jan. 8, 1929. Chem. Abs., vol. 23, 1929, p. 1420.

MeOH is made by circulating gas containing a ratio of $H_2 : CO_2$ far greater than the theoretical proportions required for the reaction, whereas the reaction pressure is maintained by adding a gas containing C oxides and H_2 in substantially theoretical proportions.

604. EGUCHI, T., AND KANEDA, S. (Nippon Synthetic Petroleum Co.). [Lubricating Oil From Polymerization and condensation of Olefin Hydrocarbons.] Japanese Patent 175,929, Mar. 29, 1948. Chem. Abs., vol. 44, 1950, p. 8634.

Synthetic petroleum from CO and H_2 or cracked kerosine containing less olefins is used as a raw material for preliminary polymerization with catalyst. Low-boiling fractions are removed, and the residue is used for regular polymerization.

EICKMEYER, A. G. *See* abs. **3860.**

EILBRACHT, H. *See* abs. **271, 3307.**

605. EISENHUT, A., AND AUERHAHN, A. (I. G. Farbenindustrie A. G.). Catalytic Hydrogenation of Carbon Oxides. United States Patent 1,704,732, Mar. 12, 1929; appl. filed Sept. 30, 1924. Chem. Abs., vol. 23, 1929, p. 2000.

Oily liquid obtained by the catalytic hydrogenation of C oxides under pressure and containing oxygenated organic compounds of a higher order than MeOH is separated into fractions, and the fractions are treated with condensing agents to obtain motor fuels, solvents for cellulose esters or for natural or artificial resins, and detergents. The residue from the fractionation may be purified and used as a resin for lacquers and varnishes.

EISENHUT, O. *See* abs. **3920.**

EISENSTECKEN, F. *See* abs. **3305.**

EKHOLM, E. L. *See* abs. **3272.**

606. ELIAN, J. (Syndicat d'étude et d'exploitation des carburants de synthèse). [Synthesis of Hydrocarbons From Water Gas.] French Patent 879,959, Mar. 10, 1943; appl. filed Mar. 4, 1942. Chem. Zentralb., 1943, II, p. 1167.

See United States Patent 2,369,548 (abs. **609**).

607. ———. [Synthesis of Hydrocarbons, Particularly Those Corresponding to Gasoline.] Belgian Patent 440,751, Apr. 30, 1941. Chem. Abs., vol. 36, 1942, p. 5979.

Catalyst used consists of higher carbides of Fe, Ni, or Co.

See United States Patent 2,369,548 (abs. **609**).

608. ———. [Synthetic Process for Preparing Hydrocarbons, Particularly Gasoline.] Italian Patent 392,-831. Chem. Zentralb., 1943, II, p. 1167.

See United States Patent 2,369,548 (abs. **609**).

609. ———. Synthetic Process for Preparing Hydrocarbons, Particularly Gasoline. United States Patent 2,369,548, Feb. 13, 1945; appl. filed Feb. 25, 1942, in Belgium Mar. 4, 1941 (*Cl. 260–449.6*). Chem. Abs., vol. 39, 1945, p. 3147.

Preparation of an Fe, Co, or Ni carbide catalyst promoted by Cu oxide for the Fischer-Tropsch synthesis. The pure metal in a finely divided state is introduced in a tube made of steel, ceramic, or quartz and heated in an electric oven to 250°–450° C. while passing a gas, CO, CH_4, etc., capable of giving up its C or using C itself in a sealed tube and constantly rotating the tube. Then the carbide is cooled, using an inert gas, N_2, He, very rapidly to a very low temperature, preferably lower than —190° C., and then crushed and a suitable amount of powdered Cu or alkali metal oxide is added and the carbide is agglomerated under pressure while heating moderately. Using Fe carbide prepared in this manner, 155 gm. of hydrocarbons for each $m.^3$ of water gas used are obtained.

610. ELIOT, T. Q., GODDIN, C. S., AND WEAVER, J. C. (Stanolind Oil & Gas Co.). Extractive Distillation of Oxygenated Organic Compounds. United States Patent 2,607,719, Aug. 19, 1952; appl. filed Apr. 15, 1949, Serial No. 87,698; 7 claims (*Cl. 202–39.5*). Chem. Abs., vol. 47, 1953, p. 5422.

Crude and complex organic mixtures obtained by the hydrocarbon synthesis process, involving the reduction of CO with H_2 in the presence of a fluidized Fe catalyst, can be separated and recovered in substantially pure form by being subjected to a series of extractive distillations with H_2O. The method relates particularly to the separation of ethanol, isopropanol, methyl-ethyl ketone, methyl-propyl ketone, butyraldehyde, and ethyl acetate. The concentration of H_2O in the column ranges 90–99 mol. %. The heat requirequirements are 80–120 B. t. u. per lb. of bottoms to give a bottom tower temperature of 82°–94° and an overhead temperature of 68°–77°. By using only H_2O as an extractive distillation agent, sharp separations can be made between the several constituents, which not only boil very close together but form numerous azeotropes.

611. ELLIOTT, M. A., CLARK, E. L., AND STORCH, H. H. Production of Hydrocarbon Synthesis Gas From Coal. United States Patent 2,634,286, Apr. 7, 1953; appl. filed Nov. 7, 1949, Serial No. 126,002; 2 claims (*Cl. 260–449.6*).

Low-S-content synthesis gas suitable for Fischer-Tropsch process is produced from the low-S-content residue char obtained by the direct hydrogenation of coal in the dry fluidized state. The residue char is passed directly from the hydrogenation zone to the gasification zone, thus reducing handling costs and avoiding losses in energy, which would normally attend discharge of the char from the hydrogenation zone to atmospheric temperature and pressure. 1 literature ref., 2 foreign patents, and 4 United States patents cited.

612. ELOUARD, L. [Synthesis of Hydrocarbons.] French Patent 908,013, Mar. 28, 1946; appl. filed May 31, 1944. Chem. Zentralb., 1949, III, p. E–236.

An aqueous solution of NH_4HCO_3 is decomposed at 1,500°–1,600° over alumina to CO and H_2 and the gas mixture converted over Co or Ni catalysts into hydrocarbons. The residual CO is converted to CO_2 and then with aqueous NH_3 to NH_4HCO_3. The alumina mass is made of alumina, C, and binder and then converted by the decomposition of NH_4HCO_3 into AlN. This is converted with aqueous NaOH to gaseous NH_3 and water vapor as well as to $NaAlO_2$ liquor, which is split by CO_2. The Al_2O_3 H_2O formed thereby is dehydrated and agglomerated. The soda solution is causticized with $Ca(OH)_2$ and the CO_2 evolved changed with gaseous NH_3 to NH_4HCO_3. The NaOH is returned to the AlN decomposition.

ELVINS, O. C. *See* abs. **2501.**

ELWORTHY, E. G. *See* abs. **1987, 1988.**

613. ELWORTHY, H. S. Gas for Illuminating, Heating or Power Purposes. United States Patent 943,627, Dec. 14, 1909; appl. filed May 15, 1905.

Gas rich in CH_4 is made by destructively distilling carbonaceous material, separating therefrom the hydrocarbons other than CH_4, mixing water gas therewith, and afterwards passing the gas over metallic Ni at a suitable temperature for producing CH_4 and H_2O.

614. ———. [Methane Production.] German Patent 191,026, Aug. 1, 1905. Chem. Abs., vol. 2, 1908, p. 1633.

Process of producing a gas, composed principally of CH_4, by leading a mixture of the oxides of C and H_2 in the heat over catalytic metals (Ni or the like), wherein the C oxides and H_2 required in the process are obtained in the known manner by heating a mixture of water gas and steam with a reduction of H_2O to H_2 and oxidation of CO to CO_2 and the separation of the latter.

615. ———. Process of Producing a Gas Composed Principally of Methane. United States Patent 191,026, Aug. 1, 1905. Chem. Abs., vol. 2, 1908, p. 1633.

A mixture of the oxides of C and H_2 are passed over catalytic metals such as Ni. The C oxides and H_2 are obtained by heating a mixture of water gas and steam with a reduction of H_2O to H_2 and oxidation of CO to CO_2.

616. ELWORTHY, H. S., AND WILLIAMSON, E. H. [Gas Production.] German Patent 190,201, May 14, 1905. Chem. Abs., vol. 2, 1908, p. 1211.

Process of producing a gas rich in CH_4 by leading a mixture of H_2 and CO or CO_2, or both, over metallic Ni, $CO+3H_2=CH_4+H_2O$; $CO_2+4H_2=CH_4+2H_2O$. The CO and CO_2 in various commercial gases may be so treated.

617. ———. [Increasing Methane Content and Gas Mixtures.] German Patent 183,412, May 14, 1905. Chem. Abs., vol. 2, 1908, p. 345.

Process of giving or increasing the CH_4 content in such gas mixtures as contain, in addition to H_2, CO or CO_2, or both, by leading the gases over metallic Ni, characterized in that H_2 is added in excess, whereby the CH_4 content is materially increased. A part of such H_2 may be substituted by CH_4.

618. ———. Increasing Methane in Gas Mixtures. British Patent 183,412, May 14, 1905. Chem. Abs., vol. 2, 1908, p. 345.

CH_4 content in gas mixtures containing H_2 and CO or CO_2 is increased by passing the gas mixture over metallic Ni. H_2 is added in excess.

619. ———. Manufacture of Gas Consisting Chiefly of Methane or Marsh Gas for Illuminating, Heating, and Power Purposes. British Patent 12,461, May 31, 1902. Jour. Soc. Chem. Ind., vol. 22, 1903, p. 900.

Water gas obtained by any of the usual methods is mixed with H_2 in sufficient quantity to convert the C present as CO and CO_2 into CH_4 and to convert the O_2 into H_2O, and the gaseous mixture is passed over metallic Ni at a suitable temperature, whereupon the following reactions occur: (1) $CO+3H_2\rightarrow CH_4+H_2O$. (2) $CO_2+4H_2\rightarrow CH_4+2H_2O$. The Ni acts as a catalytic agent. The reactions may be effected in 2 stages, a temperature of 250° C. being suitable for attacking the CO and 350° C. for the dioxide. The 26 claims relate to modifications in the process, to production of the H_2 required from metallic iron and steam, to production of metallic Ni in suitable form, and various forms and combinations of plant.

620. ———. Manufacture of Gas for Illuminating, Heating, and Power Purposes. British Patent 14,333, June 25, 1904. Jour. Soc. Chem. Ind., vol. 24, 1905, p. 1006.

Coal gas is purified in the usual way, and hydrocarbons other than CH_4 are removed by scrubbing with paraffin oil. The gas is passed over metallic Ni at a temperature of 250° C. The CO and H_2 are converted into CH_4 and H_2O according to the equation of $CO+3H_2\rightarrow CH_4+H_2O$. If necessary H_2 may be added to the gas before treatment. If CO_2 is present as well as CO the gas is treated 1st at 250° C. as above, and then at 350° C. to convert the CO_2 also into CH_4 according to the equation $CO_2+4H_2\rightarrow CH_4+2H_2O$. After treatment, the hydrocarbons that were removed by scrubbing may be restored to the gas. Instead of coal gas alone, a mixture of coal gas with water gas, Dowson gas, or the like, with or without the addition of H_2, may be used. Such a mixture may be prepared by passing water gas through a superheater and then through a column of fresh coal. The hot gas effects the destructive distillation of the coal, and the coke may be used for the production of the water gas.

621. ———. Process of Producing Gas Rich in Methane. British Patent 190,201, May 14, 1905. Chem. Abs., vol. 2, 1908, p. 1211.

Gas rich in CH_4 is produced by leading a mixture of H_2 and CO or CO_2, or both, over metallic Ni—$CO+3H_2=CH_4+H_2O$; $CO_2+4H_2=CH_4+2H_2O$. The CO and CO_2 in various commercial gases may be so treated.

622. EMERSON, W. S., AND LONGLEY, R. I., Jr. (Monsanto Chemical Co.). Oxo Aldehydes. United States Patent 2,624,764, Jan. 6, 1953. Chem. Abs., vol. 47, 1953, p. 11,234.

Hydrolysis of alkoxydihydropyrans (I) prepared by condensing acroleins or vinyl ketones and vinyl ethers) in the presence of an acid in a solvent and at temperatures slightly above normal room temperature yields oxo aldehydes. Thus, 2-ethoxy-2-methyl-3, 4-dihydro-2H-pyran, 50 gm., H_2O 100, and concentrated HCl 10 ml. are stirred 30 min. at 20°–40°, neutralized with $NaHCO_3$, saturated with NaCl, extracted 3 times with Et_2O 100 ml., the extracts diluted with hexane 150 and C_6H_6 100 ml., the Et_2O distilled, the residue refluxed under a Dean and Stark trap to remove H_2O and EtOH, and distilled in a Lecky-Ewell column to give 31 gm. 5-oxohexanal, b_{15} 87°–89°. Similarly prepared are the following hexanals: 5-oxo-3-phenyl, b_2 133°–137°, 5-oxo-2-methyl, 5-oxo-3-methyl, 5-oxo-4-methyl. In addition, preparation of 5-oxo-3-(2-furyl)-5-phenyl and 5-oxo-5-cyclohexylpentanol were reported by analogous methods.

623. ENGEL, W. F. (Shell Development Co.). Gas Purification. United States Patent 2,537,448, Jan. 9, 1951; appl. filed Apr. 22, 1947. Serial No. 743,187, in the Netherlands May 22, 1946; 10 claims (*Cl. 23–3*). Chem. Abs., vol. 45, 1951, p. 3147.

Gas of relatively high thermal stability is purified without altering its composition. A mixture of CO and H_2 containing about 2 vol. of H_2 per l. of CO, having a S content of 120 mg. per $m.^3$, and a Cl content of 10 mg. per $m.^3$ of gas, was purified by contact with a catalyst consisting of active C and KOH at 550° atmospheric pressure and a throughput rate of 40 l. of gas per l. of catalyst per hr. The S or Cl, present in the untreated gas in an organically combined form, was found to be unaffected by treatment with NaOH. The catalyst had a K content of 30 wt. %. The purified gas obtained during 20 hr. of continuous operation had an average overall S content of only 2 mg. and Cl content of 1 mg. per $m.^3$ of gas.

See abs. **1086, 1087, 1098, 1099, 1100.**

ENGELHARDT, F. *See* abs. **1909.**

624. ENTREPRISE GÉNÉRALE DE CHAUFFAGE INDUSTRIEL PILLARD FRÈRES & CIE. Gasification of Solid or Liquid Fuels. British Patent 688,915, Mar. 18, 1953. Chem. Abs., vol. 47, 1953, p. 8349.

Describes method and apparatus for gasification of liquid or finely pulverized combustible material such as lignite fines or other pulverized solid or liquid fuels to give gas containing a high percentage of CH_4. Combustibles, free O_2, and steam are injected by tangential nozzles into a tubular furnace where primary gasification takes place at 1,100° and approximately 20 atm. This gas then enters a conical section of the furnace where additional steam is introduced, and a water-gas shift reaction takes place at 600°–700°. The gas then enters a widened 3d section where it is cooled to 300° by secondary steam, which flows through pipes around this section. Formation of CH_4 by hydrogenation of CO occurs in this section and is aided by high pressures and low temperatures. The gas produced contains 60–70% CH_4 and H_2 on a CO_2-free basis.

625. Ericsson, G. Closure for High-Pressure Vessels Used for Synthesizing Chemicals, etc. United States Patent 2,213,161, Aug. 27, 1940; appl. filed Oct. 13, 1936, Serial No. 105,364; 1 claim (*Cl. 220–3*). Chem. Abs., vol. 35, 1941, p. 351.

Various structural details.

626. Établissements Brunon-Vallette & cie. (S. A. r. l.), and Société anon. de Gas Comprimé. [Apparatus for Catalytic, Highly Exothermic Gas Reactions.] French Patent 891,202, Mar. 1, 1944. Chem. Abs., vol. 47, 1953, p. 7839.

Reactor is submerged in cylinder or transformer oil, which is heated by an electric coil and cooled by H_2O. It is claimed that the reactor is especially suitable for exothermic reactions between CO and H_2 in presence of Raney Ni, hence it may be used for the enrichment of city gas with CH_4.

Etherington, L. D. *See* abs. **3255.**

627. Etienne, A., and Du Chaffaut, R. (E. I. du Pont de Nemours & Co.). Carrying Out Exothermic Catalytic Chemical Reactions. United States Patent 1,962,301, June 12, 1934; appl. filed Apr. 26, 1928. British Chem. Abs., 1935, B, p. 385.

In the operation of an exothermic reaction in a catalyst that is cooled by the ingoing gases, greater latitude of control is attained by dividing the catalyst into portions of unequal size and the gases into corresponding streams in parallel and in adjustable proportion during the preliminary heat-exchange pass.

Everett, E. F. *See* abs. **488.**

628. Evering, B. L., and Peters, E. F. (Standard Oil Co. of Indiana). Conversion of Olefins, Carbon Monoxide, and Hydrogen. United States Patent 2,606,939, Aug. 12, 1952; appl. filed June 25, 1949, Serial No. 101,462; 9 claims (*Cl. 260–683.15*).

Process for the conversion of an olefin, CO, and H_2 to a predominantly straight chain, normally liquid olefinic hydrocarbon containing more C atoms per molecule than the original olefin and boiling substantially within the gasoline boiling range. It comprises contacting a feed stock made up of the olefin and 5–40 vol. % of a mixture of H_2 and CO having a mol ratio of $H_2 : CO = 0.5 : 10$ with an alkali-promoted (0.5% K_2O) Fe catalyst at about 350°–425° and 250–1,500 p. s. i. g.

629. Eversole, J. F. (Carbide & Carbon Chemicals Corp.). Dehydrogenation of Methanol. United States Patent 2,010,427, Aug. 6, 1935. Chem. Abs., vol. 29, 1935, p. 6251.

For making gaseous mixtures of CO and H_2, MeOH is catalytically decomposed by passing the MeOH vapors over a catalyst consisting of reduced Cu and Ni as essential active constituents at a temperature of about 350°–400°. Describes apparatus.

630. ——— (Carbide & Carbon Chemicals Corp.). Methanol Catalyst. Canadian Patent 359,414, July 28, 1936. Chem. Abs., vol. 30, 1936, p. 6391.

MeOH is prepared by passing C oxides with H_2 at 300°–375° under a pressure of 3,000–4,000 p. s. i. and at a space velocity of 18,000–30,000 vol. per vol. per hr. over a catalyst initially comprising essentially 26–65% ZnO, 25% CrO_3, 1.5–35% CuO, and about 13% FeCr. The catalyst is contained within a vessel having inner surfaces composed of an austenitic alloy steel containing both Cr and Ni. The catalyst is active in promoting the synthesis of MeOH and produces better yields with less total hydrogenation to form hydrocarbons than other catalysts.

F

Faatz, A. C., Jr. *See* abs. **168.**

631. Fabrique nationale de produits chimiques et d'explosifs Soc. anon. Distilling Solid Carbonaceous Materials. British Patent 296,443, Sept. 2, 1927. Chem. Abs., vol. 23, 1929, p. 2555.

Before carbonizing coal, lignite, peat, or oil shale, oxidizing agents, such as oxides of Fe or Mn or carbonates of alkali metals or alkaline earth metals, are added to the charge. The yield of tar is increased, and a porous coke is obtained, which contains metal oxides or finely divided metals and may be used as a catalyst in synthetic processes such as production of condensable hydrocarbons and alcohols from CO, H_2, and gaseous hydrocarbons produced in the distillation. Pulverulent Fe ore, residues of roasted pyrites, or Mn ore may be added and the residue together with the associated coke transferred to a reducing apparatus.

Faldini, M. *See* abs. **2524.**

632. Falk-Hultgren, N., and Vidstrand, E. H. [Combustible Liquid.] Danish Patent 18,827, July 11, 1913. Chem. Abs., vol. 9, 1915, p. 2452.

Combustible liquid similar to benzine is manufactured by heating a mixture of CO or CO_2 and H_2 to at least 2,000°. In the reaction are formed, besides H_2O, hydrocarbons, which condense upon cooling to a readily volatile benzine-like liquid.

See also French Patent 457,174 (abs. **3830**).

633. ———. [Combustible Liquid.] Norwegian Patent 24,576, Jan. 18, 1913. Chem. Abs., vol. 9, p. 2452.

In the manufacture of a combustible liquid, compounds of the CH_4, ethylene, or acetylene series, such as the dry distillation products from peat, coal, etc., are heated with H_2O to 2,000°. The resulting liquid consists of a mixture of several heavy hydrocarbons and their isomers and in composition is intermediate between the CH_4 and the ethylene series.

See also French Patent 457,174 (abs. **3830**).

634. Farbwerke vorm. Meister Lucius and Brüning. Methane. British Patent 146,110, June 21, 1920. Chem. Abs., vol. 14, 1920, p. 3428.

Methane is prepared catalytically by passing a mixture of CO and excess of H_2 through a series of furnaces containing heated contact material such as pumice carrying active Ni, the composition of the gases being adjusted at each passage by the addition of CO, so that the amount of the latter does not exceed about 1/5, by vol., of the H_2 present, and the gases being freed from H_2O vapor after each passage through a furnace. Thus, between each pair of furnaces there is a condenser and a connection with suitable measuring device for introducing a measured quantity of CO, the gases used containing originally a large excess of H_2. In place of H_2, purified illuminating gas may be employed, and a purified water gas may be substituted for CO. The traces of H_2 finally remaining in the gases may be

removed by passage over CuO, or the CH_4 may be liquefied by cooling the gases.

635. ———. Methane. British Patent 146,114, June 22, 1920. Chem. Abs., vol. 14, 1920, p. 3428.

In the later stages of the process described in British Patent 146,110 (abs. **634**), that is, after a high concentration of CH_4 has been attained, CO_2 in an amount corresponding to about ¼ of the H_2 remaining is added instead of further addition of CO; the H_2O vapor is removed after each passage as before. In an example, the first set of furnaces taking CO and H_2 is heated to 290° and the furnaces through which the gases are passed subsequent to addition of CO_2 are heated to 390°. Excess of CO_2 may be removed from the gases by absorption by lime, etc. and the residue of H_2 by heated CuO.

636. ———. Methane. British Patent 161,924, May 12, 1921; appl. filed Aug. 10, 1920. Chem. Abs., vol. 15, 1921, p. 2444.

Process described in the principal patent for manufacturing CH_4 from CO and H_2 is modified by diluting the mixture with gases that are indifferent to the process to regulate the temperature of the reaction, more particularly in the earlier stages. The dilution may be effected by employing a quantity of H_2, as compared with CO in excess of the proportion 1 : 5; or the gases may be diluted with CH_4, which may be derived from the process itself. In the latter case, the gases may be repeatedly passed through a single contact furnace, the H_2O and a proportion of the highly concentrated CH_4 being withdrawn after each passage, while to the entering gases are added quantities of CO and H_2 equivalent to the CH_4 withdrawn, the relative proportions of CO and H_2 in the reaction gases being maintained at about 1 : 5; the last traces of H_2 in the CH_4 may be subsequently removed. This is an addition to British Patent 146,110 (abs. **634**).

637. ———. [Production of Methane.] French Patent 521,054, July 6, 1921; appl. filed July 24, 1920. Chem. Zentralb., 1921, IV, p. 910.

Mixture of CO and H_2 containing an excess of H_2 is passed over heated catalysts in a series of furnaces, and, after each removal of H_2O vapor, fresh CO is added in an amount not exceeding ⅕ of the H_2 present, and finally, when desirable, the residual H_2 is removed in known manner.

———. *See* abs. **834.**

638. FARENHOLTZ, W. A., HUBBE, G., AND HUBBE, H. Apparatus for Mixing Gases and Liquids in the Oxidation of Hydrocarbons of High Molecular Weight Into Fatty Acids and Alcohols. British Patent 515,720, Dec. 12, 1939. Chem. Abs., vol. 35, 1941, p. 5905.

Gives various structural, technical, and operative details.

639. ———. Oxidation of Paraffin Hydrocarbons. British Patent 507,521, June 16, 1939. Chem. Abs., vol. 34, 1940, p. 446.

Paraffins that are liquid under the conditions of treatment are oxidized in the presence of salts of metals of the 6th, 7th, or 8th group of the periodic system together with free higher carboxylic acids; for example, fat (stearic or linoleic), resinic, or naphthenic acids, if desired with the addition of compounds, fat or resinic acid salts, carbonates or bicarbonates, of the alkali or alkaline-earth metals, Mg included. Mn or Co oxalate, palmitate or stearate, Co resinate, Fe naphthenate, $MnCl_2$, $FeCl_3$, bichromates, and U nitrate are suitable salts.

640. ———. Oxidizing Hydrocarbons. British Patent 506,104, May 23, 1939. Chem. Abs., vol. 33, 1939, p. 9321.

Fatty acids, alcohols, etc. are produced by oxidizing hydrocarbons of high molecular weight with gaseous oxidizing agents in more than 1 reaction vessel, a current of oxidizing gas being passed through the vessels in succession and additional oxidizing gas being introduced into 1 or more of the vessels disposed in succession in relation to the flow of the gas. The material to be oxidized may be passed through the reaction vessels in the same direction as the current of gas but at a slower rate than the latter. If aliphatic alcohols are to be produced, the reaction medium is kept strongly acid. Gives examples of the oxidation of paraffin with the use of Mn stearate, Mg stearate, and fatty acid as catalyst.

See also French Patent 837,524 (abs. **3808**).

FÄRHÄUSER, F. *See* abs. **946.**

641. FARLOW, M. W., AND HERRICK, E. C. (E. I. duPont de Nemours & Co.). Catalytic Hydrogenation of Carbon Monoxide to Orientable, Essentially Hydrocarbon Polymers. United States Patent 2,652,372, Sept. 15, 1953; appl. filed July 10, 1951, Serial No. 236,086; 12 claims (*Cl. 260–2*).

Claim 1. An essentially hydrocharbon polymer orientable by cold-drawing, which is the reaction product of CO and H, said hydrocarbon polymer melting above 130° C., having an inherent viscosity of at least 1.1, measured at 0.1% concentration in tetrahydronaphthalene at 125° C., and being capable of forming tough films having a density of at least 0.97, based on the annealed film and having a stiffness modulus >150,000 p. s. i., and a microtensile breaking strength of at least 100,000 p. s. i., based on the relaxed, drawn dimension of a film of said polymer.

642. FASCE, E. V. (Standard Oil Development Co.). Selective Oxidation Process Producing Fatty Acids and Alcohols. United States Patent 2,537,577, Jan. 9, 1951; appl. filed Nov. 10, 1948, Serial No. 59,421, 5 claims (*Cl. 260–413*). Chem. Abs., vol. 45, 1951, p. 4738.

Organic mixture from the Oxo process having a high aldehyde content, olefins, and alcohols is oxidized in the liquid phase with an O_2-containing gas and a metallic soap catalyst. The branched-chain compounds in the mixture are converted into acidic compounds and the straight-chain compounds into predominantly alcohols; these are separated in the usual manner.

———. *See* abs. **2565.**

643. FAUSER, G. [Apparatus for Exothermic Reactions Under Pressure and at High Temperature.] Italian Patent 450,478, July 21, 1949. Chem. Abs., vol. 45, 1951, p. 913.

Apparatus consists mainly of a high-pressure H_2O circulation inside the reaction chamber for removing the excess heat produced by the reaction.

644. ——— (Montecatini Società generale per l'industria mineraria e chimica). [High-Pressure Reactor for Liquid-Phase Syntheses.] Italian Patent 448,038, May 6, 1949. Chem. Abs., vol. 45, 1951, p. 4102.

Reactor is made of ordinary steel for its shell and of corrosion resistant steel for the inner body. The inert carrier liquid flows into the jacket between shell and inner body and effectively keeps the corrosive reactants from coming into contact with the shell. The reactants are led by tubes into the inner body, and reactant mixture, including inert carrier, flows out the top.

645. FAWCETT, E. W., GIBSON, R. O., AND IMPERIAL CHEMICAL INDUSTRIES, LTD. Formic Acid. British Patent 447,492, May 19, 1936. Chem. Abs., vol. 30, 1936, p. 6764.

HCOOH is produced by the reaction of CO and H_2O at at least 2,000 atm. and 175°–250°. Catalysts, such as H or metal halides, metal oxides, and nonvolatile acidic oxides, may be present.

646. FEILER, P. (I. G. Farbenindustrie A. G.). [Liquid Hydrocarbons.] German Patent 719,375, Apr. 8, 1942; appl. I 44,241, filed Apr. 17, 1932 (*Cl. 12 o–1.06*). FIAT Reel AA–88, frames 4,182–4,183; PB 70.273; Chem. Abs., vol. 37, 1943, p. 1,849.

Heating of CH_4 and other gaseous hydrocarbons over 600° C in the presence of O_2 results in the formation of liquid compounds. Excessive C deposition in the apparatus is avoided by adding 5% of O_2 to the gas stream.

FEISST, W. *See* abs. **13, 2144, 2808, 2809, 2810, 2811, 2812, 2813, 2814.**

647. FEISST, W., NEWELING, H., AND ROELEN, O. (Hydrocarbons Synthesis Corp.). Converting Carbon Oxides Into Higher Hydrocarbons. United States Patent 2,238,726, Apr. 15, 1941; appl. filed Dec. 4, 1936, Serial No. 114,186, in Germany Dec. 10, 1935; 9 claims (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 4777.

Reaction is effected between C oxides and gases containing free H_2, substantially free from other reactants, at about 180°–250° in the presence of a catalyst such as one of Co, Th oxide, and kieselguhr. Nonvolatile reaction products are periodically removed from the catalyst, at a temperature not materially above the reaction temperature, as by use of H_2 or extraction with benzine, before these reaction products impair the efficiency of the catalyst by over about 5%.

648. FEISST, W., ROELEN, O., AND SCHUFF, W. (Alien Property Custodian). Synthesis of Multilink Hydrocarbons From Hydrogen and Carbon Monoxide. United States Patent 2,369,956, Feb. 20, 1945; appl. filed Oct. 14, 1941, APC No. 414,926, in Germany Oct. 6, 1936; 9 claims (*Cl. 260–449.6*). Chem. Abs., vol. 39, 1945, p. 3148.

Co catalyst, used to exhaustion in the Fischer-Tropsch synthesis, is treated with a rapidly flowing stream of H_2 at 350° C. In 2 hr. it removes from the catalytic mass 80%–85% of organic substances in the form of a paraffin m. p. 60°–65°. The H_2-treated catalyst is cooled, then moistened with H_2O and dissolved in HNO_3. The catalytically active metals are precipitated with a soda solution from the metal salt solution thus obtained, after purification by filtration. The washed and dried catalyst is then reduced with H_2 and is again available for use.

FELLER, A. *See* abs. **3295.**

649. FETTERLY, L. C. (N. V. de Bataafsche Petroleum Maatschappij). [Extractive Crystallization of Hydrocarbons From Their Mixtures With Urea by Formation of Crystalline Complexes.] French Patent 963,978, July 26, 1950; appl. filed Mar. 30, 1948. Chem. Zentralb., 1951, I, p. 2382.

Straight-chain hydrocarbons form crystalline complex compounds, whereas the hydrocarbons with branch chains, especially isoparaffins as well as aromatic and naphthenic hydrocarbons, remain unchanged. The process consists in treating the hydrocarbon mixture with aqueous or alcoholic saturated solutions of urea. The crystalline complex formation and separation is especially influenced by the temperature, for example, the quantity of hydrocarbons tending toward the formation of complexes is increased with decrease in temperature. In most cases the operation is carried on between 20°–0°. Through temperature regulation crystalline fractions separate, which contain hydrocarbons of different molecular weights; for example, at temperatures >30° only straight-chain hydrocarbons with at least 6 C atoms form crystalline complexes. Therefore, it is easy to separate the straight-chain gaseous hydrocarbons from the higher molecular paraffin hydrocarbons.

650. ——— (Shell Development Co.). Extractive Fractionation of Organic Compounds. United States Patent 2,520,715, Aug. 29, 1950; appl. filed Mar. 29, 1947, Serial No. 738,213; 5 claims (*Cl. 260–674*). United States Patent 2,520,716, Aug. 29, 1950; appl. filed Nov. 28, 1947, Serial No. 788,693; 10 claims (*Cl. 260–676*). Chem. Zentralb., 1951, I, p. 2220.

Organic compounds, which form crystalline complex compounds with urea or thiourea, are separated by fractionation. The organic compounds are treated with urea or thiourea in presence of a selective solvent agent, which does not dissolve the complex compound. According to another process, an acid anhydride (SO_2, NO_2, acetic anhydride), which forms a further complex compound with the original complex compound, is used in place of the solvent agent. Example: A mixture of normal and branched alcohols, containing an average of 10–14 C atoms obtained by the oxo synthesis, is treated with a concentrated solution of urea in liquid SO_2 and the solid complex compound immediately separated; this method, after separation and decomposition with H_2O, yields the normal alcohols without the presence of isomers.

651. ——— (Shell Development Co.). Extractive Fractionation Process. United States Patent 2,549,372, Apr. 17, 1951; appl. filed Apr. 15, 1947, Serial No. 741,676; 7 claims (*Cl. 260–666*). Chem. Abs., vol. 45, 1951, p. 8545.

Flowsheet is presented for the extractive fractionation of organic compounds. Extractive crystallization with urea has been found suitable for large-scale separations. Urea forms crystalline complexes with organic compounds of straight-chain structure. Thiourea is useful in forming complexes with organic compounds having a branched configuration or cycloaliphatic structure. An extensive list of compounds that can be thus treated is presented.

652. ——— (Shell Development Co.). Extractive Fractionation Process. United States Patent 2,588,506, Mar. 11, 1952; appl. filed Apr. 15, 1947, Serial No. 741,677; 15 claims (*Cl. 260–666*).

Mixtures of organic compounds are treated with urea and/or thiourea to form crystalline complexes, which are separated from the raffinate and then decomposed to recover the active organic compounds present. Such decomposition or regeneration can be effected by simple or steam distillation by applying a solvent for the complex-forming agent, by heating, or by applying a solvent for a particular fraction of the regenerated organic compounds. The raffinate may be fractionated by distillation, solvent extraction, or extractive fractionation with a complex-forming agent other than the one originally employed. The raffinate may be subjected to conversion processes such as isomerization, alkylation, hydrogenation, or by formation of other complexes. Gives an extensive list of organic compounds that form complexes with urea or thiourea.

653. ——— (N. V. de Bataafsche Petroleum Maatschappij). [Fractional Extraction and Crystallization of Hydrocarbon Mixtures in the Form of Complex Compounds With Urea and Thiourea.] French Patent 964,694, Aug. 22, 1950; appl. filed Apr. 15, 1948. Chem. Zentralb., 1951, I, p. 2383.

Isomeric hydrocarbon mixtures, such as octane and isooctane and hydrocarbons, which were obtained by alkylation, isomerization, and aromatization, may be separated. To facilitate the fractional separation, a part of the complex mixture from a preceding operation is added to the initial mixture. Normal paraffins and olefins, strongly unsaturated compounds, normal alcohols with at least 6 C atoms, as well as etherlike compounds such as acetals, dioxan, paraldehyde and esterlike compounds such as amylacetate, amines, acid amides, and mercaptans form crystalline complexes

with urea. To the hydrocarbons that form complexes with thiourea belong branched and naphthenic hydrocarbons such as isobutane, isopentane, 2,2-dimethylpropane, isohexane, and 2-methylpentane.

654. ——— (N. V. de Bataafsche Petroleum Maatschappij). [Fractional Extraction and Extractive Crystallization of Isomeric Hydrocarbon Mixtures.] French Patent 969,716, Dec. 26, 1950; appl. filed July 27, 1948. Chem. Zentralb., 1951, I, p. 2109.

Hydrocarbons containing at least 6 C atoms are separated by urea or thiourea, which selectively forms crystalline compounds with normal paraffin hydrocarbons, olefins, alcohols, ethers, etc. This patent describes the separation of octane and isooctane. Likewise straight-chain hydrocarbons are separated from branched-chain, cyclic, aromatic, and naphthenic hydrocarbons. Thiourea forms crystalline complex compounds with branched or cycloaliphatic hydrocarbons, whereas straight-chain hydrocarbons do not react.

655. ——— (N. V. de Bataafsche Petroleum Maatschappij). [Separation of Branched Aliphatic and Aromatic as Well as Cyclic and Naphthenic Hydrocarbons From Mixtures With Other Hydrocarbons and Hydrocarbon Compounds by Adding Urea or Thiourea Which Forms Crystalline Complex Compounds With Isoparaffins, Cyclic or Naphthenic Hydrocarbons.] French Patent 964,693, Aug. 22, 1950; appl. filed Apr. 15, 1948. Chem. Zentralb., 1951, I, p. 1104.

656. ——— (Shell Development Co.). Thiourea-Hydrocarbon Complexes and Process for Preparing Same. United States Patent 2,499,820, Mar. 7, 1950; appl. filed Feb. 21, 1947, Serial No. 730,182; 16 claims (*Cl. 260–666*). Chem. Abs., vol. 44, 1950, p. 5090.

It has been found that isoparaffins, naphthenes, isoolefins, and cyclo-olefins readily form crystalline complexes with thiourea. The formation of these compounds makes possible the separation, concentration, and purification of specific petroleum hydrocarbons from impurities. A list of 164 hydrocarbons that form complexes with thiourea is presented. Describes preparation of many thiourea-hydrocarbon complexes.

657. Field, E., and Hill, B. L. (Standard Oil Co. of Indiana). Higher Alcohols From Aldehydes. United States Patent 2,587,576, Mar. 4, 1952; appl. filed Dec. 2, 1950, Serial No. 198,918; 10 claims (*Cl. 260–638*).

Normal aldehydes having 2–4 C atoms per mol. are subjected to 120°–200° and 1,000–10,000 p. s. i. g. in the presence of CO and H_2, in a mol ratio of about 2 : 1 to 1 : 4 and about 0.01–0.2 gm.-atoms of Co per mol of reactant aldehyde as a Co carbonyl or Co hydrocarbonyl. By maintaining the reactants under these conditions long enough to establish a mol velocity of not more than 10 mols of aldehyde per hr. per gm.-atom of Co, a condensation hydrogenation of the aldehyde is effected and a polymeric primary alcohol derivative is obtained having at least 2 times as many C atoms per mol. as the aldehyde employed. Thus, acetaldehyde will produce some *n*-butanol, propionaldehyde will produce primarily hexanol, and *n*-butraldehyde will produce octyl alcohol. Addition of H_2O to the reaction enhances the tendency of these aldehydes to form the condensation products. The solvent for the reaction can be any hydrocarbon solvent. The catalyst can be added as preformed Co carbonyl or hydrocarbonyl or as an aqueous Co salt in a H_2O solution or suspended in oil, or as a H_2O-insoluble compound, such as a slurry or dust of powdered metallic Co. If the catalyst is not preformed 0.1–5% of an inorganic S compound, such as NH_4HS or H_2S, that will convert Co to CoS is introduced into the reactant zone to ensure initial reaction and conversion. In 1 example using acetaldehyde the product contained 11% ethanol, 20% *n*-butanol, 30% 2-methyl-1-pentanol, and a balance of bottom distillation products, with paraldehyde the product contained 2% ethanol, 11% butanol, 38% mixed hexanols, about 34% mixed octanols, and 15% higher boiling products.

658. Fiorelli, F. [Gas Production.] Italian Patent 384,203, July 8, 1940. Chem. Zentralb., 1942, I, p. 3062.

In the continuous production of synthesis gas from fuels containing solid, volatile constituents by gasification with O_2 and steam, the gas formed in the distillation zone is so introduced into a layer of coke at increased temperature that between the distillation zone and the gasification zone a decomposition zone is formed in which the hydrocarbons are decomposed.

659. ———. [Vertical Oven for Synthesizing Gas.] German Patent 719,874, Apr. 18, 1942; appl. F 84,479, filed February 1938 (*Cl. 26 a–2*). Chem. Abs., vol. 37, 1943, p. 2163.

Construction and operation of an oven for the production of gas from lignite and desulfurizing of the gas.

Fiorillo, F. *See* abs. **3801.**

660. Fischer, E., and Donath, B. Hydrocarbons. British Patent 479,931, Feb. 9, 1938. Chem. Zentralb., 1938, II, p. 470; Chem. Abs., vol. 32, 1938, p. 4999.

Hydrocarbons are produced from CO and H_2 at over 1,500 atm. and the requisite temperature without a catalyst, the pressure being developed in successive compression stages. Describes apparatus,

See also French Patent 825,379, (abs. **661**).

661. ———. [Synthetic Hydrocarbons.] French Patent 825,379, Mar. 2, 1938. Chem. Abs., vol. 32, 1938, p. 6256.

In making hydrocarbons from CO, CH_4, C_2H_6, and other gases containing much C and H_2 by combination with H_2, very high pressures are used. The pressure increases in at least 5 stages from atm. up to 5,000 atm. Describes apparatus.

See also British Patent 479,931 (abs. **660**).

662. Fischer, F. [Apparatus for Producing Hydrocarbons From Methane.] German Patent 583,851, Sept. 13, 1933; appl. F 71,554 filed Jan. 21, 1930 (*Cl. 12 o–1.03*). FIAT Reel AA90, frames 1,346–1,349; PB 70,275; Chem. Abs., vol. 28, 1934, p. 776.

Addition to German Patent 578,311 (abs. **667**).

663. ———. Catalytic Purification of Gases. British Patent 282,634, Dec. 24, 1926. Chem. Abs., vol. 22, 1928, p. 3715.

Gases such as water gas (which may be first freed from H_2S) are treated for the removal of S compounds other than H_2S by using a catalyst of precious metal such as Au or Ag, which convert the S compounds in the presence of H_2 to H_2S without causing any other change in the gas. The gas is then further treated by a usual method for removing the H_2S formed. Silverized asbestos may be used at a temperature of 200°–300°.

See also United States Patent 1,754,371 (abs. **3636**).

664. ——— (Studien- und Verwertungs-G. m. b. H.). Catalytic Synthesis of Aliphatic Hydrocarbons, as in Production of Light Liquid Hydrocarbons. United States Patent 2,149,515, Mar. 7, 1939; appl. filed Apr. 15, 1935. Chem. Abs., vol. 33, 1939, p. 4270.

Method of increasing the yield in the catalytic synthesis of aliphatic hydrocarbons having more than 1 C atom in the molecule from CO and H_2, in which the synthesis is carried out in stages, involves effecting partial conversion of the mixture of CO and H_2 in the first stage to the extent of $< \frac{2}{3}$ the available quantity,

removing the reaction products, and subsequently subjecting the mixture of CO and H_2 to partial conversion in the succeeding stages, each time after separation of the reaction products, and completing the conversion in the final stage.

See also abs. **680** and **684**.

665. ———. Higher Hydrocarbons From Methane. British Patent 319,340, Sept. 22, 1928. Chem. Zentralb., 1930, II, p. 620; Chem. Abs., vol. 24, 1930, p. 2468.

Hydrocarbons such as C_2H_4 and C_6H_6 are obtained from CH_4 by passing it through a furnace operating on the regenerative system. The furnace is hot blasted by combustion gases and cooled again by passage of the CH_4. Catalytically active lining or filling bodies such as silica or silica gel may be used, but the presence of Fe, Ni, or Co should be avoided. Describes various details.

See also French Patent 686,040 (abs. **675**).

666. ———. [Hydrocarbons.] German Patent 571,-898, Mar. 9, 1933; appl. filed Dec. 10, 1930 (*Cl. 12 o–1.03*). FIAT Reel AA–90, frames 1,440–1,441; PB 70,275; Chem. Abs., vol. 27, 1933, p. 4239.

Liquid aliphatic hydrocarbons are prepared by treating oxides of C with H_2 at pressures near normal by the aid of metallic contact agents containing activated Ni. Any CH_4 formed is reconducted over the catalyst to form liquid hydrocarbons. In the example, the catalyst is prepared by suspending pure kieselguhr in H_2O, adding $Ni(NO_3)_2$ and $Th(NO_3)_4$, precipitating with NaOH, and finally washing and drying. This catalyst is activated by reduction in a stream of H_2 at 350°. CO and H_2 are then passed over it in the proportions 1:2 at about 180°. CH_4 is first formed. This is returned over the catalyst to obtain higher homologs. Finally, C_6H_6 occurs in the liquid hydrocarbons forming the product. The catalyst should be free from Cu.

667. ———. [Hydrocarbons From Methane.] German Patent 578,311, June 12, 1933; appl. F 66,881, filed Sept. 23, 1928 (*Cl. 12 o–1.03*). FIAT Reel AA–90, frames 1,442–1,446; PB 70,275; Chem. Abs., vol. 27, 1933, p. 4239.

CH_4 is heated to >1,000° in a regenerative apparatus, which is alternately heated by combustion gases and cooled by the CH_4. The period during which the CH_4 is heated is preferably <1 sec. The apparatus should be lined and packed with material that does not promote the deposition of C, for example, silica gel C_2H_2, olefins, and liquid hydrocarbons of the benzene type are obtained. Gives examples.

668. ———. Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. Australian Patent 4,773, Apr. 28, 1932; appl. filed Nov. 2, 1931. Chem. Zentralb., 1932, II, p. 2237.

In the synthesis of hydrocarbons at ordinary or slightly raised pressure and temperature but below that at which CH_4 is mainly formed, Ni catalysts are used that are free from Cu and have been made by being precipitated together with activated substances such as Th, Al, and Ce from their solutions on porous substances and then reduced by H_2. The operating temperature for these catalysts lies at 150°–250°; for example, 180° for a gas mixture of $CO:H_2=1:2$.

669. ———. [Oxygenated Organic Compounds.] German Patent 546,336, Feb. 5, 1930. Chem. Abs., vol. 26, 1932, p. 3263.

Coal, peat, wood, mineral oil, and bitumen, or their extracts or distillation products, are treated with O_2 or gases containing O_2 at a raised pressure and at atmospheric or raised temperature in the presence of H_2O, steam, or other noncombustible fluid, the reaction vessel being made of or lined with Ag or an alloy rich in Ag. Carriers of O may be present, for example, salts of Fe, Mn, or Cu. The products are mainly acids. Gives examples.

670. ———. [Synthesis Gas From Hydrogen and Carbon Monoxide.] German Patent 685,291, Dec. 15, 1939; appl. filed July 17, 1935. Chem. Zentralb., I, 1940, p. 1605.

Water gas generator is hot-blasted with O_2 and steam, the gasifying operation is performed with H_2 and hydrocarbons or CH_4. The 2 gases are mixed. Heat exchange between the hot-blasting and gasifying stages is practiced.

671. Fischer, F., and Koch, H. (Studien- und Verwertungs-G. m. b. H.). "Knock-Proof" Gasoline and Lubricating Oil. United States Patent 2,128,994, Sept. 9, 1938; appl. filed July 10, 1935. Chem. Abs., vol. 32, 1938, p. 8764.

Process that comprises passing water gas at about 200° and at about atm. pressure in contact with a hydrogenation catalyst, subjecting the reaction products to distillation at a temperature up to about 125°, separating the distillate, continuing distillation up to about 250°, heating the 2d distillate after separation from the paraffinic residue obtained, under stirring in the presence of a polymerization catalyst to about 120°, purifying the oil layer thereby obtained, distilling same at ordinary pressure up to 250°, and continuing the distillation up to 200° under a high vacuum for the recovery of a 3d distillate and of a residue, which is adapted for use as a lubricant, and cracking the 3d distillate together with the paraffinic residue to recover knockproof benzine. Describes arrangement of apparatus.

672. Fischer, F., and Pichler, H. Aromatic and Unsaturated Hydrocarbons From Methane. British Patent 316,126, July 23, 1928. Chem. Zentralb., 1930, I, p. 3384; Chem. Abs., vol. 24, 1930, p. 1649.

CH_4 is heated to 1,000°–1,100° for not more than 1 sec., suitably 0.05–0.2 sec. The CH_4 may be diluted with coke gas, and ordinary or reduced pressure may be used. C_6H_6 and other aromatic hydrocarbons are formed, and the H_2 produced may be reconverted into CH_4 by reaction with CO or CO_2 in the presence of a Ni catalyst or used for hydrogenating the hydrocarbons produced or other materials.

See also French Patent 686,040 (abs. **675**).

673. ——— (Studien- und Verwertungs-G. m. b. H.). [Catalysts for Synthesizing Hydrocarbons.] Italian Patent 363,948, no date. Kainer, pp. 18, 19, 84, 149, 154.

See French Patent 841,043 (abs. **3665**) and German Patent 738,091 (abs. **679**).

674. ———. (Studien- und Verwertungs-G. m. b. H.). [Flow of Gases in Catalytic Reactions.] German Patent 708,500, July 23, 1941; appl. St. 55,966, filed Mar. 14, 1937 (*Cl. 12 g–4.01*). TOM Reel 274, frames 1,286–1,293; TOM Reel 49, frames 533–540; Chem. Abs., vol. 37, 1943, p. 2623.

For long contact layers and temperature-sensitive exothermal reactions, the contact of the gas with the granular catalyst is so arranged that the gas flows along gas-permeable walls on the other side of which is the catalyst. The contact of the gas and the catalysts and the drawing off of the reaction products from the contact mass takes place by flow or diffusion through the pores of these walls.

675. ———. [Hydrocarbons.] French Patent 686,040, Dec. 10, 1928. Chem. Zentralb., 1931, I, p. 1708; Chem. Abs., vol. 24, 1930, p. 5764.

See British Patents 316,126 (abs. **672**) and 319,340 (abs. **665**).

676. ——— (Hydrocarbon Synthesis Corp.). Hydrocarbons From Gases Containing Carbon Monoxide

and Hydrogen. United States Patent 2,257,457, Sept. 30, 1941; appl. filed July 23, 1938, Serial No. 220,919, in Germany July 31, 1937; 9 claims (*Cl. 260–449*). Chem. Abs., vol. 36, 1942, p. 250.

Process of producing aliphatic solid, liquid, or readily liquefiable hydrocarbons from gas mixtures containing CO and H_2 in the presence of an Fe catalyst comprises passing a mixture of CO and H_2 under an operating pressure of 2–100 atm. and at 220°–320° over an Fe catalyst that has been subjected to a preliminary treatment with CO under a pressure considerably lower than the operating pressure subsequently employed.

677. ——— (Studien- und Verwertungs-G. m. b. H.). [Paraffin.] French Patent 828,893, no date. Kainer, p. 211.

See German Patent 731,295 (abs. **3684**) and Italian Patent 352,611 (abs. **3683**).

678. ——— (Studien- und Verwertungs-G. m. b. H.). Process for Producing Iron Catalysts. German Patent Appl. St 60,795, filed May 23, 1941 (*Cl. 12 o–1.03*). TOM Reel 100.

A process for producing precipitated Fe catalysts for the synthesis of hydrocarbons from H_2 and the C oxides consisting in decomposing an Fe salt solution at temperatures <50° with soda to such an extent that no precipitate is formed and then heating the solution to boiling after the following precipitation step. The precipitate is then washed, alkalized with 0.125–1% K_2CO_3, and dried at 100°–120°. Example: 1 kg. of an acid Fe nitrate solution obtained by dissolving 900 gm. of Fe shavings in 10 l. of dilute HNO_3 (density 1.12) is decomposed at room temperature in 4 l. of soda solution. The Fe solution becomes dark red without a precipitate being formed. The solution is filtered, and 10 l. of the solution are diluted with 25 l. of H_2O and heated to boiling, made slightly alkaline, and after precipitating heated to boiling for 1 min. The precipitate is then filtered and washed until alkali-free and then alkalized with 0.25% of K_2CO_3 and dried at 110°. The completed catalyst is solid, dark-brown to black in color, and shows a lustrous fracture. Before use for the synthesis process, the catalyst is pretreated for 3 days with a 1:2 mixture of CO: H_2 at 250° and 1 atm. On passing a synthesis gas of CO: H_2=3:2 over it at 15 atm. and 250°, 150 gm. of solid, liquid and gasol hydrocarbons are obtained per $m.^3$ of gas. The catalyst will last for many years.

679. ——— (Studien- und Verwertungs-G. m. b. H.). [Process for the Production of Higher Hydrocarbons From Carbon Monoxide and Hydrogen Under Increased Pressure.] German Patent 738,091, July 1, 1943; appl. St 58,896 filed July 7, 1939 (*Cl. 12 o–1.03*). FIAT Reel AA–90, frames 1,490–1,492, PB 70,275; TOM Reel 101, Doc. PQ–21, 576–NID; Meyer Transl., PC–S–II Fischer-Tropsch, vol 6, chap. 170, 1949, p. 18; Chem. Abs., vol. 38, 1944, p. 4122.

Fe catalysts are used for synthesizing hydrocarbons from CO and H_2 at 10–30 atm. and 200°–300°. Before use the catalyst is pretreated with CO or gases containing CO at 230°–350° and a pressure amounting to a fraction of 1 kg. per $cm.^2$. The catalyst is prepared by precipitation from Fe nitrate solution and contains about 0.1% of alkali. The time of pretreatment is about 24 hr. at a rate of 400 l. of CO per kg. of Fe per hr. The best synthesis results are obtained with a gas of composition CO: H_2=1.8:1, a pressure of 15 kg. per $cm.^2$, and a temperature of 235°. The gas contraction amounts to 55% with virtually a complete conversion of the CO. Yields of solid, liquid, and gasol hydrocarbons are 150 gm. per N $m.^3$ of CO+H_2 mixture, without any lessening of catalyst actvity in 3 mo. of operation.

680. ——— (Studien- und Verwertungs-G. m. b. H.). [Process for the Production of Hydrocarbons From Carbon Monoxide and Hydrogen.] German Patent Appl. St 56,856, filed Nov. 25, 1937 (*Cl. IV d–12 o*). TOM Reel 100.

Higher hydrocarbons are produced by synthesis from a gas mixture containing CO and H_2 in at least equal proportions at temperatures of 230°–320° and pressures of 2–100 atm. in presence of an Fe catalyst that has been pretreated at ordinary pressure or at any other pressure lower than that at which the succeeding synthesis is carried out, by CO or a gas containing it at about 250°, and until the gas contraction has attained about 30%. The catalyst is prepared by thermal decomposition up to 300° of Fe nitrate and contains about 0.25% of K_2CO_3 based on the Fe content.

681. ——— (Studien- und Verwertungs-G. m. b. H.). [Process for the Production of Hydrocarbons From Carbon Monoxide and Hydrogen.] German Patent Appl. St 60,409, filed Jan. 22, 1941 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 382–385; TOM Reel 100.

Higher hydrocarbons are produced by carrying out the process at pressures > atmospheric (10–30 atm.) and at 180°–230° over Fe catalysts and with a synthesis gas of composition CO: H_2=1:3 or 4. The catalyst is prepared by precipitation from Fe nitrate and pretreated at 0.1 atm. and 325° with CO. By carrying out the synthesis in 2 or 3 repeated steps, the yield of liquid products can be increased from 60–70 gm. per $m.^3$ of gas to 110 and 140 gm., respectively.

682. ——— (Studien- und Verwertungs–G. m. b. H.). [Process for the Production of Paraffin.] German Patent Appl. St 56,469, filed July 30, 1937 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 361–364; PB 83,253; TOM Reel 100.

Process in general refers to the production of solid paraffin from CO and H_2 in presence of a catalyst containing Co at < 250° and 2–50 atm. The preferred operating conditions are as follows: Synthesis gas CO: H_2=1:2; catalyst produced by precipitation and consisting of Co–Th–kieselguhr; pressure 5–20 atm. with the gases remaining in the contact chamber for a period proportional to the increase in pressure; for example, at 10 atm., it would remain 10 times as long as at 1 atm.; temperatures 180°–200°. The best yield, 150–160 gm. per $m.^3$ of gas, is obtained under the above conditions.

683. ——— (Studien- und Verwertungs-G. m. b. H.). Process for the Production of Solid, Liquid and Easily Liquefiable Aliphatic Hydrocarbons From Carbon Monoxide and Hydrogen. German Patent Appl. St 61,859, filed May 5, 1942 (*Cl. 12 o–1.03*). TOM Reel 100.

For the production of the hydrocarbons an Fe catalyst is used, which has been pretreated with CO at 200°–500°, preferably 240°–325°, and at atm. pressure. The catalyst is prepared by precipitation from an Fe nitrate solution by means of soda. The precipitate is washed until free from alkali, alkalized by 0.125% K_2CO_3, dried at 110°, and granulated. The induction is performed at atm. pressure and 260°–290° by passing over it 400 l. per hr. of CO until CO_2 formation attains a constant value, followed by conversion with 400 l. per hr. of synthesis gas CO: H_2=3:2 at 15 atm. and 240°. The gas contraction amounts to 50% and a yield of 130–150 gm. per N $m.^3$ of synthesis gas is obtained.

684. ——— (Studien- und Verwertungs-G. m. b. H.). [Process for the Production of Solid, Liquid, and Easily Liquefied Aliphatic Hydrocarbons From Carbon Monoxide and Hydrogen.] German Patent Appl. St 56,470, filed July 30, 1937 (*Cl. IV d–12 o*). TOM Reel 134, sec. Ib, item 6, 7 pp; TOM Reel 100.

A synthesis gas consisting of CO: H_2=3:2 is passed over an Fe catalyst at 2–50 atm. pressure and < 320°. The catalyst consists of Fe and Cu in proportions of 4 to 1; it is made by dissolving Fe–II–Cl and Cu–II–

Cl in H_2O, precipitated with Na_2CO_3, washed until free from alkali, impregnated with 0.125% K_2CO_3, dried at 110°, granulated, and deposited on a carrier. Induction of the catalyst takes place at > 200° and a pressure below that of the succeeding synthesis (or at 240° and atm. pressure) with synthesis gas in volume ratio of $CO : H_2 = 1 : 2$, and until the gas contraction attains a maximum of about 30% in about 3 days time. The following conversion may then be carried out at 15 atm. and 260° with a synthesis gas of composition $CO : H_2 = 3 : 2$ and at a rate of 400 l. of gas per kg. Fe per hr. Contraction amounts to 50% and the yield of hydrocarbons to 130–150 gm. per $m.^3$ of gas, of which 80–90 gm. is solid and liquid hydrocarbons and 50 gm. easily liquefiable benzine.

685. ——— (Studien- und Verwertungs-G. m. b. H.). [Production of Hydrocarbons From Carbon Monoxide and Hydrogen.] Hungarian Patent 122,138, no date.

See German Patent Appl. St 56,470 and St 56,856 (abs. **684** and **680**).

686. ——— (Studien- und Verwertungs-G. m. b. H.). [Production of Hydrocarbons From Carbon Monoxide and Hydrogen.] Hungarian Patent 123,067, no date.

See German Patent Appl. St 56,470 and St 56,856 (abs. **684** and **680**).

687. ———. Production of Hydrocarbons Having a High Carbon Content From Hydrocarbons Having a Low Carbon Content. United States Patent 1,940,209, Dec. 19, 1933; appl. filed July 15, 1931, Serial No. 551,052, in Germany July 18, 1930; 9 claims (*Cl. 260–170*). British Chem. Abs., 1934, B, p. 917; Chem. Abs., vol. 28, 1934, p. 1353.

Aliphatic gaseous hydrocarbons are converted into hydrocarbons of higher C content, for example, $CH_4 \rightarrow C_2H_2$, by passing a mixture of the initial gas with O_2 in amount insufficient for complete combustion through a reaction zone at above 1,000° under conditions giving a reaction time of less than 0.01 sec. The products are cooled by admixture with cold gas immediately on leaving the hot reaction zone. The amount of O_2 used is preferably such that that ratio $CO : H_2$ in the resulting gas is approximately 1 : 2, so that after removal of the C_2H_2 the gas may be used for the synthesis of benzine.

688. ——— (Studien- und Verwertungs-G. m. b. H.). [Solid Aliphatic Hydrocarbons.] German Patent 705,528, Apr. 30, 1941; appl. St. 57,429, filed May 10, 1938 (*Cl. 12 o–1.03*). TOM Reel 134, item III–1, 4 pp.; Chem. Zentralb., 1941, II, p. 839; Chem. Abs., vol. 36, 1942, p. 1943.

Process for the production of solid aliphatic hydrocarbons from H_2 and the C oxides at < 300°, preferably at 150°–280°, and at increased pressure, particularly > 30 atm., using a catalyst of Ru. The catalyst is prepared by conversion of metallic Ru with caustic potash and K nitrate into K ruthenate, which is dissolved in H_2O and converted at boiling temperature with MeOH into Ru dioxide, which is precipitated, filtered, washed, and dried. Reduction takes place with synthesis gas, $CO : H_2 = 1 : 2$, at atmospheric pressure and about 150°. At a temperature of 195° and 100 atm. pressure, 1 l. of $CO–H_2$ mixture per gm. Ru per hr. is passed over the catalyst yielding per $m.^3$ of gas 150–160 gm. of hydrocarbons, ⅔ of which is solid, oil-free paraffin, and the rest liquid hydrocarbons. The life of the catalyst is virtually unlimited. The paraffin is white and melts at 118°–120°.

689. ——— (Hydrocarbon Synthesis Corp.). Solid Paraffin Products From Carbon Monoxide and Hydrogen. United States Patent 2,206,500, July 2, 1940; appl. filed July 16, 1937, Serial No. 153,924, in Germany Aug. 1, 1936; 6 claims (*Cl. 260–449*). Chem. Abs., vol. 34, 1940, p. 7295.

Describes apparatus and a process of producing paraffin products solid at ordinary temperature, which comprises treating CO with H_2 at 125°–250° under a pressure above 4 atm. in the presence of a solid catalyst containing Co as the main active ingredient coated with paraffin solid at room temperature, approximately 1 l., measured under atmospheric pressure and at room temperature, of the mixture of CO and H_2, being hourly brought into contact with the quantity of catalyst, which contains 1 gm. Co, and causing all but a thin coating of paraffin to drip off from the catalyst to prevent clogging of the cavities existing between the individual catalyst particles.

690. ——— (Hydrocarbon Synthesis Corp.). Synthesis of Paraffin From Carbon Monoxide and Hydrogen. United States Patent 2,243,897, June 3, 1941; appl. filed July 23, 1938, Serial No. 220,918, in Germany July 30, 1937; 4 claims (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 5508.

Process of producing solid paraffin from a mixture of CO and H_2 in the presence of a Co catalyst and under superatmospheric pressure (p') involves maintaining the gas mixture in the reaction zone for about a period of time (t') as determined by the equation $t' : t = p' : p$, in which t= the time required to obtain maximum output when operating under a pressure of 1 atm. (p), and p' is the pressure in atmospheres under which the reaction is carried out.

691. ——— (Studien- und Verwertungs-G. m. b. H.). [Synthesizing Hydrocarbons From Carbon Monoxide and Hydrogen.] German Patent 716,853, Jan. 8, 1942; appl. St 57,532 filed June 4, 1938 (*Cl. 12 o–1.03*); Chem. Abs., vol. 38, 1944, p. 2478.

CO and H_2 are brought in contact with a catalyst suspended in H_2O or aqueous solutions at a temperature below the point at which Co reacts with H_2O to form CO_2 and H_2.

692. Fischer, F., and Roelen, D. [Hydrocarbons From Carbon Monoxide and Hydrogen.] Austrian Patent 153,194, no date.

See German Patent 672,731 (abs. **693**).

693. ——— (Studien- und Verwertungs-G. m. b. H.). [Hydrocarbons From Carbon Monoxide and Hydrogen—Temperature Regulation.] German Patent 672,731, Mar. 9, 1939; appl. St 51,786 filed Feb. 3, 1934 (*Cl. 12 o–1.03*); FIAT Reel AA88, frames 03,424–03,427; PB 70,273; Chem. Abs., vol. 33, 1939, p. 6338.

In the catalytic reduction of CO by H_2 to form branched-chain hydrocarbons, the temperature is regulated by heated oil flowing in tubes embedded in the catalyst. Apparatus is indicated.

694. Fischer, F., and Schrader, H. [Process for Reduction or Hydrogenation With Formates.] German Patent 370,975, Mar. 9, 1923; appl. filed Aug. 23, 1920. Chem. Zentralb., 1923, IV, p. 536.

Formates are used in presence of H_2O under pressure at temperatures >100°. Gives example for the hydrogenation of low temperature phenols, b. 250°–340°, in alkali solutions with sodium formate to neutral oils insoluble in alkali as well as of moist brown coal to oily or resinous products.

695. Fischer, F., and Tropsch, H. [Alcohols and Other Oxygen-Containing Compounds by Catalytic Reduction of Carbon Monoxide at High Temperatures and Pressure.] German Patent 411,216, Mar. 26, 1925; appl. filed Nov. 3, 1922. Chem. Zentralb., 1925, I, p. 2748.

Catalysts are used that contain compounds of Rb or Cs or both.

696. ———. Gas Purification. Canadian Patent 266,382, Dec. 7, 1926. Chem. Abs., vol. 21, 1927, p. 1003.

S-containing C compounds are catalytically hydrogenated, and the H_2S thus formed is adsorbed.

See also British Patent 254,288 (abs. **707**).

697. ———. [Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen.] German Patent 577,069, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 174.

698. ———. Hydrocarbons. British Patent 255,818, July 21, 1925. British Chem. Abs., 1927, **B**, p. 695; Chem. Abs., vol. 21, 1927, p. 2906.

By effecting reaction between oxides of C and H_2 at a temperature lower than that required for production of CH_4, with the particular catalyst employed, homologs of CH_4, such as C_2H_6 and C_3H_8, are produced. With a catalyst of ZnO and finely divided Fe, CH_4 only is obtained at 480°, but at 380° a mixture of CH_4 80% and homologs 20% is obtained; whereas at 300° only 10% of CH_4 is formed, together with 90% of higher hydrocarbons. Simple catalysts, except Ni and others that produce only CH_4, may be also employed. Normal reduced or increased pressure may be used.

See also Austrian Patent 119,038 (abs. **705**).

699. ———. [Hyrocarbons.] German Patent 484,337, Oct. 16, 1929; appl F 59,419, filed July 22, 1925 (*Cl. 12 o–1*). FIAT Reel AA–88, frames 3,796–3,798; PB 70,273; Chem. Abs., vol. 24, 1930, p. 1119.

Paraffin hydrocarbons containing a plurality of C atoms in the molecule are prepared from H_2 and oxides of C by passing these gases over a suitable catalyst at a temperature lower than that at which the catalyst promotes the production of CH_4 only. The reaction may be conducted at reduced, ordinary, or slightly raised pressure. Suitable catalysts are mixtures of ZnO with Fe, or Cu with Fe, or Co with Cu; pure Ni is not suitable. Gives examples.

See also British Patent 255,818 (abs. **698**).

700. ———. [Hydrocarbons.] German Patent 531,004, Aug. 7, 1931; appl. F 59,533, filed Aug. 7, 1925. FIAT Reel AA88, frames 3,738–3.739; PB L70,273; Chem. Abs., vol. 25, 1931, p. 5432.

In preparing hydrocarbons from H_2 and oxides of C, as described in German Patent 484,337 (abs. **699**), mixtures of metals with oxygenated compounds of metals are used as the catalysts; for example, a mixture of Co and ZnO.

701. ———. [Hydrocarbons.] German Patent 567,069, Dec. 27, 1932; appl. F 62,091, filed Sept. 15, 1926 (*Cl. 12 o–1*). FIAT Reel AA–88, frames 4,001–4,002; PB 70,273; Chem. Abs., vol. 27, 1933, p. 1499.

Hydrocarbons are treated in known manner with steam and/or CO_2, to produce a gas mixture of the water-gas type, and this mixture is led over a catalyst at atmospheric pressure to produce other hydrocarbons. Gives an example in which natural CH_4 is led with CO_2 over spongy Fe at 950°, and the resulting gas is led at 270° and atmospheric pressure over a mixture of Co and ZnO, giving liquid hydrocarbons of the benzine type. The residual gases are returned to the process.

702. ———. [Hydrocarbons From Hydrogen and Oxides of Carbon.] German Patent 524,468, May 7, 1931; Appl. F 62,373 filed Nov. 2, 1926 (*Cl. 12 o–1*); FIAT Reel AA–89, frames 435–436; PB 70,274; Chem. Abs., vol. 25, 1931, p. 3664.

The method of German Patent 484,337 (abs. **699**) is improved by lowering the reaction temperature; for example to 240°, whereby the life of the catalyst is prolonged, and completely colorless products are obtained. The reaction may be effected under pressures up to 10 atm. Gives examples.

703. ———. Paraffinic Hydrocarbons. United States Patent 1,746,464, Feb. 11, 1930; appl. filed Apr. 1, 1926, Serial No. 99,163, in Germany July 21, 1925. Chem. Abs., vol. 24, 1930, p. 1649.

See German Patent 484,337 (abs. **699**).

704. ———. Paraffins. Canadian Patent 265,063, Oct. 19, 1926. Chem. Abs., vol. 21, 1927, p. 918.

Paraffins with more than 1 C atom are obtained by treating oxides of C in the presence of H_2 by catalytic agents and under normal pressure at temperatures that are lower than those at which, for the catalytic agents used, CH_4 is formed exclusively, the employment of such catalyzers as pure Ni being excluded.

705. ———. [Process for Producing Paraffin Hydrocarbons.] Austrian Patent 119,038, Apr. 15, 1930, Aug. 15, 1930.

See British Patent 255,818 (abs. **698**) and French Patent 613,200 (abs. **706**).

706. ——— (Ruhrchemie A. G.). [Producing Paraffin Hydrocarbons.] French Patent 613,200, Nov. 10, 1926; appl. filed Mar. 22, 1926. Chem. Zentralb., 1927, II, p. 2109.

See British Patent 255,818 (abs. **698**), and Austrian Patent 119,038, (abs. **705**).

707. ———. Removing Sulfur From Gases. British Patent 254,288, Jan. 20, 1927; appl. filed June 29, 1925. Chem. Abs., vol. 21, 1927, p. 2552.

C–S compounds in gas are converted into H_2S by catalysis in the presence of H_2, and the H_2S is then absorbed; preferably metals such as Pb and Sn are used, which may be mixed with inorganic bases or acid anhydrides. Pb chromate, Ca plumbate, Cu and CuO, and infusorial earth may be used or Pb acetate may be applied to porous earthenware.

708. ———. [Synthesis Catalyst.] Swiss Patent 125,468, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 150.

See United States Patent 1,746,464 (abs. **703**).

709. Fischer, F., Koch, H., and Gilfert, W. (Studien- und Verwertungs-G. m. b. H.). [Process for the Conversion of High-Boiling Hydrocarbons into Lower-Boiling Hydrocarbons.] German Patent Appl. St 63,927, filed Mar. 8, 1944 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 248–253; TOM Reel 100.

As catalyst for the cracking-hydrogenation process, use is made of a mixture of H_2O-free $AlCl_3$ and H_2O-free HCl in the vol. proportions of 1 $AlCl_3$ to 0.5 or more of HCl. The process is carried out at <200° (preferably at 100° or below) and under a partial pressure of H_2 of at least 50 atm. Example: 25 gm. of a synthesis product from CO and H_2 b. 200°–450° and free from olefins were treated in a glass lined autoclave with 17 gm. $AlCl_3$ and 31 gm. HCl under a H_2 pressure at 50° and 200 atm. After a 2-hr. treatment and separation of the mixture, the hydrocarbon had the following composition, in wt. %: 38% isobutane, 21% isopentane, 19% isohexane, 11% isoheptane, 4% isooctane, 7% isononane and higher boiling isoparaffins. Gives other examples.

710. Fischer, F., Pichler, H., and Buffleb, H. (Studien- und Verwertungs-G. m. b. H.). [Process for Producing Formic Acid From Carbon Monoxide and Water.] German Patent Appl. St 61,649, filed Mar. 14, 1942 (*Cl. IV d–12 o*). TOM Reel 100.

Process for the production of formic acid from CO or CO-containing gases and H_2O in the liquid phase. at high pressures, preferably > 1,000 atm. and at temperatures not over 200°, in presence of a catalyst consisting of 1–10 *N* H_2SO_4, preferably about 5*N*.

711. Fischer, F., Pichler, H., and Ziesecke, K. (Studien- und Verwertungs-G. m. b. H.). [Process for the Catalytic Production of Hydrocarbons.] German Patent Appl. St 62,438, filed Nov. 5, 1942 (*Cl 12 o–1.03*). TOM Reel 100.

The method for producing branched hydrocarbons from CO and H_2 using ThO_2 as the catalyst has been improved by substituting pressures preferably > 100 atm. (200–500 atm.) and 350°–450°. Under these conditions liquid, branched, aliphatic, and cyclic hydrocarbons are produced almost entirely. For the production of an active catalyst, basic $Th(CO_3)_2$ is precipitated from a dilute $Th(NO_3)_4$ solution with soda and the precipitate thoroughly washed free from alkali with boiling H_2O and dried at 300° in a stream of air. Addition to German Patent Appl. St 61,125 (abs. **3685**).

712. ——— (Studien- und Verwertungs-G. m. b. H.). [Process for the Production of Antiknock Hydrocarbons.] German Patent Appl. St 62,589, filed Dec. 14, 1942 (*Cl. IV d–12 o*). TOM Reel 100; TOM Reel 134, item IV–4, 4 pp.

In producing branched aliphatic hydrocarbons from CO and H_2, German Patent Appl. St 62,438 (abs. **711**), with a ThO_2 catalyst, the Th can be replaced wholly or in part by other oxides from the 3d to the 6th group; for example, the oxides of Al, W, Zr, or the rare earths. At 200–500 atm. and > 350° these catalysts will produce branched aliphatic hydrocarbons and at still higher temperatures, cyclic hydrocarbons. The activity of the catalyst is increased by adding a small amount of ZnO (Al_2O_3: ZnO=4 : 1). By passing synthesis gas at the rate of 400 l. per l. of catalyst per hr. at 300 atm. and 410°, a yield of 100 gm. per N $m.^3$ of inert-free gas of gasol and liquid hydrocarbons is obtained. These liquid products consist almost entirely of branched, aliphatic hydrocarbons, 80% of which are isobutane and isobutene.

713. Fischer, G., and Biederbeck, H. (Ruhrchemie A. G.). [Removal of Carbon Dioxide From Technical Gases.] German Patent 699,843, Nov. 7, 1940 (*Cl. 26 d–8.02*). Chem. Abs., vol. 35, 1941, p. 7157.

CO_2 is absorbed by slightly moistened (10–20% moisture) solid $Ca(OH)_2$. The absorbent 0.5–1 cm. in size, is packed in a tower through which the gases are passed. To purify 1,000 $m.^3$ per hr. of a gas containing 3% CO_2, a capacity of 20 $m.^3$ is required, as compared with 45 $m.^3$ required by the ordinary method.

714. Fischer, H. G. M., and Welty, A. B., Jr. (Standard Oil Development Co.). Gasification of Carbonaceous Materials. United States Patent 2,618,544, Nov. 18, 1952; appl. filed June 29, 1951, Serial No. 234,412; 7 claims (*Cl. 48–206*).

Temperature in a conversion zone such as a water gas generator is maintained by withdrawing a portion of the carbonaceous material from the generator, burning a portion of that withdrawn under conditions to produce the maximum amount of CO_2, and recycling the heated remainder to the generation zone. In burning to CO_2, 3 times as much heat is generated than when burning to CO. This minimizes the amount of C and air required to generate a given amount of useful heat.

Fischer, K. *See* abs. **3922.**

715. Fleming, H. W. (Phillips Petroleum Co.). Separation of Oxygen-Containing Chemical Compounds. United States Patent 2,586,928, Feb. 26, 1952; appl. filed Jan. 4, 1949, Serial No. 69,233; 11 claims (*Cl. 260–488*).

Presents method for separating the close-boiling, difficultly separable mixtures of organic compounds containing aldehydes, ketones, esters, and alcohols obtained by the hydrogenation of CO. A typical mixture contains *n*-butyraldehyde, methyl ethyl ketone, ethyl acetate, ethyl alcohol, and H_2O. To accomplish the separation formic acid is added to the mixture in an amount stoichiometrically equivalent to the alcohol and acetate content, the alcohol and acetate being converted to the corresponding formate with the resultant formation of H_2O and acetic acid. A small amount of H_2SO_4 is added to catalyze the reaction. The products have the following boiling points: ethyl formate 54.3°, butyraldehyde–H_2O azeotrope 68°, methyl-ethyl ketone–H_2O azeotrope 73.45°, H_2O 100°, and acetic acid 118.1°. This mixture can be separated easily by a simple distillation.

716. ——— (Phillips Petroleum Co.). Solvent Extraction of Oxygenated Organic Compounds. United States Patent 2,580,750, Jan. 1, 1952; appl. filed May 8, 1949, Serial No. 92,192; 6 claims (*Cl. 260–450*).

Describes a process for recovering the organic acids, alcohols, aldehydes, and ketones from the normally liquid hydrocarbon mixture obtained by the catalytic hydrogenation of CO in the presence of an Fe catalyst. The organic acids are 1st removed by washing with NaOH. Then ethylene glycol is added to the acid-free mixture in a volumetric ratio of 0.5 : 1–1.5 : 1 at <100° to selectively extract the alcohols and aldehydes from the hydrocarbon phase. The extracted aldehydes react with ethylene glycol to form acetals and the alcohols are separated by simple distillation. The acetals are then hydrolyzed by addition of H_2O in a volumetric ratio of H_2O : alcohol-free extract 0.5 : 1–1 : 1 and by heating to 100°–150°. The acetals are thus resolved to re-form the aldehydes, which are recovered by distillation. The raffinate is then extracted in a 2d step with ethylene glycol in a ratio of 1 : 1–4 : 1 to separate the ketones, which are recovered by distillation.

717. Fleming, H. W., and Cromeans, J. S. (Phillips Petroleum Co.). Separation of Oxygenated Organic Compounds. United States Patent 2,586,929, Feb. 26, 1952; appl. filed Apr. 18, 1949, Serial No. 88,092; 3 claims (*Cl. 260–488*).

Method is provided for resolving difficulty separable oxygenated compounds resulting from the catalytic hydrogenation of a C oxide, specifically a mixture of EtOH, methyl–*n*–propyl ketone, and H_2O. The separation is effected by adding enough formic or acetic acid or a mixture thereof to esterify at least part of the EtOH to the corresponding ester. A trace of mineral acid (4 drops of concentrated H_2SO_4 in 200 ml. of the mixture) is added to catalyze the esterification reaction. The ester is then removed by distillation or other suitable means in the form of either the ester alone or an azeotrope of the ester, EtOH, and H_2O.

718. Fleming, H. W., and Friedman, A. H. (Phillips Petroleum Co.). Treatment of Synthetic Gasoline. United States Patent 2,615,036, Oct. 21, 1952; appl. filed Feb. 16, 1948, Serial No. 8674; 5 claims (*Cl. 260–450*).

Synthetic gasoline produced by the Fischer-Tropsch process and b. 37°–205° may be improved in octane rating by separating a 1st fraction containing oxygenated organic compounds and b. >90°–95° and a 2d fraction containing oxygenated organic compounds and b. <90°–95°. The 1st fraction is treated within the temperature range 316°–427° with bauxite to effect removal of the chemically combined O at 0–200 p. s. i. and a space velocity 1–10 liquid volume of catalyst per hr. and then mixing the 1st and 2d fractions. The gasoline thus produced is stable, colorless, and of 70–75 ASTM clear and 80–90 Research clear octane ratings. The original untreated gasoline was unstable and had an ASTM clear octane rating of 55–65.

719. Fohlen, J. L. [Liquid Hydrocarbons by Synthesis.] French Patent 33,568, Apr. 27, 1927. Chem. Zentralb., 1929, I, p. 2468.

Process of the main patent can also be applied to the production of alloys and in electrometallurgy, also, gases such as H_2S, NH_3, HCl can be injected. Addition to French Patent 631,927 (abs. **720**).

720. ———. [Manufacture of Liquid Hydrocarbons From Water Gas.] French Patent 631,927, Apr. 14, 1927. British Chem. Abs., 1930, B, p. 406.

Liquid hydrocarbons are obtained when H or water gas, steam, and CH_4 or ethane are injected into a blast furnace and the exit gases are led over a Ni, Co, or Pt catalyst at 100°–450° C., preferably under pressure. With a Zn oxide catalyst alcohols are obtained; with Al chloride, polymerized products.

721. ———. [Synthetic Fuels.] French Patent 37,076, Dec. 23, 1927. Chem. Abs., vol. 25, 1931, p. 1060.

Carbonaceous materials used for reduction of an ore and manufacture of synthetic liquid fuels are present in higher % than in a simple metallurgical operation. The yield in liquid fuels is increased by using a speed for ascending gases higher than the speed of the descending solids.

See French Patent 631,927 (abs. **720**).

722. ———. [Synthetic Organic Compounds.] French Patent 680,585, Dec. 27, 1928. Chem. Abs., vol. 24, 1930, p. 3799.

Pure metals and synthetic organic compounds are prepared by the pyrogenic decomposition of metal carbonyls in the presence of gases such as H_2, water gas, and gaseous hydrocarbons, or a mixture of these with or without free CO.

Food Machinery & Chemical Corp. *See* abs. **205, 3883.**

723. Ford, T. A. (E. I. du Pont de Nemours & Co.). Hydrogenation of Carboxylic Acids to Alcohols. United States Patent 2,607,807, Aug. 19, 1952. Chem. Abs., vol. 47, 1953, p. 4895.

Describes process for preparation of alcohols in good yields by liquid-phase hydrogenation of unsubstituted carboxylic acids in the presence of a Ru hydrogenation catalyst at relatively low temperatures. Thus AcOH 120 and RuO_2 1.8 gm. were charged into a shaker tube, and the mixture was shaken 10 hr. at 147°–170° under 700–950 atm. of H_2. Distillation of the reaction mixture produced EtOH as its aqueous azeotrope; 88% conversion of AcOH to EtOH was accomplished. In general, the pressures used may vary 500–1,500 atm.; the preferred temperature range is 120°–200°. Any Ru-containing catalyst may be employed, and any unsubstituted aliphatic mono- or di-carboxylic acid may be converted to the corresponding alcohol.

724. Franceway, J. A. (Standard Oil Development Co.). Restoring the Activity of Hydrogenation Catalysts. United States Patent 1,904,218, Apr. 18, 1933. Chem. Abs., vol. 27, 1933, p. 3320.

For reactivation of catalysts used in the hydrogenation of carbonaceous materials with free H_2 under a pressure $>$ 20 atm., the bulk of the carbonaceous material is removed from the catalyst and the surface of the catalyst is etched (suitably with a mixture of steam and NH_3).

725. Françon, J. (Distillers Co., Ltd.). Formaldehyde. British Patent 517,740, Feb. 7, 1940. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 229. Chem. Abs., vol. 35, 1941, p. 6982.

Manufacture of CH_2O from CO and H_2 is carried out by the joint action of heat and a catalyst prepared from Ni as pure as possible to which is added a small proportion (up to 5% of the catalyst) of activators formed by Zn, Pb, Mn, Mg, Fe, and Si.

726. ———. (Société industrielle des carburants et solvants). Hydrogenation Catalysts. United States Patent 2,132,613, Oct. 11, 1938. Chem. Abs., vol. 33, 1939, p. 332.

A process for depositing catalytic metals, such as Ni, on metallic supports, such as Ni, Fe or Cr, comprises heating the supports to $>$ 100° and leading a gaseous organometallic compound, such as $Ni(CO)_4$, over the heated supports so as to cause decomposition of the organometallic compound at the surface of the heated supports and precipitation of metal from the compound upon the supports.

727. ———. Manufacture of Formaldehyde. British Patent 450,449, Jan. 5, 1935. British Chem. Abs., 1936, B, p. 973.

A Ni catalyst on a metal support is used in presence of a promoter (1–5% of Ag, V, Co, Cd, or Cu), preferably at 180°–225°, the lower temperature being employed for mixtures rich in H_2. For purification the gas mixture may be passed successively over Fe, Cu, Ni, and metallized (Cu) porous C. The catalyst may be regenerated at intervals by a reverse current of N_2 or steam, or steam may be added to the gas mixture. The metal support is preferably Ni, Cr, or Al.

728. ———. Manufacture of Formaldehyde. United States Patent 2,111,469, Mar. 15, 1938; appl. filed Dec. 31, 1935, Serial No. 57,063, in Great Britain Jan. 5, 1935; 10 claims (*Cl. 260–138*). Chem. Abs., vol. 32, 1937, p. 3773.

In producing HCHO from CO and H_2 these gases, after treatment for removal of catalyst poisons, are passed at 180°–225° C. over Ni particles deposited on a metal support and aided by a metal promoter.

729. Françon, J., and Distillers Co., Ltd. Catalysts. British Patent 519,874, Apr. 9, 1940; appl. filed Aug. 3, 1938, Serial No. 22,980, and July 11, 1939, Serial No. 20,214. Chem. Abs., vol. 36, 1942, p. 632.

Catalytic Ni-containing materials for hydrogenating and dehydrogenating reactions and especially for the synthesis of CH_2O from CO and H_2 are produced by converting pure Ni or Ni hydrate into basic Ni nitrate by the action of HNO_3 at a temperature below 40°, converting the nitrate into Ni hydrate, reducing the Ni hydrate to Ni and incorporating into the latter 1 or more of the activators Co, Cu, Ag, Zn, Pb, Mn, Mg, Fe, or Si.

730. Frankenberg, W. G. (Hydrocarbon Research, Inc.). Catalytic Reduction of Carbon Oxide by Hydrogen. United States Patent 2,507,510, May 16, 1950; appl. filed Apr. 30, 1947, Serial No. 745,116; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 7046.

Liquid hydrocarbons boiling in the gasoline range are produced from CO and H_2 with Ti boride as fluidized catalyst, temperature 260°–399° F. The catalyst may be used in an unsupported state or on conventional carriers. Borides of V, Cr, Mn, Zr, Cb, Mo, Ma, Hf, Ta, W, Re, Th, Pa, and U may be used. 1 literature ref., 1 foreign patent, and 3 United States patents cited.

731. ——— (Hydrocarbon Research, Inc.). Catalytic Reduction of Carbon Oide by Hydrogen. United States Patent 2,531,420, Nov. 28, 1950; appl. filed Apr. 30, 1947, Serial No. 745,117; 4 claims (*Cl. 260–449*). Chem. Abs., vol. 45, 1951, p. 1326.

Nitrides of elements from Groups IV–A, V–A, VI–A, and VII–A, such as Ti, V, Cr, Mn, Zr, Cb, Mo, Ma, Hf, Ta, W, Re, Th, Pa, and U, are active as Fischer-Tropsch catalysts. Formation of normally liquid hydrocarbons is favored over formation of gaseous hydrocarbons. CO_2 production is usually moderate. The catalysts may be used individually or in combination with each other or with known catalysts and activators. Optimum temperature and pressure conditions are specific for each catalyst but lie in the ranges 400°–70° F. and atmospheric —500 p. s. i. Apparatus design may follow typical known processing equipment. 1 literature ref., 2 foreign patents, and 3 United States patents cited.

732. ——— (Hydrocarbon Research, Inc.). Catalytic Reduction of Carbon Oxide by Hydrogen. United

States Patent 2,539,414, Jan. 30, 1951; appl. filed Apr. 30, 1947, Serial No. 745,115; 1 claim (*Cl. 260–449*).

CO and H_2 are contacted with a carbide of an element from Groups IV–A, V–A, VI–A, and VII–A. The carbide may be combined with typical Fe and Co catalysts. For example W carbide in combination with a typical Fe catalyst may be prepared by dissolving W carbide in molten Fe, pulverizing the resulting product. The technique of cemented carbide formation may be used. Pure W carbide, with or without promoter, may be used. Temperature 400°–700° F. and pressure atmospheric up to 500 p. s. i. are used. 1 literature ref, 3 foreign patents, and 3 United States patents cited.

733. FRANKENBURG, W. G., AND LAYING, E. T. (Hydrocarbon Research, Inc.). Hydrocarbon Synthesis. United States Patent 2,600,399, June 17, 1952; appl. filed July 11, 1947, Serial No. 760,498; 12 claims (*Cl. 260–449.6*). Chem. Abs., vol. 46, 1952, p. 8352.

Synthesis of hydrocarbons and oxygenated hydrocarbons by the reaction of H_2, CO, and CO_2 in the presence of an Fe synthesis catalyst at about 500°–750° F. and superatmospheric pressure with the consumption of at least 80% of the CO supplied to form the desired products is improved by use of a reactant gas containing >about 15 mole % CO and <about 2 mole % H_2O, based on the total moles of CO, H_2, and CO_2 present. The flow of gas is in conformance with the equation: $\log_e(K+50)=-0.1548A-0.1075G-0.001512T+\log_e 279.8$, where K is <15, A is the ratio of moles H to moles CO in the feed gas, G is the ratio of moles CO_2 to moles CO in the feed gas, and T is the absolute temperature in °K. By this process the production of CO_2 is limited to <15%, and CO_2 can even be consumed in the reaction.

See also British Patent 671,652 (abs. **734.**).

734. ——— (Hydrocarbon Research, Inc.). Synthesis of Hydrocarbons. British Patent 671,652, 1952. Fuel Abs., 1952, abs. 517; Chem. Abs., vol. 46, 1952, p. 8352.

In the catalytic manufacture of normally liquid hydrocarbons over an Fe catalyst at 500°–750° F. and under elevated pressures, CO_2 formation is controlled so that the CO in the feed is consumed essentially in the formation of desired products.

735. ——— (Hydrocarbon Research, Inc.). Synthesis of Hydrocarbons and Oxygenated Hydrocarbons. United States Patent 2,510,096, June 6, 1950; appl. filed Jan. 11, 1947, Serial No. 721,538; 13 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 9658.

Invention provides a limited range of operation within which the feed gas composition may be adjusted to control net CO_2 production to the desired value. With upper limits of 15% CO and 3%, preferably 1%, H_2O vapor and with lower limits of 15% CO_2 and 2.5 : 1 = H_2 : CO ratio, it is simply necessary to adjust until the specific predetermined conditions are met. In general the conditions thus determined are also favorable to suppressing formation of light hydrocarbon gases such as CH_4. Fluidized Fe catalyst is used. Temperature range is 550°–700° F. and pressure 200–250 p. s. i. 1 literature ref., 1 foreign patent, and 7 United States patents cited.

FRANKENBURGER, W. *See* abs. **2428, 2429.**

736. FRANKENBURGER, W., ZIMMERMANN, W., AND MAYRHOFER, K. (I. G. Farbenindustrie A. G.). [Carrying Out Chemical Reactions in Gases and Vapors.] German Patent 528,740, Feb. 5, 1927; Chem. Abs., vol. 25, 1931, p. 5223.

Gases or vapors are caused to react in a vessel by the aid of a glowing cathode. Examples describe H_2–CO and C_2H_4–H gas reactions. Describes apparatus. Addition to German Patent 458,756.

737. FRANKLIN, R. G. Catalyst. Canadian Patent 280,008, May 8, 1928. Chem. Abs., vol. 22, 1928, p. 2818.

Catalyst for the production of oxygenated organic compounds from CO and H_2 is prepared by causing a soluble Cr compound to react with $ZnCO_3$.

738. ——— (Imperial Chemical Industries, Ltd.). Catalysts for Methanol Production. United States Patent 1,774,432, Aug. 26, 1930; appl. filed Oct. 13, 1927. Chem. Abs., vol. 24, 1930, p. 5045.

In preparing a catalyst for producing MeOH and other oxygenated organic compounds from CO and H_2, a soluble acidic Cr compound such as CrO_3 is caused to react with an excess of a $ZnCO_3$, and the precipitate formed is dried and heated to effect decomposition and reduction of the carbonate.

See also French Patents 642,318 and 672,797 (abs. **1626 and 1625**).

739. ——— (Imperial Chemical Industries, Ltd.). Catalytic Production of Methanol. United States Patent 1,878,390, Sept. 20, 1932. Chem. Abs., vol. 27, 1933, p. 312.

For reactions such as the production of MeOH from CO and H_2, a catalyst is used comprising Zn and Cr oxides (which are prepared from the mixed carbonates by heating).

———. *See* abs. **3358.**

740. FRANKLIN, R. G., AND SYNTHETIC AMMONIA & NITRATES, LTD. Catalysts for Methanol Synthesis. British Patent 293,056, Dec. 23, 1926. Chem. Abs., vol. 23, 1929, p. 1420.

Catalysts suitable for promoting the interaction of CO and H_2 are prepared by heating a mixture of basic Zn and Cr carbonates. Gives several examples.

See British Patent 290,399 (abs. **741**).

741. ———. Synthesis of Methanol. British Patent 290,399, Nov. 15, 1926. Chem. Age., vol. 18, 1928, p. 579; Chem. Abs., vol. 23, 1929, p. 851.

Catalysts for the production of MeOH and other oxygenated organic compounds from CO and H_2 are prepared by heating a mixture comprising $ZnCO_3$ or basic Zn carbonate and a Cr compound such as Zn chromate or basic Zn chromate.

FRANZEN, H. *See* abs. **2082.**

742. FRANZEN, H., AND LUTHER, M. (I. G. Farbenindustrie A. G.) [Organic Acids From Hydrocarbons.] German Patent 489,938, Oct. 29, 1927. Chem. Abs., vol. 24, 1930, p. 2142.

Organic acids are obtained from hydrocarbons, especially paraffins, by saponifying the crude oxidation products of the hydrocarbons and treating with mineral acid. In an example, the crude oxidation product of paraffin is cooked for 3 hr. with excess of NaOH, diluted with hot H_2O, and stirred with mineral acid. Gives another example.

743. FREE, G. (Badische Anilin und Soda-Fabrik). [Sulfonic Acids or Their Salts From Paraffinic Hydrocarbons.] German Patent 804,571, Apr. 26, 1951; appl. filed Apr. 24, 1949 (*Cl. 12 o.*) Chem. Zentralb., 1951, II, p. 1679.

Crude materials such as petroleum, middle oils, or synthetic hydrocarbons are aromatized in the liquid or vaporous state in the presence of catalysts, such as silicates or alumina, capable of being impregnated with metal oxides at about 450°–650°. The reaction products, particularly the middle factions, are sulfonated and neutralized. Detergents are obtained.

See abs. **2336, 2337, 2660, 2661, 2662, 2663.**

744. FREJACQUES, J. L. M. (Cie des produits chimiques et électrométallurgiques). [Methods of Manufactur-

ing Fuels.] German Patent Appl. —, filed Mar. 6, 1939; APC SN 260,214.

Method of manufacturing fuels from CO and H_2 in presence of a catalyst constituted of a mixture of oxides, including at least 1 oxide of the group consisting of Li, Na, K, Rb, and Cs and at least 1 of the group Zn, Cd, Hg, Cr, Mo, W, Mn, and Re, under conditions of pressure, temperature, and rate of flow corresponding to the formation of alcohols and hydrocarbons, which are mostly unsaturated, without substantial formation of MeOH, dehydrating to transform the alcohols into hydrocarbons, separating the liquid hydrocarbons from the gaseous hydrocarbons, and polymerizing the latter into liquid hydrocarbons.

745. FREY, F. E. (Phillips Petroleum Co.). Converting Normally Gaseous Hydrocarbons Into Products of Higher Molecular Weight. United States Patent 2,180,672, Nov. 21, 1939; appl. filed May 16, 1936, Serial No. 80,160 (*Cl. 196–10*). Chem. Abs., vol. 34, 1940, p. 1684.

Decribes arrangement of apparatus and a process which involves passing normally gaseous hydrocarbons such as a mixture high in CH_4 admixed with oxides of C into contact with a catalytic oxide of Al, Th, Zr, or Cr at 150°–350° to produce hydrocarbons of higher molecular weight.

746. FREY, U. [Catalysts for the Synthesis of Hydrocarbons From CO_2 and H_2.] French Patent 958,160, Mar. 3, 1950; appl. filed Dec. 29, 1947. Chem Zentralb., 1951, I, p. 1406.

Catalysts consist of a mixture of 1,000 gm. white P, 100 CaO powder, 100 Cu turnings, 10 MgO, and 3,000 H_2O. A mixture of 90% CO_2 and H_2 is passed through the catalyst, after which the gas mixture leaving the catalyst is heated to 150° and contacted with molten S at 130°. After injection of steam the gas-steam mixture is cooled. The condensed H_2O is separated, and the gas-hydrocarbon mixture partly liquefied in a compressor at 30 atm. Gives diagram.

747. FREYERMUTH, G. H. (Standard Oil Development Co.). Hydrogen From Steam and Hydrocarbons. United States Patent 1,970,695, Aug. 21, 1934; appl. filed Dec. 23, 1929. Chem. Abs., vol. 28, 1934, p. 6256.

Mixture of steam and hydrocarbon vapor or CH_4 is passed at a suitable reaction temperature, which may be about 425°–980°, over a catalytic mass comprising a mixture of Ni with a powdered fused aluminosilicate containing excess alumina and a small amount of an earth oxide, such as CaO.

FRIED, F. *See* abs. **3937.**

748. FRIEDMAN, A. H. (Phillips Petroleum Co.). Distribution for Inlet Gas. United States Patent 2,654,659, Oct. 6, 1953; appl. filed Dec. 18, 1947; Serial No. 792,515; 3 claims (*Cl. 23–288*).

Claim 1. Apparatus for the synthesis of hydrocarbons by contacting synthesis gas mixtures comprising CO and H_2 with a finely divided catalyst, which comprises an upright, elongated reaction chamber closed at its upper end; a reactant material outlet conduit connected to the upper portion of said chamber; heat exchange means positioned within said chamber; a downward and inward tapering, conical distribution chamber attached to and closing the lower end of said reaction chamber; a sole reactant material inlet conduit communicating with the apex of said distribution chamber; a first reticular member positioned between said reaction and distribution chambers for supporting said finely divided catalyst thereabove; a catalyst inlet conduit communicating with the lower portion of said chamber and located above said first reticular member; a second reticular member positioned between said reactant material inlet conduit and said distribution chamber; catalyst inlet means in said chamber above said first reticular member and a fixed mass of granular solid particles inert to the reactants and larger than the openings in said reticular members disposed between said reticular members.

749. ——— (Phillips Petroleum Co.). Method for Replacing Deactivated Hydrocarbon Synthesis Catalyst With Fresh Catalyst. United States Patent 2,573,559, Oct. 30, 1951; appl. filed June 21, 1948, Serial No. 34,177; 6 claims (*Cl. 260–449.6*).

A deactivated fluidized catalyst of the type utilized in the catalytic synthesis of hydrocarbons and of oxygenated compounds and having an average particle size of 40- to 400-mesh is reactivated by introducing a fresh fluidizable catalyst, differing by at least 10-mesh size from the average particle size of the catalyst present, into the reaction zone in suitably measured amounts, so that the catalytic operation is not interfered with, and withdrawing a like portion of deactivated catalyst from the reaction zone at a point below the upper level of the fluidized catalyst bed, then separating the withdrawn catalyst by difference in particle size into fresh and deactivated portions and returning the fresh catalyst to the reaction zone. These steps are continued until the fluidized bed of deactivated catalyst has been substantially replaced by fresh catalyst. The exchange may take 20–48 hr.

750. ——— (Phillips Petroleum Co.). Preparation of Solid Hydrocarbons. United States Patent 2,500,533, Mar. 14, 1950; appl. filed Sept. 6, 1946, Serial No. 695,305; 3 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 4656.

Feed gas 50 vol. % N_2: 16CO: 34H_2 is passed to a reactor or series of reactors containing a catalyst such as metallic Co: ThO_2: kieselguhr=100: 18: 100 parts by weight. Pressure is 100 p. s. i., temperature 200° C., and space velocity 100–200 vol. per vol. catalyst per hr. Wax is produced in high yield. 2 foreign and 2 United States patents cited.

751. ——— (Phillips Petroleum Co.). Process for Reactivating Catalysts. United States Patent 2,540,109, Feb. 6, 1951; appl. filed May 15, 1946, Serial No. 669,793; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 4024.

Catalyst from Fischer-Tropsch synthesis is reactivated by contact with synthesis gas at a space velocity substantially < that for the synthesis reaction and < that at which any substantial yield of hydrocarbons is effected (0–10 vol. synthesis gas per vol. catalyst per hr.). Reaction conditions of temperature and pressure are maintained until the wax is removed. Then the flow rate is increased to the space velocity desired for the reaction. 1 literature ref. and 2 United States patents cited.

752. ——— (Phillips Petroleum Co.). Regeneration of a Carbonized Fischer-Tropsch Catalyst. United States Patent 2,605,234, July 29, 1952; appl. filed Dec. 1, 1947, Serial No. 788,983; 8 claims (*Cl. 252–411*).

Fluidized metallic catalyst, which has been deactivated by surface deposition of C, is regenerated by being suspended in a gas inert to the surface deposited C and there caused to come into contact with itself or with some of the reactivated catalyst at a high velocity, so that the surface is abraded and the surface C removed and carried away in the effluent gas stream. Example: A fluidized Fe catalyst of 100- to 250-mesh, whose activity had declined to only 70% conversion at a space velocity of 1,500 vol. synthesis gas per vol. of catalyst per hr., was treated with H_2 at 300° at a linear velocity of 1 ft. per sec. per 5 hr. When synthesis was resumed in the reactor, the activity of the catalyst had increased to 90% conversion at a space velocity of 2,500 vol. synthesis gas per vol. of catalyst per

hr. and at a substantially lower tempertaure than before.

———. *See* abs. **718, 1079.**

753. FRIEDMAN, A. H., AND MORAN, J. N. (Phillips Petroleum Co.). Catalyst for the Synthesis of Hydrocarbons by Reduction of Carbon Monoxide With Hydrogen and Process of Utilizing Same. United States Patent 2,588,511, Mar. 11, 1952; appl. filed Apr. 11, 1949, Serial No. 86,858; 6 claims (*Cl. 260–449.6*). Chem. Abs., vol. 46, 1952, p. 5295.

Hydrocarbons are synthesized by contacting a synthesis gas comprising CO and H_2 in the ratio of 1.8 : 1–2.2 : 1 with a catalyst consisting essentially of a reduced, ground, fused mixture of Fe oxide in elemental form and a mixed silicate of Al and an alkali or alkaline-earth metal (feldspar) in approximately equal proportions. The preferred reaction conditions comprise 5–20 atm. pressure, 175°–325° temperature, a flow rate of 1,000–30,000 vol. synthesis gas per hr. per vol. of catalyst, and a fluidized state. Comparative yields under similar operating conditions were, for the Fe catalyst, 4.5 cc. of liquid product per hr. plus some C and wax and, for the Fe-feldspar catalyst, 6 cc. of liquid per hr. without C or wax.

754. ——— (Phillips Petroleum Co.). Feldspar–Iron–Alkali Fischer-Tropsch Catalyst and Its Preparation. United States Patent 2,488,530, Nov. 22, 1949; appl. filed Feb. 10, 1947, Serial No. 727,726; 11 claims (*Cl. 252–459*). Chem. Abs., vol. 44, 1950, p. 1672.

Fe oxide is fused with a mixed silicate of Al and an alkali or alkaline earth metal. The fused mixture is ground and reduced, usually with H_2, to convert the Fe oxide substantially to elemental Fe. The bulk density of the Fe catalyst is 1.8 or lower. Example: Fe wire burned in O_2 was mixed with equal weight of feldspar and fused in an oxyhydrogen flame. It was ground to 65- to 100-mesh. The bulk density was 1.8. After reduction 60 cc. of catalyst was reacted with synthesis gas $H_2 : CO = 2 : 1$ at 150 p. s. i. and 320° C., using 2,500 vol. of synthesis gas per vol. catalyst per hr. The yield was 6 cc. liquid product per hr., substantially all in gasoline range. After 54 hr. there was no wax on the catalyst and no C formation. A similar experiment using Fe wire without the feldspar yielded 4.5 cc. liquid product per hr. with some C and wax formation. 4 United States patents cited.

755. FRIEDMAN, L. D., AND HUGHES, W. B. (Cities Service Oil Co.). Refining of Organic Compounds. United States Patent 2,544,308, Mar. 6, 1951; appl. filed July 3, 1946, Serial No. 681,420; 16 claims (*Cl. 260–450*).

Gives process for purification of synthesized alcohols by removal of carbonyl impurities. Adding a carbonyl-condensing agent such as aldehydes or ketones in the presence of a basic condensation catalyst results in conversion of the carbonyl compounds into complexes of higher molecular weight and lower volatility. A highly purified product and valuable hydroxy by-products are recovered. 3 literature refs., 3 foreign patents, and 5 United States patents cited.

FRIEDRICHSEN, W. *See* abs. **2532.**

FROELECKE, E. *See* abs. **3240.**

756. FROELECKE, E., LÜBEN, R., MEYER, K., AND SCHALLER, P. (Ruhrchemie A. G.) [Separation of Thorium From Materials Containing Iron and Thorium.] French Patent 847,409, Oct. 10, 1939; appl. filed Dec. 12, 1938. Chem. Abs., vol. 35, 1941, p. 5084.

To the acid solution of the metals is added an excess of alkali carbonate. The Fe and some of the Th is precipitated. The precipitate is dissolved and reprecipitated. All but about 0.4% of Th is obtained in solution. The Th is then precipitated by boiling with a little NaOH. The first precipitation is at 40°–50°, the second at 80°–90°.

757. ——— (Ruhrchemie A. G.). [Separation of Thorium From Materials Containing Iron and Thorium.] French Patent 847,409, Oct. 10, 1939; appl. R 101,219, R–374, filed Jan. 8, 1938 (*Cl. VI–40 a*). Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 4, chap. 131, 1949, p. 14; Chem. Abs., vol. 35, 1941, p. 5084.

See French Patent 847,409 (abs. **756**).

FUJIMURA, K. *See* abs. **1868.**

758. FUJIMURA, K., AND TSUNEOKA, S. (Kyoto Imperial University). [Manufacture of Gasoline by Reduction of Carbon Monoxide.] Japanese Patent 106,560, June 15, 1934; appl. filed Apr. 5, 1933. U. S. Naval Tech. Mission to Japan, Index No. X–38(N)–7, encl. (D), 1946, p. 247.

Normal-pressure Ni-catalyst: Utilization of impure Ni (Cu <0.5%).

759. FUJITA, K. [Gaseous Hydrocarbons, Mainly Beside Methane, From Reduction of Carbon Monoxide.] Japanese Patent 156,456, May 11, 1943. Chem. Abs., vol. 44, 1950, p. 309.

Over the mixed catalyst of Fe, Cu, Mn, H_3BO_3, and K_2CO_3 (100 : 25 : 2 : 20 : 3), prepared by adding the last 2 to the precipitate from a mixed solution of $Fe(NO_3)_2$, $Cu(NO_3)_2$, and $Mn(NO_3)_2$ with K_2CO_2, was passed, at 300° with space velocity 200, a mixed gas of CO and H_2 (1 : 1) to give CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, C_4H_{10}, C_4H_8 and liquid hydrocarbons mixed in weight ratio 10 : 8.5 : 5.6 : 15.4 : 18.8 : 7 : 11.4 : 23.3.

FUJITA, T. *See* abs. **1869, 1874, 3706, 3707.**

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760. GABRIEL, C. L., AND BROWN, B. K. Methanol. Canadian Patent 271,569, June 14, 1927. Chem. Abs., vol. 21, 1927, p. 3626.

MeOH is produced by passing a gaseous mixture consisting of 1 vol. CO and 5 vol. H_2 over a Cu–Zn alloy catalyst containing some oxides at 280° and at a pressure of about 20 atm.

761. ——— (Commercial Solvents Corp.). Methanol Synthesis. United States Patent 1,875,722, Sept. 6, 1932. Chem. Abs., vol. 27, 1933, p. 103.

Catalyst is used comprising a Cu–Zn alloy in which the Cu predominates, with a surface comprising partly reduced oxides of the alloy.

762. GALLO, S. G. (Standard Oil Development Co.). Alcohol Recovery From Hydrocarbon Oils. United States Patent 2,610,977, Sept. 16, 1952. Chem. Abs., vol. 47, 1953, p. 854.

Oil-soluble aliphatic alcohols containing 8–18 C atoms per mol. are recovered from solution in hydrocarbons by a 2-stage extraction process; this comprises (1) extracting the alcohol solution with an aqueous aliphatic alcohol solvent, such as MeOH, to obtain an extract consisting of the alcohol in the solvent and the hydrocarbon as raffinate; and (2) extracting the 1st extract with a low-boiling hydrocarbon to separate the alcohol from the aqueous solvent. The low-boiling hydrocarbon is finally separated from the alcohol. The process is particularly applicable to the recovery of higher oxygenated compounds from crude oils obtained by the catalytic hydrogenation of CO.

763. GÁLÓCSY, Z., AND KOLLER, K. [Generator Gas.] Hungarian Patent 104,905, Jan. 16, 1933. Chem. Abs., vol. 27, 1933, p. 4060.

Solid, liquid, or gaseous fuels are burned with O_2 or air mixed with O_2. Overheating is prevented by injecting in superheated steam. The mixture of fuel gases and water gas thus produced is led through the ignited column of a generator working with liquid slag so as to form $CO+H_2$.

764. GAMBURG, D. Y. [Iron Catalyst.] Russian Patent 68,429, May 31, 1947. Chem. Abs., vol. 43, 1949, p. 5135.

Molten magnetite, together with activating additions, is cast into sheets. The latter are oxidized with steam and then reduced at a temperature not above 450° by the method of Russian Patent 54,406 (abs. **765**).

765. ———. [Iron Catalyst for Ammonia Synthesis.] Russian Patent 54,406, Jan. 31, 1939. Chem. Abs., vol. 35, 1941, p. 3046.

α–Fe obtained by reduction of magnetite is repeatedly oxidized with steam, and the Fe_2O_3 formed is reduced with H_2 at not above 450° to form crystals not larger than 10^{-5} to 10^{-6} cm.

766. GARBO, P. W. (Hydrocarbon Research, Inc.). Generator of Synthesis Gas. United States Patent 2,520,925, Sept. 5, 1950; appl. filed Jan. 22, 1947, Serial No. 723,547; 11 claims (*Cl. 48–212*). Chem. Abs., vol. 44, 1950, p. 11,069.

Reaction zone of the generator comprises several concentric tubes of porous material, such as ZrO_2, MgO, or alundum, capable of being formed into rigid shapes. The gaseous reactants are fed separately into adjacent sections; the O_2 of high purity (80–95%) is preheated to 600° F. and the hydrocarbon stream at 1,000° F. A pressure difference of 10–40 p. s. i. is maintained while the feed gases pass under 200–300 p. s. i. pressure. The porous barrier may be impregnated with a catalyst, such as NiO, ThO_2, or SrO. To remove C deposition in pores, the feed gases are switched periodically into alternate sections.

767. ——— (Hydrocarbon Research, Inc.). Process and Apparatus for the Synthesis of Hydrocarbons. United States Patent 2,539,415, Jan. 30, 1951; appl. filed Mar. 14, 1947, Serial No. 734,666; 9 claims (*Cl. 260–449.6*).

Fluid catalyst is held in dense phase by recycling gaseous reaction products upward through the contact mass while fresh feed reactants are introduced, preferably above the point of introduction of the recycle stream, through perforated or porous tubes, which extend vertically in the reaction zone. Any required number of inlet conduits may be used. The introduction of the reactant gases and their mixing with the recycle gas flow are instantaneous and uniform throughout the fluidized catalyst mass. Fe, Ni, Co, and Ru, with or without support, may be used. 6 United States patents cited.

768. ——— (Hydrocarbon Research, Inc.). Separating Powdered Catalysts From Exothermically Reactive Gases. United States Patent 2,526,651, Oct. 24, 1950; appl. filed Aug. 2, 1945, Serial No. 608,394; 11 Claims (*Cl. 260–449.6*).

Control of exothermic reaction of gaseous suspension of unreacted vapors and powdered catalyst is achieved by introducing an agent such as NH_3, H_2S, or thiophene, which depresses the activity of the catalyst. In hydrocarbon synthesis NH_3, 5–15% by volume of CO represses the hydrogenation. For example, in synthesizing hydrocarbons using Fe catalyst, 2 or 3 fluidizing reactors, preferably of decreasing capacity, are arranged serially with means for withdrawal of products between reactors. At these withdrawal points there is a preceding separation of entrained catalyst in presence of NH_3. ⅓–⅔ of the CO will be converted in the 1st reactor, the rest in subsequent steps. In oxidation of toluene and naphthalene, lead tetraethyl, Fe pentacarbonyl, and I vapor may be used as repressors; in oxidation of MeOH, Cl- or S-containing compounds; in destructive hydrogenation of mineral oils, steam, or O_2. 1 foreign and 13 United States patents cited.

769. ——— (Hydrocarbon Research, Inc.). Synthesis Gas. United States Patent 2,526,652, Oct. 24, 1950; appl. filed Oct. 2, 1946, Serial No. 700,819; 9 claims (*Cl. 48–212*). Chem. Abs., vol. 45, 1951, p. 1326.

Temperature of a high-temperature reaction, such as the formation of synthesis gas from CH_4 and O_2, is controlled by absorbing the heat of reaction in a granular solid thermophore. The O_2 feed is preheated by contact with the thermophore. The partly cooled thermophore then preheats the less stable CH_4 feed to such a temperature that thermal decomposition is avoided. Thus 1/16-in. SiC pellets are heated to 2,300° F. in a reaction zone. The hot thermophore is passed countercurrent to incoming 98% O_2 introduced at atmospheric temperature at 2,880 cu. ft. per hr. and withdrawn at 2,200° F. The thermophore at 900° F. is brought into contact in a 2d preheating zone with natural gas containing CH_4, 75%, higher hydrocarbons, 13%; and H_2, 10% introduced at atmospheric temperature at 3,900 cu. ft per hr. and discharged at 800° F. The thermophore is withdrawn at 200° F. and is recirculated. The preheated streams are mixed in the reaction zone and form a gas containing N_2, 2%; CH_4, 2%; CO_2, 5%; and the remainder H_2 and CO in the molar ratio of 2:1.

770. ——— (Hydrocarbon Research, Inc.). Synthesis of Hydrocarbons in the Presence of a Fluid-Phase Catalyst. United States Patent 2,576,931, Dec. 4, 1951; appl. filed June 25, 1949, Serial No. 101,403; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 46, 1952, p. 2783.

Vertical cylindrical reactor holding a fluidized catalyst mass is continuously supplied at its lower end with an upflowing stream of synthesis gas in the ratio of $H_2:CO=1.5:1$ to 3.0:1. Operating temperatures are about 600°–650° F. and pressures, 400 p. s. i. The catalyst consists of solid particles varying from 60 to 400-mesh prepared by reducing magnetite and promoted by about 1% Al_2O_3 and 1.5% K_2O. The linear velocity of the gases flowing up through the catalyst is about 0.3–1.5 ft. per sec., or enough to hold the mass in uniform dense fluid phase condition. Catalyst is continuously drawn off from the bottom of the reactor, elevated, and reintroduced into the reaction zone at the pseudoliquid level of the catalyst mass, thereby effecting a continual downward movement of the catalyst in the reaction zone at about 3 ft. per sec. The total recovery of C_3+ hydrocarbons including the minor proportions of oxygenated compounds amounts to 1.51 gal. per 1,000 cu. ft. of synthesis gas, whereas without circultation of the catalyst the total recovery is only 1.32 gal.

771. GARBO, P. W., AND RIBLETT, E. W. (Hydrocarbon Research, Inc.). Stagewise Process for the Hydrogenation of Carbon Monoxide. United States Patent 2,567,932, Sept. 18, 1951; appl. filed Apr. 30, 1948, Serial No. 24,124; 14 claims (*Cl. 260–449.6*).

Synthesis gas containing a particulate Fe catalyst is passed through the 1st reaction zone under about 1,000°–1,250° F. and a short residence time of about 0.1–1 sec., so that substantially all of the CO is converted to CH_2 groups, and then through the 2d larger reaction zone at a temperature about 300° less than before and with a considerably longer reaction time to effect polymerization of the generated CH_2 groups to organic compounds. The catalyst passes through

the 2d reaction zone as a dense fluidized mass and is then withdrawn, separated from the reaction products, and returned to the 1st zone.

772. GARNER, P. J., AND MILLS, S. E. (Shell Development Co.). Olefins. United States Patent 2,642,466, June 16, 1953. Chem. Abs., vol. 47, 1953, p. 8,999.

An improvement in the process for producing olefins by vaporphase thermal cracking is described by which the difficultly vaporizable fraction resulting from a processed paraffin wax is subjected to thermal soaking for 0.25–4 hr. at 390°–460° before reprocessing.

773. GARNER, P. J., GOLDSBROUGH, L. N., AND BUYERS, T. B. (Shell Development Co.) Separation of Straight-Chain Hydrocarbons by Means of Urea Complexes. United States Patent 2,518,677, Aug. 15, 1950; appl. filed May 10, 1949, Serial No. 92,518, in Great Britain July 7, 1948; 16 claims (*Cl 260–676*). Chem. Abs., vol. 45, 1951, p. 3406.

Straight-chain hydrocarbons are separated from admixture with branched-chain and cyclic hydrocarbons by bringing the mixture into contact with an aqueous urea solution to selectively form crystalline molecular complexes of urea with the straight-chain hydrocarbons.

A small amount of wetting agent such as 0.2–0.6 gm. per l. of the urea solution of an alkali-metal alkyl sulfate, for example, Na 2-decyl sulfate and a neutral water-soluble electrolyte (10–60 gm. per l. alkaline-earth, alkali-metal, or ammonium salt) are added to the reaction mixture to promote association of the complex crystals with the aqueous solution and aid in depressing emulsification.

GARRETT, R. C. *See* abs. **3640.**

774. GARRISON, A. D. (Texaco Development Corp.). Method and Apparatus for Gasifying Carbonaceous Material. United States Patent 2,516,974, Aug. 1, 1950; appl. filed Dec. 4, 1946, Serial No. 713,895; 4 claims (*Cl. 48–206*).

Carbonaceous solid fuel is subjected at elevated temperature to the action of H_2O vapor with production of H_2 and CO. The H_2 is diffused through a permeable wall of gasification zone and subjected to combustion in the vicinity of the exterior or effusion surface so as to heat the wall to a high temperature. The heat is transmitted from the diffusion wall to the reactants in the gasification zone to supply part of the heat for the endothermic reaction. The solid fuel may be in a fluidized state. 2 foreign and 4 United States patents cited.

775. ——— (Texaco Development Corp.). Method of Effecting Dissociative Conversion of Organic Compounds. United States Patent 2,516,973, Aug. 1, 1950; appl. filed July 11, 1946, Serial No. 682,908; 6 claims (*Cl. 48–214*).

Natural gas or other hydrocarbon is used for starting material in a process similar to that described in United States Patent 2,516,974 (abs. **774**). The pores in the diffusion barrier have cross-sectional dimension of 1 micron. The synthesis gas has a H_2 : CO ratio approximately 2 : 1. 6 United States patents cited.

776. ——— (Texaco Development Corp.). Preparation of Hydrogen and Carbon Monoxide Gas Mixtures. United States Patent 2,621,117, Dec. 9, 1952; appl. filed Mar. 11, 1947, Serial No. 733,838, 8 claims (*Cl. 48–196*). Chem. Abs., vol. 47, 1953, p. 2964.

Synthesis gas is produced by reaction of carbonaceous reactant with O_2. A stream of the O_2-containing gas is charged to the reaction zone. A stream of carbonaceous reactant is charged to the reaction zone annularly about the O_2 stream to surround the O_2 stream. The carbonaceous material is in sufficient amount to react with all of the O_2 with formation of completely oxidized reaction products. An additional stream of carbonaceous reactant is charged to the reaction zone into intimate contact with reaction products immediately following their formation. These react to form a final product gas. 13 United States patents cited.

777. ——— (Texaco Development Corp.). Process for Preparing Synthesis Gases. United States Patent 2,566,936, Sept. 4, 1951; appl. filed Jan. 4, 1947, Serial No. 720,272; 3 claims (*Cl. 252–373*).

Synthesis gas composed essentially of H_2 and CO in the ratio 2 : 1 is produced from a hydrocarbon gas, such as natural gas and steam, by passing the same over a refractory material, heated previously to about 3,600° F. by the combustion of tail gas from a previous operation, air, steam, and CH_4, whereby it is cracked to gases and C and the latter deposited upon the refractory material. Cracking is continued until the temperature of the refractory is reduced to 3,000°–3,400° F. When the cracked gases are withdrawn, a mixture of steam and hydrocarbon gas is passed over the C on the refractory material at 1,800°–3,000° F. thereby effecting reaction of steam with the C and the hydrocarbon gas with production of H_2 and CO in the molar ratio desired. Diagram.

GÄRTNER, H. *See* abs. **2016.**

GARWOOD, W. E. *See* abs. **3218.**

GAS LIGHT & COKE CO. *See* abs. **912.**

778. GAUCHER, L. P. (The Texas Co.). Catalytic Process for the Synthesis of Hydrocarbons and the Like From Hydrogen and the Oxides of Carbon. United States Patent 2,436,962, Mar. 2, 1948; appl. filed Dec. 6, 1945, Serial No. 633,248, 5 claims (*Cl 2260–449.6*). Chem. Abs., vol. 42, 1948, p. 3932.

This patent is the same as United States Patent 2,436,957 (abs. **588**), except that the recycle gas contains no olefinic hydrocarbons, these having been polymerized and removed. The reactor feed, as before, contains about 1–4 vol. of recycle gas per volume of fresh feed.

779. ——— (The Texas Co.). Conversion of Hydrocarbon Gas Into Carbon Monoxide and Hydrogen. United States Patent 2,483,132, Sept. 27, 1949; appl. filed Feb. 21, 1946, Serial No. 649,291; 15 claims (*Cl. 48–196*). Chem. Abs., vol. 44, 1950, p. 823.

Synthesis gas is prepared by partial combustion of hydrocarbon gas. The O_2 for combustion is divided into 2 streams, and the stream containing 60–75% of the total O_2 is mixed with the hydrocarbon gas, preheated to 1,000°–1,200° F., and led to the furnace, where it meets the minor O_2 stream preheated to 1,600° F. containing 25–40% of the total O_2 required.

780. ——— (The Texas Co.). Production of Carbon Monoxide and Other Gases From Carbonaceous Materials. United States Patent 2,558,746, July 3, 1951; appl. filed Feb. 10, 1948, Serial No. 7,446; 5 claims (*Cl. 48–206*).

Coal, ground to small size, surface dried so that there is no tendency for the powder to agglomerate, but moisture remains in the pore space within the coal particle itself. The coal is fed into the generator into intimate contact with concentrated free O_2. The dry exterior surface of the coal particle reacts violently with the gas, rapidly releasing heat, which in turn heats the interior of the particle so rapidly that it disintegrates or explodes because of the expansion of steam generated in the pores. This further reduces the size of the particles. The resulting powdered coal then reacts with additional O_2 to heat the particle individually to the reaction temperature. Superatmospheric pressure is preferably used. The heated powdered coal and resulting gases produced by oxidation pass directly to an endothermic zone to which preheated steam is supplied, where the reactions for CO

and H_2 production take place. 2 United States patents, 1 foreign patent, and 1 literature ref. cited.

———. *See* abs. **591, 592, 593.**

781. GAUS, W. (I. G. Farbenindustrie A. G.). Motor Fuel. United States Patent 1,775,674, Sept. 16, 1930; appl. filed May 7, 1926, Serial No. 107,464. Chem Abs., vol. 24, 1930, p. 5466.

Gasoline is mixed with not over 12%, by volume, of crude synthetic MeOH, which contains other compounds, such as iso-BuOH.

782. GAUS, W., AND LAPPE, F. (Badsche Anilin- und Soda-Fabrik.). Motor Fuel by Hydrogenation of Carbon Monoxide. United States Patent 1,591,526, July 6, 1926; appl. filed Apr. 29, 1924, Serial No. 709,799. Chem. Abs., vol. 20, 1926, p. 3228.

Liquid product is obtained by the hydrogenation of CO and CO_2 under high pressure by catalysis, and this product, containing a trace of Fe carbonyl, is used directly or after purification as a fuel or ingredient of fuel mixtures.

783. GAUS, W., MITTASCH, A., AND SCHLECHT, L. (I. G. Farbenindustrie A. G.). Metal Carbonyls. United States Patent 1,812,399, June 30, 1931; appl. filed June 29, 1929, Serial No. 374,938; in Germany July 5, 1928. Chem. Abs., vol. 25, 1931, p. 4981.

Metal such as Fe capable of forming a carbonyl, in mixture with an inert liquid such Fe carbonyl, which is a solvent for CO, is acted on with a gas containing CO, the metal and liquid being kept in motion against each other.

784. GAVRILOV, V. S. [Utilization of the Heat of Reaction in the Formation of Ammonia or Methanol.] Russian Patent 44.237, Sept. 30, 1935. Chem. Abs., vol. 32, 1938, p. 3102.

Gases are brought into contact with the catalyst in 2 stages, with preheating before each stage by utilization of the heat of reaction.

785. ———. [Utilization of the Heat of Reaction in the Formation of Ammonia or Methanol.] Russian Patent 44,238, Sept. 30, 1935. Chem. Abs., vol. 32, 1938, p. 2792.

Heat exchange arrangement of the catalyst box of the column used in the synthesis is effected by using liquid Hg for the heat exchange medium. The vapors of Hg are then used as a heating medium in a steam boiler.

786. "GAZOLINA" SPOLKA AKCYJNA. [High-Grade Hydrocarbons From Natural Gas.] Yugoslav Patent 14,031, Mar. 25, 1937. Chem. Zentralb., 1938, II, p. 812.

Natural gas is subjected to the action of a mixture of CO and steam in presence of a catalyst at 700°–1,300° whereby a synthesis gas is obtained consisting mainly of CO and H_2. This synthesis gas is then contacted with a suitable catalyst at a determined temperature and pressure to obtain a desirable end product.

787. GEE, W. P. (Texaco Development Co.). Generation of Synthesis Gas. United States Patent 2,630,378, Mar. 3, 1953; appl. filed July 23, 1949, Serial No. 106,367; 6 claims (*Cl. 48–206*). Chem. Abs., vol. 47, 1953, p. 4065.

Synthesis gas can be obtained from high-boiling liquid hydrocarbons relatively deficient in H. The hydrocarbons are reacted at 1,600°–2,600° F. with high purity free O_2 in a regulated amount substantially below that stoichiometrically necessary to convert the hydrocarbon completely to H_2 and CO. High-boiling hydrocarbons are converted into solid carbonaceous material. The carbonaceous solids are separated and reacted in a separate succeeding step with a mixture of steam and high purity O_2 in relative proportion effective to maintain the reaction zone autogeneously at high temperature. 6 United States patents cited.

See also British Patent 672,165 (abs. **3742**).

GEĬMAN, I. B. *See* abs. **265.**

GEISER, N. *See* abs. **373.**

788. GEISSLER, —. (I. G. Farbenindustrie A. G.). [Process for Obtaining Organic Compounds.] German Patent Appl. I 76,503, OZ 14,523 filed Dec. 21, 1943 (*Cl. IV d–12 o*). TOM Reel 23, item 15, frames 183–185; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 5, chap 150, 1949, p. 18.

In separating organic compounds, such as alcohols, ketones, and the like, from their mixtures with hydrocarbons by treating the mixture in a liquid or dissolved condition with adsorbing substances such as active gels, the adsorbed organic compounds are removed with H_2O or aqueous mixtures instead of with solvents. Example: 12 parts, by weight, of a fraction of a product, b. 180°–230°, obtained by the hydrogenation of CO and containing 40% of alcohols besides hydrocarbons, diluted with double the amount of petroleum ether, and brought into contact with 25 parts, by weight, of a wide-pored silica gel. The gel is washed with petroleum ether to remove the hydrocarbons and shaken well several times with cold H_2O. An oily layer is formed with the H_2O, which when dried contains 3.1 parts, by weight, of a product containly 97% alcohol.

789. GEL'MS, I. E. [Removal of Ceresin From the Catalyst for the Synthesis of Hydrocarbons.] Russian Patent 66,906, Aug. 31, 1946. Chem. Abs., vol. 41, 1947, p. 4634.

The synthesis of hydrocarbons from water gas is hampered by deposition of ceresin on the catalyst, This ceresin is readily removed by passing alkali-containing water gas and synthol alternately over the catalyst. Preferably the synthol is used in quantities sufficient to remove the ceresin only from the lower part of the catalyst.

GEMASSMER, —. *See* abs. **1035.**

GEMASSMER, A. *See* abs. **3907.**

GENERAL ANILINE & FILM CORP. *See* abs. **367.**

GERCHIKOVA, S. Y. *See* abs. **265.**

GERICKE, P. H. *See* abs. **805, 806.**

GERMAN, I. F. *See* abs. **1742.**

790. GESELLSCHAFT, FÜR LINDE'S EISMASCHINEN A. G. [Gaseous Mixture Rich in Hydrogen.] German Patent 699,489, Oct. 31, 1940 (*Cl. 12i–1.01*). Chem. Abs., vol. 35, 1941, p. 7157.

$2H_2+CO$ is generated from CH_4 in a special 2-compartment oven filled with coke. Enough O_2 to effect the conversion and maintain the right temperature (1,300°) is fed through the bottom of the oven. H_2O vapor is added to both the feed gas and the O_2. The 2 compartments operate alternatingly. The oven is provided with a device to tap the slag.

791. ———. [Production of a Gas Containing Carbon Monoxide and Hydrogen for the Fischer-Tropsch Benzine Synthesis.] Belgian Patent 436,077, Apr. 11, 1940; appl. filed Aug. 22, 1939, in Germany Aug. 22, 1938. Chem. Zentralb., 1940, II, p. 1818.

Gas mixture rich in H_2 and CO_2 is cooled in cold exchange with periodical conversion to the dewpoint of CO_2.

792. ———. [Synthesis Gas.] French Patent 863,521, no date. Chem. Zentralb., 1942, I, p. 3287.

Gas mixtures rich in H_2 and CO are cooled periodically to the dewpoint of CO_2.

See Belgian Patent 436,077 (abs. **791**).

———. *See* abs. **1799, 1800.**

793. GESSMANN, W., AND SHALDERS, E. W. Hydrocarbons. Canadian Patent 282,392, Aug. 14, 1928. Chem. Abs., vol. 22, 1928, p. 4128.

Easily boiling hydrocarbons are produced by passing a mixture of unsaturated hydrocarbons and a gas containing carbon oxide and H_2 without applying heat and at normal pressure, over a catalyzer subjected to chemically active light rays. The catalyst consists of a mixture of pure powdered electrolytic Cu, W, and pumice-stone powder treated with a dilute caustic alkaline lye and quickly dried.

794. ———. Synthesis of Low-Boiling-Point Hydrocarbons. British Patent 299,820, June 30, 1927. Schmidt, J., Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 150; Chem. Abs., vol. 23, 1929, p. 3476.

See Canadian Patent 282,392 (abs. **793**).

795. ———. [Volatile Hydrocarbons.] French Patent 636,568, June 25, 1927. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 150; Chem. Abs., vol. 23, 1929, p. 604.

See Canadian Patent 282,392 (abs. **793**).

796. GEWERKSCHAFT AUGUSTE. [Hydrocarbon Synthesis.] Austrian Patent 159,617, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 174.

See French Patent 815,200 (abs. **798**), and United States Patent 2,213,415 (abs. **3351**).

797. ———. Hydrocarbons. British Patent 487,250, June 17, 1938. Chem. Abs., vol. 32, 1938, p. 9095.

In the synthesis of hydrocarbons from CH_4 and CO or CO_2 under high pressure, a mixture of these reactants that would give rise to an endothermic reaction ("fundamental reaction") is modified by replacing part of the CH_4 by a mixture of H_2 or H_2O and CO and/or CO_2 that will form CH_4 exothermically by a so-called "steering reaction." The fundamental reaction and the steering reaction are combined in such ratio that the resulting free energy of the net reaction, calculated according to the method of Lewis and Randall, does not exceed 5,500 gm.-cal. per mol. of the product and may be negative. The molecular proportion of CH_4 to C oxides in the reaction mixture is at least 0.25. Among examples, the fundamental reaction of 17 $CH_4+7\ CO=3\ C_8H_{18}+7\ H_2O$, which is strongly endothermic, is combined with the exothermic reaction $15\ H_2+5\ CO=5\ CH_4+5\ H_2O$, to give a total reaction of $4\ CH_4+4\ CO+5\ H_2=C_8H_{18}+4\ H_2O$, with a free energy of −849 cal. per mol.; a mixture of H_2, 38%; CO, 31%; and CH_4, 31% is forced at 1,000 cu. m. per hr. through a contact tube filled with Fe–Mo catalyst at 850 atm. and 250°; the product is 315 kg. of hydrocarbons, mainly C_8H_{18}, per hr.

798. ———. [Hydrocarbons.] French Patent 815,200 July 7, 1937. Chem. Abs., vol. 32, 1938, p. 1276.

Hydrocarbons are prepared by passing a mixture of H_2, CO, and CH_4 through a Fe-Mo contact tube under high pressure and temperature. Thus, a mixture containing H_2, 38%; CO, 31%; and CH_4 31% yields C_8H_{18} and H_2O. Gives other examples.

See abs. **3351**.

799. GEWERKSCHAFT MATHIAS STINNES. [Motor Fuels.] French Patent 838,841, Mar. 16, 1939. Chem. Abs., vol. 33, 1939, p. 7079.

Properties of gas oils for use as motor fuels are improved by mixing with oils poorer in H, the predominant nature of which is unsaturated or aromatic, with a H content below 12%, particularly of about 7–9%. The added oils may be those obtained by hydrogenating coal or extraction products from coal under pressure, with or without catalysts.

800. GEWERKSCHAFT VICTOR, STICKSTOFFWERKE. [Apparatus for Synthesizing Benzine From Carbon Monoxide and Water by the Contact Process.] German Patent 681,979, Oct. 5, 1939; appl. G 91,506, filed Nov. 8, 1935 (*Cl. 12 o–1.03*). FIAT Reel AA 88, frames 3,418–3,420; PB 70,273; Chem. Abs., vol. 36, 1942, p. 2393.

Tubes that carry the cooling agent are of greater diameter at the point where the gases enter the synthesis reactor than in the remainder of the reactor.

801. ———. [Working Up Kogasin.] German Patent Appl. G 92,034, no date (*Cl. 12 o–1.01*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 64.

Fischer-Tropsch Kogasin is treated by taking a medium-boiling fraction (150°–250°) and cracking it in the vapor phase. The cracked products are condensed in the presence of Friedel-Crafts catalysts and freed by distillation of the lower boiling fractions.

———. *See* abs. **211**.

GIBSON, J. W. *See* abs. **283**.

GIBSON, R. O. *See* abs. **645**.

GICAUDAN CORP. *See* abs. **1796**.

802. GIESEN, J., HANISCH, H., AND DALLY, M. (I. G. Farbenindustrie A. G.). Purifying Alcohols. German Patent 671,261, Feb. 6, 1939 (*Cl. 12 o–5.02*). Chem. Abs., vol. 33, 1939, p. 3391.

See United States Patent 2,099,475 (abs. **804**).

803. ——— (I. G. Farbenindustrie A. G.). Purifying Methanol. United States Patent 2,115,553, Apr. 26, 1938. Chem. Abs., vol. 32, 1938, p. 4610.

Crude product obtained by catalytic hydrogenation of C oxides under pressure is mixed with H_2O and centrifuged to separate the mixture into an upper oily layer containing the separable impurities and a lower MeOH–H_2O layer.

804. ——— (I. G. Farbenindustrie A. G.). Purifying Synthetically Produced Alcohols. United States Patent 2,099,475, Nov. 16, 1937. Chem. Abs., vol. 32, 1938, p. 191.

In the purification of crude anhydrous alcohols separated from the mixture of alcohols obtained by the catalytic hydrogenation of C oxides, and alcohol of lower boiling point, such as MeOH, is added to the crude alcohol, and the resulting mixture is subjected to fractional distillation.

805. GIESEN, J., HANISCH, H., AND GERICKE, P. H. (I. G. Farbenindustrie A. G.). [Purification of Methanol.] German Patent 720,733, Apr. 9, 1942 (*Cl. 12 o–5.01*). Chem. Abs., vol. 37, 1943, p. 2392.

Synthetic MeOH is purified by distillation in the presence of slight amounts of chromic acid. The latter is fed into approximately the middle of the column in such quantities that the H_2O collecting at the bottom of the column is nearly neutral.

See also British Patent 500,745 (abs. **1337**) and United States Patent 2,242,463 (abs. **806**).

806. ——— (W. E. Currie). Purification of Synthetic Methanol. United States Patent 2,242,463, May 20, 1941; appl. filed Aug. 23, 1938, Serial No. 226,256, in Germany Sept. 10, 1937; 2 claims (*Cl. 202–57*). Chem. Abs., vol. 35, 1941, p. 5518.

Synthetic MeOH obtained by the catalytic hydrogenation of CO_2 can be purified by distillation under pressure, using chromic acid as a counter-current wash liquid, withdrawing this from the bottom of the column while the deodorized MeOH escapes from the top of the column.

GILBERT, W. I. *See* abs. **2389**.

807. GILBERT, W. I., AND MONTGOMERY, C. W. (Gulf Research & Development Co.). Synthesizing Hydrocarbons. United States Patent 2,579,663, Dec. 25, 1951; appl. filed Dec. 15, 1948, Serial No. 65,527; 5 claims (*Cl. 260–449.6*).

Normally, liquid hydrocarbons are produced by contacting a mixture of CO and steam, in a mol. ratio of CO : steam=1 : 1 to 2 : 1, with a catalyst consisting of Fe about 50–100% reduced from the oxide and of Co about 40–80% reduced from the oxide at 100–600 p. s. i. and 500°–600° F.

GILFERT, W. *See* abs. **709.**

808. GILLER, F., AND WINKLER, F. (I. G. Farbenindustrie A. G.). [Desulfurizing Water Gas.] German Patent 701,758, Dec. 19, 1940 (*Cl. 26 d–13.10*). Chem. Abs., vol. 35, 1941, p. 8263.

Organically bound S is removed from water gas by passing the latter through activated C impregnated with oxidizing agents. The activated C is prepared according to German Patent 463,772 (abs. **3946**). Suitable oxidizing agents are: Nitrates, chromates, dichromates, manganates, persulfates, and perborates.

809. ——— (I. G. Farbenindustrie A. G.). [Removing Organically Bound Sulfur From Water Gas.] German Patent 702,605, Jan. 16, 1941 (*Cl. 22 d–13.10*). Chem. Abs., vol. 35, 1941, p. 8263.

Describes change in procedure whereby the gas to be desulfurized is mixed with oxidants, for example, Cl, H_2O_2, O_3, and the mixture passed through activated C. The latter is not necessarily impregnated with oxidants as required in German Patent 701,758 (abs. **808**). In the case, for example, the gas is mixed with Cl and the activated C is saturated with Na_2CO_3. Also the gas to be purified can be mixed with NO or NH_3, and, in this case, it is advisable to add a base to the activated C.

810. GILLESPIE, B. G. (Standard Oil Development Co.). Carbon-containing Fischer-Tropsch Catalyst and Its Preparation. United States Patent 2,608,535, Aug. 26, 1952; appl. filed May 9, 1947, Serial No. 747,125, divided, and this appl. Mar. 26, 1948, Serial No. 17,380; 9 claims (*Cl. 252–447*). Chem. Abs., vol. 47, 1953, p. 8995.

Improved Fe catalyst, which has a reduced tendency toward C formation and a shorter activation period, is obtained by sintering red Fe oxide in a reducing atmosphere and by incorporating into the catalyst before sintering about 2–10%, by weight, of the Fe of powdered activated C. About 10 wt. % of an alkali-metal compound may be added as promoter.

811. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,552,422, May 8, 1951; appl. filed May 9, 1947, Serial No. 747,125; 4 claims (*Cl. 260–449.6*).

Catalyst for the CO–H_2 reaction is prepared by combining Fe oxide with finely divided C and an alkali-metal promoter, subjecting the resulting composite to sintering in a reducing atmosphere, and then grinding the sintered material to a fluidizable particle size. The sintering reduces the tendency toward C formation and disintegration but also partly inactivates the catalyst so that it must be subjected to a long activation treatment at synthesis conditions before it reaches a degree of activity useful for practical operation. Addition of the C is found to reduce the time needed for the activation treatment. 7 United States patents and 1 foreign patent cited.

812. ——— (Standard Oil Development Co.). Method for Forming Synthesis Gas. United States Patent 2,496,342, Feb. 7, 1950; appl. filed Sept. 7, 1945, Serial No. 615,083; 2 claims (*Cl. 252–373*). Chem. Abs., vol. 44, 1950, p. 3702.

Cu on activated C is used as catalyst in reacting CH_4 or gas containing it with CO_2. The catalyst is prepared by placing activated C (4-mesh) in a vessel fitted with means for introducing liquid and a connection with a vacuum pump. The C is heated to 300°–600° F. for several hr. under vacuum. The C is cooled to 200° F., or lower still, under vacuum. Enough hot, saturated Cu nitrate solution is added to immerse the C. Air is admitted, and the C is kept immersed for 1 hr. It is then removed, drained, and heated slowly to 400° C. to drive off nitrous fumes. When the last of the nitrate has been decomposed, the residual nitrous fumes are displaced by air or N_2 to avoid formation of explosive mixtures of H_2 and N oxides. H_2 is passed in to reduce the Cu oxide at 400° C. The catalyst has a bulk density about 0.52 gm. per ml. and contains 10–15 wt. % of Cu. The Cu is in finely divided state. 1 foreign and 5 United States patents cited.

813. ——— (Standard Oil Development Co.). Red-Iron Oxide Type Fluid Catalyst for Hydrocarbon Synthesis. United States Patent 2,496,343, Feb. 7, 1950; appl. filed June 4, 1946, Serial No. 674,371; 4 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 3702.

Fluidizable Fe catalysts are obtained by subjecting Fe oxides to a sintering treatment and grinding. Reduction may be applied before grinding. Red Fe oxide, preferably less than 30 microns, is best. It may be impregnated with activator such as K carbonate before sintering. Suitable sintering temperature is 1,200°–1,600° F. in a reducing atmosphere but may be considerably higher, 1,600°–2,700° F., in a nonreducing atmosphere. 8 United States patents cited.

GILLILAND, E. R. *See* abs. **2043.**

814. GILLILAND, E. R., MORRELL, C. E., CARLSON, C. S., AND ROBERTSON, N. C. (Standard Oil Development Co.). [Extractive Distillation of Alcohols from Closely Boiling Aqueous Mixtures.] United States Patent 2,551,593, May 8, 1951; appl. filed Jan. 28, 1947, Serial No. 724,840; 13 claims (*Cl. 202–39.5*). Chem. Abs., vol. 46, 1952, p. 521.

Controlled use of H_2O as a reflux medium is the method by which closely boiling oxygenated organic compounds, particularly H_2O-miscible alcohols, are separated. Flowsheets of the apparatus are given, along with tables listing boiling points of various oxygenated compounds and their azeotropes.

GIRDLER CORP. *See* abs. **2754.**

815. GIROD, P. [Treating Petroleum or Its Derivatives and Synthesizing Hydrocarbons.] French Patent 839,061, Mar. 23, 1939. Chem. Abs., vol. 33, 1939, p. 8391.

Processes for cracking crude petroleum, if desired with hydrogenation, so as to obtain lighter products; processes for hydrogenating coal or lignite at high temperature and pressure in presence of a catalyst so as to obtain gaseous, liquid, or solid hydrocarbons; processes for hydrogenating CO, for example, using water gas enriched with H_2 at 200° in presence of a catalyst; and similar processes are accelerated by effecting them in presence of an electric arc of high or low frequency or of a high-tension direct-current arc.

GODDIN, C. S. *See* abs. **610.**

GOEHRE, O. *See* abs. **2336, 2337.**

816. GOETHEL, H., AND TRAMM, H. Lubricating Oils From Conversion Products of the Hydrogenation of Carbon Monoxide. United States Patent 2,172,441, Sept. 12, 1939; appl. filed Aug. 18, 1936, Serial No. 96,594, in Germany Aug. 24, 1935; 6 claims (*Cl. 196–50*). Chem. Abs., vol. 34, 1940, p. 258.

Describes arrangement of apparatus. Hydrocarbon mixtures obtained in the catalytic conversion of mixtures of CO and H_2 and made up of fractions that are liquid at room temperature, boil above 150°, and comprise a substantial portion boiling closely above 150° are cracked to yield unsaturated hydrocarbons. This mixture is polymerized in the presence of a catalyst.

817. GOETHEL, H., SCHALLER, P., AND TRAMM, H. Manufacture of Lubricating Oils. United States Patent 2,199,200, Apr. 30, 1940; appl. filed Oct. 13, 1937, Serial No. 168,794, in Germany Oct. 24, 1936, 5 claims (*Cl. 196–78*). Chem. Abs., vol. 34, 1940, p. 6442.

Lubricating oil is made from a cracked benzine rich in olefins. Synthetic gasolines (Fischer-Tropsch process) are used. Their olefin content may vary widely, but their successively higher boiling fractions must follow a specified density curve closely if a satisfactory lubricant is to be produced. The synthetic gasoline is cracked under conditions that yield such a density curve and then condensed in presence of $AlCl_3$ for 12 hr. at about 160° C.

818. GOHR, E. J. (Standard Oil Development Co.). [Continuous Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen by the Fluidization Process.] French Patent 943,737, Dec. 31, 1946, Mar. 16, 1949, in United States June 25, 1946. Chem. Zentralb., 1950, I, p. 1174.

Catalyst is maintained in the reaction zone through which the gases pass from bottom to top in the form of a lower dense phase and a superimposed dilute phase. By suitably measuring the catalyst volume, care is taken that the degree of conversion of the CO always amounts to more than 95 vol %. The upper boundary line of the denser phase is allowed to rise by adding a further amount of catalyst when the process has been in operation for 500–1,000 hr. The flow velocity of the gases through the fluidized catalyst mass is so chosen that the density of the catalyst amounts to about 2.4 kg. per l. The pressure is kept above normal pressure, and the time of contact is increased whenever the activity of the catalyst slackens.

GOLDSBROUGH, L. N. *See* abs. **773.**

819. GOLDSBY, A. R. (The Texas Co.). High-Antiknock Motor-Fuel Hydrocarbons. United States Patent 2,257,074, Sept. 23, 1941; appl. filed July 8, 1939, Serial No. 283,429; 4 claims (*Cl. 196–10*). Chem. Abs., vol. 36, 1942, p. 647.

Describes arrangement of apparatus and a process that involves catalytically converting a mixture of CO and H_2 to a synthetic hydrocarbon mixture composed mainly of hydrocarbons having from 1 to about 10 C atoms per molecule, composed largely of normal olefins including normal butylenes, and being comparatively free from aromatic and naphthenic constituents, separating from this synthetic mixture gasoline hydrocarbons boiling up to about 390° F., having a relatively high content of normal butylenes and a relatively low content of isobutylene, and treating these gasoline hydrocarbons with a paraffin hydrocarbon fraction comprising isobutane in the presence of concentrated H_2SO_4 in the substantial absence of isobutylene and aromatic hydrocarbons, whereby isobutane is alkylated to produce normally liquid saturated hydrocarbons having a high antiknock value and boiling within the range for motor fuel.

820. ——— (The Texas Co.). Manufacture of High-Antiknock Motor Fuel Hydrocarbons by Catalytic Conversion of Carbon Monoxide and Hydrogen. United States Patent Reissue 22,205, Oct. 20, 1942; appl. filed Apr. 14, 1942. Chem. Abs., vol. 37, 1943, p. 1849.

Reissue of original United States Patent 2,257,074 (abs. **819**).

821. ——— (Texaco Development Corp.). Method of Manufacturing High Antiknock Synthesis Gasoline. United States Patent 2,461,153, Feb. 8, 1949; appl. filed Apr. 14, 1945, Serial No. 588,309; 8 claims (*Cl. 260–450*).

Gives a process for obtaining high antiknock gasoline by combination of hydrocarbon synthesis, alkylation, isomerization, and catalytic conversion. In the example, the hydrocarbon synthesis products are fractionated to the following % by vol.: 8% C_4 hydrocarbons; 25% C_5–C_7 light naphtha, 35% C_8, 400° F. end point heavy naphtha, 20% diesel fuel, and paraffin wax. One vol. of light naphtha is contacted at 25° F. with 10 vol. 90% H_2SO_4 (H_2O content 2%) for 2 min., 97% of the olefins are removed. The acid-olefin extract is alkylated with isobutane in a molar ratio of 5 : 1 of the equivalent olefin content, at 50° F., acid to hydrocarbon ratio in the reactor 1 : 1, contact time 20 min. Aviation alkylate of 350° F. end point, octane 84 is produced in yield 80% by vol. on basis of naphtha charged or 190% by weight of equivalent olefin content converted to C_4. The remaining paraffin raffinate is treated with 98% H_2SO_4 at 60° F. in proportion of 10 lb. acid per bbl. paraffin raffinate of zero bromine number. This is isomerized in presence of fortified Al chloride-kerosine complex having a heat of hydrolysis of 340 cal. per gm., and with 2% HCl on the weight of the raffinate, 1 vol. of mixed butanes per vol. of raffinate, temperature 235° F. 9% by weight of isobutane to the raffinate charge is produced with 88% of a 110°–297° F. gasoline isomate, octane 73. The heavy naphtha is hydroformed with Mo oxide-alumina catalyst using recycle gas (70% H_2) at rate of 2,300 cu. ft. per bbl. feed, temperature 975° F., pressure 200 p. s. i., space velocity 0.5. A yield of 78% by weight of naphtha charge of debutanized aviation hydroformate, end point 364° F., octane 74 is obtained. The hydroformate naphtha is nearly saturated with a bromine number of 8. 8% by weight of C_4 hydrocarbons are produced. The C_4 fraction with isobutane is alkylated, charging 99% H_2SO_4, 5 : 1 molar ratio of isobutane to butylene, temperature 40° F., 1 : 1 vol. ratio of acid to hydrocarbons. The yield is 190% by weight on olefins charged of aviation alkylate, 350° F. end point, octane 92. The composite has an octane number of 80 and good lead susceptibility 4.5 cc. tetraethyl lead per gal. gives 100 octane gasoline. 11 United States patents cited.

GOLDSCHMIDT, A.-G. *See* abs. **3303.**

822. GOODSON, L. B., AND GUYER, J. A. (Phillips Petroleum Co.). Fluid-Type Catalytic Reaction Chamber. United States Patent 2,606,097, Aug. 5, 1952. Chem. Abs., vol. 47, 1953, p. 1923.

Describes reaction chamber for fluid vapor-solid contacting, which separates the solid material from gases by a simple means. The chamber is cylindrical with a conical bottom. A vertical tube, the reaction zone (I), extends up from the bottom inside chamber into an upper 1st settling zone (II), which is connected with the lower 2d settling zone (III) by a small annular space around (I). Starting with a solid catalyst in (III), the vaporized feed enters the bottom of (I), and the catalyst is drawn along with it through a Venturi-type injector. The mixture passes into (II) where the catalyst settles out, and the mixture passes down into (III) through the annular space with enough velocity that the vapors rising to the outlet, at the top of (III), carry very little catalyst. For example, in the hydrogenation of a kerosine, this material was fed into a preheater at the rate of 2 bbl. per hr., and the vapors, together with 2,000 standard $ft.^3$ of H per bbl. of hydrocarbon, fed into (I). The system pressure was 500 p. s. i. This gave a linear velocity in (I) of 4.4 ft. per sec. and in (II) of 0.2 ft. per sec. With catalyst of 100- to 140-mesh having a particle density of 4 gm. per cc. at a linear velocity up to 2.5 ft. per sec., very little catalyst is carried out of (I). At 2.5–6.0 ft. per sec. the amount of catalyst carried varies with the velocity. Allowance for exothermic or endothermic reactions is made by appropriate control of preheat temperature. The catalyst can be regenerated in the same vessel by blowing air

through it. The application of such a reaction chamber to such processes as catalytic cracking, reforming, Fischer-Tropsch, and others, is obvious.

823. Gordon, K., and Imperial Chemical Industries, Ltd. Effecting Reactions With Circulating Gases. British Patent 432,574, July 30, 1935. Chem. Abs., vol. 30, 1936, p. 535.

In carrying out reactions with circulating gases, the gases are purified by being passed in rapid, cocurrent flow with a liquid absorbent, which removes in each operation only a small proportion of the undesired constituents. Specific applications are destructive hydrogenation, NH_3 synthesis, and MeOH synthesis.

824. ———. Heating Hydrogen Under Pressure for Ammonia or Methanol Synthesis, Destructive Hydrogenation. British Patent 317,131, May 12, 1928. British Chem. Abs., 1929, B, p. 814; Chem. Abs., vol. 24, 1930, p. 1948.

Heating of H_2-containing gases under high pressure is effected by bubbling through a bath of molten metal. Describes an apparatus.

825. Gorin, E., and Gorin, M. H. (Socony-Vacuum Oil Co.). Conversion of Dimethyl Ether. United States Patent 2,456,584, Dec. 14, 1948; appl. filed Nov. 18, 1946, Serial No. 710,476; 8 claims (*Cl. 260–668*). Chem. Abs., vol. 43, 1949, p. 3435.

Dimethyl ether is converted to liquid hydrocarbons by the following steps: 18.2 mol. % of dimethyl ether and 81.8 mol. % of isobutane is passed over an alumina–silica catalyst at 370° C., 150 p. s. i. pressure, and a space velocity of 6.8 vol. of gaseous mixture per vol. of catalyst per min. The product mixture contains CH_4, normally gaseous hydrocarbons containing 2–4 C atoms per mol., normally liquid hydrocarbons and H_2O are separated from the product mixture. The gaseous hydrocarbons are recycled, and the liquid hydrocarbons are recovered. Since MeOH may be readily produced from synthesis gas obtained by reaction of steam with natural gas or coal, or by partial oxidation of CH_4, this invention provides an indirect method for conversion of coal or natural gas to liquid hydrocarbons. 3 United States patents cited.

Gorin, M. H. *See* abs. **1825.**

826. Gorin, M. H., and Abrams, A. J. (Socony-Vacuum Oil Co., Inc.). Synthesis Gas. United States Patent 2,485,875, Oct. 25, 1949. Chem. Abs., vol. 44, 1950, p. 1677.

Synthesis gas consisting of H_2 and CO is manufactured from natural gas, steam, and CO_2 in a 5-stage process, comprising: (1) Bringing the natural gas, steam, and CO_2 obtained in the manner described subsequently into countercurrent contact with hot, liquefied Sn or Pb under nonflooding conditions in a reaction zone packed with a porous, refractory solid at temperatures high enough to react with formation of H_2 and CO; (2) separating the H_2 and CO from the metallic vapor contained in the gaseous effluent from step (1) by scrubbing the effluent with liquefied metal in a separate vessel; (3) circulating part of the liquid metal from step (1) to a vessel containing $CaCO_3$ to cool the metal, to condition it for pumping to a metal-preheating step, and to decompose the $CaCO_3$ to CaO and CO_2; (4) circulating the remainder of the liquid metal from step (1) through a plurality of refractory-packed heat exchangers in countercurrent flow to separate streams of natural gas and steam to preheat these gases before introducing them as feed to step (1); and (5) passing the preheated streams of natural gas and steam from step (4) and CO_2 from step (3) to the reaction zone of step (1). The process may be carried out in 1, 2, or 3 stages, as desired.

827. Goring, G. E. (Pittsburgh Consolidation Coal Co.). Gasification of Carbonaceous Solids. British Patent 688,096, Feb. 25, 1953. Chem. Abs., vol. 47, 1953, p. 7762.

Char is completely gasified in a fluidized-bed process with heat-recovery features. The feed is forced into the bottom of an annular upward-moving bed, where it is preheated by product gas. The hot char overflows into the interior fluidized bed, where it is gasified with O_2 and steam. The product gas in passing down through the outer annular bed is cooled to about 1,150° F. and freed of entrained solids.

See also British Patent 658,542 (abs. **2760**).

828. Gornowski, E. J., and Nelson, K. J. (Standard Oil Development Co.). Gasification of Carbonaceous Solids. United States Patent 2,633,416, Mar. 31, 1953; appl. filed Dec. 3, 1947, Serial No. 789,424; 6 claims (*Cl. 48–203*). Chem. Abs., vol. 47, 1953, p. 6122.

Synthesis gas is produced from coal, steam, and O_2 in a multistage, fluidized-bed process. The crushed coal is conveyed at a pressure of 30–500 p. s. i. to the preheater, where it is heated with product gas to 250°–300° F. in the upper section and to 500°–700° F. in the lower section. The preheated coal is then partly carbonized in the generator at 1,700° F. with steam and O_2. The residue passes to a furnace for generation of the steam. The product gas preheats the steam to 1,550° F. and the O_2 to 800° F., then passes to the coal preheater.

829. ——— (Standard Oil Development Co.). Gasification of Carbonaceous Solids. United States Patent 2,633,417, Mar. 31, 1953; appl. filed Feb. 28, 1952, Serial No. 273,986; 14 claims (*Cl. 48–206*). Chem. Abs., vol. 47, 1953, p. 6122.

Carbonaceous solids to be gasified are dried and preheated in direct heat exchange with hot gases produced in the gasification stage. The gases flow upward through 2 or more fluidized beds of solids to which the solids feed is supplied countercurrently to the gases that serve simultaneously as heating and fluidizing medium. The process allows utilization of the available waste heat of the product gases at different temperature levels in an order affording the greatest heat transfer efficiency and maximum heat recovery. The savings of O_2 and process coal may amount to 10–20%. Carbonaceous solids are gasified at a relatively high C concentration of 30–70% by weight of the solids held in the gasification zone. C losses are avoided by feeding the high C gasification residue directly to the combustion zone where their sensible and potential heat content is converted into steam. In this way the generator size is kept at a minimum. About 15,000–30,000 B. t. u. of sensible heat per 100 lb. coal fed to the generator.

Gottschall, W. *See* abs. **2141, 2142, 2143.**

830. Gottschall, W., Kolling, H., and Hagemann, A. (Ruhrchemie A. G.). Process of Oxidizing Paraffinic Hydrocarbons. United States Patent 2,602,812, July 8, 1952; appl. filed Aug. 8, 1949, Serial No. 109,238; 15 claims (*Cl. 260–451*).

In reacting paraffinic hydrocarbons, consisting of the hard paraffin or the diesel oil fraction produced by the catalytic hydrogenation of CO, with concentrated H_2SO_4 and NO_2 as oxidants, the oxidation effect is greatly increased by using H_2SO_4 of 70–90% concentration.

831. Goudet, A. [Conversion of Methane Into a Petroleumlike Liquid.] French Patent 31,758, Dec. 9, 1925. British Chem. Abs., B, 1928, p. 844.

Fission of CH_4 into olefins and H_2 is facilitated by passing the gas at the higher temperatures over a layer

of CaF_2 to which may be added sulfides, selenides, or tellurides.

See also French Patent 613,146 (abs. **832**) and British Patent 255,493 (abs. **3446**)

832. ———. [Hydrocarbon Fuel From Methane.] French Patent 613,146, 1925. British Chem. Abs., 1927, B, p. 868.

See British Patent 255,493 (abs. **3446**).

833. ———. [Transformation of Methane Into Gasoline or the Like.] French Patent 32,666, May 26, 1926. Chem. Abs., vol. 22, 1928, p. 4790.

Methane is treated with Ni, Fe, or Co or their compounds at a pressure up to 1,000 kg. per $cm.^2$, the migration of the H being facilitated by the addition of alkali or alkaline earth metals or of Cl, Br. I, S, Se, or Tl. The methane may be mixed with Hg vapor and submitted to an electrical field giving a difference of potential. This is an addition to French Patent 613,146 (abs. **832**).

See also French Patent 31,758 (abs. **831**)

834. GRAF, R. (Ferbwerke vormals Meister Lucius & Brüning). [Nitriles.] German Patent 848,947, Sept. 11, 1952 (*Cl. 21 o–11*). Chem. Abs., vol. 47, 1953, p. 5425.

Saturated aliphatic or cycloaliphatic hydrocarbons with CNCl in the presence of organic peroxides at moderately elevated temperature, 50°–60° C., give nitriles useful as intermediates in the preparation of amines by hydrogenation or saturated aliphatic or cycloaliphatic carboxylic acids by saponification. Suitable initial materials are BuH, hexane, heptane (I), dodecane, cetane, iso-BuH, 2—BuCHEt, cyclohexane (II), and its alkyl derivatives; moreover hydrocarbon mixtures as they are produced by the hydrogenation of petroleum fractions or by the CO hydrogenation; di-Ac_2O_2 or Bz_2O_2 or peroxides of the general formula RSO_2O_2. Ac produced by treating saturated hydrocarbons with SO_2 and O_2 in the presence of Ac_2O, are suitable catalysts. Adding cyclohexylsulfonyl acetyl peroxide (III) 40 to (II) 400 and CNCl 63 with stirring at 30°, raising the temperature (with intensive reflux-cooling) within 6 hr. to 50°, extracting the (II) layer repeatedly with H_2O, and removing the excess (II) by distillation, gives hexahydrobenzonitrile 50 parts by weight, b_{10} 65°. Similarly are prepared: A mixture of isomeric cyanoheptanes, b_{23} 84°–95°, from (I), (III), and CNCl; a mixture of isomeric cyanoisooctanes, colorless oil, b_{25} 70°–105°, N content 10.4%, from isooctane (obtained by hydrogenation of dimerized isobutylene) (III), H_2O, and CNCl.

835. GRAHAME, J. H. (Texaco Development Corp.). Catalytic Synthesis of Hydrocarbons. Canadian Patent 464,546, Apr. 18, 1950; appl. filed Aug. 28, 1947, Serial No. 563,858; in the United States Sept. 19, 1946, 13 claims.

Hot synthesis gas is passed in heat-exchange relation with a hydrocarbon conversion catalyst until the latter is heated to an elevated conversion temperature. The synthesis gas is then passed over the synthesis catalyst to promote the direct synthesis of normally liquid hydrocarbons. The hydrocarbon conversion catalyst is withdrawn from the synthesis gas stream, and a portion of the synthesis hydrocarbons is passed over it until the hydrocarbons are converted. The converted liquid hydrocarbons are recovered and the normally gaseous hydrocarbon products of conversion recycled to the synthesis catalyst in admixture with the synthesis-gas feeds.

836. ——— (The Texas Co.). Catalytic Synthesis of Hydrocarbons. United States Patent 2,464,501, Mar. 15, 1949; appl. filed Sept. 19, 1946, Serial No. 697,960; 13 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 4447.

Synthesis gas leaves the generator at about 2,100° F. and is cooled to about 1,200° F. in a waste-heat boiler. From there it passes in direct heat exchange with a combination isomerization-dehydrogenation catalyst such as silica–alumina–thoria complex mixed with a second catalyst of 10% chromite on alumina. The synthesis gas passes upward through the catalyst, leaving the bed at about 600° F. The catalyst is discharged at the lower portion of the preheating vessel at about 1,150° F. The synthesis gas, temperature 600° F., goes from the preheater to the reactor containing a typical fluidized Fe catalyst. Cooling coils hold the temperature at 600° F., and the pressure is 200 p. s. i. Products are withdrawn. Gases are condensed, the water layer separated, and the liquid hydrocarbons and the gaseous residue preheated to 900° F. and passed in direct contact with the catalyst withdrawn from the preheater at 1,150° F. Temperature in this zone is approximately 1,000° F., with a gaseous hourly space velocity of 1,000. Gasoline of 80 octane is obtained. The gaseous fraction is recycled with partial venting to relieve the accumulation of CH_4, N_2, etc. The invention is adaptable to any type of conversions with endothermic requirements at temperatures about 700° F. and a catalyst relatively inert to the synthesis-gas stream. 2 United States patents cited.

837. ——— (The Texas Co.). Conversion of Synthetic Hydrocarbons Containing Oxygenated Compounds to Hydrocarbons of High Octane Value. United States Patent 2,452,121, Oct. 26, 1948; appl. filed Nov. 26, 1947, Serial No. 788,325; 7 claims (*Cl. 260–450*). Chem. Abs., vol. 43, 1949, p. 2421.

Hydrocarbon fraction containing dissolved oxygenated compounds resulting from the phase separation at a temperature 200°–300° F. and a pressure 150–550 p. s. i. is subjected to catalytic treatment with an alumina catalyst at 700°–900° F. The space velocity is 1–10 liquid vol. hydrocarbon per vol. catalyst per hr. Isomerization of the olefinic constituents takes place and the oxygenated organic compounds are converted to olefins and isomerized. Thus, the catalytic treatment effects conversion of alcohols and other oxygenated compounds to motor fuel hydrocarbons of high antiknock value.

838. ——— (Texaco Development Corp.). Synthesis of Hydrocarbons. United States Patent 2,503,724, Apr. 11, 1950; appl. filed Apr. 16, 1947, Serial No. 741,867; 9 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 7516.

Products from a primary reaction zone, particularly byproduct CO_2 and H_2, are supplied to a secondary reaction zone together with the fresh feed synthesis gas. The reaction is controlled to give additional hydrocarbon product. Example: H_2 : CO :: 1.5 : 1 is passed through a primary reaction zone containing fluidized Al–Th catalyst, 20% alumina and 80% thoria, pressure 300 atm., and temperature 805° F. The gaseous products are removed, reduced in pressure to 200 p. s. i., condensed, and separated at 70° F., with recovery of liquid product in motor gasoline boiling range. C_4 fractions are recovered from this gas and the residue is passed to a secondary reaction zone containing fluidized Fe catalyst promoted with alumina and potassium oxide, pressure 200 p. s. i. and temperature 600° F. This stream is mixed with additional fresh synthesis gas, ratio 1 part synthesis gas, 2 parts tail gas from the primary zone. The gaseous products are recovered as from the primary zone. The separated gases are recycled at a rate 2 : 1 on basis of the mixed synthesis gas. Unrecycled portions are treated for recovery of C_4 hydrocarbons, fractionated for removal of normal butane, and supplied directly to an alkylation system. The feed to the secondary zone, excluding recycle, is substantially free of water vapor and contains H_2 : CO :: 3 : 1 and slightly under 40 mol. % CO_2 on basis of

total reactant content. The CO_2 is largely consumed. 1 literature ref. and 10 United States patents cited.

839. GRASSHOF, H. (I. G. Farbenindustrie A. G. "In Auflösung"). [Separation of Alcohols From Carbon Monoxide Hydrogenation Products.] German Patent 811,348, Aug. 20, 1951 (*Cl. 12 o–5₀₁*). Chem. Abs., vol. 47, 1953, p. 5666.

MeOH and higher alcohols, especially iso-BuOH, are separated from the crude products resulting from the hydrogenation of CO by extraction with a solvent boiling below MeOH in which MeOH is poorly soluble, for example, pentane, amylene, or their mixtures, followed by washing the extract with 70–90% aqueous MeOH and distillation.

———. *See* abs. **3436, 3437, 3438.**

840. GRASSNER, F. (I. G. Farbenindustrie A. G.). [Freeing Gases Containing Carbon Monoxide From Volatile Iron Compounds.] German Patent 499,652, June 16, 1925. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 214; Chem. Abs., vol. 24, 1930, p. 4562.

Gases containing CO (except MeOH) are freed from volatile Fe compounds, especially $Fe(CO)_x$, by leading them over burned lime, BaO, SrO, Al_2O_3, MgO, magnesite, pumice stone, fragments of earthenware, diatomaceous masses or active H_2SiO_3 at high temperatures.

———. *See* abs. **2428, 2429.**

841. GREATHOUSE, L. H. Catalyst for Ammonia Synthesis. United States Patent 1,618,004, Feb. 15, 1927. Chem. Abs., vol. 21, 1927, p. 1168.

Catalyst is prepared by mixing substances such as Fe_2O_3 (or MnO_2) and Al, and after effecting fusion by exothermic reaction, subjecting the material to reduction, for example, by H_2 in the catalytic chamber.

842. GRECO, G. (Montecatini). [Synthesis Gas.] Italian Patent 446,318, Mar. 16, 1949. Chem. Abs., vol. 45, 1951, p. 1754.

Conventional method of synthesis gas manufacture from gaseous aliphatic hydrocarbons is modified as follows: No external heat is used, but the reaction starts with partial combustion of the hydrocarbons; the gas mixture so obtained is then injected into the catalyst chamber. The air or O_2 needed for the combustion should be 10% more than that required by the reaction $2CH_4+O_2=2CO+4H_2$. Gives a design of the oven and of the catalyst chamber.

GREEN, S. J. *See* abs. **68, 71.**

843. GREENE, F. C. (In Situ Gases, Inc.). Generation of Synthesis Gas. United States Patent 2,466,945, Apr. 12, 1949; appl. filed Feb. 21, 1946, Serial No. 649,295; 10 claims (*Cl. 262–71*).

Sythesis gas is produced in situ from a geological formation having a deposit of combustible material therein by a method claimed in detail. 2 literature refs. and 1 United States patent cited.

844. GRÉNÉ, P. G. [Hydrocarbon Synthesis.] French Patent 629,407, Apr. 28, 1926. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 174; Chem. Zentralb., 1928, I, p. 778.

Combination of coal gasification and hydrocarbon synthesis.

845. GRENIER, R. J. A. [Catalysts for the Preparation of Hydrogen and Alcohol.] French Patent 634,747, May 20, 1927. Chem. Abs., vol. 22, 1928, p. 3965.

See British Patent 271,523 (abs. **846**).

846. ———. Hydrogen and Methanol. British Patent 271,523, May 22, 1926. Chem. Age, vol. 17, 1927, p. 115; Chem. Abs., vol. 22, 1928, p. 1658.

Reactions involving the use of CO, such as the reaction between CO and steam for producing H_2 and reaction between CO and H_2 for producing MeOH, are effected in the presence of porous C, preferably wood charcoal, as catalyst.

847. GRESHAM, W. F. (E. I. du Pont de Nemours & Co.). Amides. United States Patent 2,542,766, Feb. 20, 1951. Chem. Abs., vol. 45, 1951, p. 7138.

Substituted propionamides are prepared in as high as 65–75% yield by treating CO, RR'NH, where R and R' are H or alkyl groups, and compounds containing a —C=C— group such as olefins, unsaturated nitriles, acids, and esters, at 150°–350°, over 50 atm., preferably 160°–260° and 100–2,000 atm., in the presence of organic compounds of Co, such as the carbonyl compounds, or salts of carboxylic acids. C_2H_4 1.1, NH_3 1.0, CO 1.2, C_6H_6 0.8, and Co naphthenate 0.002 mol. were passed continuously through a tube at 259° and 605 atm. with a contact time of 4 min. to give a 10.9% conversion to $EtCONH_2$ and smaller amounts of Et_2CO and $HCONH_2$. The heel after distillation usually contains Co and is in itself a satisfactory catalyst and can be recycled.

848. ——— (E. I. du Pont de Nemours & Co.). Catalytic Process for Preparing Alcohols. United States Patent 2,535,060, Dec. 26, 1950; appl. filed June 15, 1949, Serial No. 99,343; 9 claims (*Cl. 260–449*).

Alcohols, and more particularly straight chain primary hydroxyalkanes, are prepared by introducing $H_2:CO=1.5:1-3:1$, and a hydroxylated solvent into a reactor and heating the mixture with a Ru catalyst and an alkaline reagent, pH preferably 7.8–11.5, pressure 200–1,000 atm., and temperature 150°–300° C. The liquid hydroxyl-containing reaction medium may be H_2O or an alcohol such as a primary hydroxyalkane having 1–10 C atoms per mol. 90%–98% of the product is straight-chain, primary alcohols ranging from small amount of MeOH to alcohols with 2–15 C atoms per mol. 3 United States patents cited.

849. ——— (E. I. du Pont de Nemours & Co.). Conversion of Saturated Aliphatic Carboxylic Amides to Nitriles. United States Patent 2,439,426, Apr. 13, 1948. Chem. Abs., vol. 42, 1948, p. 6841.

Saturated aliphatic amides are dehydrated to nitriles in the presence of a catalyst, which simultaneously converts CO and H_2O to H_2 and CO_2. The yield is improved because the endothermic heat of dehydration is partly compensated by the exothermic heat of conversion. Preferred catalysts are chromites of Fe, Ni, or Mn. The preferred amide: $CO+H_2O$ ratio is 1:4 to 1:20 and the preferred $CO:H_2O$ ratio is 2:1 to 1:2. The reactants are passed over the catalyst at 320°–450°. In an example EtCN was prepared from $EtCONH_2$ in 90.9% yield. In addition 3.2% Et_2CO was obtained.

850. ——— (E. I. du Pont de Nemours & Co.). Esters of Cyclic Acetals and Carbon Monoxide. United States Patent 2,364,438, Dec. 5, 1944. Chem. Abs., vol. 39, 1945, p. 4632.

Of particular interest is the reaction product of 1,3-dioxolane and CO. The reaction is carried out at a wide range of temperatures, under superatmospheric pressures of CO and in the presence of an acid catalyst. Suitable catalysts are inorganic acids (HCl, H_2SO_4, and H_3PO_4), inorganic acid salts, nonmetal halides, such as BF_3, as well as organic acids. The product is cooled on an ice bath, H_2SO_4 53 is added to 1,3-dioxolane 175 parts. The polymerized dioxolane is placed in a Ag-lined pressure vessel, CO added under 200–700 atm., and the temperature raised to 88°–122°. The product is dissolved in a MeOH–Et_2O mixture, neutralized with Na_2CO_3, and the Na_2SO_4 formed filtered off. The excess Et_2O is evaporated, 3 parts of H_2SO_4 and enough MeOH to bring it to 400 parts are added; this is boiled for 2 hr. to esterify, neutralized with NaOMe, and fractionated. The Me (2-hydroxyethoxy) ace-

tate, $HOCH_2CH_2OCH_2CO_2Me$, b_1 64°–69° was a saponification number of 420. In place of dioxolane, dioxanes, dioxins, various other related compounds, and their polymers can be used.

851. ——— (E. I. du Pont de Nemours & Co.). Ether Esters. United States Patent 2,449,471, Sept. 14, 1948. Chem. Abs., vol. 43, 1949, p. 1055.

Ketenes and ortho aliphatic carboxylic acid esters react to form dialkoxy monocarboxylic acid esters of the formula $(RO)_2CR_1CXYCO_2R$, where R is alkyl or aryl and R′, X, and Y are H, alkyl, or aryl. The ketene is passed into the ortho ester at —80° to 150°, using an acid or Friedel-Crafts-type catalyst. Thus, ketene is bubbled 1.5 hr. into 33.2 gm. $HC(OEt)_3$ and 0.9 gm. BF_3 with stirring at 0°, 3 gm. $NaHCO_3$ added, the mixture filtered, and the filtrate distilled from 1 gm. $NaHCO_3$, giving 21.9 gm. Et β, β–diethoxy–proprionate, $b_{1.5}$58.5°, n_D^{25} 1.4088.

852. ——— (E. I. du Pont de Nemours & Co.). Glycol and Glycerol and Their Esters. British Patent 655,237, July 11, 1951. Chem. Abs., vol. 46, 1952, p. 7115.

Process for preparing glycol (I) and glycerol and their esters by heating CO and H_2 in the presence of a catalyst at a temperature >150° and a pressure of 2,000–5,000 atm. Thus, CO and H_2 (1 : 1 mol. ratio) heated in the presence of AcOH containing 0.035 gm. $Co(OAc)_2$ per cc. at 184°–242° and 3,000 atmospheric pressure yield mainly $(CH_2OAc)_2$ and $C_3H_5(OAc)_3$. The same products, together with lower boiling esters, mainly EtOAc and PrOAc, are obtained by heating a 2 : 1 mol. CO–H_2 mixture under the same conditions 1 hr. at 225°–246°. If the above reaction is carried out in the absence of AcOH but in the presence of H_2O, the reaction product is a mixture of (I) and (I) formates. Other catalysts that can be used in this procedure are Mn naphthenate, Cu–Zn chromite, $Sn(OAc)_2$, $Pb(OAc)_2$, ZnO_2, Sb_2O_3, Mn chromite, and Cr carbonyl.

853. ——— (E. I. du Pont de Nemours & Co.). Organic Oxygen-Containing Compounds. United States Patent 2,462,738, Feb. 22, 1949. Chem. Abs., vol. 43, 1949, p. 5035.

MeOH with CO at 200°–300° under 200–1,500 atm. pressure gives AcOMe. $Co(OAc)_2$ serves as the catalyst. Small amounts of H_2 increase the reaction rate. MeOH 64, $Co(OAc)_25$, and H_2O 72 parts, heated in a Ag-lined shaker tube under 600–710 atm. CO at 220°, gave 7% conversion to MeOAc in 0.5 hr. When a mixture of H_2 and CO in the ratio 1 : 3 was used the conversion was 25% in 0.5 hr.

854. ——— (E. I. du Pont de Nemours & Co.). Preparation of Polyfunctional Compounds. United States Patent 2,636,046, Apr. 21, 1953; appl. filed Oct. 16, 1948, Serial No. 55,016; 8 claims (*Cl. 260–449.6*).

When an oxide of C is reacted with H_2 at 1,500–5,000 atm., particularly > 1,400 atm., polyfunctional O-containing organic compounds such as ethylene glycol, higher polyhydric alcohols, and esters of polyhydric alcohols can be obtained very readily and in excellent yield. The reaction may be carried out in vapor or liquid phase. Inert organic solvents may be used. 2 foreign and 3 United States patents cited.

855. ——— (E. I. du Pont de Nemours & Co.). Preparing Polyhydric Alcohols and Related Products. United States Patent 2,570,792, Oct. 9, 1951; appl. filed Dec. 8, 1949, Serial No. 131,938; 9 claims (*Cl. 260–449*). Chem. Abs., vol. 46, 1952, p. 5076.

Polyhydric alcohols, such as ethylene glycol are prepared by reacting CO with H_2 under a pressure 2,000–5,000 atm. and 150°–400° in the pressure of a Mn–Zn–Cr catalyst. The best ratio of CO : H_2 is 3 : 1–1 : 3. The process may be performed in the presence of an inert liquid diluent, such as H_2O, which facilitates removal of heat from the reaction mixture and also may prevent formation of hydrolyzable products, such as esters.

856. ——— E. I. du Pont de Nemours & Co.). Process for Preparing High-Molecular-Weight Hydrocarbons. United States Patent 2,632,014, Mar. 17, 1953; appl. filed Nov. 3, 1951, Serial No. 254,804; 3 claims (*Cl. 260–449*).

Polymethylenes are prepared by introducing H_2, CO, and H_2O into a reaction vessel. The mol ratio of CO : H_2 is initially > 1 : 1 and preferably 2 : 1–12.5 : 1. The reactants are heated in presence of a Ru-containing catalyst and an acidic reagent (maintaining a pH < 2) at a pressure of 200–800 atm. and a temperature of 180°–225° C. The polymethylenes have m. p. 126°–129° C. and inherent viscosities of 0.33–0.36, measured at 0.25% concentration in tetrahydronaphthalene at 125° C. 1 United States patent cited.

857. ——— (E. I. du Pont de Nemours & Co.). Recovery of Hydrogen Fluoride-Boron Trifluoride Catalysts. United States Patent 2,462,739, Feb. 22, 1949. Chem. Abs., vol. 43, 1949, p. 3949.

Mixtures (I) of MeC_6H_4CHO (II), HF, and BF_3 are formed in the catalytic preparation of (II) from toluene and CO. (I) is treated with 1 mol. NaF at —40°, warmed to 25°, and the precipitate washed with toluene to give 92% recovery of (II). Similarly LiF gives 95% (II); CaF_2 also is effective. The complex $(LiF)_2$–HF–BF_3 heated 115 min. at 336°–374° gives quantitative recovery of HF and BF_3, and at 302°–317° gives 98.7 and 81.5%, respectively. The complex CaF_2–HF–BF_3 in 15 hr. at 300° gives a high recovery of BF_3 but very little HF. In 90 min. at 458°–514° a 20% recovery of HF and BF_3 is obtained from the NaF–HF–BF_3 complex. Treatment of (I) at —40° with 1 mol. NaF and 3 CaF_2 gives 100% removal of HF and BF_3; the heating of the precipitate for 150 min. at 387°–395° allows 45% recovery of HF and BF_3.

858. ——— (E. I. du Pont de Nemours & Co.). Synthesis of Carboxylic Acids. United States Patent 2,432,474, Dec. 9, 1947. Chem. Abs., vol. 42, 1948, p. 1961.

Carboxylic acids are prepared by the reaction of a polyalkylene cyclic monoether with CO in the presence of a Ni carbonyl catalyst. Thus, $NiCl_2.6\ H_2O$, 23.8; $Ni(CO)_4$, 17.1; tetrahydrofuran, 72.1; and H_2O, 70.3 gm. are heated in a Cu-lined shaker tube at 290°–315° with CO at 740–800 atm. The ether extract of the reaction mixture is fractionated to yield 31.9 gm. of an acid fraction b_{20} 75°–97°, neutralization equivalent 106; 17.8 gm. acid b_1 up to 131°; and 6.4 gm. solid acidic residue. The main fraction is resolved by redistillation into $EtCHMeCO_2H$ and $BuCO_2H$.

859. Gresham, W. F., and Brooks, R. E. (E. I. du Pont de Nemours & Co.). Acrolein. United States Patent 2,402,133, June 18, 1946. Chem. Abs., vol. 40, 1946, p. 6093.

In the presence of a hydrogenation catalyst, acrolein (I) was produced directly from CO, H_2, and vinyl compounds of the type ROCH : CH_2, where R is an acyl radical, in accordance with the following equation: CH_2 : CHOR + CO + H_2 → I + ROH. For example, a mixture containing 137.6 gm. CH_2 : CHOAc (II), 20 gm. of reduced sintered CoO catalyst, and 1 gm. hydroquinone was heated to 78°–92° for 1 hr. at 200–310 atm., with an equimolecular mixture (III) of CO and H_2. The resulting product contained (I) (27% conversion) and MeCH(OAc)CHO (IV) (20% conversion).

860. ——— (E. I. du Pont de Nemours & Co.). Anhydride Synthesis. United States Patent 2,549,453, Apr. 17, 1951. Chem. Abs., vol. 45, 1951, p. 8551.

Organic carboxylic acid anhydrides are prepared from olefins with CO and carboxylic acids or substances that yield carboxylic acids. $EtCO_2H$ (I), 74; $Ni(CO)_4$, 10; and C_2H_4, 28 gm. heated 15 min. in a Cu-lined pressure-resistant vessel with CO at 272°–293° under 600–810 atm. gave 39% conversion to $(EtCO)_2O$ (II). H_2O, 18; $Ni(CO)_4$, 5; and C_2H_4, 56 gm. with CO at 280° and 800 atm. gave a liquid containing (II). CO, 0.5; C_2H_4, 0.36; (I), 1.0; and $Ni(CO)_4$, 0.11 mole passed through a Cu-lined converter at 263° under 605 atm. with a contact time of 4.9 min. gave 183 lb. per cu. ft. per hr. of (II).

861. ——— (E. I. du Pont de Nemours & Co.). Aryl Esters. United States Patent 2,467,206, Apr. 12, 1949. Chem. Abs., vol. 43, 1949, p. 6234.

Various aryl esters are prepared by the reaction of a phenol, CO, and an olefinic compound in the presence of a Ni or Co catalyst under pressure. Thus, when PhOH, 47.1; C_6H_6, 100; $(EtCO_2)_2Ni$, 10; and C_2H_4, 28 gm. are heated 25 min. in a Cu-lined pressure vessel at 292°–300° under 260–700 atm. CO distillation of the product gives 87.3% $EtCO_2Ph$.

862. ——— (E. I. du Pont de Nemours & Co.). Carboxylic Acids From Olefins, Carbon Monoxide, and Water. United States Patent 2,448,368, Aug. 31, 1948. Chem. Abs., vol. 43, 1949, p. 669.

Organic carboxylic acids are prepared by treating 0.1–10 (preferably 0.8–2) mols. unsaturated compounds containing at least 1 nonaromatic C:C bond with 0.1–20 (preferably 0.8–5) mols. CO and 1 mol. H_2O in the presence of 0.05–30% (based on the total weight of the reactants) Ni or Co carbonyl at 150°–500° (preferably 175°–375°) under 50–3,000 (preferably 500–1,500) atm. in the absence of inorganic acidic substances. Any inert liquid, for example, carboxylic acids, ketones, cyclohexane, or C_6H_6, may be used as reaction medium; however, the reaction may be conducted in the absence of any added medium, using CO_2 as a diluent to suppress the water-gas reaction. The carbonyl catalyst may be introduced as such or formed in situ under conditions of the reaction. The synthesis eliminates excessive corrosion of equipment and utilizes cheap, available raw materials and may be conducted in liquid or vapor phase, operating either batchwise or continuously, using a fixed-bed, solid, or fluidized catalyst. Recovery of the catalyst (75–80%) is effected by direct distillation of the reaction product under a blanket of CO and separation of the acid from the product. For example, 9 cc. distilled H_2O, 10 gm. Ni carbonyl, 44 gm. CO_2 (to suppress the water-gas reaction), and 28 gm. C_2H_4 are heated 30 min. at 300°–375° under 450–740 atm. of CO and the product distilled to yield 30.3 gm. (80%–90%) crude $EtCO_2H$. Employing Co propionate in place of the Ni carbonyl and omitting the CO_2 diluent in the above example, 46% $EtCO_2H$ and 14.5% Et_2CO are obtained at 234°–250° and 660–830 atm. of CO. Similarly 18 cc. H_2O, 10 gm. Ni carbonyl, 44 gm. CO_2, and 42.1 gm. propene are heated 1 hr. at 314°–334° under 595–765 atm. of CO to yield 67 gm. pale brown liquid, chiefly 2 parts $PrCO_2H$ and 1 part iso-$PrCO_2H$. Likewise, 56 gm. $Me_2C:CH_2$, 10 gm. Co, and 9 cc. H_2O were heated 2.2 hr. at 318°–322° under 450–700 atm. of CO; distillation yielded a fraction, b_{23-4} 60°–130°, which was a mixture of $Me_2C:CH_2$ polymers and O_2-containing organic compounds.

863. ——— (E. I. du Pont de Nemours & Co.). Methoxyethanol. United States Patent 2,429,878, Oct. 28, 1947. Chem. Abs., vol. 42, 1948, p. 923.

An equimolecular mixture of CO and H_2 at 600–700 atm. in a Ag-lined shaker, containing 38.1 gm. methylal, 115 gm. Me_2O, and 20 gm. reduced sintered Co oxide catalyst, gave, after 53 min. at 200°–235° at a minimum pressure of 600 atm., methoxyethanol, b. 123°–124.5°, in good yields.

864. ——— (E. I. du Pont de Nemours & Co.). 1,1,2-Trialkoxyethanes. United States Patent 2,449,470, Sept. 14, 1948. Chem. Abs., vol. 43, 1949, p. 675.

1,1,2-trialkoxyethanes are prepared by heating dialkyl formals with CO and H_2 in the presence of an alkanol and 0.1–20% (based on the total weight of the reaction mixture) Ni or Co catalyst at 100°–350°, preferably 125°–170°, under a pressure of at least 10 atm., preferably 400–1,000 atm., the initial molecular ratio of dialkyl formal to alkanol being 2:1–1:20 and of CO to H_2 3:1–1:3. For example, 38.1 gm. $H_2C(OMe)_2$, 160 gm. MeOH, and 20 gm. reduced sintered Co oxide catalyst are treated with a mixture of CO and H_2(1:1) injected into an Ag-lined shaker tube at 550–750 atm., the mixture shaken 15 min. at 160°–170° with intermittent additions of CO–H mixture to maintain a pressure of at least 600 atm., unconverted $H_2C(OMe)_2$ (50%) and MeOH (88%) recovered by fractional distillation, and 25 ml. distilled H_2O added to the residue, giving $(MeO)_2CHCH_2OMe$ (I) as a homogeneous H_2O azeotrope, b. 93°–94°, containing 30% H_2O and 70% (I). Saturation of the azeotrope with K_2CO_3 yielded an upper layer (30 gm.), which was dried with Na_2SO_4 and distilled to yield (I), b_{50} 56°–59°, b. 126°–127.5°, n^{25} 1.3901. Substituting iso-BuOH for MeOH in the above example gave a mixture of $(iso\text{-}BuO)_2CHCH_2OCH_2CHMe_2$ and $(iso\text{-}BuO)_2CHCH_2OMe$. Similarly, 83.2 gm. $H_2C(OEt)_2$, 92 gm. absolute EtOH, and 20 gm. reduced, fused Co catalyst heated 30 min. at 200°–214° with $CO:H_2$(2:1) at 700 atm., and the products cooled and distilled yielded 6.0 gm. $EtOCH_2CH_2OH$, b_{30} 53°–56°, and 7.5 gm. $(EtO)_2CHCH_2OEt$, b_{30} 73°–75°. The compounds thus prepared are useful as solvents and intermediates for the manufacture of unsaturated ethers.

865. ——— (E. I. du Pont de Nemours & Co.). Production of Esters From Olefinic Compounds, Carbon Monoxide, Hydrogen, and Organic Carboxylic Acids. United States Patent 2,549,455, Apr. 17, 1951; appl. filed Jan. 28, 1948, Serial No. 4,935; 13 claims (*Cl. 260–488*).

Object of the process is to direct the Oxo reaction between olefinic compounds, CO, H_2, and organic carboxylic acids to the formation of esters exclusively, while suppressing the formation of aldehydes, ketones, and other O-containing organic compounds. The process comprises reacting CO and H_2 simultaneously with an olefin hydrocarbon and a saturated organic carboxylic acid at temperature 140°–375° and pressure 325–5,000 atm. in the presence of a catalyst containing a Co or Ru salt dissolved in the reaction mixture, the mol. ratio of $CO:H_2$=1:3 to 3:1. Any olefin hydrocarbon containing 2–20 or more C atoms per molecule and any saturated organic carboxylic acid may be employed.

866. ——— (E. I. du Pont de Nemours & Co.). Production of Ketones From Secondary Alcohols, Olefins, and Carbon Monoxide. United States Patent 2,526,742, Oct. 24, 1950; appl. filed Dec. 20, 1945, Serial No. 636,262; 14 claims (*Cl. 260–586*). Chem. Abs., vol. 45, 1951, p. 2017.

Saturated secondary alcohols and olefins are treated with CO in the presence of Co catalysts (reduced Co oxide hydrogenation catalyst and Co salts of carboxylic acids) at pressures > about 50 atm. at 100°–500°, preferably 225°–300°. Thus, 150 gm. iso-PrOH, 10 gm. Co propionate, and 14 gm. C_2H_4 heated 30 min. to 250°–261° under 625–755 atm. CO gave Me_2CO and Et_2CO; addition of reduced Co oxide gave almost 100% conversion.

867. ——— (E. I. du Pont de Nemours & Co.). Reaction Between Olefinic Compounds, Carbon Monoxide, and Hydrogen in the Presence of a Metal Carbonyl Catalyst. United States Patent 2,497,303,

Feb. 14, 1950; appl. filed May 23, 1945; Serial No. 595,475; 3 claims (*Cl. 260–604*). Chem. Abs., vol. 44, 1950, p. 4492.

Outstanding results are obtained with Co, Ni, and Fe carbonyls. Amount of catalyst is preferably 0.1–10%, based on total weight of the reaction mixture, but Co carbonyl will exert an effect even when present to an extent of only 200 parts per 1,000,000 or less. In synthesis of O-containing compounds from ethylene, CO, and H_2 at pressures below 300 atm., the following 2 reactions occur: (1) $CH_2{=}CH_2{+}CO{+}H_2{\rightarrow}CH_2CH_2CHO$; (2) $2\ CH_2{=}CH_2{+}CO{+}H_2{\rightarrow}CH_3CH_2COCH_2CH_3$. According to the invention the effect of pressure above 375 atm. is to suppress (2), making possible the formation of aldehyde (1) in high yield. The pressure may be 3,000 atm. or higher. Molar ratio of CO : H_2 : olefin is 1 : 2 : 1–2 : 4 : 1. CO under high pressure is effective in suppressing thermal decomposition of thermally unstable carbonyls such as Co carbonyl. An inert liquid, such as xylene or diethyl benzene, may be used as reaction medium. When the catalyst is to be recovered by separating the aldehydric product at elevated temperature under high CO pressure, the boiling point of the medium should be above the boiling point of the principal aldehyde. Gives 14 examples. 2 literature refs., 1 foreign patent, and 3 United States patents cited.

868. ——— (E. I. du Pont de Nemours & Co.). Synthesis of Polyhydroxy Compounds. United States Patent 2,451,333, Oct. 12, 1948. Chem. Abs., vol. 43, 1949, p. 673.

Poly-HO compounds are produced by reaction between HCHO, CO, and H_2 in the presence of a hydrogenating catalyst, preferably a Co derivative and an inert solvent, such as HCO_2Me. Thus, paraformaldehyde 31.6 gm., HCO_2Me 123 ml., and sintered Co oxide catalyst 10 gm. were heated in a Ag-lined shaker tube 2 hr. at 150°–157° and 500–700 atm. pressure of a gas, which was 11 vol. CO to 2 vol. H_2. On distillation there was obtained 6.8 gm. mixed poly-HO compounds, b_3 58° to b_6 174°. The product may be further hydrogenated in MeOH solution with Cu chromite catalyst to give ethylene glycol and glycerol and other lower molecular products.

869. Gresham, W. F., and du Pont de Nemours, E. I., & Co. Primary Alcohols. British Patent 638,754, June 14, 1950. Chem. Abs., vol. 44, 1950, p. 9473.

Primary normal alcohols are the principal product from olefins, CO, and H at 275°–375° pressures > 300 atm., and in the presence of a Cu–Cr–Co catalyst. A 16 : 8 : 1 mixture of H_2–CO–propylene passed over a 1 : 0.1 : 0.05 Cu–Cr–Co catalyst at 288° and 1,000 atm. gave liquid products containing 88% BuOH, and 12% iso-BuOH.

See also British Patent 637,999 (abs. **878**).

870. Gresham, W. F., and Hardy, J. V. E. (E. I. du Pont de Nemours & Co.). Metallic Carbonyls. United States Patent 2,473,993, June 21, 1949. Chem. Abs., vol. 43, 1949, p. 9398.

CO, H_2, and a Co or Ni salt of a carboxylic acid at 50–1,200 atm. and 100°–375° give Co or Ni carbonyl, which is recovered from the reaction mass at 50°–100° by blowing with CO and scrubbing the exit gas with an organic solvent. Outstanding results are obtained at 100–1,000 atm. partial pressure of CO, and with an initial H_2 : Ni ratio of 1 : 1–3 : 1 and an initial CO : H_2 ratio of 25 : 1–500 : 1. $EtCO_2H$ is a suitable solvent for both reaction and recovery.

871. Gresham, W. F., and Hill, A. J., Jr. (E. I. du Pont de Nemours & Co.). Process for Synthesis of Higher Aliphatic Oxygen-Containing Compounds. United States Patent 2,640,074, May 26, 1953; appl. filed May 18, 1949; Serial No. 94,046; 2 claims (*Cl. 260–497*).

Claim 1. Process that comprises reacting butadiene with CO and H at a reaction temperature within the range of 135°–200° C. under 2,500–5,000 atm. pressure in a liquid alkanoic acid medium in the presence of a Co compound dissolved in the said alkanoic acid whereby a reaction product of the said butadiene, CO, and H_2 is obtained, said reaction product having an O_2 atom attached to an acyclic hydrocarbon radical, the number of C atoms in the said acyclic hydrocarbon radical being at least 9 and not greater than 21.

872. Gresham, W. F., and Kubico, M. (E. I. du Pont de Nemours & Co.). Primary Alcohol Composition. United States Patent 2,609,397, Sept. 2, 1952; appl. filed July 24, 1948, Serial No. 40,623; 1 claim (*Cl. 260–632*).

Normally liquid, highly branched primary tridecanol has a b.p. 103°–112° at a pressure of 4 mm. It is a hydrogenation product of the highly branched C_{13} aldehyde obtained by simultaneous reaction of CO and H_2 with tetrapropylene in the presence of a hydrogenation catalyst.

873 Gresham, W. F., and McAlevy, A. (E. I. du Pont de Nemours & Co.). Treatment of Olefinic Compounds With Carbon Monoxide and Hydrogen. United States Patent 2,564,104, Aug. 14, 1951. Chem. Abs., vol. 46, 1952, p. 4561.

O-containing compounds are prepared from olefinic unsaturated compounds with CO and H_2 in the presence of an inert reaction medium in which is dissolved a catalyst consisting of a salt of Co, Ni, or Cu at 150°–250° and under a pressure 550–1,500 atm. Thus, 5.42 gm, AcOK, 4.58 gm. $Co(OAc)_2 \cdot 4\ H_2O$, 100 cc. H_2O, and 28 gm. C_2H_4 heated 85 min. at 175°–182° and 600–700 atm. with CO and H_2, in a ratio 1 : 2, and distilled, yielded 2.5 gm, EtCHO, b. 48°, and 10.8 gm. EtCH : CMeCHO, $b._{102}$ 76°–83°.

874. Gresham, W. F., and Schweitzer, C. E. (E. I. du Pont de Nemours & Co.). Preparation of Polyfunctional Compounds. United States Patent 2,534,-018, Dec. 12, 1950; appl. filed Aug. 11, 1949, Serial No. 109,802; 7 claims (*Cl. 260—449.6*).

Polyfunctional O-containing organic compounds are prepared by reacting a CO or CO_2 and H_2 in presence of CO fluoride in aqueous or alcoholic medium at 150°–400° C. The reaction is $n\mathrm{CO}+(n+1)\mathrm{H_2}=\mathrm{H(CHOH)}n\mathrm{H}$, n being an integer greater than 1. Pressure is 2,000–5,000 atm. Either vapor or liquid phase may be used. The reaction may be carried out in the presence of an esterifying reactant, such as acetic acid, whereby esterification of the hydroxyl groups in the compound, $\mathrm{H(CHOH)}n\mathrm{H}$ can occur, at least in part. 5 United States patents cited.

875 Gresham, W. F., and Tabet, G. E. (E. I. du Pont de Nemours & Co.). Aromatic Aldehydes. United States Patent 2,485,237, Oct. 18, 1949. Chem. Abs., vol. 44, 1950, p. 2027.

Aromatic aldehydes (I) are obtained by the reaction of aromatic hydrocarbons with CO in the presence of a BF_3–HF catalyst at —80° to 50° under superatmospheric pressure. The catalyst can be recovered and reused. (I) may be oxidized to aromatic carboxylic acids. (I) include BzH, p-MeC_6H_4CHO, 2,4–, 2,5-$Me_2C_6H_3CHO$, 2,4,6-$Me_3C_6H_2CHO$, p-PhC_6H_4CHO, and 1-$C_{10}H_7CHO$.

876. Gresham, W. F., Brooks, R. E. and Bruner, W. M. (E. I du Pont de Nemours & Co.). Methyl 4-Oxobutyrate. United States Patent 2,549,454, Apr. 17, 1951. Chem. Abs., vol. 45, 1951, p. 8551.

Olefins with CO and H_2 give a mixture of aldehydes and ketones. If the reaction is carried out at pressures above 300 atm., high yields of aldehydes are obtained

to the almost total exclusion of ketones. Reduced, fused Co catalysts (10 gm.), 75 cc. Et_2O, and 42.1 gm, MeCH : CH_2 heated 2 hr. at 108°–120° under 470–790 atm. in a Ag-lined shaker tube with a 1 : 2 mixture of CO and H_2 gave 69.9 gm. PrCHO. C_2H_4, 140, CO, 140; H_2, 20; and cyclohexane, 900 gm. were pumped for 1 hr. through a Ag-lined tube 20 in. long, containing 65 cc. metallic Co catalyst, at 140° under 700 atm., to give 90% EtCHO. Cyclohexene (82.1 gm.), 75 cc, Et_2O, and 10 gm. Co catalyst containing 3% Cu processed 2 hr in a Cu-lined shaker tube under 580–790 atm. of CO : $4H_2$ at 110°–112° gave 41.5 gm. hexahydrobenzaldehyde b_{19-20} 55°–60° CH_2 : $CHCO_2Me$ (43 gm.), 0.5 gm. p–$C_6H_4(OH)_2$, 100 cc. HCO_2Me, and 10 gm. Co catalyst processed 1 hr. in a shaker tube with CO : $2H_2$ under 390–730 atm. at 145°–167° gave 57.4% Me4–oxobutyrate, b_{10} 62°. H_2O (100 cc.), 10 gm. reduced 65% Co–35% Fe catalyst, and 28 gm. C_2H_4 heated 1.5 hr. at 110°–178° under 550–730 atm. of CO : $2H_2$ in a stainless-steel shaker tube gave 13.3 gm. EtCHO and 15 gm. EtCH : CMeCHO, b. 135°–139°.

877. ——— (E. I. du Pont de Nemours & Co.). Synthesis of Aldehydes. United States Patent 2,437,600, Mar. 9, 1948; appl. filed June 7, 1945, Serial No. 598,208; 11 claims (*Cl. 260–604*). Chem. Abs., vol. 42, 1948, p. 4196.

Describes process for the synthesis, particularly of saturated and unsaturated aldehydes, by reacting an olefinic hydrocarbon having 2–8 C atoms per molecule and containing a nonbenzenoid olefinic unsaturation with CO and H_2. The initial molal ratio of CO : H_2 is about 1 : 1.5–1 : 10, at 75°–250° and 325–3,000 atm. A hydrogenation catalyst such as Ni, Co, Fe, Cu, and Ru and their mixtures and compounds, in combination with inert substances such as kieselguhr or the like or with promoters such as ThO_2, Mn, etc., is used. The effect of pressure in selectively favoring aldehyde formation is very pronounced at the above molal ratios, yields of aldehydes as high as 70–100% being obtained under the above conditions.

878. Gresham, W. F., Brooks, R. E., and du Pont de Nemours, E. I., & Co. Catalytic Production of Aldehydes, Acetals, and Alcohols. British Patent 637,999, May 31, 1950. Chem. Abs., vol. 44, 1950, p. 9473.

Co, Ni, and Fe carbonyls are effective and recoverable catalysts for the liquid-phase reaction of an olefin, CO and H_2. Ketones are inhibited at pressures > 375 atm., and the products are mainly aldehydes. H_2, CO, and C_2H_4 in a molar ratio 1 : 2 : 1 led through a Cu-lined tube concurrently with 2% Co carbonyl in xylene at 140° and 700 atm. gave 48.5% conversion of C_2H_4; yield of propionaldehyde 3.15 lb. per hr. per $ft.^3$.

879. Gresham, W. F., Brooks, R. E., and Grigsby, W. E. (E. I. du Pont de Nemours & Co.). Synthesis of Diethyl Ketone. United States Patent 2,473,995, June 21, 1949; appl. filed June 19, 1946, Serial No. 677,922 (*Cl. 260–597*). Chem. Abs., vol. 44, 1950, p. 1130.

Diethyl ketone is synthesized by heating a mixture of C_2H_4, CO, and H_2 containing initially more than 1 molecule of C_2H_4 per mol. of H_2 and having an initial CO : H_2 molal ratio of from about 5 : 1–20 : 1 at a reaction temperature of about 50°–350° in the presence of a Co catalyst under a pressure of 325–1,500 atm., and thereafter separating diethyl ketone from the reaction product.

880. Griffin, L. I., Jr. (Standard Oil Development Co.). Catalyst Purification. United States Patent 2,487,867, Nov. 15, 1949; appl. filed July 11, 1945, Serial No. 604,349; 6 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 1673.

Catalyst contaminated in the reaction of CO and H_2 is reactivated by destructive hydrogenation of the contaminants and treatment with a wash solvent. The temperature for the hydrogenation is 450°–750° F. and the pressure up to 750 p. s. i. The synthesis catalyst also promotes the hydrogenation. 9 United States patents cited.

881. ——— (Standard Oil Development Co.). [Catalytic Production of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 954,643; appl. filed Oct. 24, 1947, issued Dec. 28, 1949, in United States Nov. 9, 1946. Chem. Zentralb., 1950, II, p. 488.

Hydrocarbons are synthesized from CO and H_2 with simultaneous introduction of steam. Fe, Ni, or Co in suspended fluidized form is used as the catalyst, Fe being preferred. A part of the catalyst is removed from the reaction zone during the synthesis, regenerated, and returned to the process to avoid as far as possible the deposition of C on the catalyst. The operating temperature lies 260°–399° and at a pressure of 52.5 atm.

882. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,468,494, Apr. 26, 1949; appl. filed Dec. 7, 1944, Serial No. 567,063; 2 claims (*Cl 260–449.6*). Chem. Abs., vol. 43, 1949, p. 7213.

A portion of the catalyst is removed from the reaction zone to a washing zone in which a liquefied, normally gaseous hydrocarbon such as butane is circulated through the catalyst and removed through a filter to a recovery zone. The hydrocarbon is flashed off, and the liquid products and wax are recovered as a residue. The liquefied hydrocarbon is condensed and returned to the washing zone. The liquid- and wax-free catalyst is at least partly dried and returned to the reaction zone as a suspension in the synthesis gas. 1 literature ref., 1 foreign patent, and 10 United States patents cited.

883. ——— (Standard Oil Development Co.). Synthesis of Hydrocarbons. United States Patent 2,498,838, Feb. 28, 1950; appl. filed Sept. 12, 1945, Serial No. 615,859; 9 claims (*Cl. 260–449.6*) Chem. Abs., vol. 44, 1950, p. 7045.

In carrying out the Fischer-Tropsch synthesis, a major portion of the product gases is recycled directly to the catalyst at the temperature of its withdrawal. The minor portion goes to a recovery system, but the tail gas is also recycled to the catalyst. The total gas recycle is less than 20 times and at least 1.5 times the vol. of fresh feed gas. The gas keeps the catalyst in motion and controls the temperature. 6 United States patents cited.

884. Griffin, L. I., Jr., and Jahnig, C. E. (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,436,568, Feb. 24, 1948; appl. filed Sept. 19, 1946, Serial No. 697,976; 8 claims (*Cl. 260–449.6*). Chem. Abs., vol. 42, 1948, p. 3934.

This patent refers to regeneration of used catalyst by washing with a solvent to remove wax and like deposited contaminants. The catalyst is of the fluidized, suspended type, the activity of which is maintained by gradually withdrawing the contaminated portion, washing it with a solvent, and then discharging it into a settling zone where water is added, the solvent removed, and the water-catalyst slurry returned to the reactor. The slurry is fed directly to the reaction zone at a rate responsive to the temperatures existing in the reaction zone, thus utilizing the water to control the temperature therein.

885. Griffin, L. I. Jr., and Krebs, R. W. (Standard Oil Development Co.). [Synthetic Hydrocarbons.] French Patent 955,866, appl. filed Nov. 20, 1947, issued Jan. 20, 1950, in United States Nov. 22, 1946. Chem. Zentralb., 1950, II, p. 339.

Hydrocarbons with 3 or more C atoms are produced from CO and H_2, the ratio of CO : H_2 being at least 3 H_2 : 1 CO, preferably 4–6 H_2 : 1 CO. The synthesis gas therefor is made from a mixture of CH_4, H_2O, and CO_2 which contains 20–60% CO_2 and 20–60% H_2O. According to an example, the synthesis gas is made from a mixture of 40% CH_4, 40% H_2O, and 20% CO_2 and in the presence of Ni at 700°–870°. A synthesis gas, which contains 64% H_2, 16% CO, and 16% CO_2, yields at 343° and 28 atm. C_3 and C_4 hydrocarbons beside higher molecular hydrocarbons and water-soluble alcohols.

GRIGSBY, W. E. *See* abs. **879.**

886. GRISENTHWAITE, A. T., AND RUSCHIN, K. (Power-Gas Corp., Ltd.). Ammonia Synthesis Gas. British Patent 685,962, Jan. 14, 1953. Chem. Abs., vol. 47, 1953, p. 6637.

NH_3 synthesis gas is prepared by gasification of solid fuels containing volatile material with air or steam. The fuel is separated into 2 fractions—1 high and 1 low in volatile material. The high-volatile fraction is used to reduce Fe oxide, which is used in turn to obtain gases rich in H_2 by treatment with steam. The oxidized low-volatile fraction is subjected to the water-gas shift reaction, and the product is mixed with the H_2-rich gas in the desired N_2 : H_2 ratio.

887. GRISWOLD, H. L. (Coast Reduction, Inc.). Apparatus for Generating Gases Such as Carbon Monoxide and Hydrogen From Natural Gas and Air. United States Patent 2,338,506, Jan. 4, 1944; appl. filed Dec. 30, 1940, Serial No. 372,228; 5 claims. Chem. Abs., vol. 38, 1944, p. 3802.

Various details of a generator having a cylindrical body portion and communicating wing chambers extending from it, which are of substantially semicircular cross section, with electrodes in these chambers extending through them at an inclination such that the lower ends of the electrodes are closer to each other than their upper ends. This placement serves to facilitate desirable heat transfer.

GROGER, R. *See* abs. 1040.

888. GROOMBRIDGE, W. H., AND NEWNS, J. E. Catalysts. British Patent 507,419, June 9, 1939. Chem. Abs., vol. 34, 1940, p. 598.

Metallic compositions, particularly for use as catalysts in the hydrogenation of C compounds, especially CO, are obtained by heating a mixture, preferably finely divided, of a heavy metal oxide with another metal of higher affinity for O to obtain a porous structure of 1 heavy metal oxide permeated with and acting as a support for an oxide of the other heavy metal, which is then reduced with a gaseous reducing agent to form a porous nonfriable structure of the heavy metal of lower affinity for O permeated with the metal of higher affinity for O. Examples describe the preparation of catalysts by heating CuO with Ni or Co at 900°; the products are broken to about 0.25-in. mesh and reduced by water gas at 350°; the catalysts may be used for the conversion of CO and H_2 to CH_4. Other substances may be applied to or incorporated in the metallic compositions. ThO_2 may be applied or incorporated to give a catalyst suitable for synthesizing hydrocarbons from CO and H_2. The catalysts also are suitable for other reactions, such as conversion of EtOH to Me_2CO or reactions in which the metals combine with and remove O and halogens from compounds.

889. ———. Catalysts. British Patent 507,420, June 9, 1939. Chem. Abs., vol. 34, 1940, p. 598.

Metallic composition comprising Fe and Cu is obtained by heating a mixture of finely divided Fe and CuO to above 600° form a hard, sintered mass comprising Cu_2O permeated with Fe oxide, which is, after being broken into granules, reduced, for example, with water gas or producer gas at 500°–800°. The product is used particularly for the manufacture of H_2 from steam, as in the Lane process, or from liquid H_2O under pressure, as in the Bergius process.

890. ——— (Celanese Corp. of America). Metallic Composition. United States Patent 2,234,246, Mar. 11, 1941; appl. filed Nov. 26, 1938 (*Cl. 252–257*). Chem. Abs., vol. 35, 1941, p. 3780.

Metallic composition suitable as a catalyst for the hydrogenation of C compounds comprises a porous structure of an oxide of 1 heavy metal such as cuprous oxide permeated with an supporting the oxide of another heavy metal such as Co oxide having a higher affinity for O_2. A mixture of the 2 in substantially equal proportions is heated to sintering and then reduced in a stream of water gas at about 350°. Such a catalyst is suitable for hydrogenating CO to hydrocarbons.

891. GROOMBRIDGE, W. H., AND PAGE, R. Catalytic Purification of Gases. British Patent 507,593, June 19, 1939. Chem. Abs., vol. 34, 1940, p. 611.

Gas mixtures, particularly CO and H_2, are freed from S by passage at an elevated temperature, 400°–600°, over a catalyst comprising Fe_2O_3 and ZnO; for example, Fe_2O_3 60–80% and ZnO 40–20%. In the gas of gas mixtures such as water gas the ratio between CO and H_2 may be altered to make the product suitable for conversion into CH_4 or higher hydrocarbons or oxygenated compounds such as aliphatic alcohols by conducting the process with the addition of H_2O vapor. Where possible, the catalytic treatment is preceded by a washing with alkali solution to remove as much of the S as possible, and it is followed by a similar washing to remove the remaining S.

892. ———. Exothermic Chemical Process. British Patent 551,312, Feb. 17, 1943. Chem. Abs., vol. 38, 1944, p. 2478.

Describes method and apparatus used in producing hydrocarbons from CO and H_2 on a commercial scale and for other exothermic chemical reactions, especially those carried out in the vapor phase.

893. ——— (Celanese Corp. of America). Treatment of Sulfur-Containing Gases Such as Water Gas. United States Patent 2,239,000, Apr. 22, 1941; appl. filed Nov. 16, 1938, Serial No. 240,790, in Great Britain Dec. 17, 1937; 6 claims (*Cl. 252–373*). Chem. Abs., vol. 35, 1941, p. 4941.

Process for treating S-containing gas mixtures containing CO and H_2 is given to facilitate subsequent removal of S by alkali and to decrease the proportion of CO. The mixture is suitable for the synthesis of hydrocarbons by passing the gas at a temperature of 400°–600° in admixture with H_2O vapor, over a mixture of ferric and Zn oxides.

GROSS, H. W. *See* abs. **1025, 1026, 1027, 1031, 2835.**

894. GROSS, W. (Metallgesellschaft A. G.). [Process for Making Catalysts for Use in Producing Liquid and Solid Hydrocarbons.] German Patent Appl. M145,617, July 17, 1939 (*Cl. IV d–12o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 271; TOM Reel 35, bag 3,440, item 64, 9 pp.

Catalysts containing Fe together with difficultly reducible metal compounds and/or Fe and Cu oxides, which have been precipitated from the nitrates onto kieselguhr supports by means of alkali, are used in producing liquid and solid, as well as oxygenated, organic compounds from CO and H_2 at atmospheric or higher pressure. The kieselguhr is pretreated with the boiling alkali solution, preferably KOH, which is to be used for the precipitation. The precipitation of the metal salts takes place by stirring the salt solution

into the alkali solution containing the kieselguhr. Precipitation is completed when the catalyst slurry has a pH value of 7.5–11, preferably 9–10. After precipitation of the catalyst, water glass is added.

GROSSELFINGER, F. B. *See* abs. **37.**

GROVER, R. K. *See* abs. **1859.**

895. GRUETTER, T. W. Use of Catalysts for Promoting Combustion in Furnaces. British Patent 276,300, Aug. 23, 1926. Chem. Abs., vol. 22, 1928, p. 2456.

Catalysts such as base metal oxides, for example, oxides of Cu, Ni, Co, or Fe, may be applied to porous supports such as bricks or may be injected into fuels.

See also French Patent 651,194 (abs. **1002**).

896. GUINOT, H. M., AND USINES DE MELLE. [Hydrogenation Catalysts.] French Patent 973,322, Feb. 9, 1951. Chem. Abs., vol. 47, 1953, p. 3330.

CuO, preferably on an inert support such as SiO_2 or pumice stone, is reduced by H_2, at 150° in tubes surrounded by H_2O. N_2 may first be passed over the CuO and H_2 gradually admitted to replace the N_2. The space around the tubes is at a predetermined pressure associated with the temperature of the reduction. Organic substances are then reduced by passing them with H_2 through the tubes. Examples are: (1) With 40 tubes 2.5 m. long and 76 mm. diameter, and 350 l. of pastilles of CuO or pumice stone, the intertube space is heated to 135° by passing in steam, with the pressure kept at 4 kg. per $cm.^2$ When the CuO has been reduced, 120 l. Me_2CO per hr. is passed in with 20 times the theoretical amount of H_2 at 150°. The yield of iso-PrOH is theoretical, with 240 l. Me_2CO per hr. the yield is 87%. (2) Similarly 90 l. MeCH : CHCHO per hr. at 160° gives 100% BuOH. (3) PrOH : CEtCHO (75 l. per hr.) at 160° gives a quantitative yield of BuCHEt CH_2OH, with a reduced mixture of CuO activated by CeO. (4) Furfural (90 l. per hr.) at 170° gives a mixture of 2-methylfuran 40 and furfuryl alcohol 60%. (5) AcH at 65° and 187 mm. pressure gives 100% EtOH.

GULF OIL CORP. *See* abs. **436, 437, 438.**

GULF RESEARCH & DEVELOPMENT CO. *See* abs. **446, 587, 807, 1059, 1060, 1061, 1062, 1093, 2387, 2388, 2389, 2390, 2391, 2392, 3867, 3868.**

897. GUNNESS, R. C. (Standard Oil Co.). Hydrocarbon Synthesis. Canadian Patent 475,545, July 24, 1951; appl. filed July 25, 1947, Serial No. 562,236, in the United States Apr. 24, 1941; 4 claims.

Method of converting low molecular weight hydrocarbon gases into hydrocarbons of higher molecular weight, which comprises mixing the hydrocarbon gases with CO_2, recycled gas from the synthesis gas, and steam in such proportions as to provide an atomic proportion of H, C, and O of about 4 : 1 : 1, contacting the mixture with a reforming catalyst at a sufficiently high temperature and for a sufficient time to convert the mixture chiefly into H_2 and CO whereby a make gas is produced having a H_2 : CO ratio of about 2 : 1, suspending a synthesis catalyst in the make gas, maintaining the temperature of the catalyst suspension at a level in the approximate range 225°–425° F. and substantially constant and uniform by directly admixing relatively cool materials with the mixture in a synthesis zone, continuing the contact of make gas with suspended catalyst in the synthesis zone for a period of time sufficient to effect synthesis, then separating suspended catalyst from gases and reaction products, separating unreacted gases and low molecular weight hydrocarbon gases from high-molecular-weight reaction products, and recycling the unreacted gases and low-molecular-weight hydrocarbon gases to the mixing step.

898. ——— (Standard Oil Co.). Hydrocarbon Synthesis. United States Patent 2,533,666, Dec. 12, 1950; appl. filed Dec. 29, 1945, Serial No. 638,412; 8 claims (*Cl. 260–449.6*).

Natural gas is first freed from H_2S and organic S compounds by scrubbing with a solvent such as monoethanolamine or triethanolamine. If necessary, the scrubbing is followed by another scrubbing with a strong caustic solution. The desulforized gas is then mixed with such proportions of CO_2, steam and/or O_2 as to give a gas mixture of atomic ration H : C : O= 4 : 1 : 1 for Co catalyst and 4 : 1 : 1–2 : 1 : 1 for Fe catalyst. The gas mixture is contacted with a reforming catalyst, such as a mixture of oxides of Ni, Fe, and Mn in proportion 1 : 1 : 0.5. Synthesis gas H_2 : CO= 2 : 1–1 : 1 results. The synthesis reactor is a vertical tower that contains no heat exchange surfaces but that may be bounded by heat exchange surfaces. Catalyst is suspended by upflowing synthesis gas. Temperature is controlled by cooling either catalyst or incoming gases or both in a zone outside the synthesis zone. Complete separation of catalyst from reaction products takes place in a settling zone above the reactor. The catalyst is stripped with hot gas before it is cooled and recycled to the synthesis zone. 9 United States patents cited.

899. ——— (Standard Oil Co. of Indiana). Regeneration of a Hydrocarbon Synthesis Catalyst. United States Patent 2,462,861, Mar. 1, 1949; appl. filed Mar. 29, 1947, Serial No. 738,054; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 3994.

Describes process for regeneration of powdered Fe catalyst used in the Fischer-Tropsch process. The spent catalyst is heated at 1,000°–1,200° F. in an oxidizing atmosphere until its C content is reduced to 7–9%. During this step the catalyst is maintained in fluidized condition by upward-flowing air. The catalyst is then activated by injecting H_2 into the catalyst mass at 1,100°–1,300° F. 1 foreign and 2 United States patents cited.

900. ——— (Standard Oil Co.). Synthesizing Hydrocarbons. British Patent 647,155, 1950. Fuel Abs., vol. 9, III, 1951, abs. 1780.

CO and H_2 are contacted with a synthesis catalyst under synthesis conditions, which comprise employing a finely divided catalyst maintained in a suspended, dense phase liquidlike condition in the synthesis zone, by introducing the CO–H_2 mixture at the base of the zone and passing gases upward therein at a low velocity, separating unreacted gases and reaction products from the suspended catalyst and removing untreated gases and light, normally gaseous products from the heavier reaction products.

901. ——— (Standard Oil Co. of Illinois). Synthesizing Hydrocarbons. United States Patent 2,347,682, May 2, 1944. Chem. Abs., vol. 39, 1945, p. 177.

Normally gaseous hydrocarbons, preferably natural gas are first freed from H_2S and organic S compounds by scrubbing with a suitable solvent, such as monoethanolamine or triethanolamine following by scrubbing with a strong caustic solution. The desulfurized gas is mixed with CO_2 to obtain a H : C : O ratio of 4 : 1 : 1. The mixture is brought in contact with a reforming catalyst, (I) of metal oxides of VIII group of the periodic table, unsupported or supported on the commonly used carriers. I is preferably a mixture of oxides of Ni, Fe, and Mn with the proportions of 1 : 1 : 0.5. The temperature of this operation is 1,400°–1,650° F. with pressure from atmospheric to 150 lb. per sq. in. or higher and contact time of 10–30 sec. The product consists chiefly of H_2 and CO in proportion of 2 : 1. This so-called synthesis gas is piped to a reactor where the bulk density of the suspended catalyst is great enough and the gas velocity low enough to maintain a dense opaque phase of suspended catalyst and yet prevent its settling out of the gases, preferably at 10–40 lb per cu. ft., with a gas velocity of 0.5–1.5 ft.

per sec. The temperature is kept at 325°–395° F. for maximum liquid yields. The product is cycled to a settling zone provided with a plurality of centrifugal separators, where the catalyst is removed partly by settling and partly by centrifuging. The gaseous reaction product is further stripped of the catalyst by passing through electrostatic separators and steam. The cleaned gas is fractionated or the C_3 and C_4 hydrocarbons separated by an absorption system. Describes apparatus.

902. ——— (Standard Oil Co.). [Synthetic Production of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 953,555; appl. filed Sept. 26, 1947, issued Dec. 8, 1949, in United States Apr. 24, 1941. Chem. Zentralb., 1950, II, p. 488.

Hydrocarbons are synthesized from CO and H_2 in presence of a suspended and fluidized catalyst, the synthesis gas being introduced from below and passed upwards through the reaction zone, the gaseous and vaporous products being drawn off above. The entrained catalyst is separated from the gaseous and vaporous products centrifugally and then returned to the reaction zone.

903. GUTEHOFFNUNGSHÜTTE OBERHAUSEN A. G. Gas Mixture Containing Carbon Monoxide and Hydrogen. British Patent 343,160, Nov. 15, 1928. Chem. Abs., vol. 27, 1933, p. 830.

H_2O or H_2O vapor is passed through a bed of coke, which is between the poles of a high-frequency generator, so that luminous discharges take place in the coke. The content of CO and H_2 can be varied by varying the frequency and voltage of the current and rate of flow of the H_2O or H_2O vapor.

904. ———. [Method of Quenching and Transporting Used Catalysts.] German Patent Appl. —, PA 852,505, filed Dec. 11, 1942. FIAT Reel B–196, frames 4–6; PB 83,253.

To prevent afteroxidation of a quenched and exhausted hydrogenation catalyst during the time of storage, the H_2O used for quenching contains suitable catalyst poisons, such as H_2S, alkalies such as caustic soda, NH_3, alkali or alkaline earth hydroxide, SO_2, SO_3, or phenols, which react with the used catalyst substance and inactivate it against oxidation.

905. GUTHARDT, K. (F. Krupp Germaniawerft A. G.). [Heat Exchanger for Exothermal Catalytic Gas Reactions.] German Patent 692,836, May 30, 1940 (*Cl. 12 g—4.02*). Chem. Abs., vol. 35, 1941, p. 4252. Gives structural details.

906. GUTHRIE, R. G., AND WILBOR, O. J. (Peoples Gas Byproducts Corp.). Re-Forming Fuel Gases for Use in the Bright Heat-Treatment of Metals. United States Patent 2,164,403, July 4, 1939; appl. filed Mar. 31, 1937. Chem. Abs., vol. 33, 1939, p. 8390.

Method of reforming fuel gas of known composition containing hydrocarbon constituents that are combinable with H_2O vapor to render it suitable for use as an atmosphere for the bright heat treatment of metals comprises intimately agitating the fuel gas in contact with a relatively stationary body of H_2O to produce substantially complete saturation of the gas with H_2O vapor at a predetermined temperature and a predetermined pressure, the temperature and pressure being such with respect to the combinable hydrocarbons present in the gas that the ratio of H_2O vapor to combinable hydrocarbons present in the saturated gas is substantially exact for complete reaction of all of the H_2O vapor with all of the combustible hydrocarbon constituents to produce CO and H_2, and then subjecting the saturated gas to reforming temperature to reform the hydrocarbons and H_2O vapor into CO and H_2. Prescribes apparatus.

GUY, W. R. F. *See* abs. **2093.**

907. GUYER, J. A. (Phillips Petroleum Co.). Combined Hydrocarbon Conversion—Hydrocarbon Synthesis Process. United States Patent 2,518,775, Aug. 15, 1950; appl. filed Aug. 29, 1947, Serial No. 771,332; 3 claims (*Cl. 260–449.6*).

Contaminated used catalyst from hydrocarbon conversion is treated with steam and O_2 in a regeneration zone at 1,100°–1,800° F., pressure up to 25 atm. absolute. The regeneration gas has a steam : O_2 ratio in range of 9 : 1–1 : 4 vol. The regeneration effluent gas is suitable synthesis gas for Fischer-Tropsch synthesis. The ration of CO_2 : CO in volume % is 56 : 44. CO_2 and H_2O are removed. The synthesis gas is contacted with a Fischer-Tropsch catalyst at 340°–700° F. and a pressure 1–20 atm. The effluent is separated into gasoline and heavier oil fractions. The heavier fraction is recycled to the cracking step. 8 United States patents cited.

———. *See* abs. **822.**

908. GWYNN, M. H. Catalysts Suitable for use in Hydrogenating Carbon Monoxide, Hydrofining Various Oils, "Doctor Sweetening" Light Petroleum Distillates, etc. United States Patent 2,319,453, May 18, 1943; appl. filed May 31, 1940, Serial No. 338,233; 7 claims (*Cl. 252–255*). Chem. Abs., vol. 37, 1943, p. 6439.

Highly active hydrated and black catalytic surfaces or surface layers are prepared by treating a metal such as Co or Ni, or a readily reducible ferromagnetic alloy with an aqueous solution of a chlorite, suitably after roasting and treatment with steam. Gives numerous details of different treatments.

908. ——— (Allied Chemical & Dye Corp.). Cleaning Metal Catalysts With Alcoholic Caustic Solution. United States Patent 2,473,880, June 21, 1949; appl. filed Aug. 11, 1942, Serial No. 454,429; 3 claims (*Cl. 252–414*). Chem. Abs., vol. 43, 1949, p. 6763.

Deposits of resinous materials are removed from hydrogenation catalysts such as Ni, Cu, Co, Pt, and Pd catalysts of supported or unsupported, stationary or powdered type by treatment with a solution of caustic alkali in an aliphatic alcohol or ketol. The temperature range is 150°–300° C., and the preferred alcoholic solvent is ethylene glycol. Alcohols or ketols boiling below 150° C. may be used when the solution is maintained under superatmospheric pressure high enough to prevent undue volatilization of the solvent at the temperatures used for treating the catalyst. After treatment with the caustic alkali solution, the catalyst is washed with H_2O to remove the resinous material, which has been made H_2O-soluble but not removed by the solution. The catalyst may be used without further treatment or may be subjected to reactivation, for example, by immersion in a solution of nitrate of the catalytic metal followed by decomposition of the nitrate. In a train of converters connected in series, it may be necessary to remove resin only from the catalyst near the reaction zone; the remainder of the catalyst may be shifted toward the inlet end and fresh catalyst introduced at the outlet end of the zone. 4 literature refs., 3 foreign patents, and 11 United States patents cited.

H

HAAYMAN, P. W. *See* abs. **3365.**

HABESHAW, J. *See* abs. **188.**

910. HAENSEL, V. (Universal Oil Products Co.). Catalysts Containing Alumina, Combined Halogen, and

Platinum. United States Patent 2,611,749, Sept. 23, 1952. Chem. Abs., vol. 47, 1953, p. 2474.

Catalyst suitable for conversion reactions, such as the reforming of hydrocarbons, is prepared by intimately mixing 0.1–8% of a combined halogen with Al_2O_3, mixing therewith finely divided PtS formed by precipitation from a solution of a Pt salt in an aqueous organic solvent, and subsequently calcining the resulting Al_2O_3–combined halogen–PtS composite to form a supported catalyst containing 0.01–1% Pt. The catalyst is particularly suitable for the destructive hydrogenation or hydrocracking reactions in which hydrocarbon oils heavier than gasoline are converted to produce lower boiling products, particularly gasoline. It also may be used for hydrogenation reactions, such as the hydrogenation of unsaturated hydrocarbons, cyclic hydrocarbons, alcohols, ketones, and acids to the corresponding saturated products, or for oxidation of olefins to form olefin oxides, oxidation of alcohols, and ketones.

911. ——— (Universal Oil Products Co.). Hydrocarbon-Conversion Catalysts. United States Patent 2,636,863, Apr. 28, 1953. Chem. Abs., vol. 47, 1953, p. 11,716.

A catalyst for hydrocarbon conversion which minimizes cracking or controls it at a low level is composed of Al_2O_3 plus 0.01–1% Pt, with or without halogen (0.05–3% F or 0.2–8% Cl).

912. HAFFNER, A. E., AND PEXTON, S. (Gas Light & Coke Co.). Water Gas Enriched With Hydrogen. British Patent 517,530, Feb. 1, 1940. Chem. Abs., vol. 35, 1941, p. 7157.

Mixture of water gas and steam leaving the generator is passed into a contact chamber where it is brought in contact with an Fe oxide catalyst for promoting the reaction between CO and steam to produce H_2 and CO_2. Describes apparatus.

913. HAGEMANN, A. (Alien Property Custodian). Preparation of High-Grade Antiknock Motor Fuels. United States Patent 2,403,524, July 9, 1946; appl. filed Mar. 10, 1941, APC No. 382,639, in Germany Feb. 8, 1940; 6 claims (*Cl. 260–449.6*).

Unsaturated, low-molecular hydrocarbons obtained by cracking high-molecular hydrocarbons are selectively polymerized to convert only the unsaturated isohydrocarbons. The resulting products are treated with CO and H_2 at pressures of 50–200 atm. and temperatures of at least 300°. Alcohols are thus formed that are dehydrated at normal pressure into alkenes having branched chains. These are subsequently hydrogenated, producing an aviation fuel of high octane number.

914. ——— (Ruhrchemie A. G.). [Process for Producing High-Performance Motor Fuels.] German Patent 733,749, Mar. 4, 1943; appl. R 108,271, R 533, filed Sept. 6, 1940 (*Cl. 12 o–1.06*). FIAT Reel AA–88, frames 4,141–4,142; PB 70,273; TOM Reel 177, frames 1,605–1,608; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 33, 1948, p. 82; Chem. Abs., vol. 38, 1944, p. 1094.

High-grade fuels are obtained from CO hydrogenation. The C_3–C_4 fraction of the primary product is polymerized and hydrogenated. The C_7–C_{10} fraction is aromatized. The products resulting from the individual treatment of these fractions are then combined.

915. ——— (Ruhrchemie A. G.). [Production of Lubricants.] French Patent 874,483, Aug. 7, 1942; appl. filed Aug. 4, 1941. TOM Reel 36, bag 3,451, item 8.

For production of lubricants by polymerization of the hydrogenation products of CO with $AlCl_3$ or other polymerization agents, materials are used that are obtained through the use of water gas at a recycle ratio of 1:3–1:5. Mixtures b. 150° and above, preferably 220° and above, are suitable as raw materials.

916. ——— (Ruhrchemie A. G.). [Production of Lubricants.] Norwegian Patent 65,217, Sept. 14, 1942; appl. filed July 9, 1941. TOM Reel 36, bag 3451, item i.

See French Patent 874,483 (abs. **915**).

917. ——— (Ruhrchemie A. G.). [Production of Lubricants.] Swedish Patent 106,009, Dec. 1, 1942; appl. filed July 25, 1941.

See French Patent 874,483 (abs. **915**).

———. *See* abs. **830**.

918. HAGEMANN, A., AND TRAMM, H. (Ruhrchemie A. G.). [Benzine-Like Substances.] German Patent 730,995, Dec. 24, 1942 (*Cl. 12 o–1.06*). Chem. Abs., vol. 38, 1944, p. 635.

Benzine-like substances are obtained by polymerizing olefinic hydrocarbons. The polymerization is done under pressure at an elevated temperature. As the polymerization progresses, the rate of flow of the unpolymerized part is gradually slowed down. This is conveniently done, for example, by gradually increasing the cross-sectional area across which the gas flows.

919. HAGEMEYER, H. J. (Eastman Kodak Co.). Ketene Condensation Products With Aldehydes. United States Patent 2,466,420, Apr. 5, 1949. Chem. Abs., vol. 43, 1949, p. 5037.

Ketene (I) (2 mols.) is slowly added to Ni butyrate 1 gm. in furfural 200 cc. with high-speed stirring; the exothermic reaction keeps the mixture at 30°–40°. The reaction mixture contains mostly β–2–furyl–β–propional–acetone, as shown by distillation at 1 atm. with decarboxylation and formation of 30 gm. 2–vinylfuran (II). $Ba(OAc)_2$ at 45° gave 34 gm. (II), Co isobutyrate 34 gm. (II), and Zn butyrate 27 gm. (II). Yields of (II) without catalyst and outside the temperature range 30°–60° were low. Passage of (I) 84 into Hg $(OAc)_2$ 2 gm. in BzH 200 cc. at 45° gave mostly β–phenyl–β–propionolactone, converted by 30 min. reflux and distillation to 41 gm. styrene, b. 143°–144°. Other β-substituted β–propionolactones prepared are the *m*–nitrophenyl, 5–methyl–2–furyl, 5–chloro–2–furyl, 2–naphthyl, and *p*–propylphenyl derivatives.

920. ——— (Eastman Kodak Co.). Manufacture of Carboxyl Compounds. United States Patent 2,593,440, Apr. 22, 1952; appl. filed Apr. 22, 1948, Serial No. 22,714; 6 claims (*Cl. 260–533*).

Lower aliphatic acids are prepared by reacting lower aliphatic olefins with CO and H_2O at 150°–400° and 40–700 atm. in the presence of a 3-component catalyst comprising (1) a chloride of a carbonyl-forming metal from group 8, (2) a metal selected from the group consisting of Ni and Co, and (3) a promoter comprising an alkali-metal halide. 19 examples.

921. ——— (Eastman Kodak Co.). Processes for the Production of Oxygenated Compounds. United States Patent 2,576,113, Nov. 27, 1951; appl. filed Apr. 22, 1948, Serial No. 22, 713; 8 claims (*Cl. 260–604*). Chem. Abs., vol. 46, 1952, p. 5074.

Describes method for producing oxygenated organic compounds such as aldehydes, ketones, alcohols, and the like, specifically carbonyl compounds such as propionaldehyde and butyraldehyde, by reacting an aliphatic olefin with CO and H_2. Reaction is carried out at elevated temperatures and pressures within the range 50°–250° and 40–700 atm. in the presence of a buffered metalsalt catalyst containing a H_2O-soluble salt of Co or Fe with a buffering agent consisting essentially of an alkali metal salt of an aliphatic carboxylic acid. The preferred catalyst materials are the Co and Fe salts of the lower aliphatic carboxylic acids and Co basic carbonate. Promoters are usually em-

ployed in the form of salts of the aliphatic carboxylic acids. A typical catalyst composition contains 20 parts of Co acetate, 6 of Na acetate, 2 Mg acetate, and 0.75 part of Th acetate dissolved in H_2O. Gives 13 typical examples.

HAGER, G. F. *See* abs. **1103.**

922. HAGY, J. D. (Stanolind Oil & Gas Co.). Gas Processing for the Synthesis of Hydrocarbons. United States Patent 2,493,454, Jan. 3, 1950; appl. filed Dec. 15, 1944, Serial No. 568,315; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 2221.

Compressed air, natural gas, and a small amount of recycled gas are raised to reaction temperature by combustion of a part of the gas with all of the air within a combustion case. The remaining gas is bled into the hot gases from the combustion case at the entrance to the reformers. The reaction within the reforming case is very nearly adiabatic. The synthol feed gas so produced is supplied to the reactor using fluidized catalyst. Bayonet type tube assembly removes heat directly from the reactor. Saturated steam at 200 p. s. i. is generated within the tube assembly. Control of rate of heat removal may be either by variation of steam pressure or by control of the number of tubes in operation. The product is cooled by direct contact with H_2O. Product is recovered from the uncondensed gases by adsorption on activated C. Ordinarily 2 gas re-formers, 6 synthol reactors, and 2 product-cooling towers of the types described may be used in a plant producing 5,000 bbl. liquid product per day from 76,400 M cu. ft. per D of natural gas. 16 United States patents cited.

923. HALE, C. C. (Standard Oil Development Co.). Recovery of Organic Acids From Dilute Aqueous Solution. United States Patent 2,537,133, Jan. 9, 1951; appl. filed Dec. 18, 1948, Serial No. 66,107; 4 claims (*Cl. 260–450*). Chem. Abs., vol. 45, 1951, p. 3147.

Dilute acid solutions are reacted with a Bi compound, preferably an oxide, or a mixture of Bi compounds in the case of acetic acid, a basic Bi acetate is precipitated, which, after ordinary drying, has the formula BiOAc. The acids are regenerated from the Bi fatty acid salt precipitate and recovered in commercial strengths. 2 literature refs. cited.

924. HALE, C. H. (Standard Oil Development Co.). Iron Removal From Aldehyde Synthesis Process. United States Patent 2,604,491, July 22, 1952; appl. filed Apr. 1, 1949, Serial No. 84,878; 14 claims (*Cl. 260–598*).

In the 3-stage process for conversion of CO, H_2, and olefins to oxygenated organic compounds, the products of the 1st step containing dissolved salts and the carbonyls and molecular complexes of the metal catalyst are treated in the 2d step to remove the dissolved catalyst material from the mixture before the 3d or hydrogenation step. To accomplish this the primary reaction product, from which the bulk of the dissolved metal has been removed by heat treatment and stripping, is treated in a reflux zone with an aqueous alkaline treating agent at temperatures ranging from room temperature to the boiling point of the effluent, whereby a precipitate of Fe and Co hydroxide is obtained with recovery of a liquid product comprising oxygenated organic compounds substantially free of dissolved and dispersed Co and Fe. The alkaline treating agent may be an alkali metal hydroxide or carbonate, or an organic derivative of NH_3, such as a tetra-alkyl ammonium hydroxide.

925. ——— (Standard Oil Development Co.). Topped Oxo Alcohol Treatment by Caustic and Air. United States Patent 2,595,785, May 6, 1952; appl. filed Oct. 8, 1949, Serial No. 120,423; 3 claims (*Cl. 260–638*). Chem. Abs., vol. 46, 1952, p. 6814.

Crude, H_2O-immiscible alcohols having 6–14 C atoms and produced by the Oxo synthesis contain substantial amounts of impurities in the form of acids, free carbonyls, aldehydes, acetals, and esters, which are detrimental to the odor, color, and plasticizing properties of the products. These impurities can be removed by extracting crude alcohols in the liquid phase with an aqueous caustic solution of 1–25% concentration at temperatures 150°–175° with simultaneous exposure to an O_2-containing gas, as air, at least 1 time before distillation. The treatment should be applied as quickly as possible to the crude alcohol after the hydrogenation stage. The mixture is allowed to stratify into a lower aqueous layer and an upper alcohol layer, which is separated. The alcohol is washed free of caustic and then distilled to give a purified alcohol product relatively free of ester color-forming impurities, including aldehydes and acetals. Treatment can generally be carried out at or near atmospheric pressure for only a short period.

926. HALE, C. H., AND STARR, C. E., JR. (Standard Oil Development Co.). Treatment of Topped Oxo Alcohol With Molecular Oxygen and Caustic.] United States Patent 2,595,786, May 6, 1952; appl. filed June 1, 1950, Serial No. 165,608; 9 claims (*Cl. 202–57*). Chem. Abs., vol. 46, 1952, p. 6814.

Unstable S compounds are removed from Oxo-process alcohols of the C_4–C_{20} range by superatmosphere molecular–O_2 oxidation in the presence of aqueous caustic; then the treated alcohols are distilled. Special conditions disclosed are the use of air of O_2 pressures of as high as 300 p. s. i. g. and temperatures 100°–250°.

See also United States Patents 2,595,763 (abs. **314**) and 2,595,785 (abs. **925**).

927. HALE, W. J. Organic Anhydrides. United States Patent 2,117,554, May 17, 1938; appl. filed Sept. 27, 1934, Serial No. 745,831; 16 claims (*Cl. 260–123*). Chem. Abs., vol. 32, 1938, p. 5004.

Organic compound containing a labile H atom adjacent to a nonmetallic element other than C (such as HOAc to form Ac_2O) is treated with CO $<$ 5–1,000 atm. pressure and at temperatures of —10° to —20° in the presence of an H halide, such as HCl, and a metal salt, such as Cu_2Cl_2, and the anhydride formed is distilled. Gives various examples, with details.

HALLER, W. *See* abs. **3918, 3919, 3921.**

HAMA, Y. *See* abs. **3715.**

928. HANFORD, W. E. (M. W. Kellogg Co.). Dehydration of Organic Acids. United States Patent 2,578,698, Dec. 18, 1951; appl. filed Sept. 24, 1948, Serial No. 51,107; 13 claims (*Cl. 260–450*).

Aqueous solution of a fatty organic acid obtained in the catalytic hydrogenation of CO is separated by contacting the solution with a solvent comprising a dialkyl amide of an organic acid to produce an extract phase and a raffinate phase and then separating the phases. Example: 100 cc. of an aqueous solution of acetic acid was admixed with 100 cc. of dimethylamide of oleic acid, the mixture was allowed to settle in an extract phase and a raffinite phase, and these were separated. The partition ratio used in judging the extraction efficiency (defined as the gm. of acetic acid per 100 cc of the extract, or solvent, layer, divided by the gm. of acetic acid per 100 cc. of the raffinate, or H_2O, layer) was found to be 1.18, whereas the % of H_2O present in the 2 phases were found to be 5.2 and 94.7%, respectively. Gives other examples utilizing the dimethylamides of tolylstearic and of phenylstearic acids.

HANISCH, F. *See* abs. **2815, 2816, 2819, 2820, 2821.**

HANISCH, H. *See* abs. **802, 803, 804, 805, 806.**

929. HANKE, F. (Krupp Treibstoffwerk G. m. b. H.). [Refining Synthetic Benzine Hydrocarbons.] German Patent 719,449, Mar. 12, 1942; appl. K 155,906, filed Nov. 1, 1939 (*Cl. 23 b–1.05*). Chem. Abs., vol. 37, 1943, p. 1852.

Benzine synthesized at low pressure from CO and H_2 is 1st treated with organic polyhydroxy compounds, preferably such that can be esterified with organic bases. These liquids are then removed, and the benzine is washed with NaOH and/or H_2O.

930. HANS, A. J. E. [Coke-Oven Gas.] French Patent 817,767, Sept. 10, 1937. Chem. Abs., vol. 32, 1938, p. 2327.

Gas is subjected to an oxidizing cracking at a high temperature in the presence of O_2, whereby the CH_4 is converted to H_2 and CO. The H_2 and N_2 in the resulting gases are separated in a liquefaction apparatus and used for the production of NH_3. The CO may be used along with H_2 for the synthesis of MeOH.

931. HANSEN, F. J. M. [Hydrogenation of Coal.] French Patent 647,981, Jan. 28, 1928. Chem. Abs., vol. 23, 1929, p. 2555.

Coal, hydrocarbons, or C are hydrogenated by the action of an electric arc or sparks from a condenser discharge between electrodes immersed in a solvent for the products. One electrode is made of, or contains, a catalytically active metal such as Ni or contains a salt such as $NiCO_3$, which becomes dispersed in the liquid. Gives examples of the hydrogenation of coal and water gas.

932. HANSGIRG, F. Furnace Gases Low in Nitrogen and Suitable for Synthetic Purposes. United States Patent 2,337,551, Dec. 28, 1943. Chem. Abs., vol. 38, 1944, p. 3458.

Describes apparatus, and a process is employed for producing gases consisting largely of H_2 and CO, which involves employing substantially N_2-free O_2 together with inflammable hydrocarbon gases low in N_2 as a blast gas in metallurgical reduction processes carried out in furnaces requiring the use of a blast, as in the reduction of iron ore. CH_4-rich waste gases from oil-synthesis and coal-hydrogenation processes, coke-oven gas, or natural gas may be used.

933. ———. [Production of Synthesis Gas.] Italian Patent 373,541, Apr. 28, 1939. TOM Reel 41, bag 2744, item 23.

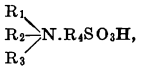
See United States Patent 2,337,551 (abs. **932**).

934. ———. (Österreichische-amerikanische Magnesit A.-G.) [Reaction of Carbon Monoxide and Steam.] Austrian Patent 139,830, Dec. 10, 1934 (*Cl. 12a*). Chem. Abs., vol. 29, 1935, p. 2673.

See French Patent 770,608 (abs. **2550**).

935. HARBAN, A. A., AND JOHNSON, C. E. (Standard Oil Co. of Indiana). Extraction of Oxygenated Compounds. United States Patent 2,522,619, Sept. 19, 1950; appl. filed Sept. 30, 1949, Serial No. 118,746; 15 claims (*Cl. 260–450*). Chem. Abs., vol. 45, 1951, p. 848.

Gives process for selective extraction of one or more neutral, oxygenated, oil-soluble organic compounds from their mixture with hydrocarbon oils such as those produced in Fischer-Tropsch or Synol processes. An amine sulfonate is used as solvent. The amine sulfonate has the general formula



wherein R_1 and R_2 are selected from the class consisting of H_2 and saturated hydrocarbon radicals, R_3 is a saturated hydrocarbon radical, and R_4 is selected from the class consisting of saturated hydrocarbon radicals and aromatic hydrocarbon radicals.

HARDY, J. V. E. *See* abs. **870**.

936. HARLAN, J. T. (Shell Development Co.). Production of Oxygenated Compounds. United States Patent 2,504,682, Apr. 18, 1950; appl. filed Nov. 8, 1946, Serial No. 708,625; 5 claims (*Cl. 260–632*). Chem. Abs., vol. 44, 1950, p. 6876.

Oxo synthesis is carried out in at least 2 stages. Fresh synthesis gas containing a major molecular amount of CO and a minor molecular amount of H_2 is supplied to the 1st stage along with the reactant containing the ethylenic linkage, and the unreacted synthesis gas is continuously recycled in this stage. H_2, substantially free of CO, is supplied to the last stage and unreacted hydrogenating gas is recycled to this stage. Enough recycle gas from the last stage is continuously transferred to the gas stream and recycled to the 1st stage to maintain the ratio CO : H_2=1 : 1 or above. Any gas vented is from the recycle gas in the 1st stage. 5 United States patents cited.

———. *See* abs. **2048**.

HARSHAW CHEMICAL CO. *See* abs. **2695**.

HART, M. *See* abs. **3798, 3800, 3833**.

937. HART, M., HOOG, H., AND WEEDA, K. A. (Shell Development Co.). Reactivation of Cobalt Oxo Catalyst. United States Patent 2,529,236, Nov. 7, 1950; appl. filed May 1, 1948, Serial No. 24,667, in the Netherlands May 2, 1947; 3 claims (*Cl. 252–416*). Chem. Abs., vol. 45, 1951, p. 2607.

Gives method for reactivation of Co catalyst used in carbonylation of organic compounds by the Oxo process. The catalyst is subjected to a very high temperature (700°–900° C.) oxidation followed by a high temperature reduction, 400° or above. Over a pumice stone catalyst containing 8% Co, olefins and water gas were passed at a pressure of 200 atm. and 140°–180°, giving a product containing 65% aldehydes. Co was added to the olefin feed as Co salts of C_6–C_9 fatty acids from oxidation of aldehydes formed in an amount to give 0.15–0.25% Co in the olefin feed. After 700 hr. the aldehyde content of the product has decreased to 25–30%. Hydrogenation of the catalyst at 475° and 200 atm. gave only partial reactivation, the product then containing 55% aldehydes, which decreased to 25%, at which point hydrogenation was ineffective in reactivation. Superficial oxidation of a portion of this catalyst followed by repeated hydrogenation, did not improve its activity. Another portion of this catalyst was heated in air for a few min. at 700°–900° and subsequently reduced with H_2 at 475° and atmospheric pressure, giving a catalyst that yielded a product containing 68% aldehydes. Before the reactivation treatment the catalyst contained less than 0.5% C and only a trace of S, and its low activity could not be attributed to those nor to the Cu content of the catalyst near the inlet, since it is know that Cu is not harmful and in any case would not have been removed in reactivation. 6 United States patents cited.

938. HARTER, H. [Apparatus for Effecting Exothermic Catalytic Gas Reactions Under Pressure.] German Patent 589,014, Dec. 1, 1933; (*Cl. 12k–3*). Chem. Abs., vol. 28, 1934, p. 1226.

See British Patent 325,028 (abs. **939**).

939. ———. Apparatus for Exothermic Catalytic Gas Reactions. British Patent 325,028, Nov. 24, 1928. Chem. Abs., vol. 24, 1930, p. 3678.

Heat-insulating cylinder is placed between a reaction cylinder and an outer pressure-resisting wall. Describes various details of construction.

940. ———. Apparatus for Exothermic Catalytic Gas Reactions. United States Patent 1,779,092, Oct. 21, 1930; appl. filed July 9, 1927, Serial No. 204,649, in Germany Aug. 10, 1926, divided and this appl. filed

July 9, 1928, Serial No. 291,302. Chem. Abs., vol. 25. 1931, p. 176.

Describes structural features.

941. ———. [Catalyst for Ammonia Synthesis.] German Patent 647,720, July 10, 1937 (*Cl. 12k–3*). Chem. Abs., vol. 31, 1937, p. 8133.

Catalyst consists of Fe, Fe_2O_3, difficultly reducible metal oxides, and the corresponding metals. The presence of the metals is ensured by reducing their oxides by adding reducing metals, such as Ca, Mg, or Al, to the fused mass and stirring. Thus, freshly precipitated $Fe(OH)_2$ is intimately mixed with nitrates of U, Th, and Zr, dried, and heated to glowing in a current of H_2. The resulting mass of Fe, Fe_2O_3, and difficultly reducible oxides of U, Th, and Zr is given an addition of Al, Ca, and Mg well mixed and fused. The oxides of U, Th, and Zr are partly reduced by the Al, Ca, and Mg to insure the presence of some metallic U, Th, and Zr. The product is used as the catalyst for NH_3 syntheses. Gives other examples. Small amounts of Mo and W may be added with the Al.

942. ———. Gases Containing Hydrogen Produced From Those Containing Methane. United States Patent 1,920,858, Aug. 1, 1933; appl. filed Feb. 14, 1929. Chem. Abs., vol. 27, 1933, p. 4888.

Gas rich in CH_4 such as natural gas is mixed with steam, and the mixture is passed over a ferriferous catalyst in a 1st apparatus to produce H_2 and CO_2; another portion of the original CH_4-containing gas is treated with a gas rich in O_2 and the mixture is heated in a 2d apparatus to produce CO and H_2, and the products formed in the 2d apparatus are utilized for reducing and heating the catalyst material in the 1st apparatus.

943. ———. [Hydrogen-Carbon Monoxide Mixtures From Methane and Steam.] Polish Patent 10,914, Mar. 3, 1930; appl. filed June 23, 1928. Chem. Zentralb., 1931, I, p. 401.

Gases rich in CH_4, such as coke-oven or natural gas, are divided and a part treated with steam and air in presence of catalysts to form CO and H_2. The other part is treated with O_2 with or without catalysts to form CO and H_2 to be used in the first apparatus to reduce the catalyst and to recover liquid hydrocarbons. The gases formed by the reduction and remaining in the first apparatus are, after removal of CO_2 and H_2O, used for NH_3 synthesis or for hydrogenation, depending on whether they consist mainly of H_2 and N_2 or CO and H_2.

HARTFORD NATIONAL BANK & TRUST CO. *See* abs. **3365.**

HASHIMOTO, G. *See* abs. **1891.**

HATCH, G. B. *See* abs. **2632.**

944. HÄUBER, H., AND HIRSCHBECK, J. (I. G. Farbenindustrie A. G.). Ethylene From Saturated Hydrocarbons. United States Patent 2,154,676, Apr. 18, 1939. Chem. Abs., vol. 33, 1939, p. 5416.

Describes arrangement of apparatus and a process for producing C_2H_4, which comprises cracking saturated hydrocarbons such as C_3H_8 to form a substantial amount of C_2H_4, removing from the cracked product any compounds containing triple C linkages and also substances liquid under ordinary conditions of temperature and pressure, treating the remaining gases containing C_2H_4 together with higher olefins with an ammoniacal cuprous salt solution, thereby separating the olefins from the gases, expelling the olefins from the solution and then separating them by distillation into C_2H_4 and higher olefins, passing the higher olefins, together with the part of the gases not having been absorbed by the ammoniacal cuprous salt solution at an elevated temperature over a hydrogenating catalyst and subjecting the hydrogenated gas after removal of CH_4, if any is present, again to cracking to form a substantial amount of C_2H_4.

944a. ——— (I. G. Farbenindustrie A. G.). Hydrocarbon-Oil Production by Polymerizing Olefinic Gases. United States Patent 2,159,148, May 23, 1939. Chem. Abs., vol. 33, 1939, p. 7091.

Catalyst such as $AlCl_3$ or BF_3 is used for the polymerization of a gas, such as one formed by reaction of CO with H_2, containing over 30% of gaseous olefins with a preponderating proportion of butylenes and amylenes, and the polymerization product is subjected to hydrogenation and to treatment with superheated steam in the presence of a caustic alkali to produce an insulating oil.

945. ——— (I. G. Farbenindustrie A. G.). [Process for Obtaining Hydrocarbon Oils Suitable as Insulating Oils.] German Patent 746,304, July 21, 1944; appl. I 58,456, July 7, 1937 (*Cl. 12 o–1.06*). FIAT Reel AA 88, frames 4,146–4,148; PB 70,273; TOM Reel 67, item 74, frames 1,111–1,112.

Gases containing 30–40% or more of olefins with the range of propylene to amylene, such as the end gases from the conversion of CO with H_2, are polymerized until only very small amounts of unsaturated hydrocarbons remain. The liquid products are then hydrogenated at 140°–150° under a pressure of 200 atm. over a Ni catalyst. The hydrogenated oil is treated with superheated steam in the presence of about 2.5% of caustic alkali, The distillate oils, after removal of the lighter fractions as gasoline and diesel oil, contain about 51% of oil suitable for insulating oil.

946. HAUSSMANN, H., FÄRHÄUSER, F., AND SATTLER, J. (I. G. Farbenindustrie A. G.). [Textile Lubricants.] German Patent 748,836, no date. Kainer, p. 273.

Sulfonation products of high-molecular olefins from synthetic oils are used together with low-volaitile hydrocarbon oils for textile lubricants.

HAVESTADT, L. *See* abs. **3303.**

947. HAWK, C. O., STERN, N. R., AND HOFER, L. J. E. (United States of America as Represented by the Secretary of the Interior). Catalyst for the Synthesis of Hydrocarbons. United States Patent 2,449,071, Sept. 14, 1948; appl. filed Nov. 7, 1945, Serial No. 627,271; 12 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 827.

Preparation of a catalyst containing 10%–20% by weight of meta form ferric oxide, $Fe_2O_3 \cdot H_2O$ is given in the following example: Solution 1, $Fe(NO_3)_3 \cdot 9H_2O$, 1,518 gm. in 3 l. H_2O; and solution 2, K_2CO_3 (anhydrous) 856 gm. in 1.5 l. H_2O were made up and heated to 75° C. Solution 2 was then added slowly (20 min. period) to solution 1 with agitation. The temperature was maintained at 75° C. The volume of the slurry was increased to 12 l. by addition of H_2O (75° C.). The precipitate was allowed to settle and the supernatant liquor withdrawn by decantation. Over a period of 2 weeks the precipitate was washed 16 times by decantation, 8 l. of H_2O being withdrawn at each washing. The last decantation contained less than 1 part nitrate to 16,000 parts H_2O. The precipitated oxide was filtered, spread upon a plate, and air dried 114 hr. at room temperature. It was then placed in an electrically heated drying oven. The temperature was raised from room temperature to 149° C. in 9.5 hr. and held at this temperature 38.5 hr. longer. The catalyst was ground and compressed into pellets ⅛ in. in diameter and 3/32 in. long. The estimated amount of K did not exceed 0.1%. The catalyst was conditioned with synthesis gas, H_2: CO (1 : 1) for 15 hr. at atmospheric pressure and 240° C., synthesis gas H_2: CO (2 : 1) for an additional 62 hr. at the same pressure and temperature. The space velocity was about 150 per hr. (N. T. P.). At the end of this period

a synthesis gas, H_2:CO (2:3), was passed over the catalyst at 100–135 p. a. i., 250°, and a space velocity 150 per hr. (N. T. P.). For a single pass operation, using a 12-in. bed, over a 5-wk. test period the yield of hydrocarbons heavier than butane averaged 66 gm. per $m.^3$ synthesis gas (N. T. P.). During the 3d week the yield was 70 gm. per $m.^3$ synthesis gas. 3 literature refs., 4 United States patents, and 1 foreign patent cited.

948. HAYS, G. E. (Phillips Petroleum Co.). Method of Separating High-Condensation-Point Materials From Hydrocarbons. United States Patent 2,560,645, July 17, 1951; appl. filed Nov. 28, 1947, Serial No. 788,407; 5 claims (*Cl. 260–450*).

Process and equipment specifically described for removing relatively high condensation point materials from the effluent of Fischer-Tropsch synthesis reactions and further concentrating the byproducts thereof.

949. HECKEL, H. (Hydrocarbon Synthesis Corp.). Paraffinic Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,339,927, Jan. 25, 1944; appl. filed Jan. 8, 1941, Serial No. 373,704, in Germany Jan. 5, 1940; 3 claims (*Cl. 260–449.6*). Chem. Abs., vol. 38, 1944, p. 4122.

CO and H_2 (1:2 vol.) are passed at a temperature of about 160°–175° and under 5–50 atm. pressure over a Co on kieselguhr catalyst, such as one containing Co and Mn (100:15) and infusorial earth 10–20 parts by weight, the Mn serving as an activator.

———. *See* abs. **2819, 2820, 2821.**

950. HECKEL, H., AND ROELEN, O. Activated Catalyst for Hydrocarbon Synthesis, United States Patent 2,369,106, Feb. 6, 1945. Chem. Abs. vol. 39, 1945, p. 3148.

The yield of solid and liquid hydrocarbons from CO and H_2, or water gas, normally secured by means of a Fe catalyst can be increased by the use of a catalyst prepared by the coprecipitation of Fe and Ca hydroxides from solutions of the chloride or nitrate by means of alkali hydroxides. Ca and/or Mg should make up 10–50% of the total weight of the compound calculated as oxides. The mixture is easier to filter than $Fe(OH)_3$ alone. The catalyst is preferably activated by adding 2–5% of at least 1 metal from the group Ni, Co, and Cu, thus shortening the induction period. The catalyst may be supported on diatomite powder, powdered MgO, pumice, and clay. In 1 example the catalyst is reduced in water gas at 245°.

951. ——— (Hydrocarbon Synthesis Corp.). Catalysts Containing Magnesium Oxide and Cobalt for the Catalytic Hydrogenation of Carbon Oxides. United States Patent, 2,219,042, Oct. 22, 1940; appl. filed Sept. 17, 1938, Serial No. 230, 511, in Germany Sept. 27, 1937; 3 claims (*Cl. 23–236*). Chem. Abs., vol. 35, 1941, p. 1063.

Method employed for the preparation of catalysts suitable for use in the production of hydrocarbons from C oxides by hydrogenation involves precipitating together basic compounds such as the carbonates of Mg and Co from a solution of Mg and Co chlorides or nitrates containing at least approximately 10% more Mg in relation to Co than corresponds to the ratio of Mg:Co in the catalyst to be prepared, as by use of Na_2CO_3, and removing the precipitate before complete precipitation of the Mg oxide occurs. Th compounds also may be used.

952. ——— (Ruhrchemie A. G.). [Cobalt-Magnesium Catalyst for the Conversion of Carbon Monoxide-Hydrogen Mixtures.] Swedish Patent 95,639, May 9, 1939; appl. filed Sept. 23, 1938. Chem. Zentralb., 1940, I, p. 816.

Mg and Co are precipitated together or separately from solutions of the nitrates or chlorides whereby the concentration of this solution in Mg salts is equal or higher, 25–75%, than the stoichiometric ratio in which the Co and Mg should be in the finished catalyst.

953. HECKEL, W. (International Hydrocarbon Synthesis Co.). [Synthetic Paraffin.] Italian Patent 371,909, no date. Kainer, p. 213.

To produce as much paraffin as possible, the synthesis is carried out at pressures of 5–50 atm. over Co catalysts containing at least 200 gm., preferably 300 gm., of Co per l. and 5–25% of the Co as Mn activator. The best temperature lies at 160°–185°. Out of a total yield of about 120 gm, per $m.^3$ of synthesis gas, 60% of paraffin is obtained.

954. ——— (International Hydrocarbon Synthesis Co.). [Synthetic Paraffin.] Swedish Patent 104,476, no date. Kainer, p. 213.

See Italian Patent 371,909 (abs. **953**).

955. HEDBERG, D. G., JR. (Eastman Kodak Co.). Lower Aliphatic Carboxylic Acids and Ketones. United States Patent 2,510,105, June 6, 1950. Chem. Abs., vol. 44, 1950, p. 7344.

Process operating either batchwise or continuously for manufacturing $EtCO_2H$ (I) by liquid-phase reaction of C_2H_4, CO, and water at 200°–250° and pressures of 2,000–4,000 lb. in the presence of an aqueous solution of a Co-containing catalyst is presented. Yields of 50–85% of (I) with 40–80% conversion based on consumed C_2H_4, are obtained; simultaneously Et_2CO and CO_2 are formed. Optimum results are obtained with a CO : C_2H_4 ratio of 3 : 1 and aqueous solutions of Co salts of lower aliphatic acids, such as (I) or $PrCO_2H$. The catalyst, employed as 0.025–1.0 N (preferably 0.1–0.3 N) solution, is prepared by activation of an aqueous solution of the Co salt with CO at 150° and 2,000–3,000 lb. pressure, followed by removal of solids; the used catalyst is reconditioned in the same manner. To avoid inactivation of the catalyst by carbonate formation, the CO_2 content of the reaction liquid should be kept below 28%. Other Co catalysts, including Harshaw No. 268 and 542, have been investigated. Metal propionates, other than Co, appear to be inactive. *See also* United States Patent 2,448,368 (abs. **862**) and United States Patent 2,448,375 (abs. **2001**).

956. HEINEMANN, A. Formaldehyde. British Patent 179,951, May 11, 1922. Chem. Abs., vol. 16, 1922, p. 3315.

HCHO is produced by passing CO, H_2, and H_2O vapor over a contact substance at a temperature of 240°–350°. Suitable contact substances are unburned porcelain, pumice, asbestos, coke, or charcoal, preferably coated with a metallic deposit of Cu and Ni.

957. ———. [Formaldehyde.] Swedish Patent 59,281, 1922.

See British Patent 179,951 (abs. **956**).

958. ———. Formaldehyde From Carbon Dioxide and Hydrogen. United States Patent 1,460,244, June 26, 1923; appl. filed June 12, 1922, Serial No. 567,809. Chem. Abs., vol. 17, 1923, p. 2886.

See British Patent 179,951 (abs. **956**).

959. ———. [Formaldehyde From Carbon Monoxide and Hydrogen.] French Patent 551,222, 1922.

See British Patent 179,951 (abs. **956**).

960. ———. [Formaldehyde Synthesis.] Swiss Patent 99,281, no date. Schmidt, J.; Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 229.

From CO and H_2 in presence of steam at 240°–350°; porous catalysts with metallic coating.

See British Patent 179,951 (abs. **956**) and United States Patent 1,460,244 (abs. **958**).

961. ———. [Production of Formaldehyde.] Austrian Patent 100,450, no date. Chem. Zentralb., 1925, II, p. 2575.

A gas mixture consisting of CO, H_2, and steam is passed at 240°–350° over a porous catalyst of Cu or Ni on porcelain, asbestos, coke, charcoal.

See British Patent 179,951 (abs. **956**), French Patent 551,222 (abs. **959**), and United States Patent 1,460,244 (abs. **958**).

962. HEINRICH, R. L. (Standard Oil Development Co.). Olefin Polymerization Feed Stock. United States Patent 2,570,032, Oct. 2, 1951; appl. June 23, 1948, Serial No. 34,832; 6 claims (*Cl. 260–683.15*). Chem. Abs., vol. 46, 1952, p. 1748.

Mixtures of olefins, hydrocarbons, and oxygenated organic compounds, such as the reaction products from a Fischer-Tropsch synthesis, are treated with H_2S, which contains a small amount of gaseous HCl as catalyst at 5°–120° for 1 min.–6 hr. The oxygenated compounds form high-boiling compounds which are readily separated from the olefins and other hydrocarbons. The olefin-containing fraction is suitable for polymerization with a Friedel-Krafts catalyst.

963. ——— (Standard Oil Development Co.). Preparation of Olefin Lubricant Having a High Viscosity. United States Patent 2,616,916 No. 4, 1952; appl. filed Dec. 6, 1950, Serial No. 199,571; 4 claims (*Cl. 260–451*).

High-viscosity lubricating oil is made by forming a mixture of a lubricating oil polymer of an α olefin having 5–10 C atoms in the molecule and a proportional amount of 0.1–5 wt. % (1% preferred) of diphenylthiourea. The mixture is oxidized in the presence of air at 300°–600° F. for 30 min. to 16 hr. The product has an increased viscosity and a low neutralization value. Olefins that may be polymerized to produce lubricating oil polymers are the α olefins having 5–10 C atoms in the molecule including pentene-1, hexene-1. A convenient source of α olefins is the naphtha fraction produced in the Fischer-Tropsch synthesis when employing a promoted Fe catalyst. The olefinic lubricating-oil polymer will ordinarily be employed in an amount in the preferred range 97–99.5 wt. %.

964. ——— (Standard Oil Development Co.). Removal of Oxygenated Compounds From Olefins. United States Patent 2,542,516, Feb. 20, 1951; appl. filed Oct. 11, 1947, Serial No. 779,285, 6 claims (*Cl. 260–683.15*). Chem. Abs., vol. 45, 1951, p. 4440.

Oxygenated compounds are removed from olefins in the naphtha-boiling range produced by the Fischer-Tropsch hydrocarbon synthesis by treatment at 60°–100° F. with $AlCl_3$ containing 0.1–2 mol. % H_2O. The olefins treated in this way can be polymerized to lubricating oils with $AlCl_3$, and the resulting sludge can serve as the treating agent for removing oxygenated compounds.

965. ——— (Standard Oil Development Co.). Synthetic Polyolefin Lubricants. United States Patent 2,361,176, Mar. 10, 1953. Chem. Abs., vol. 47, 1953, p. 7205.

Lubricants are produced by polymerization of α-olefins containing at least 4 C atoms in the presence of a Friedel-Crafts catalyst (I) and an O-containing compound (an aliphatic alcohol, ketone, peroxide, aldehyde, or organic acid) containing <5% by weight of olefin. The quantity of catalyst in the charge exceeds that of the O-containing compound. The reaction takes place at 75°–150° F. under a pressure sufficient to maintain the liquid phase. In an example, a mixture of 1-decene 50 and $C_{16}H_{16}$ approximately 50 was treated with $AlCl_3$ 2 and MeOH 1 part by weight for 2 hr. at 100° F. to give a 73% yield of product having a viscosity of 2,598 at 100° F. and of 232 Saybolt Universal seconds at 210° F.

966. HEINZE, B., AND KING, J. A. (Cities Service Oil Co.). Separation of Alcohols and Acids From Fischer-Tropsch Synthesis Product. British Patent 672,365, May 21, 1952. Chem. Abs., vol. 46, 1952, p. 8354.

See United States Patent 2,523,248 (abs. **967**).

967. ——— (Cities Service Oil Co.). Separation of Alcohols and Acids From Fischer-Tropsch Synthesis Products. United States Patent 2,523,248, Sept. 19, 1950; appl. filed Feb. 19, 1948, Serial No. 9,428; 10 claims (*Cl. 202–42*). Chem. Abs., vol. 44, 1950, p. 11,068.

Oily and aqueous fractions from the Fischer-Tropsch synthesis are mixed if they have been separated or are taken directly from the synthesis plant and charged to a fractionating tower. The mixture is fractionated to take overhead oil and H_2O together with oil and H_2O soluble oxygenated compounds, principally alcohols with a bottoms product made up of oily constituents, H_2O, and oil- and H_2O-soluble oxygenated compounds, principally organic acids. The overhead is extracted with selected alcohol solvents such as aqueous alcohol solutions. The bottoms fraction has a lower solvent power for organic acids and particularly a low solvent power for the Na salts of the acids when the bottoms oil fraction is neutralized with an alkaline solution. 12 United States patents cited.

HEISEL, P. *See* abs. **989**.

968. HEMMINGER, C. E. (Standard Oil Development Co.). Apparatus and Process for Circulating Powdered Solid in Chemical Treatment. United States Patent 2,595,254, May 6, 1952. Chem. Abs., vol. 46, 1952, p. 6876.

Describes process in which gaseous reactants are brought into contact with a powdered material in the reaction zone. The reactants flow upward and maintain, in suspension, a solid in powdered form. The powder acts as a heat absorbing or releasing medium and thus tends to maintain the reactants within a desired temperature range, which is optimum for the reaction in question. This continuous process is adaptable to a wide range of vapor phase chemical reactions. Gives examples, including hydrogenation of hydrocarbons, Fischer synthesis, and MeOH synthesis.

969. ——— (Standard Oil Development Co.). [Catalytic Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 960,868, Apr. 26, 1950; appl. filed Feb. 9, 1948, in United States Mar. 21, 1947. Chem. Zentralb., 1950, II, p. 2270.

Synthesis is carried out under pressures of 10.5–105 atm. and at temperatures 370°–425°, preferably 370°–400°. The fluidized Fe catalyst contains 0.1–1.5 wt. % of K_2O reckoned on the Fe_2O_3. The ratio of $CO:H_2 = 1.9:0.7$ at a throughput of synthesis gas of 1.24–3.12 l. per kg. of catalyst per hr. The Fe catalyst has the following composition, in parts by weight: Fe, 67.1; O_2 (combined with the Fe), 26.1; Al_2O_3, 2.57; SiO_2, 1.37; MnO, 0.85; K_2O, 0.90; MgO, 0.11; CuO, 0.10; NiO, 0.05; particle size 0–20μ 20%, 20–40μ 17%, 40–80μ 27%, and more than 80μ 36%; conversion of CO 92.5–95.2%. The products consist of 6.1% C_1–, 8.4% C_2–, 11.1% C_3–, 65.4% C_4–hydrocarbons, and 9.0% oxygenated compounds. The C_4–fraction consists of 25% C_4–, 63% C_5–hydrocarbons, with a boiling point up to 204° and 12% above 204°. The octane No. is 75.7.

970. ——— (Standard Oil Development Co.). Contacting Solid Particles and Gaseous Fluids. United States Patent 2,444,990, July 13, 1948; appl. filed Sept. 12, 1941, Serial No. 410,525; 8 claims (*Cl. 196–52*).

Vapors or gases are passed through a reaction zone countercurrent to the flow of finely divided contacting material. The counterflow heat exchange may be used for either heating or cooling. The process may be used in synthesis of hydrocarbons from CO and H_2, as well as in catalytic cracking. 16 United States patents and 2 foreign patents cited.

971. ——— (Standard Oil Development Co.). Gaseous Fuel. United States Patent 2,605,178, July 29, 1952. Chem. Abs., vol. 46, 1952, p. 11,643.

Describes reactor to produce CO and H_2 suitable for hydrocarbon synthesis from heavy oily material or solid hydrocarbons.

972. ——— (Standard Oil Development Co.). Gasification. United States Patent 2,644,745, July 7, 1953. Chem. Abs., vol. 47, 1953, p. 8996.

Finely divided carbonaceous solids are gasified continuously while suspended in the gaseous gasifying medium, such as steam or CO_2, at temperatures above the fusion point of the ash. The heat required to support the endothermic gasification reaction and to maintain the high reaction temperatures is generated by partial combustion of the carbonaceous charge with free O_2. Gasification temperatures of preferably 1,149°–1,371° and pressures ranging from atmospheric to about 400 p. s. i. are suitable for the gasification of most carbonaceous solids, such as coals, shale, and coke. The particle size of the solids is preferably 20- to 100-mesh. The suspension of the solids in the gas mixture containing O_2 and steam or CO_2 is admitted in suitable proportions at a relatively high velocity tangentially into the gasifier so as to impart a swirling motion to the suspension.

973. ——— (Standard Catalytic Co.). Gasification of Oil Residues. United States Patent 2,346,754, Apr. 18, 1944; appl. filed Dec. 9, 1939, Serial No. 308,368; 5 claims (*Cl. 48–215*). Chem. Abs., vol. 38, 1944, p. 6525.

Crude-oil residues, pitches, cracked tars, and the like are used as raw materials to produce gases rich in free H_2. This is accomplished in a specially designed cracking unit where the hydrocarbon residue is first heated to above 750° F. to effect decomposition. The cracked gases are discharged into a reaction chamber lined with refractory material and capable of withstanding temperatures of 2,000°–3,000° F. Into this chamber is introduced the carbonaceous material in a rapidly swirling motion, together with steam and an O_2-containing gas. The volume of O_2 is carefully adjusted so as to burn a portion of the carbonaceous material and thus produce a high reaction temperature, and is approximately 0.35 lb. per 1 lb. of carbonaceous material, whereas the amount of introduced steam is 0.3–3.0 lb. of the same. The latter amount is over that required in addition to O_2 supplied to the system to oxidize the C content of residue to CO_2 and thus release its H_2 content along with that of the steam as free H_2. It is desirable to conduct the gases through several additional reactors where the high temperature is maintained. From the last reactor the gas is conducted into C collectors where the residual C is drawn off for use as such or recycled to the reactor. It may be employed with suspending gases, such as N_2, H_2 or CH_4, C_2H_6 and C_3H_8, or their mixtures. The temperature of reaction may be reduced by adding finely subdivided catalysts, such as metallic Fe, Ni, and Co, or oxides of these metals together with oxides of Groups II and III of the periodic table, for example, CaO, MgO, or Al_2O_3. The gas thus produced is rich in H_2 and contains only a minor amount of CO_2 and hydrocarbons and a large % of CO. A characteristic gas obtained by this method has the following composition: H_2, 33.5%; CO, 55%; CO_2, 6%; CH_4, 4%; and N_2, 1.5%. Such gas is useful for catalytic production of hydrocarbons by the so-called Fischer synthesis.

974. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,542,517, Feb. 20, 1951; appl. filed Sept. 26, 1946, Serial No. 669,529; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 4431.

Yields of hydrocarbons are increased in the fluid catalyst hydrocarbon synthesis operation employing an Fe catalyst by recirculating to the synthesis reactor a part of the oxygenated compounds formed with the hydrocarbons in the synthesis reactor. 5 United States patents cited.

975. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis and Method of Preparing the Catalyst. United States Patent 2,527,130, Oct. 24, 1950; appl. filed Sept. 22, 1948, Serial No. 50,671; 4 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 1326.

Carbonization tendency of Fe catalysts may be depressed by adding small amounts of Si, preferably 3–15% by weight of the Fe. Conventional promoter, 0.1–10% by weight of the total catalyst also may be used. The Si is fused with the other components and the fused mass cooled, sized, and, if desired, reduced, or powdered Si may be mixed with powdered Fe in metallic form and the promoter added by dry mixing or impregnation. The catalyst may be reduced with H_2 at 600°–1,200° F. until 60%–90% of the O_2 is removed. 2 United States patents cited.

976. ——— (Standard Oil Development Co.). [Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 959,193, Mar. 23, 1950; appl. filed Jan. 2, 1948. Chem. Zentralb., 1951, I, p. 279.

Synthesis is performed in the usual manner at 260°–385° under a pressure of 49 atm. The synthesis products thus obtained are fractionally distilled. There are thus obtained a hexane fraction up to 176° and a heavier fraction, b. 176°–205°. The C_2–C_5 olefins are polymerized. The middle fraction (up to 176°) is treated in the presence of bauxite or a SiO_2–Al_2O_3–gel catalyst, in the presence of H_2, at 455°–510° and a pressure of 1.4 atm. for 1 hr. The higher fraction (176°–205°) is treated in the same manner at 426°–524° and 0.7–3.5 atm., if desired in the presence of H_2 and with the same catalyst. The O_2-containing compounds are converted into hydrocarbons and a valuable hydrocarbon mixture obtained, which may be catalytically hydrogenated.

977. ——— (Standard Catalytic Co.). Hydrogenation of Carbon Oxides. United States Patent 2,357,894, Sept. 12, 1944; appl. filed Dec. 11, 1940, Serial No. 369,540; 4 claims (*Cl. 260–449.6*). Chem. Abs., vol. 39, 1945, p. 527.

C oxides are hydrogenated in the presence of a suspended powdered catalyst. To control the catalyst concentration and maintain the temperature of reaction within the desired critical temperature range, the reaction gases are passed through a reaction zone, the area of which becomes progressively smaller in the direction of flow of the reacting gases in a manner to compensate for the decreased volume of gases and to adjust the ratio of catalyst per vol. of unreacted gas to the desired figure.

978. ——— (Standard Oil Development Co.). Method of Making Gasoline. United States Patent 2 540,581, Feb. 6, 1951; appl. filed Sept. 18, 1946, Serial No. 697,807; 3 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 4024.

2-stage process is used in which the major part of the synthesis takes place in the 1st stage at lower temperatures and a lower H_2:CO ratio (2:1) than used in the 2d stage. The high H_2:CO ratio 2–20:1,

CO_2 : CO=5–10 : 1 in the 2d stage controls the C content of the catalyst and converts CO_2 to hydrocarbons and H_2O, owing to the water gas shift reaction. The decrease of CO_2 and H_2 in the exit gas decreases the volume of gas to the absorption equipment and results in higher yield of liquid products based on feed gas. The gas feed to the 2d stage may or may not be gases from which the lighter hydrocarbons have been removed by absorption. 2 or more single-pass reactors may be used. The 1st reactor may have a small amount of recycle vent gas feed and the 2d may be once through. The 1st may be once through and the 2d use recycle. Successively lower pressures may be used in each reactor as 450 p. s. i. in the 1st and 250 p. s. i. in the 2d. Each reactor may have its own condensing system. Different catalysts may be used. 6 United States patents cited.

979. ——— (Standard Oil Development Co.). Method of Producing Gasoline. United States Patent 2,464,505, Mar. 15, 1949; appl. filed Sept. 18, 1946, Serial No. 697,808; 3 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 3994.

Stream of synthesis gas in which powdered, Fe catalyst is suspended, 10–50 lb. per cu. ft. density, flows through an elongated reaction zone, 20–75 ft., at a velocity such that the flow of catalyst and gas is concurrent and the residence time not more than 20 sec., 3–10 sec. preferred. The temperature at the inlet is 550° F. and at the outlet 700°–750°. The pressure is 100–800 p. s. i. with a higher pressure range beginning at 350–450 p. s. i. preferred. 1 United States patent cited.

980. ——— (Standard Oil Development Co.). Pretreatment of Catalyst for Hydrocarbon Synthesis. United States Patent 2,560,345, July 10, 1951; appl. filed Dec. 23, 1947, Serial No. 793,368; 4 claims (*Cl. 260–449.6*).

Standard method of synthesizing hydrocarbons from CO and H_2 in the presence of a fluidized Fe catalyst is improved by first reducing an O_2-containing Fe catalyst with H_2 to an O_2 content of about 0.10 wt. % of the Fe, then treating the reduced catalyst with fresh synthesis gas, containing CO and H_2 in the ratio of 1–2 mol. H_2 per mol. CO at a temperature 550°–750° F. and a H_2 partial pressure of 100–150 p. s. i., for a time, 0.5–2 hr., sufficient to convert 25–50 wt. % of its Fe content into a mixture of Fe carbides, in which Fe_2C predominates. Such treatment results in less C deposition on the catalyst during synthesis and less disintegration.

981. ——— (Standard Oil Development Co.). Process of Treating a Hydrocarbon Synthesis Naphtha Product. United States Patent 2,556,275, June 12, 1951; appl. filed Sept. 11, 1946, Serial No. 696,340; 2 claims (*Cl. 260–450*).

Naphtha product produced by the hydrogenation of CO in the presence of an Fe catalyst is improved in quantity and quality by removing the oxygenated compounds contained therein. Process consists of 1st separating the fraction b. 0°–225° F. and subjecting it to the action of a dehydrating and polymerizing action, which causes the oxygenated compounds to form olefins, which are polymerized to acyclic and aromatic hydrocarbons boiling in the gasoline boiling range. The remainder of the naphtha fraction is subjected to the influence of a dehydrating catalyst only so that the oxygenated compounds contained therein will form olefins, which are already within the gasoline boiling range and so do not need to be polymerized. The 2 fractions are then combined. 4 United States and 1 foreign patent cited.

982. ——— (Standard Oil Development Co.). Processing of Hydrocarbon Synthesis Products. United States Patent 2,516,699, July 25, 1950; appl. filed Jan. 15, 1947, Serial No. 722,275; 1 claim (*Cl. 260–450*). Chem. Abs., vol. 45, 1951, p. 848.

Gasoline heart cut, C_6 to 350° F. cut, from Fischer-Tropsch synthesis, is subjected to a severe catalytic treatment, the heavy naphtha gas oil cut, 350° F. and above, is subjected to a milder catalytic treatment, and the C_2–C_5 olefins are polymerized. Bauxite or a silica-alumina (10–25 wt. % alumina) may be used. A solid phosphoric acid catalyst is used for treating the lighter fractions. Any continuous treating unit may be used, but a fluid reactor and regenerator system is preferred. Oil product is nondestructively hydrogenated and superior diesel and heating oil are recovered. 1 literature ref., 2 foreign patents, and 9 United States patents cited.

983. ——— (Standard Oil Development Co.). Removal of Carbon From the Fischer-Tropsch Catalyst. United States Patent 2,608,569, Aug. 26, 1952. Chem. Abs., vol. 47, 1953, p. 8995.

Describes an improved fluidized hydrocarbon-synthesis process wherein the C content of the catalyst is controlled by withdrawing selectively the catalyst particles with high C content. The fluidized stream of catalyst is withdrawn from the treating zone and passed to a segregation zone, which contains packing elements. Elements of the saddle type having a maximum diameter of 2 in. are most suitable. The gases flowing up through the packing in the elutriator effect a separation of the catalyst particles according to C content. The particles with the smaller C content are concentrated in the lower portion of the elutriator and returned to the reaction zone in such a quantity that the C concentration on the Fe catalyst is 15–20%. In this process, the catalyst must have a particle size of 20–200μ. Approximately 0.5–3% of the total catalyst is maintained in the elutriation zone.

984. ——— (Standard Oil Development Co.). [Simultaneous Production of Liquid Hydrocarbons and Oxygenated Compounds From Carbon Monoxide and Hydrogen.] French Patent 962,948, June 23, 1950; appl. filed Mar. 8, 1948, in United States May 24, 1947. Chem. Zentralb., 1950, II, p. 2270.

Finely powdered, fluidized Fe catalyst is used at a H_2 pressure of at least 7 atm. and a CO_2 partial pressure of at least 8.8 atm. A red Fe oxide, which has been activated with 0.5–1.0% K_2CO_3, is used as catalyst. The reaction temperature is 343°. The yield of C_4-hydrocarbons amounts to 149–168 cc. per $m.^3$ $CO+H_2$, and oxygenated products 39–43 cc.

985. ——— (Standard Oil Development Co). Synthesis of Hydrocarbons. United States Patent 2,518,315, Aug. 8, 1950; appl. filed Mar. 21, 1947, Serial No. 736,151; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 854.

Yields of more than 200 cc. C_{3+} hydrocarbons containing 60–75% gasoline, b. 100°–400° F. with research octane number of at least 80, may be obtained per $m.^3$ synthesis gas. The fluidized Fe catalyst is prepared from pyrites or sintered pure Fe and promoted with 0.1–1.5%, preferably 0.6–0.9%, K, expressed as % K_2O on Fe_2O_3. The temperature is 700°–850° F., preferably 700°–750° F. The pressure is 150–1,500 p. s. i., preferably 200–400 p. s. i. The feed-gas rate is about 20–50 *n* $ft.^3$ synthesis gas per lb. of catalyst per hr. The H_2 : CO ratio is about 0.7–1.9. The exit gases are recycled to the reactor in amount of 0–3, preferably 0–1.0 vol. per vol. of fresh feed gas. 2 literature refs. and 3 United States patents cited.

986. ——— (Standard Oil Development Co.). [Synthetic Hydrocarbons.] French Patent 953,152, Dec. 1, 1949; appl. filed Sept. 15, 1947, in United States Sept. 28, 1946. Chem. Zentralb., 1950, II, p. 366.

Synthetic hydrocarbons are made from CO and H_2 in presence of a powdered Fe catalyst containing 1.2–1.7% of K. The operation is fluidized. The advantage lies in a strongly reduced coke formation during the synthesis and in a longer activity of the catalyst.

987. ——— (Standard Oil Development Co.). Two-Stage Hydrocarbon Synthesis Operation. United States Patent 2,560,344, July 10, 1951; appl. filed Sept. 29, 1947, Serial No. 776,752; 3 claims (*Cl. 260–449.6*).

Hydrocarbons and oxygenated hydrocarbons are prepared in a 2-stage process from CO and H_2 by first contacting a mixture of these gases in molecular proportion of about 1 : 1–2 with about 2–8 vol. % H_2O in the presence of a fluidized catalyst containing about 77% Fe and 5% K_2O as promoter and about 1–3% C as carbide, the particle size being in the range 10–80μ. The temperature of the reaction is 350°–600° F., the pressure 550–700 p. s. i., the space velocity about 10 cu. ft. gas per hr. per lb. of catalyst, and a recycle to fresh feed ratio of 1–2 : 1 vol. Under the processing conditions about 75–80% of the CO–H_2 mixture is converted to oxygenated hydrocarbons. The 2d step of the process involves removing the reaction products and a portion of the used catalyst, contacting the unconverted synthesis gas with the used catalyst at 550°–750° F., 200–500 p. s. i., and a space velocity of 10–75 cu. ft. gas per hr. per lb. of catalyst, and recovering the hydrocarbons thus formed. The overall conversion of CO and H_2 in the 2 steps was above 93%. As an example of yields from step 1, 150–160 cc. of hydrocarbons heavier than C_3H_8 and C_3H_6 and the low-molecular-weight alcohols were obtained in an amount of 40–50 cc. per cu. m. of H_2 and CO consumption. In the oil layer of the reaction product, 35% of product mainly C_8–C_{15} alcohols were obtained. From step 2, the following were obtained per cu. m. of H_2 and CO consumed: 180 cc. of hydrocarbons heavier than C_3H_8 and C_3H_6 and only 20 cc. of H_2O-soluble oxygenated compounds, 20% of these hydrocarbons occurred in the oil layer. The composition of the H_2O-soluble oxygenated compounds was about 60% EtOH and *n*–PrOH with traces of MeOH, BuOH, and higher alcohols. Of the remaining 40%, about 20% was acetic and higher acids, 10% aldehydes, and 10% ketones. Diagram.

See abs. **296, 297.**

988. Hendricksen, W. E. (Hydrocarbon Research, Inc.). Catalytic Synthesis of Hydrocarbons. United States Patent 2,449,775, Sept. 21, 1948; appl. filed Aug. 24, 1946, Serial No. 692,938; 9 claims (*Cl. 260–449.6*). Chem. Abs., vol. 42, 1948, p. 9123.

Substantially pure Fe is alloyed with 0.2% by weight of Te and ground to a powder passing a 200-mesh screen, about 65% passing a 325-mesh screen. Approximately 1% by weight of K_2O and 1% of Al are chemically precipitated upon the powder, and the mass is dried. The powder is charged into a reaction vessel and subjected for 48 hr. to the passage of synthesis gas (31% CO, 62% H_2, 4% CH_4, 2% CO_2, and the rest N_2). The temperature is 625° F., and the pressure 200 p. s. i. The linear velocity of the feed gases is 1.5 ft. per sec. After the initial conditioning period of 48 hr., the catalyst assumes a condition of settled operation. Contact time is held at 10 sec. The product gases are collected and passed through a condenser operating at 70° F. The hydrocarbon layer consists of hydrocarbons boiling in the gasoline range in a yield exceeding 65% on the basis of CO. The gaseous fraction consists of CO_2, normally gaseous hydrocarbons, H_2, and a small amount of unreacted CO. The total amount of moisture condensed over any selected period of operation is greater on a molar basis than the amount of CO_2 in the gaseous products recovered, usually amounting to at least 3 molar parts for each molar part of CO_2. Similar results are obtained with an Fe–Te catalyst prepared from an alloy containing 0.2% by weight Te and about 2% by weight C, cast under conditions of slow cooling. The conditions of operation are otherwise identical. The catalyst may also be used in fixed-bed operation. Metals from the Fe group other than Fe may be used. 4 United States patents cited.

989. Hendschel, A., and Heisel, P. (I. G. Farbenindustrie A. G.). [Chlorination of Crude Fatty Acids.] German Patent 709,582, July 10, 1941 (*Cl. 12o–11*). Chem. Abs., vol. 37, 1943, p. 3624.

Fatty acids or their alkali salts are obtained from the oxidation with alkali or alkaline earth hydroxides of the higher oily fraction, which in turn is obtained in the catalytic hydrogenation of CO. The chlorination takes place in an aqueous medium. H_2O-soluble salts of S oxyacids are used as catalysts.

990. Hengstebeck, R. J. (Standard Oil Co. of Indiana). Catalytic Conversion. United States Patent 2,493,-917, Jan. 10, 1950; appl. filed Nov. 20, 1944, Serial No. 564,348; 13 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 3700.

Rotating catalyst bed, partly immersed in a cooling liquid, is used. The charge gases are introduced at one side of the bed and withdrawn at the other side. Rotation is at a velocity that will keep the catalyst at uniform temperature. When the heat capacity of the bed is great enough, a relatively nonvaporizable liquid may be used as coolant. When the heat capacity is not great enough to absorb liberated heat of reaction as sensible heat, the catalyst may be kept wet with vaporizable liquid when it is in contact with the reaction gases. The space velocity is controlled by raising and lowering the level of the liquid in which the rotating bed is partly immersed. The speed of rotation is controlled to insure reimmersion of the catalyst before it gets too hot or to insure the presence of vaporizable liquid on the catalyst from the time it emerges from the liquid layer until it is again immersed. Preferred coolants are H_2O, gasoline-boiling-range hydrocarbons, and low boiling aqueous mixtures of O-containing products of the Fischer-Tropsch synthesis itself. 1 foreign and 10 United States patents cited.

991. Henkel & Cie. G. m. b. H. Aliphatic Acids. British Patent 489,443, July 26, 1938. Chem. Abs., vol. 33, 1939, p. 645.

Higher aliphatic hydrocarbons, for example, solid and liquid paraffins, higher hydrocarbons from the benzine synthesis, are oxidized by O_2 or oxidizing agents, for example, O_3, N oxides, with or without the use of catalysts, for example, Mn, Co, Cu, Fe, Cr, Pb, V or their salts, Al salts with or without alkalies, alkaline earths or their salts, and fresh material is continuously saponified, and the unsaponified matter is continuously separated by centrifuging and returned to the oxidation process. The catalysts may be present as soaps of saturated or unsaturated fatty acids, naphthenic acids, or resinic acids. Catalysts may be omitted if some previously oxidized material is present. The separated soap may be freed from remaining unsaponifiable material by treatment with solvents, for example, Me_2CO, AcOEt. Describes apparatus.

992. ———. [Easily Oxidizable Paraffins.] French Patent 850,756, Dec. 26, 1939. Chem. Abs., vol. 36, 1942, p. 1944.

Mixture of paraffins easily oxidizable into fatty acids is obtained by subjecting the products resulting from the hydrogenation of CO to a cracking operation and hydrogenating the cracked products.

993. ———. Fatty Acids. British Patent Appl. 6,762, filed 1939.

In preparing fatty acids by oxidation, a suitable starting material can be prepared by hydrogenating

the products from the cracking of the very high melting Fischer-Tropsch waxes. The oxidation is carried out by passing air or O_2-containing gases through the wax at 80°–120°. The reaction is exothermic and requires careful control.

994. ———. Fatty Alcohols. British Patent 489,863, Aug. 4, 1938. Chem. Abs., vol. 33, 1939, p. 172.

Liquid-solid mixture of hydrocarbons obtained in the synthesis of benzine from CO and H_2 is oxidized, and the fractions consisting of acids, esters, and lactones are reduced to alcohols. The latter, which contain about 8–18 C atoms in the molecule, may be sulfonated. O_2, O_3, N oxides, and CrO_3 are suitable oxidizing agents and Mn, Ni, Co, Cu, Fe, Cr, Pb, V, or their salts, for example, soaps, may be used as catalysts. Alkalies and alkaline earths also may be present. Among examples, a synthetic benzine obtained by Franz Fischer's process is oxidized with air in the presence of a Mn soap and, after separation of unoxidized material, the product is reduced with H_2 and a Cu chromite catalyst.

995. ———. [Mixtures of Higher Alcohols and Their Derivatives.] French Patent 817,291, Aug. 31, 1937. Chem. Abs., vol. 32, 1938, p. 2143.

Liquid-solid mixture of hydrocarbons in the synthesis of gasoline from CO and H_2 is oxidized; for example, by blowing air through it, and the oxidation products are reduced to alcohols. The mixture of alcohols may be sulfonated.

996. ———. [Oxidation Products of Paraffins.] French Patent 833,064, Oct. 11, 1938. Chem. Abs., vol. 33, 1939, p. 2532.

Paraffins of high molecular weight obtained in the synthesis of petrol by the Fischer method are subjected to oxidation at 105°–120° in presence of small quantities of permanganates and caustic alkali, soap, alkali carbonate, or other alkaline substance. Fatty acids of high molecular weight are obtained.

997. ———. [Oxidized Hydrocarbons.] French Patent 816,928, Aug. 20, 1937. Chem. Abs., vol. 32, 1938, p. 2142.

Aliphatic hydrocarbons of high molecular weight are oxidized, the fatty acids formed and their derivatives converted into salts, and the mixture is pulverized or nebulized so as to distill off the volatile substances with the assistance of heat.

998. ———. [Oxidized Hydrocarbons.] French Patent 817,862, Sept. 13, 1937. Chem. Abs., vol. 32, 1938, p. 2142.

Aliphatic hydrocarbons of high molecular weight are treated with oxidizing agents, fresh material being introduced continuously. A part of the oxidized product is saponified continuously with alkaline agents; the unsaponifiable part is separated continuously by centrifuging and returned to the oxidation. A further separation of the saponified and unsaponified portions may be obtained by extraction with solvents or distillation. Describes apparatus.

999. ———. [Oxidizing Hydrocarbons.] French Patent 832,546, Sept. 28, 1938. Chem. Abs., vol. 33, 1939, p. 2532.

Synthetic hydrocarbons of high molecular weight made by the Franz Fischer process are oxidized with gases containing O_2 in the presence of small quantities of permanganates, particularly $KMnO_4$ and at below 104°.

1000. ———. [Producing a Mixture of Higher Fatty Alcohols.] Austrian Patent 155,472, Jan. 25, 1939; appl. filed Jan. 21, 1937; in Germany Feb. 17, 1936 (*Cl. 12e*). Chem. Zentralb., 1939, II, p. 525.

Hydrocarbon mixture obtained by synthesis from CO and H_2 is oxidized and subsequently reduced. The acid constituents of the oxidation products also can be converted into esters or anhydrides, and these can be reduced. The reduction also can be accomplished with alkali metals and alcohols.

1001. ———. [Recovering and Separating Aliphatic Oxygen-Containing Compounds.] French Patent 884,394, Sept. 13, 1943; appl. filed Aug. 20, 1942. Chem. Zentralb., 1944, I, p. 697.

Example: An alcohol-hydrocarbon mixture from the treatment of olefins with CO and H_2, b. 250°–370°, and having an alcohol content of 43% is heated in amounts of 2,400 parts with 30 of NaOH to boiling until 45 parts of H_2O are separated. 1,375 parts of hydrocarbons and 926 of an alcohol fraction are obtained, b. 200°–285° at 12 mm. Hg. The average OH number is 123 and the average C-atom number is 26–34. The viscous oil is suitable for cosmetics.

———. *See* abs. **1003, 2108, 2109, 2576.**

HENNICKE, W. *See* abs. **3918, 3919.**

1002. HENRY, C. [Methyl Alcohol.] French Patent 651,194, Feb. 9, 1926. Chem. Abs., vol. 23, 1929, p. 3235.

Catalysts for the preparation of MeOH from CO and H_2 are either (1) Sr and PbO ground together, preferably in the proportion of 3 Sr : PbO or (2) Zn and Bi_2O_3, preferably in the proportion of 3 Zn : Bi_2O_3.

HENSHAW, D. M. *See* abs. **433.**

1003. HENTRICH, W., LAINAU, C. A., AND KAISER, W. J. (Henkel & Cie. G. m. b. H.). Alcohols Containing Eight or More Carbon Atoms. United States Patent 2,151,106, Mar. 21, 1939. Chem. Abs., vol. 33, 1939, p. 4599.

Mixture of hydrocarbons synthesized from CO and H_2 is fractionated and a fraction containing hydrocarbons of 8 or more C atoms per molecule is subjected to oxidation, as by treatment with a stream of air at 100°–150° in the presence of a Mn soap, and the resulting oxidation products are treated with H_2 at 250°–300° under 200–250 atm. pressure in the presence of a Cu–chromite catalyst. Mixtures of alcohols thus obtained are suitable for producing sulfuric esters and sulfonates.

1004. HERBERT, W. (Metallgesellschaft A. G.). [Catalytic Conversion of Gas Mixtures Containing Carbon Monoxide and Hydrogen Into Hydrocarbons.] German Patent 744,076, Jan. 11, 1944; appl. M 138,086, May 16, 1937 (*Cl. 12 o–1.03*). FIAT Reel E 29, frames 610–611, PB 70,432; FIAT Reel AA 88, frames 3,730–3,732, PB 70,273; TOM Reel 35, item 64, 7 pp.

In the process for the catalytic conversion of CO and H_2 into aliphatic hydrocarbons at pressures > atmospheric and with use of catalysts consisting of Co, a difficultly reducible oxide, and a carrier, previously reduced catalysts are used containing at least 50 gm. of Co per l. of catalyst mass, the gas throughout being essentially $>1N m.^3$ per hr. and per kg. of metallic Co, preferably with gas recycle. Example: A catalyst consisting of Co : ThO_2 : kieselguhr = 1 : 0.2 : 1.5 and containing 5 gm. of Co was packed in an Al tube in a layer 50 cm. long, and 5 l. of a gas mixture consisting of 30% CO, 60% H_2, and 10% N_2 were passed through it per hr. at 200° and atm. pressure. The yield of higher boiling oils and gasoline per N m.^{3} of raw gas was 105 gm. for only 1 day. On raising the pressure from 1–5 atm., the gas throughput from 5–15 N l. per hr., and the temperature so far that the CO conversion was the same as at normal pressure, the yield was 100–115 gm. per N m.^{3} of raw gas, and this rate was maintained for several weeks.

1005. ——— (Metallgesellschaft A. G.). [Catalytic Conversion of Mixtures of Carbon Monoxide and Hydrogen.] German Patent 736,922, July 1, 1943; appl. M 144,243, filed Feb. 14, 1939 (*Cl. 12 o–1.03*). FIAT Reel AA–90, frames 1,567–1,570; PB 70,275;

Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 5, chap. 162, 1949, p. 51; Chem. Abs., vol. 38, 1944, p. 3802.

To provide the required amount of Co in the contact mass, the readily reducible Co compounds are reduced only 35–70%. Care is taken that the catalyst contains large quantities of diatomaceous earth. Addition to German Patent 734,993 (abs. **1024**).

1006. ——— (Metallgesellschaft A. G.). [Catalytic Process for Higher Paraffinic and Olefinic Hydrocarbons.] German Patent 736,844, May 20, 1943; German Patent Appl. M 136,573, filed Dec. 10, 1936 (*Cl. 12 o–1.03*). FIAT Reel AA–90, frames 1,486–1,489; PB 70,275; Meyer Transl. PC-S-II, Fischer-Tropsch, vol. 6, 1949, chap. 176, p. 36; Oel u. Kohle, vol. 40, No. 9/10, Mar. 1, 1944, Sch. 44; Chem. Abs., vol. 38, 1944, p. 3114.

Synthesis is carried out in 2 stages. In the 1st stage CO and H_2 are treated at approximately atmospheric pressure with the aid of catalysts that promote the formation of paraffin. At this stage the temperature is kept constant and at a level unfavorable to the formation of CH_4. In the 2d stage, which comprises 1 or more steps, the pressure is raised. The treated material may flow continually throughout the entire process or it may be taken out between the various steps.

1007. ——— (American Lurgi Corp.). Catalytic Production of Paraffin and Olefin Hydrocarbons From Gaseous Mixtures Containing Carbon Monoxide and Hydrogen. United States Patent 2,244,196, June 3, 1941; appl. filed Nov. 26, 1937, Serial No. 176,761, in Germany Dec. 2, 1936; 6 claims (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 5678.

Process for the catalytic conversion of gas mixtures containing CO and H_2 into hydrocarbons mainly of paraffinic and olefinic nature and containing more than 2 C atoms while maintaining temperatures below 300° with a catalyst suitable for forming benzine, hydrocarbon oil, and paraffin from such gases at atm. pressure and at temperatures below 300°, the catalyst containing a hydrogenating metal, and activator, and a carrier substance. The carrier substance, constituting the major portion of the catalyst, involves performing the synthesis at pressures 2–200 atm. in the presence of a catalyst having low enough activity that, when carrying out such synthesis at atm. pressure and otherwise under the same conditions of reaction, the synthesis would yield below 100 gm. of liquid and solid hydrocarbons per n m.^{3} of synthesis gas calculated on the basis of a gas containing a 100% CO and H_2 mixture.

1008. ——— (Metallgesellschaft A. G.). [Catalytic Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] German Patent 736,701, June 29, 1943; German Patent Appl. M 152,823, filed Feb. 15, 1939 (*Cl. 12 o–1.03*). FIAT Reel AA–88, frames 3,720–3,722; PB 70,273; Chem. Abs., vol. 38, 1944, p. 3114.

Olefinic and paraffinic compounds, notably benzine, high-boiling oils and paraffin, are synthesized at pressures over atmospheric with the aid of incompletely reduced Co salts and hard reducible metal compounds. The Co salts are reduced 35–70% only. The reduction is carried out at temperatures higher than the temperature of synthesis. As carrier for the reduced Co salts, substances other than diatomaceous earth are used.

1009. ——— (Metallgesellschaft A. G.). [Conversion of Carbon Monoxide and Hydrogen Into Hydrocarbons.] Belgian Patent 424,926, no date. Kainer, p. 196.

See German Patent 742,376 (abs. **1010**) and French Patent 832,967 (abs. **2265**).

1010. ——— (Metallgesellschaft A. G.). [Conversion of Carbon Monoxide and Hydrogen Into Mixtures of Hydrocarbons.] German Patent 742,376. Dec. 14, 1943; appl. M 139,535, filed Oct. 20, 1937 (*Cl. 12 o–1.03*). FIAT Reel AA 88, frames, 3,727–3,729; PB 70,273; Chem. Abs., vol. 39, 1945, p. 2636.

Hydrocarbons of a paraffinic and olefinic nature are produced by treating CO and H_2 under a pressure of 15 atm. or more in presence of a catalyst of Fe containing a promoter. The catalyst is prepared by precipitation from a solution of $Fe(NO_3)_3$ and a small amount of $Cu(NO_3)_2$ by means of KOH and is then deposited on silica gel or kieselguhr as a carrier. Na silicates act as activator. After drying the catalyst it is reduced by H_2 at 250°. This catalyst will last for several months without loss of activity if made with silicate, but without this it loses its activity rapidly and tends to produce light fractions instead of paraffins.

1011. ———. [Converting Olefinic Hydrocarbons of Low Molecular Weight Into Compounds of Higher Molecular Weight.] German Patent 748,156, Oct. 28, 1944; appl. M 139,536, Oct. 20, 1937 (*Cl. 12 o–1.03*). FIAT Reel J–5, frames 9–12; PB 70,145; FIAT Reel AA 90, frames 1,589–1,594; PB 70,275.

Olefinic hydrocarbon mixtures, particularly those obtained by the hydrogenation of CO are treated with CO or with gases containing them, if desired under pressure and with recirculation of the reaction gases, with paraffin-forming catalysts at temperatures $< 300°$, in converters in which the catalysts are washed with a cooling agent. The hydrocarbons in the gases leaving the reactor are separated into high- and low-boiling fractions and the latter recirculated. Polymerizing catalyst may be used along with the paraffin-forming catalyst or may be placed after it. The cooling agent may be the synthetic benzine from the process.

1012. ——— (American Lurgi Corp.). Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,247,087, June 24, 1941; appl. filed Dec. 13, 1937, Serial No. 179,611, in Germany Nov. 30, 1936; 7 claims (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 6423.

Process for obtaining hydrocarbons containing more than 1 C atom by the catalytic conversion of gas mixtures containing CO and H_2 (in the presence of catalysts consisting of hydrogenating metals selected from Group VIII of the periodic system, difficultly reducible metal compounds, and a preponderance of carrier substances) at an elevated temperature below that at which the CH_4 would normally be formed as the chief reaction product with the use of the same gases and the same catalysts, involves applying superatmospheric pressure during the conversion, indirectly cooling the catalyst during the conversion, passing a solvent over the catalysts during the conversion (which is adapted to free the catalysts from the paraffin formed, which is solid at room temperature to maintain the enrichment of the catalysts with such paraffin below 100% of the weight of such catalysts when free from such paraffin), and recycling at least a portion of the end gas of the synthesis.

1013. ——— (Carbo-Norit-Union Verwaltungs G. m. b. H.). [Hydrocarbons From the End Gases of Hydrocarbon Syntheses.] German Patent 737,620, July 20, 1943; German Patent Appl. C 51,932, filed Aug. 25, 1936 (*Cl. 12 o–1.03*). FIAT Reel AA–90, frames 1,493–1,495; PB 70, 275; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 6, chap. 169, 1949, p. 15; Chem. Abs., vol. 38, 1944, p. 3662–3663.

End gases are absorbed in solid absorbents and are then desorbed with steam. The absorbents are then dried and cooled with fresh synthesis gas and are ready for reuse.

1014. ——— (Metallgesellschaft A. G.). [Iron Catalysts.] German Patent Appl. M 154,969, July 27, 1942 (*Cl. IV d–12 o*). FIAT Reel R–6, frames 5,353–5,358; PB 73,554; TOM Reel 35, item 64, 8 pp.

Fe catalysts for the Fischer-Tropsch synthesis are made by precipitation from solutions of Fe salts and salts of other metals in boiling potash liquor. Especially suitable for the purpose are Fe nitrate together with Cu nitrate and nitrates of metals whose compounds are difficultly reducible by H_2 such as Zn nitrate, Cr nitrate, and the nitrates of the rare earth metals. The pH after the precipitation should exceed 7. Kieselguhr is a suitable carrier The reduction of the dried, preferably granulated catalyst, should be performed under mild temperature conditions of 250° with a large excess of H_2 until less than 20%, preferably 8%, of the Fe compounds are reduced to the metallic state.

1015. ——— (Carbo-Norit-Union Verwaltungs G. m. b. H.). [Process for the Adsorption of the Light Synthesis Products From the Hydrogenation of Carbon Monoxide.] German Patent 747,399, Oct. 2, 1944; appl. C 52,389, filed Jan. 16, 1937 (*Cl. 12 o–1.03*). FIAT Reel AA–90, frames 1,635–1,637; PB 70,275; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 7, chap. 197, 1950, p. 34.

In the adsorption of the light products from the gases occuring in the synthesis of hydrocarbons from CO and H_2, an adsorption agent, whose capacity has become greatly reduced through the treatment of the gases in the later steps of the synthesis process, is used for treating the gases in an earlier step, and the steaming-out process connected with this adsorption step is performed in situ in such a manner that regeneration of the adsorbent takes place with the liquefied synthesis products that are formed during this steaming-out step.

1016. ——— (Metallgesellschaft A. G.). [Process for the Catalytic Conversion of Gases Containing Carbon Monoxide and Hydrogen Into Olefinic and Paraffinic Hydrocarbons.] German Patent 747,730, Oct. 11, 1944; appl. M 136,985, Jan. 26, 1937 (*Cl. 12 o–1.03*). FIAT Reel AA 90, frames 1,483–1,485, PB 70,275; TOM Reel 35, item 35, 9 pp.

In preparing olefinic and paraffinic hydrocarbons by the Fischer-Torpsch synthesis method in the presence of catalysts containing Co and Th, a synthesis gas is used having the CO and H_2 essentially in the proportion of 1:2, preferably 1:1.5 or lower with pressure of about 5 atm, or more. The catalyst preferably contains $<$ 80 gm. of metallic Co per l. of catalyst and the gas $>$ 20% of inert constitutents. The content of inerts is regulated by recycling a part of the exhaust gas.

1017. ——— (Metallgesellschaft A. G.). [Producing High-Boiling Hydrocarbons, Mainly Paraffins, by the Catalytic Conversion of Gases Containing Carbon Monoxide and Hydrogen.] German Patent 744,077, Jan. 11, 1944; appl. M 138,697, July 18, 1937 (*Cl. 12 o–1.03*). FIAT Reel E 29, frames 612–613, PB 70,432; FIAT Reel AA 89, frames 131–133, PB 70,274, TOM Reel 35, item 64, 7 pp.

Gives process for producing high-boiling hydrocarbons, mainly paraffin, by catalytic conversion of CO and H_2 at raised pressure in the gas phase in converters with close-lying cooling elements. The paraffin is continuously removed as formed. A catalyst that contains $>$ 40% of a hydrogenating metal is used, and the time of contact of the gas with the catalyst is 3–10 minutes. A synthesis gas is used that contains $>$ 1 part of CO:2 of H_2, and the sum total of the CO and H_2 is over 90%. Example: 1 m.^{3} of a granular catalyst consisting of Co:ThO_2:kieselguhr in proportions, by weight, of 100:18:80 was packed into an inner element-cooled converter, and a synthesis gas of composition CO, 40.8%; H_2, 49.5%; CO_2 6.5%; CH_4, 0.3%; and N_2, 2.9% passed through it at the rate of 100 *N* m.^{3} of catalyst per hr., at a pressure of 12 atm. and a temperature of 186°. The yield under these conditions was 137 gm. of product per *N* m.^{3} of CO+H_2 converted consisting of 58% paraffin, 22% higher-boiling oils, and 20% gasoline. Under the same conditions but with a catalyst consisting of 35 parts by weight of support material to 100 parts of Co, the yield was 143 gm. of liquid product consisting of 72% paraffin, 16% higher-boiling oils, and 12% gasoline. Merely spraying instead of cooling the catalyst with a solvent liquid in accordnace with French Patent 814,853 (abs. **1275**), cut down the yield greatly and resulted in the recovery of only a very small amount of paraffin.

1018. ——— (Metallgesellschaft A. G.). [Production of High Paraffinic and Olefinic Hydrocarbons.]. German Patent 761,883, Aug. 23, 1951; appl. M 136,500 filed Dec. 3, 1936 (*Cl. 12 o*). Chem Zentralb., 1952, p. 624.

In converting gases containing CO and H_2 in a catalyst furnace having narrow layers of paraffin forming catalyst and closely lying cooling elements, operation is carried on under a pressure of 5–10 atm. with a synthesis gas containing 20% or more of inert constituents such as CH_4, higher hydrocarbons, N_2, steam, or alcohols. A part of the end gas after partial or complete removal of the reaction products is recycled to the reactor, and the fresh synthesis gas is admitted at the middle of the reaction zone or over several such zones of a catalyst furnace having several reaction zones. 4.5 ton or 15 m.^{3} of a catalyst comprising Co 33%, ThO_2 18% on kieselguhr are divided into 2 reactors in the ratio of 10:5. The reactors are connected in series and behind each one are arranged a condenser and an active C plant. Into the 1st reactor is passed at normal pressure 1,000 *N* m.^{3} of standard synthesis gas (30% CO, 60% H_2, 4% N_2, 0.5% CH_4, 5.5% CO_2), and the reaction temperature is kept at 185°. After the reaction products are separated, there remain 500 m.^{3} of residual gas that are conducted to the 2d reactor under the same conditions. Then 250 *N* cc. of residual gas remains. For every *N* cc. of inert-free entrance gas, 112 gm. of reaction products are obtained consisting of 8% paraffin (b. 320°), 25% higher boiling oils, and 57% benzine (b. up to 200°). The olefin content of the latter is 32%. The life of the catalyst is 3 months.

1019. ——— (Metallgesellschaft A. G.). [Production of Hydrocarbons by Carbon Monoxide Hydrogenation.] German Patent 744,078, Jan. 8, 1944; appl. M 139,309, filed Sept. 26, 1937 (*Cl. 12 o–1.03.*) FIAT Reel E 29, frames 614–615; PB 70, 432; FIAT Reel AA 89, frames 69–71; PB 70,274; TOM Reel 35, item 64, 6 pp.; Chem. Zentralb., 1944, I, p. 1353.

Catalysts have a long life and yield antiknock benzines (octane number 165–170) when a CO-rich synthesis gas is used. The medium pressure synthesis can be operated by recycling the synthesis gas and by passage of $<$1 l. of synthesis gas per l. of catalyst per hr.

1020. ——— (Metallgesellschaft A. G.). [Separation of Gaseous Hydrocarbon Mixtures.] German Patent 740,347, Aug. 26, 1943 (*Cl. 26 d–10.01*). Chem. Abs., vol. 39, 1945, p. 2292.

Fractions are separately absorbed at various stages of the process and then separated. At each stage the gas is washed by the next higher boiling fraction. The substance used for separating these 2 fractions at each stage is regenerated for reuse.

1021. ——— (American Lurgi Corp.). Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,224,048, Dec. 3, 1940; appl.

filed Nov. 24, 1937, Serial No. 176,373, in Germany Dec. 2, 1936; 10 claims (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 1970.

In the production of hydrocarbons by the catalytic conversion of gases containing CO and H_2 at temperatures below 300°, with catalysts suitable for forming benzine, hydrocarbon oil, and paraffin from such gases and temperatures and at atmospheric pressure, catalysts are used consisting of hydrogenating metals such as Co, difficultly reducible metal compounds such as Th oxide, and carrier substances such as kieselguhr, which constitute at least half the weight of the catalysts, and a mixture of CO and H_2 is used containing over 20% of inert constituents with a pressure of over 2 atm.

1022. ——— (American Lurgi Corp.). Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,224,049, Dec. 3, 1940; appl. filed Nov. 24, 1937, Serial No. 176,374, in Germany Nov. 30, 1936; 8 claims (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 1970.

Describes apparatus and a process similar to United States Patent 2,224,048 (abs. **1021**) in which the end gas from the catalytic conversion is recirculated after separation from it of at least part of the H_2O and hydrocarbons formed by the conversion in sufficient quantities that the partial pressure of the liquefiable hydrocarbons formed in the hot gases, leaving the catalytic agents and which have a higher critical temperature than the temperature employed in the catalytic conversion, is maintained below $0.2\sqrt{p}$, wherein p designates the positive pressure in atmospheres applied during the conversion.

1023. ——— (American Lurgi Corp.). Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. United Staes Patent 2,271,259, Jan. 27, 1942; appl. filed May 25, 1938, Serial No. 210,073, in Germany Jan. 20, 1937, 18 claims (*Cl. 260–449*). Chem. Abs., vol. 36, 1942, p. 3661.

Process is employed for the conversion of CO and H_2 into hydrocarbons with catalysts adapted to form benzine oil and paraffin under atmospheric pressure, the catalysts being arranged in a contact chamber adapted to maintain a desired reaction temperature therein, which involves maintaining a temperature in the contact chamber above 150° but below the temperature required for the exclusive formation of CH_4 with the catalysts, maintaining a velocity of the gas flow in contact with the catalysts above 1*n* l. per hr. per gm. of hydrogenating metal in the catalysts, and adjusting the pressure of the gas to a pressure above atmospheric and sufficient that the time the gases remain in contact with the catalysts is more than 45 sec. Catalysts may be used such as Co, Th oxide, and kieselguhr.

1024. ——— (Metallgesellschaft A. G.). [Synthesizing Hydrocarbons From Carbon Monoxide and Hydrogen.] German Patent 734,993, Apr. 1, 1943; appl. M 136,645 filed Dec. 19, 1936 (*Cl. 12 o–1.03*). FIAT Reel AA88, frames 3,468–3,470; PB 70,273; Chem. Abs., vol. 38, 1944, p. 1343.

CO is catalytically hydrogenated at an elevated pressure. A difficultly reducible metal oxide, preferably Co oxide, is used as the catalyst. The oxide is diluted with diatomaceous earth to give 0.5–40 gm. of effective metal catalyst per l. of contact mass.

1025. HERBERT, W., AND GROSS, H. W. (Metallgesellschaft A. G.). [Hydrogenation of Carbon Monoxide.] German Patent 763,233, Aug. 23, 1951; appl. M 143,284, filed Nov. 9, 1938 (*Cl. 12 o*). Chem. Zentralb., 1952, I, p. 625.

CO is hydrogenated to polybranched hydrocarbons and O-containing organic compounds with or without the use of elevated pressure in catalyst reactors with closely lying cooling elements. The catalysts consist of the Fe hydroxide occurring in the decomposition of bauxite with additions of alkali-, Cr- or Al-compounds or Cu or mixtures of these. Up to 20% of the $Fe(OH)_3$ can be reduced to Fe. Additions may amount to 5% or more. The mechanical stability of the catalyst can be improved by addition of 20% of cement before granulation (2–4 mm.). Removal of H_2S, organic S compounds, and resin formers from the synthesis gas is expedient. 100 N m.^{3} of standard synthesis gas containing 60% CO, 30% H_2, 10 inert gas are passed at 10 atm. pressure and 260° over a catalyst comprising $55Fe(OH)_3$, $20Al(OH)_3$ $5CuO$, $2KOH$, $15SiO_2$, and TiO_2 previously reduced with excess H_2, 8% of the $Fe(OH)_3$ is contained as free Fe. Yields are 145 gm. benzine (27%), higher boiling oil (20%), and paraffin (53%) calculated on inert-free exit gas.

1026. ——— (Metallgesellschaft A. G.). Process for Making Iron-Containing Catalysts for Carbon Monoxide Hydrogenation. German Patent 745,444, Mar. 2, 1944; appl. M 144,025, Jan. 25, 1939 (*Cl. 12 o–1.03*). FIAT Reel AA 89, frames 65–68, PB 70,274; FIAT Reel E 33, frames 118–120; PB 70,436; Chem.-Ztg., vol. 68, 1944; Chem. Abs., vol. 40, 1946, p. 1982.

Solutions of Fe salts containing also Cu compounds and compounds of metals of which the oxides are not readily reducible by H_2 are precipitated with an alkali hydroxide, preferably KOH. The quantity of the alkali hydroxide is so chosen that, throughout the entire precipitation period or at least at its end the pH of the precipitate is 7.5–11 and preferably 9–10. This is of particular importance where the Fe catalyst is carried on diatomaceous earth. The precipitate is then washed, the washing being stopped when the wash H_2O reaches a pH of 7.5. Then the catalyst is dried and reduced.

1027. ——— (Metallgesellschaft A. G.). [Working-Up the Reaction Gases of Carbon Monoxide Hydrogenation.] German Patent 747,731, Oct. 11, 1944; appl. M 147,722, May 1, 1940 (*Cl. 12 o–1.03*). FIAT Reel AA 88, frames 3,605–3,609, PB 70,273; TOM Reel 35, item 64, 12 pp.

In working-up the gases from the hydrogenation of CO, particularly when performing the synthesis with gas recycle, the gases, after separation of the high-boiling, liquid products discharged from the converter, are washed with aqueous liquors containing alcohol under saturation with H_2O vapor and then condensed as usual. The liquors used for the washing may be those aqueous alcoholic solutions occurring in the further working-up of the reaction gases.

1028. HERBERT, W., AND METALLGESELLSCHAFT A. G. [Hydrocarbon Synthesis.] British Patent 507,366, June 14, 1939; appl. filed Apr. 25, 1938. Chem. Abs., vol. 34, 1940, p. 614.

In the synthesis of hydrocarbons, mainly paraffinic and olefinic, from CO and H_2 with catalysts known for the synthesis of benzine, oil, and solid paraffin and temperatures $<$ those yielding only CH_4 are used. The gas throughout is kept >1 l. (calculated at normal pressure and temperature) per hr. per gm. of hydrogenating metal in the contact mass, and the reaction chamber or the pressure, or both, is made so large that the time of contact of the gas with the contact mass is $>$ than 45 sec. The temperature is so regulated that the heat generated, calculated as heat load per m.^{2} of cooling surface of the cooling members embedded in the contact mass, at the gas pressure of p atmosphere does not exceed 500 $\sqrt[3]{p}$ kcal. per hr. Recycling of gases after removal of reaction products increases the catalyst life and reduces the formation of solid paraffin. A Co–Th–kieselguhr catalyst may be prepared by precipitating a mixture of the metal nitrate solutions and kieselguhr with K_2CO_3, granulating and reducing. It contains Co, 33%; ThO_2, 6%; and

kieselguhr, 61%. The contact chamber is divided into 2 stages. Part of the reaction products are withdrawn immediately. Gases containing H_2, 2 vols. and CO, 1 vol. are caused to react at 180° and normal pressure. The throughput is 1 l. per hr. per gm. of Co. The time of stay is 36 sec. and the heat load per $m.^2$ is 240 kcal. per hr.

1029. HERBERT, W., AND RUPING, H. (Carbo-Norit-Union Verwaltungs-G.m.b.H.). [Removing Sulfur and Resinifying Substances From Gases Destined for Catalytic Conversion, Particularly Carbon Monoxide–Hydrogen Mixtures (Generator Gas, Water Gas, Coking Gas).] German Patent 735,662, Apr. 15, 1943 (*Cl. 26 d–8.04*). Chem. Abs., vol. 38, 1944, p. 4122.

See French Patent 849,527 (abs. **304**).

1030. HERBERT, W., AND WEITTENHILLER, H. (Metallgesellschaft A. G.) [Hydrocarbons From Carbon Monoxide and Hydrogen.] German Patent 746,887, Aug. 30, 1944; appl. M 146,080, filed Sept. 14, 1939 (*Cl. 12 o–1.03*). FIAT Reel AA–90, frames 1,625–1,628; PB 70,275; TOM Reel 35, item 64, 11 pp.; TOM Reel 67, item 76, frames 1,131–1,133; Chem.-Ztg., vol. 69, No. 2, 1945; Chem.-tech. Übersicht, p. 9; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 5, chap. 158, 1949, p. 40.

Process is described for producing hydrocarbons from gases containing CO and H_2 with Co catalyst at 180°–230° and 3–20 atm. in 2 or more stages. The fresh catalyst is 1st used in the 2d vessel for as long a time as it will be used in the 1st vessel. After 1 or 2 months the gas flow increases to about 2,000–4,000 $m.^3$ per 800–1,000 kg. of Co in the catalyst per hr. Under these conditions CH_4 formation noticeably increases, and the conversion of CO and H_2 decreases. Hereupon the catalyst is transferred to the 1st vessel and used at lower gas flow of about 1,000 $m.^3$ per 800–1,000 kg. of Co in the catalyst per hr. The gas composition is regulated to a CO : H_2 ratio of about 1 : 1.7 or 1 : 1.98 before entrance into the next higher stage by adding H_2-containing gases.

1031. HERBERT, W., SCHALL, A., AND GROSS, H. W. (Metallgesellschaft A.-G.). [Catalyst for Hydrogenation of Carobn Monoxide.] German Patent 736,977, July 6, 1943; appl. filed July 24, 1938 (*Cl. 12 o–1.03*). Chem. Abs., vol. 38, 1944, p. 3786.

Fe nitrate mixed with diatomaceous earth and a small quantity of a metal that activates nitrates is heated. Simultaneously air is passed in so that part of the N_2 is driven off. Then the Fe is reduced with gases containing H_2 at a temperature $< 300°$. The reduction is carried to such an extent that only 5–10% of the theoretically reducible Fe is actually reduced to the metallic state.

1032. HERBERTS, K., & Co. [Paints and Varnishes.] German Patent Appl. H 173,528, no date (*Cl. 22 g–10.01*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 612.

Distillation residues of the oxidation products of CO hydrogenation are saponified with aqueous NH_4OH+ aliphatic alcohols and emulsified.

See also German Patent 742,666 (abs. **2748**).

———. *See* abs. **1074, 2016, 2748.**

1033. HERBST, W. A. (Standard Oil Development Co.). Process for the Manufacture of Synthesis Gas. United States Patent 2,631.933, Mar. 17, 1953; appl. filed Oct. 15, 1947, Serial No. 780,072; 5 claims (*Cl. 48–196*). Chem. Abs., vol. 47, 1953, p. 6637.

Hydrocarbon gases such as CH_4 or natural gas are contacted with turbulent, fluidized metal oxide particles capable of oxidizing the gases to CO and H_2 at a temperature experimentally shown to give optimum yields. Then the fluidized O carrier is passed through a classifier, preferably a packed vessel, where the agglomerates are segregated from the particles of satisfactory fluidity. The satisfactory particles are returned to the process for reoxidation. The classifying step allows both the hydrocarbon oxidation and the metal oxide carrier regeneration steps to be carried out at higher temperatures than would be possible if the agglomerates were not removed. For effective operation the carrier particles in CH_4 or natural gas oxidation step should be 10–300μ in size, with 75% being larger than 44μ. With the classification stage and the higher operating temperatures (1,400°–1,800° F. in the gas oxidizer and 1,600°–2,000° F. in the regenerator), the particles of smaller size tend to be more readily agglomerated and the particles larger than 250–300μ are continuously removed. 5 United States patents cited.

1034. ——— (Standard Oil Development Co.). Synthesis of Hydrocarbons. United States Patent 2,467,-803; appl. filed Aug. 14, 1947, Serial No. 768,540; 8 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 6810.

To reduce C formation in a multistage conversion process, fresh synthesis gas is used with aged Fe catalyst to effect 60–90% of the CO conversion at moderately high conversion levels. The catalyst is aged to the equivalent of 500–2,000 or more cu. ft. of CO converted per lb. of catalyst. The unconverted reactants are contacted with relatively fresh Fe catalyst, <1,000 cu. ft. of CO converted per lb. of catalyst, at low conversion levels to complete the conversion. Catalyst fines may be removed and oxygenated compounds withdrawn between stages. 7 United States patents cited.

HERCULES POWDER Co. *See* abs. **3338.**

1035. HEROLD, —, WENZEL, —, AND GEMASSMER, —. (I. G. Farbenindustrie A. G.). [Production of Oxygenated Organic Compounds.] German Patent Appl. I 74,736, OZ 14,118, filed Apr. 1, 1943 (*Cl. IV d–12 o*). FIAT Reel 172, frame 377; PB 25,616; TOM Reel 19, item 144, frames 1,680–1,683; Meyer Transl. PC–S–V, Oxo, vol. 2, chap. 34, 1948, p. 10.

Raw material for the process is the oxygenated organic compounds mixed with olefins, which were obtained in a previous conversion of CO with H_2 <250° and at medium pressure over an Fe catalyst. Example: A fraction b. 160°–180° from a product obtained by passing water gas over a fused Fe catalyst at 194° and 25 atm. (54% alcohols, 26% olefins, 2.2 esters and 7.3% aldehydes) is contacted with a Co catalyst having kieselguhr as the carrier and small amounts of Th and Mg oxides as the promoter. Then a CO+H_2 mixture is added at 250 atm. pressure and the conversion performed at 135°. The product is then hydrogenated at 250 atm. and 180°, separated from the catalyst, esterified with boric acid, and the neutral oil not esterified was removed. The Boric acid ester is saponified and alcohols recovered.

HEROLD, P. *See* abs. **3907.**

1036. HEROLD, P., AND ASINGER, F. (I. G. Farbenindustrie A. G.). [High-Molecular Aliphatic Chlorohydrocarbons.] German Patent 740,677, Nov. 2, 1943; appl. I 67.560, filed Aug. 1, 1940 (*Cl. 12 o–2.01*). FIAT Reel AA–90, frames 1,031–1,034; Chem. Abs., vol. 40, 1946, p. 588.

Sulfonic acid chlorides of high-molecular aliphatic hydrocarbons, such as those obtained by the hydrogenation of CO, which can be either liquids or solids at ordinary temperatures, are heated in an inert solvent at a temperature below the boiling point of the sulfonic acid chloride, preferably at 100°–200°, and in the absence of substances that have a polymerizing effect on olefins.

1037. HEROLD, P., AND LANGHEINRICH, H. (I. G. Farbenindustrie A. G.). Organic Compounds Containing Oxygen by Reduction of Carbon Oxides With Hydrogen. United States Patent 1,743,214, Jan. 14, 1930; appl. filed Nov. 8, 1927, No. 231,986. Chem. Abs., vol. 24, 1930, p. 1389.

Organic compounds containing O are obtained, either alone or in conjunction with hydrocarbons, by reducing oxides of C with H_2 under diminished, ordinary, or slightly elevated pressure up to about 20 atm. and at an elevated temperature, if the operation be carried out <300°, the catalyst employed consisting of Fe containing small additions of alkalies or alkaline earths or compounds of the same having an alkaline reaction and being used alone or in conjunction with other substances, carriers or activating substances, for example, Cu. The resulting products are partly solid and partly liquid and gaseous. In contrast to the conditions in the production of hydrocarbons alone, less H_2O and more CO_2 are formed, and merely traces of the lower members of the paraffin series of hydrocarbons are produced. The solid products are yellow to yellowish brown and contain, besides white paraffin, m. about 65°, brown, viscous resins containing O. The liquid portions have a yellow-green to yellow-brown color and boil at approximately 40°–200°. They, too, contain paraffins. Their sp. gr. is 0.74–0.80 and their Br value about 0.25–0.45. The O is contained in amounts up to about 10%. The H_2O of condensation contains alcohol and, in addition to CO_2, organic acids volatilizable by steam. Gives examples.

1038. ——— (I. G. Farbenindustrie A. G.). [Production of Oxygen-Containing Organic Compounds.] Russian Patent 10,025, June 29, 1929; appl. filed Nov. 1, 1927. Chem. Zentralb., 1931, I, p. 2828.
See British Patent 280,522 (abs. **1191**).

1039. HEROLD, P., KAUFMANN, H., AND WOERNER, A. Manufacture of Hydrocarbons. United States Patent 2,371,890, Mar. 20, 1945; appl. filed Nov. 14, 1940, in Germany Feb. 8, 1939.

The preparation of a catalyst for the distinctive hydrogenation of solid and liquid carbonaceous materials (coal, tar, and mineral oils) or the production of hydrocarbon oils from mixture of CO and H_2. Bleaching earths are treated with an aqueous solution of salts of Mg, Al, Mn, Fe, Co, or Ni. An example gives the composition of German bleaching earth. The catalyst is especially well suited for use in reactions at temperatures of 200° or 300°–700° C., under pressures of 10–500 atm.

1040. HEROLD, P., SMEYKAL, K., AND GROGER, R. (I. G. Farbenindustrie A. G.). [Refining Alcohols.] German Patent 697,756, Sept. 26, 1940 (*Cl. 12 o–5.02*). Chem. Abs., vol. 35, 1941, p. 6597.
See British Patent 494,985 (abs. **1518**)

1041. HEROLD, P., SMEYKAL, K., ASINGER, F., AND VON DER HORST, H. D. (I. G. Farbenindustrie A. G.). [Organic Sulfur Compounds.] German Patent 715,846, Dec. 4, 1941 (*Cl. 12 o–23.03*). Chem. Abs., vol. 38, 1944, p. 2050.

The reaction products containing S and O, and halogen obtained when liquid saturated aliphatic hydrocarbons are acted upon by a halogen and SO_2 are made to react with alcohols or phenols.

1042. ——— (I. G. Farbenindustrie A. G.). [Organic Sulfur Compounds.] German Patent 723,116, June 11, 1942 (*Cl. 12 o–23.03*). Chem. Abs., vol. 38, 1944, p. 2050.

Organic compounds containing halogen, S, and O, such as are obtained by simultaneous action of halogen and SO_2 on saturated aliphatic hydrocarbons, are made to react with alcohols or phenols. Addition to German Patent 715,846 (abs. **1041**).

HERRICK, E. C. *See* abs. **641.**

HESS, H. V. *See* abs. **29, 30, 31, 32, 264.**

1043. HESS, H. V., AND ARNOLD, G. B. (The Texas Co.). Extraction of Alcohols From the Fischer-Tropsch Synthesis Product. United States Patent 2,558,557, June 26, 1951; appl. filed Sept. 13, 1946, Serial No. 696,912; 1 claim (*Cl. 260–450*).

Azeotropic mixture of C_2 and C_3 alcohols, separated from the aqueous phase of the products of the Fischer-Tropsch conversion, is used for the extraction of higher boiling alcohols through the hydrocarbon phase. The alcohol-free hydrocarbon fraction obtained from this extraction is used to extract the lower boiling alcohols from the aqueous azeotropic mixture containing them. 5 United States patents and 2 literature refs. cited.

1044. ——— (The Texas Co.). Production of Hydrocarbons and Oxygenated Compounds. United States Patent 2,558,556, June 26, 1951; appl. filed Aug. 6, 1946, Serial No. 688,624; 3 claims (*Cl. 260–450*).

In the conversion of CO and H_2 into a mixture comprising hydrocarbons, H_2O, and O-containing compounds, which are mainly aliphatic alcohols, an improvement is claimed, which comprises effecting separation of the mixture at an elevated temperature of about 200°–350° F. and elevated pressure into a gas phase, a hydrocarbon phase containing substantially all of the C_3 and higher alcohols in addition to a substantial part of the ethyl alcohol produced in the conversion, and a H_2O phase containing a minor % of the alcoholic conversion products, fractionating the hydrocarbon phase into a gasoline fraction and a gas oil fraction, separating C_2 and C_3 alcohols from the gasoline fraction, and using the C_2 and C_3 alcohols to extract oxygenates from the gas-oil fraction. 4 United States patents and 3 literature refs. cited.

1045. HESS, H. V., ARNOLD, G. B., AND DRABKIN, M. L. (Texaco Development Corp.). Carbon Monoxide and Hydrogen Synthesis Products. British Patent 676,710, July 30, 1952. Chem. Abs., vol. 46, 1952, p. 11,644.

Synthesis products from the catalytic conversion of CO and H_2 are heated in the vapor phase at 500°–1,000° F. with an alkaline earth mixture to hydrolyze esters to acids and alcohols and decarboxylate acids to hydrocarbons and ketones.

1046. ——— (The Texas Co.). Process for Treating Synthesis Product. United States Patent 2,653,960, Sept. 29, 1953; appl. filed Mar. 26, 1949, Serial No. 83,732; 7 claims (*Cl. 260–450*).

Claim 1. A process for treating a product containing H_2O, hydrocarbons and O_2-containing organic compounds, comprising alcohols, esters, acids, aldehydes, and ketones and which is obtained by the catalytic conversion of CO and H_2 into synthetic fuel, which comprises separating the synthesis product obtained by catalytic conversion of synthesis gas into a gas phase and a liquid phase comprising oil and H_2O phases; contacting said entire liquid phase in the vapor state at a temperature of 500°–1,000° F. with a solid basic material selected from the group consisting of alkali metal compounds, alkaline earth compounds, and mixtures thereof, whereby esters are hydrolyzed to alcohols and acids and acids are decarboxylated to hydrocarbons and ketones; cooling said base-treated liquid phase; separating said base-treated liquid phase into an oil fraction and a H_2O fraction; vaporizing said oil fraction containing oxygenates mainly in the form of alcohols and ketones; contacting said oil fraction with a particulate adsorbent at a temperature of 400°–700° F., whereby said O_2-containing organic compounds, mainly alcohols and ketones, are adsorbed on said adsorbent; separating said adsorbent containing O_2-containing organic compounds adsorbed thereon from said vaporized oil fraction; and recovering O_2-contain-

ing organic compounds comprising mainly alcohols and ketones from said separated adsorbent.

1047. ——— (The Texas Co.). Vapor-Phase Treatment of Combined Gasoline and Water Phases of Synthesis Product With a Basic Compound. United States Patent 2,591,699, Apr. 8, 1952; appl. filed Nov. 14, 1949, Serial No. 127,201; 9 claims (*Cl. 260–450*).

Product obtained by the catalytic conversion of CO and H_2 to liquid fuel is separated at 200°–400° F. and 150–500 p. s. i. into a gas phase, a H_2O phase, and an oil phase, the gas phase being recycled to the reaction zone where the CO and H_2 are converted into liquid hydrocarbons. The oil phase is separated into a gasoline fraction and a gas-oil fraction, the former being combined with the H_2O phase. The composite thus formed is vaporized and treated at about 500° F. with a basic compound such as Na_2CO_3. This has the effect of hydrolyzing the H_2O- and oiil-soluble esters boiling in the gasoline range to alcohols and acids and of decarboxylating the H_2O- and oil-soluble acids boiling in the gasoline range either to hydrocarbons or ketones. After the treatment with the basic compound, the composite is cooled and separated into a gaseous fraction, a H_2O phase, and a gasoline phase. The gaseous fraction is recycled to the reaction zone, while the alcohols and ketones are separately removed from the H_2O and the gasoline phases.

HEUNICKE, W. *See* abs. **3890.**

1048. HEUTRICH, W., LAINAU, C. A., AND JAKOB, W. [Production of Fatty Alcohol Sulfonates.] German Patent Appl. —, filed Mar. 24, 1937; APC 132,770.

Waste products (8–18 C) from the Fischer-Tropsch gasoline synthesis are utilized for the preparation of fatty alcohol sulfonates. The liquid-solid hydrocarbons are oxidized to produce acids, then reduced to the corresponding alcohols and sulfonated.

1049. HIBSHMAN, H. J., (Standard Oil Development Co.). Hydrocarbon Synthesis Process. United States Patent 2,463,875, Mar. 8, 1949; appl. filed Sept. 18, 1946, Serial No. 697,806; 3 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 4447.

Reactant gases are removed from the synthesis zone and are scrubbed, preferably countercurrently, with a heavy petroleum oil such as an asphalt having a specific gravity 0.80–1.02 and a softening point less than 300° F. The temperature should not vary more than 50°–100° F. from the temperature maintained in the synthesis zone. The pressure should be kept, preferably, as high as that of the synthesis zone. At an absorption temperature of 200° F. a satisfactory oil rate is 4 bbl. oil per bbl. of product provided the pressure is about 50 p. s. i., at 300° and 410° F., 4 bbl. oil per bbl. of product is satisfactory at 215 and 450 p. s. i. By this process considerable quantities of relatively low-boiling hydrocarbons are not absorbed in the medium but are recycled to the synthesis zone and converted to higher boiling hydrocarbons. 3 United States patents cited.

1050. ——— (Standard Oil Development Co.). Recovery of Organic Oxygen-Containing Compounds From Mixtures of Hydrocarbon Oils. United States Patent 2,626,276, Jan. 20, 1953; appl. filed Dec. 13, 1947, Serial No. 791,592; 4 claims (*Cl. 260–450*). Chem. Abs., vol. 47, 1953, p. 4075.

The mixture of O_2-containing compounds and hydrocarbon oils is extracted with S dioxide in conjunction with a wash solvent insoluble in S dioxide, preferably in a liquid-liquid extraction whereby the O_2-containing compounds dissolve in the S dioxide forming the extract phase, leaving the raffinate phase composed substantially of the hydrocarbons and the wash solvent. 1 literature ref., 3 foreign patents, and 5 U. S. patents cited.

1051. ——— (Standard Oil Development Co.). Separating Normal Paraffins From Isoparaffins by a Solid Adsorption Process. United States Patent 2,620,363, Dec. 2, 1952. Chem. Abs., vol. 47, 1953, p. 2473.

Isoparaffins may be separated from normal paraffins by the following adsorption process, which avoids complete regeneration of the adsorbent. *n*–Pentane is adsorbed from a mixture of *n*–pentane and isopentane; the *n*–pentane is desorbed by treating with isohexane obtained from a separate adsorption system; the isohexane–*n*–pentane mixture is separated by normal distillation. The same scheme is used for recovering adsorbed *n*–hexane by deadsorbing it with isopentane and then separating it by distillation.

1052. HIBSHMAN, H. J., AND DOLPH, R. N. (Standard Oil Development Co.). Process for Segregating Oxygenated Hydrocarbons. United States Patent 2,542,521, Feb. 20, 1951; appl. filed Aug. 6, 1948, Serial No. 42,818; 5 claims (*Cl. 260–450*). Chem. Abs., vol. 45, 1951, p. 4431.

Process consists of contacting a mixture of hydrocarbons with silica gel at the top of a vertical tower, so that the oxygenated compounds will be adsorbed onto the gel and the mass will move downward into the lower part of the tower where it comes into contact with a C_1–C_4 alcohol, which acts as a desorbent for most of the oxygenated compounds except the acidic ones. The desorbed oxygenated compounds are removed as a side stream from the tower, the acidic oxygenated compounds from the bottom, and the fraction of hydrocarbons, which have not been adsorbed, from the top of the tower. 1 literature ref. and 3 United States patents cited.

1053. HIDAKA, T., AND OTHERS (Nissan Chemical Industries Co.). [Recovery of Hydrogen Sulfide in the Gaseous Mixture as Free Sulfur.] Japanese Patent 4,338, Oct. 22, 1952. Chem. Abs., vol. 47, 1953, p. 8997.

Water gas containing a small amount of H_2S is passed through an absorption tower containing yellow earth ($Fe_2O_3 \cdot 3H_2O$) molded into granules with 2% NaOH; when the weight of absorbent increases 30–33% of the weight, inert gas containing a small amount of O_2 is passed through to heat at about 50° by the heat of reaction, and to separate the free S, and the S is extracted with liquid NH_3 to recover 96–98% of the S in the absorbent. The regenerated absorbent is then recycled.

HILBERATH, F. *See* abs. **2629, 2630, 2631.**

HILL, A. J., JR. *See* abs. **871.**

HILL, B. L. *See* abs. **657.**

1054. HILL, B. N. (Standard Oil Development Co.). Treatment of Hydrocarbon Synthesis Naphtha. United States Patent 2,651,654, Sept. 8, 1953; appl. filed Jan. 21, 1949, Serial No. 71,775; 9 claims (*Cl. 260–450*).

Claim 1. A method for removing contaminating compounds from a naphtha fraction obtained by contacting a gaseous mixture of CO and H_2 with a suitable catalyst under conversion conditions to form a mixture of hydrocarbons and oxygenated organic compounds, which comprises washing a contaminated naphtha fraction consisting of said mixture of hydrocarbons and oxygenated organic compounds with an aqueous solution of an alkali metal hydroxide; removing said aqueous solution from contact with said naphtha fraction; contacting the washed naphtha fraction with an alcoholic solution containing no more than 30% of H_2O in which has been dissolved a treating reagent selected from the class consisting of hydroxylamine and its inorganic salts in an amount within 0.2–2 parts of alcoholic solution for each part of

washed naphtha; removing said alcoholic solution from contact with said naphtha; washing said treated naphtha with an aqueous solution of alkali-metal hydroxide; removing said naphtha from contact with said alkali metal hydroxide solution and distilling said naphtha to recover a fraction having a boiling range substantially identical to the boiling range of the contaminated naphtha.

1055. HILL, B. N., AND WADLEY, E. F. (Standard Oil Development Co.). [Separating Organic Oxygenated Compounds.] French Patent 971,154, Jan. 15, 1951; appl. filed Sept. 8, 1948. Chem. Zentralb., 1952, I, p. 3568.

Reaction products of the conversion of CO with H_2 comprising hydrocarbons and organic oxygenated compounds, mainly alcohols, are separated into a liquid and a gaseous phase. The liquid phase is treated with an aqueous alkali solution of 10°–20° Bé to remove the organic acids. The aqueous solution is separated from the hydrocarbon layer, and the latter is fractionated to obtain an ester-free product.

1056. ——— (Standard Oil Development Co.). [Treating Hydrocarbon Mixtures.] French Patent 970,850, Jan. 9, 1951; appl. filed Aug. 25, 1948. Chem. Zentralb., 1952, I, p. 1269.

To separate by distillation oxygenated organic compounds from the mixture of hydrocarbons obtained as product of the Fischer-Tropsch synthesis, the latter is passed over a mixture of the alkali salts of mineral oil sulfonates of a lubricating oil or a lubricating oil extract and an alkali hydroxide. The hydrocarbon distillate passes over virtually free from oxygenated compounds.

1057. ——— (Standard Oil Development Co.). Treatment of Synthetic Naphtha. United States Patent 2,544,317, Mar. 6, 1951; appl. filed Nov. 28, 1947, Serial No. 788,632; 8 claims (*Cl. 260–450*). Chem. Abs., vol. 45, 1951, p. 4920.

Oxygenated organic compounds, including ketones, aldehydes, and esters, are removed from synthetic crude petroleum from Fischer-Tropsch synthesis by distilling the crude in presence of a treating reagent, such as the lubricating-oil fraction, an alkali metal sulfonate, and an alkali metal hydroxide. This distillate fraction b. <600° F. is recovered. The alkali metal hydroxide is preferably Na hydroxide. The alkali metal sulfonate is preferably Na sulfonate. K and Li compounds may be used in both cases. 1 United States patent cited.

1058. HILL, L. R. (M. W. Kellogg Co.). Synthesis of Organic Compounds. United States Patent 2,560,171, July 10, 1951; appl. filed Mar. 3, 1947, Serial No. 731,899; 3 claims (*Cl. 260–449.6*).

Describes improved process for producing organic compounds by introducing a feed mixture containing H_2 and CO in a mol ratio of H_2 : CO between 0.7 : 1 and 10 : 1 into a reaction zone through which a gaseous mixture is passed upward at 0.5–40 ft. per sec. in presence of a fluidized catalyst and under conditions such that a major part of the CO is converted. The reaction zone is maintained at 350°–750° F. and 50–500 p. s. i. g. A gaseous effluent is withdrawn from the reaction zone, a part recycled in a volumetric ratio of recycle gas to fresh feed of between 1 : 1 and 2 : 1. Hot regenerated catalyst is introduced into the mixture of recycle gas and fresh feed, the temperature differential between catalyst and feed is decreased and the catalyst returned to the reaction zone. The unrecycled effluent is subsequently cooled and condensed, and the organic products are recovered. Using a reduced Fe catalyst under the conditions described a conversion of 70–100% of CO has been observed. The oil and H_2O yields have been as much as 100 and 120 cc. per $m.^3$, respectively. Substantial amounts of oxygenated compounds have been recovered.

———. *See* abs. **488, 2196, 2202.**

HILLARD, G. O. *See* abs. **2585, 2586.**

1059. HIRSCH, J. H. (Gulf Research & Development Co.). Catalytic Apparatus. United States Patent 2,585,462, Feb. 12, 1952; appl. filed Dec. 19, 1947, Serial No. 792,825; 7 claims (*Cl. 23–288*).

Various structural and operative details are presented. Process and apparatus are adapted for use in any chemical reaction employing a solid catalyst and involving the removal or supply of large amounts of heat from or to the reaction zone. The desired objects are achieved by contacting the fluid reactants with one or more fixed beds of catalyst, each of which has its own heat exchange means and independently operating circulating means for moving the fluid reactants through the catalyst bed and over heat exchange means back to the circulating means, all disposed within a single reaction vessel.

1060. ——— (Gulf Research & Development Co.). Manufacture of Synthesis Gas. United States Patent 2,614,915, Oct. 21, 1952; appl. filed Nov. 24, 1947, Serial No. 787,829; 3 claims (*Cl. 48–203*). Chem. Abs., vol. 47, 1953, p. 1361.

Synthesis gas from finely divided coal, steam, and O_2 may be represented stoichiometrically by the reactions:

$$3\ C+4\ H_2O \rightarrow CO_2+4\ H_2+2\ CO$$
$$2\ C+3\ H_2O \rightarrow CO_2+3\ H_2+CO.$$

Since these reactions are endothermic, sufficient O_2 and excess coal are added to cause the reaction

$$C+O_2 \rightarrow CO_2.$$

This exothermic reaction supplies the heat for the endothermic synthesis gas reactions, and the production of synthesis gas goes on continuously. The temperature in the combustion chamber is 2,000°–2,500° F. Both the steam and the O_2 are preheated to 1,000° F. The system is operated under a pressure of 300 p. s. i., and the synthesis gas expands to 200 p. s. i. Enough residual heat is left in the expanded synthesis gas to generate and superheat the steam and to preheat the O_2. Furthermore, the synthesis gas may be obtained at about 100° F. and about 190 p. s. i.; suitable conditions for hydrocarbon synthesis. 3 literature, refs. 3 foreign patents, and 7 United States patents cited.

1061. ——— (Gulf Research & Development Co.). Method and Apparatus for Conducting Chemical Reactions. United States Patent 2,488,406, Nov. 15, 1949; appl. filed Nov. 25, 1947, Serial No. 787,884; 4 claims (*Cl. 260–449.6*).

In the exothermic reactions such as synthesis of hydrocarbons from CO and H_2, the temperature is controlled by continuously removing a portion of the dense fluidized catalyst downward from the catalyst bed into a mixing zone, where it is diluted and made less dense by addition of more reactant gases. The less dense stream is then passed upward through a cooling zone back into the reactor, where the dense catalyst bed is formed again. 13 United States patents cited.

1062. HIRSCH, J. H., AND BOEGEL, M. J. (Gulf Research & Development Co.). Production of Gas Comprising Hydrogen and Carbon Monoxide. United States Patent 2,578,475, Dec. 11, 1951. Chem. Abs., vol. 46, 1952, p. 2271.

Gas mixture with a high ratio of H_2 to CO is secured by introducing into a spark-ignition internal-combustion engine a mixture of a hydrocarbon gas, such as natural gas with O_2 such that the molecular ratio of O_2 to natural gas varies 0.75–0.9 : 1. This mixture is compressed and ignited just before the top of the stroke.

Gives an equation for determining desirable relations between pressure and gas-O_2 ratios. The products are quickly released to atmospheric pressure; this cools them so that no further reaction occurs. H_2-CO ratios as high as 1.6 : 1 can be obtained in this manner.

1063. HIRSCH, S. Oxidation of Paraffinic Hydrocarbons. United States Patent 2,391,236, Dec. 18, 1945; appl. filed Aug. 25, 1943, Serial No. 500,005; 17 claims (*Cl. 260–451*). Chem. Abs., vol. 40, 1946, p. 1866.

Paraffinic hydrocarbons of high molecular weight are oxidized to fatty acids in a 4-stage process comprising (1) heating the paraffin to liquefy it, but not to a temperature about 150°; (2) intimately admixing with the liquid paraffin catalytic amounts of a heavy metal soap and a metal persalt, the latter at least being carried by an emulsion of H_2O, a H_2O-soluble soap, and an oleaginous material consisting of a fat or fatty acid; (3) dispersing through the emulsion a gas containing O_2 and a minor amount of moisture; and (4) separating the products. When using normally solid hydrocarbons, the final products and fatty acids are white and have the consistency, color, odor, and ease of saponification of coconut-oil fatty acids.

HIRSCHBECK, J. *See* abs. **944, 944a, 945.**

HOCHSCHWENDER, K. *See* abs. **1946, 1947.**

1064. HOCHSCHWENDER, K., WILLFROTH, E., AND SCHUNCK, W. (I. G. Farbenindustrie A. G.). [Oily Products.] German Patent 565,459, Jan. 20, 1924. Chem. Abs., vol. 27, 1933, p. 2543.

Products are obtained by the method of a gas mixture of CO and H_2 being used in the proportions suitable for forming MeOH. The gas mixture is passed at 450°–500° through a tube of Mn bronze containing an Fe-free contact agent consisting of $(NH_4)_2Cr_2O_8$, ZnO and K_2CO_3. Addition to German Patent 553,785 (abs. **1946**).

1065. HOCKBERGER, W. G. (Standard Oil Development Co.). [Catalytic Production of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 963,475, July 11, 1950; appl. filed Mar. 19, 1948, in United States June 11, 1947. Chem. Zentralb., 1950, II, p. 2271.

Operation is performed with an Fe catalyst at 289°–427° and under 5–50 atm. The catalyst consists of a precipitated, reduced Fe oxide or of reduced pyrite residue, which have been activated by addition of the oxides, hydroxides, carbonates, chlorides, or fluorides of Na or K. Other suitable catalysts are those used in the synthesis of NH_3 from N_2 and H_2 and contain 1.5% of Al_2O_3. The quantity ratio of $CO : H_2$ in the synthesis gas is 1 : 0.5–3.0. The liquid hydrocarbon oil formed in the synthesis, which contains considerable amounts of unsaturated hydrocarbons, is subjected to a cracking treatment on bauxite at 427°–537° and 1–10 atm., whereby mainly the hydrocarbons of the gas oil series are cracked, and the proportion of light hydrocarbons is increased. The bauxite used for the cracking catalyst is activated by dehydrating at 537°–649°, to a H_2O content $<10\%$, preferably $<3\%$.

1066. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,545,954, Mar. 20, 1951; appl. filed June 11, 1947, Serial No. 754,029; 5 claims (*Cl. 260–450*). Chem. Abs., vol. 45, 1951, p. 4912.

Total oil including gasoline and gas oil range hydrocarbons produced from CO and H_2 is treated with bauxite at conditions of temperature, pressure, and throughput that cause cracking of the gas-oil constituents. The temperature is 800°–1,000° F., pressure 1–10 atm. absolute, and throughput 0.5–2 vol. liquid feed per vol. bauxite. The bauxite is regenerated either continuously or at intervals considerably more frequent than in conventional bauxite reforming of gasoline-range hydrocarbons. Steam added to the feed will prevent excessive C deposition on the bauxite. Steam concentrations of 20–70 mol. % are suitable. 1 foreign and 2 United States patents cited.

1067. ——— (Standard Oil Development Co.). Recovery of High-Boiling Alcohols by Activated Alumina. United States Patent 2,619,497, Nov. 25, 1952. Chem. Abs., vol. 47, 1953, p. 1925.

Describes commercially feasible process for the selective adsorption and recovery of specific oxygenated compounds, such as alcohol, from fuel fractions in the gasoline-kerosine-diesel-oil range, with minimum adsorption of aromatic hydrocarbons, by using a solid adsorbent containing high proportions of alumina. To demonstrate the process, a known mixture was prepared containing 20 vol. C_9 alcohols, 20 vol. C_{10} aromatic tetrahydronaphthalene, and 60 vol. C_{12} paraffins, all boiling in the range of 350°–375° F. Approximately 200 cc. of the mixture in 200 cc. isohexane was percolated through a vertical glass tube, 1 in. diameter by 8 ft. long, packed with 50- to 200- mesh active alumina at 90°–95° F. Isohexane was added until the liquid leaving the bottom of the tube had the same refractive index as the isohexane, at which time the filtrate cuts were grouped as a 1st fraction, and all succeeding cuts were accumulated as the 2d fraction. EtOH (3 l.) was added to the column, and the 2d fraction was distilled to remove the isohexane and EtOH. This fraction, amounting to 20% of the original mixture, was exactly the same as the percentage of C_9 alcohols known to be present. Inspection of the fraction showed an API gravity of 37.2 (38.7 for the original C_9 alcohols) and a refractive index n_D^{20} of 1.43319 (1.43182 for the C_9 alcohols).

1068. HODGES, L. P. (Standard Oil Development Co.). Removal of Oxygenated Organic Compounds From Hydrocarbons. United States Patent 2,581,102, Jan. 1, 1952; appl. filed Oct. 25, 1948, Serial No. 56,447; 3 claims (*Cl. 260–450*).

Method for removing oxygenated organic compounds from a raw feed naphtha obtained from the synthesis of CO and H_2 over an Fe catalyst, which comprises mixing the liquid naphtha with a reagent consisting of 90–50% by weight of a polyethylene glycol having a molecular weight 400–4,000 and 10–50% by weight of an alkali metal hydroxide to form a liquid mixture. The mixture is charged into a fractionation zone and heated to evaporate the fractions b. 600° F., leaving a condensate substantially free of oxygenated compounds. Using this process, hydrocarbon mixtures containing olefins and oxygenated organic compounds including ketones can be refined and made suitable for the production of synthetic lubricant polymers.

1069. ——— (Standard Oil Development Co.). Separation of Oxygenated Organic Compounds From Synthetic Naphtha. United States Patent 2,584,269, Feb. 5, 1952; appl. filed Oct. 25, 1948, Serial No. 56,448; 4 claims (*Cl. 260–45*).

Crude naphtha containing approximately 20 wt. % oxygenated organic compounds, including ketones, aldehydes, carboxylic acids, and esters, and obtained from the synthesis of CO and H_2 over an Fe catalyst is freed from these compounds by mixing the hydrocarbon fraction thereof with about 5–30 vol. % of a treating reagent comprising solvent extract of a lubricating-oil fraction, an alkali metal naphthenate, and an alkali metal hydroxide. The reagent may consist of 90–99% by weight of a hydrocarbon fraction b. above 600° F., 1–10% of Na naphthenate, and 10–50% of NaOH. The mixture thus prepared is distilled and a fraction obtained boiling in the range of gasoline substantially free of oxygenated organic compounds.

1070. HODGSON, M. A. E. (Imperial Chemical Industries, Ltd.). Reactors for Catalyzed Reactions.

British Patent 680,865, Oct. 15, 1952. Chem. Abs., vol. 47, 1953, p. 4665.

Converter (I) is provided for reactions in which at least 1 component in the liquid phase is brought into contact with at least 1 other component in the liquid or gaseous phase and in which there is present 1 solid component, such as a catalyst or heat reservoir. The (I) contains at least 1 sheet of gauze positioned to ensure that any part of the solid components is within a desired horizontal distance from the sheet. The gauze consists of material wetted by the liquid components under the reaction conditions and has a weave in the form of galloon netting. Thus, in the direct catalytic hydration of propylene to isopropanol (II) at a pressure of 250 atm. and at 270° over a solid pelletted catalyst consisting essentially of a blue oxide of W, an output of (II) of 0.14 kg. per l. of catalyst bulk space per hr. was obtained. The (I), modified with 22 cylinders of stainless-steel galloon netting all coaxial with the (I) and spaced at regular intervals of 2 in. so that no point in the (I) was >1 in. distant from the nearest wire cylinder, produced an (II) output of 0.20 kg. This (I) is particularly applicable to reactions that use solid catalysts, such as the carbonylation of olefins by CO and H_2 to aldehydes or alcohols and the hydrogenation of creosote or fuel oil.

1071. HOESCH-BENZIN G. m. b. H. [Filling Catalyst Furnaces.] German Patent 754,540, no date; appl. H 165,125 (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 77.

In filling a catalyst furnace for the Fischer-Tropsch benzine synthesis, the catalyst is freed from dust directly while being poured into the catalyst furnace.

1072. ———. [Method for Improving the Efficiency of Catalyst.] German Patent Appl. H 158,604, PA 109, 780, filed Feb. 9, 1939 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 188–191; PB 83,253.

Efficiency of fresh Fischer-Tropsch catalysts is improved on induction by moistening or impregnating them with H_2O. The vertical catalyst tubes are filled with H_2O up to a certain level. The catalyst is charged into the tubes and the H_2O withdrawn to keep it at a constant level until the required amount of catalyst is charged when the excess H_2O is withdrawn and warm, 40°–60°, synthesis gas is admitted to expel the last of the H_2O. The reactor is then gradually heated to operating temperature. This method lowers the activity of the fresh catalyst by carrying off the too rapid evolution of heat thus reducing the formation of CH_4 and increasing the production of liquid products.

1073. ———. [Recovery of Fatty Acids.] German Patent Appl. H 168,380, no date (*Cl. IV d–12 o.*) Auszüge deut. Patent-Anmeldungen, vol. 6, p. 81.

Fatty acids are recovered from the spent neutralization liquors of the Fischer-Tropsch benzine synthesis by acidifying the alkaline spent liquors and washing out the free fatty acids with solvents.

HOFER, L. J. E. *See* abs. **947.**

1074. HOFFMAN, G. (K. Herberts & Co., formerly Otto L. Herberts). [Pencil Leads and Crayons.] German Patent 736,617, May 13, 1943 (*Cl. 22 g–2.01*). Chem. Abs., vol. 38, 1944, p. 3059.

In preparing pencil leads and crayons, the wax is replaced by Zn salts of oxidation products from CO hydrogenation products. Preferred are Zn salts of oxidation products with 8–14 C atoms.

1075. HOFFMANN, E. [Process for the Continuous Oxidation of Paraffins.] German Patent Appl. H 164,747, PA 162,433, filed Mar. 1, 1941 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 484–487; PB 83,253.

In the continuous oxidation of paraffins with air of O_2-containing gases, where the occurrence of dark-colored oxidation products are to be avoided, a smaller part of the raw paraffins is passed in parallel flow with the oxidizing agent at higher temperature and pressure continuously through a heated tube zone, then combined with the greater quantity of unoxidized material, and both passed continuously at lower temperature and pressure through a temperate tube zone. This method is claimed to give a lighter-colored product with less of the oxyfatty acids.

1076. HOGAN, J. P. (Phillips Petroleum Co.). Preconditioning Hydrocarbon-Synthesis Catalyst. United States Patent 2,644,829, July 7, 1953. Chem. Abs., vol. 47, 1953, p. 8995.

Describes process for eliminating the undesirably high initial activity of Fischer-Tropsch-type catalysts. Fresh or regenerated catalyst is brought into contact with a mixture of H_2 and CO at the desired reaction temperature, but at lower than normal pressure and space velocity. The pressure and space velocity are then increased slowly over a period of 5–15 hr. to the desired reaction conditions, when the reaction may be continued as usual. Thus a low reaction rate is maintained while the catalyst activity is high.

1077. ——— (Phillips Petroleum Co.). Pretreatment of Hydrocarbon Synthesis Catalyst. United States Patent 2,532,621, Dec. 5, 1950; appl. filed Apr. 22, 1947, Serial No. 743,171; 6 claims (*Cl. 260–449.6*).

Fresh or newly regenerated Fischer-Tropsch catalyst is contacted with CO–H_2 synthesis gas under conditions of total recycle of effluent gas while the reaction temperature is slowly raised until reaction begins. The reaction temperature is then slowly increased to desired operating temperature, and the effluent gas is withdrawn at such a rate that the CO content of the effluent gas is allowed to increase to a definite concentration, during which period the temperature is increased to the desired operating point. Only enough additional synthesis gas required to maintain reaction pressure is charged to the reactor. 2–10 hr. is required. The CO content of the effluent gas increases from 2–3 to 6–12 mol. %. After this breaking in period, the Fischer-Tropsch synthesis is carried out as usual. 4 United States patents cited.

1078. HOGAN, J. P., AND BANKS, R. L. (Phillips Petroleum Co.). Catalyst Fluidization. United States Patent 2,606,104, Aug. 5, 1952; appl. filed Apr. 12, 1948, Serial No. 20,384; 2 claims (*Cl. 23–289*).

Describes apparatus for providing improved distribution and fluidization of the catalyst within the reaction zone and for promoting a high degree of contact between the synthesis gas and the catalyst. These conditions are obtained primarily by installing conical, perforated baffles within the reaction chamber.

1079. HOGAN, J. P., AND FRIEDMAN, A. H. (Phillips Petroleum Co.). Regeneration of Catalyst. United States Patent 2,608,568, Aug. 26, 1952; appl. filed Apr. 12, 1948, Serial No. 20,383; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 47, 1953, p. 8995.

Hydrocarbon synthesis catalyst, the catalytic activity of which is decreased by deposition of reaction products thereon, is regenerated by interrupting the flow of synthesis gas to the reaction zone and recycling the tail gases thereto after separating therefrom the C_5 and higher boiling reaction products. The method is applicable to both fluidized and fixed catalyst beds and requires 1–3 hr. for completion.

1080. HOLDER, C. H. (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,530,243, Nov. 14, 1950; appl. filed Sept. 7, 1946, Serial No. 695,525; 1 claim (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 1751.

Character of product gases is controlled by controlling the C content of the catalyst in the reaction

zone. As the C content increases, the catalyst particles become more buoyant and tend to concentrate in the upper packed area of the reactor. The buoyant catalyst particles are withdrawn from the upper packed area, regenerated, and returned at a point lower in the reactor in an area free of packing elements. The packing should provide interstices having a length as compared to diameter of not greater than 15 : 1; also it should be at least 10 times as long as the largest particle to be fluidized. 6 United States patents cited.

1081. ——— (Standard Oil Development Co.). Production of Alcohols From Carbon Monoxide and Hydrogen. United States Patent 2,569,380, Sept. 25, 1951; appl. filed June 11, 1946, Serial No. 676,077; 15 claims (*Cl. 260–449.5*).

In the course of the catalytic synthesis of hydrocarbons from CO and H_2, varying amounts of oxygenated compounds, such as aldehydes, ketones, alcohols, etc., are produced. These compounds can be converted into more valuable alcohols by simple hydrogenation in the presence of conventional hydrogenation catalysts, such as Ni or its oxides, Cr, Mo, and W sulfides, at 400°–700° F., 50–250 p. s. i., and space velocities 0.5–5.0 vol. per vol. per hr. The hydrogenating agent consists of tail gas from the process itself. Alcohols may be recovered from the hydrogenated product by simple distillation.

1082. ——— (Standard Oil Development Co.). Reduction of Carbon Formation in Hydrocarbon Synthesis. United States Patent 2,628,968, Feb. 17, 1953; appl. filed Sept. 30, 1948, Serial No. 51,984; 3 claims (*Cl. 260–449.6*).

High yields unaccompanied by excessive C formation and catalyst disintegration is obtained by operating a hydrocarbon synthesis in 2 stages. A catalyst of low activity is used in the first reactor, followed by a catalyst of relatively high activity in the second reactor operating at substantially higher pressure than the first reactor. The feed from the first synthesis stage is converted to the extent of about 80% in the 2d zone, giving an overall conversion of about 95%. It is possible to use a feed of relatively low H_2 : CO ratio such as 1.5 : 1. 7 United States patents cited.

1083. ——— (Standard Oil Development Co.). Two-Stage Process for the Synthesis of Hydrocarbons. United States Patent 2,483,771, Oct. 4, 1949; appl. filed Jan. 2, 1948, Serial No. 291; 9 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 1673.

Exit gases from the fluid solids hydrocarbon synthesis reactor are freed of the bulk of entrained catalyst in gas-solids separators, then they pass to an oil scrubbing device where the exit gas is freed of catalyst fines. The oil and catalyst fines then pass to a centrifugal separator, and the resulting slurry passes to a Dorr thickener. The purified scrubber oil is returned to the scrubber. The thickened catalyst-oil stream is sent to a liquid or foam phase hydrocarbon synthesis unit. The catalyst fines are particularly rich in promoter. The invention provides a particularly attractive method for manufacturing high-melting paraffin waxes with m. p. 200°–250° F. 3 United States patents cited.

———. *See* abs. **3986.**

HOLMES, W. C., & Co., LTD. *See* abs. **433.**

1084. HOLMGREN, T. A. F. [Formaldehyde.] Swedish Patent 53,822, Feb. 21, 1923. Chem. Abs., vol. 17, 1923, p. 3345.

Describes process in which water gas is brought into contact with metals or metal compounds.

1085. ———. [Formaldehyde Synthesis.] Swedish Patent 53,824, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 229.

Synthesis from CO and H_2 at 200°–500° in process of metals or metallic compounds.

See also Swedish Patent 53,822 (abs. **1084**).

HOOG, H. *See* abs. **937, 1098, 1099, 1100, 3908.**

1086. HOOG, H., ENGEL, W. F., AND KOOME, J. (Shell Development Co.). Catalytic Refining of Hydro-Carbon Alcohols. United States Patent 2,525,354, Oct. 10, 1950; appl. filed Dec. 5, 1949, Serial No. 131,254, in the Netherlands Dec. 17, 1948; 9 claims (*Cl. 260–643*). Chem Abs., vol. 45, 1951, p. 2014.

Crude synthetic alcohols contaminated with aldehydic and olefinic impurities (as obtained by the Oxo process) are refined by catalytic vaporphase hydrogenation at 80°–200° with stationary beds of a solid Ni silicate catalyst. Such a catalyst is prepared as follows: To a boiling solution of 420 gm, Na_2CO_3 (4.5 l.) is added Na metasilicate solution containing 56 gm. SiO_2 (0.5 l.) and then a boiling $Ni(NO_3)_2$ solution containing 200 gm. Ni (5 l.). The precipitate is filtered, washed with 24 l. H_2O at 90°, dried at 110° for 10 hr., pulverized, and sifted, and this powder (380 l.) with activated powdered Surinam bauxite (223 l.) and powdered graphite (6 l.) compressed into pellets and reduced with 200 l. H_2 per hr. for 24 hr. at 275°–300°.

1087. ——— (N. V. de Bataafsche Petroleum Maatschappij). [Refining Synthetic Alcohols.] Netherlands Patent 69,049, Dec. 15, 1951. Chem. Abs., vol. 47, 1953, p. 141.

Synthetic alcohols, prepared from CO+H_2 or from olefins by the Oxo process, are refined by hydrogenation in the presence of a Ni catalyst. The refining is carried out in the presence of a stationary catalyst, disposed in the reaction space. The catalyst contains at least 25%, preferably > 35%, by wt. of Ni, calculated as metallic Ni, which in praparing the catalyst is partly precipitated in the form of a silicate, in an example the catalyst is prepared as follows: 0.5 l. of a Na silicate solution (containing 56 gm. SiO_2) is added to 4.5 l. of a boiling solution of 420 gm, Na_2CO_3, then, in the course of 1 min., 5 l. of a boiling solution of $Ni(NO_3)_2$ containing 200 gm. Ni is added, and the precipitate is filtered, washed with H O at 95°, dried at 110°, crushed, and sieved. Of this powder, 380 gm. is mixed with 223 gm, powdered bauxite and 6 gm. powdered graphite, and the mixture is compressed to 3- by 5-mm. pellets and reduced with H at 300°. A C_9 alcohol prepared by the Oxo synthesis, containing 4.7% aldehydes, is led over the catalyst at 150° with H under 150 atm., the end product cotaining 0.04% aldehydes, and phthalates prepared from the alcohols are H_2O-clear. Ordinary Ni catalyst containing 10% Ni gave alcohols with 0.80% aldehydes, giving brown phthalates.

1088. HOPFF, H. (I. G. Farbenindustrie A. G.). [Oxygenated Organic Compounds.] German Patent 512,718, Nov. 6, 1927. Chem. Abs., vol. 25, 1931, p. 1258.

Aliphatic hydrocarbons are subjected to the action of CO in the presence of anhydrous $AlCl_3$ at temperatures <100° under pressure. Gives several examples. In one, normal C_5H_{12}, CO and $AlCl_3$ are heated to 60° in a high-pressure bomb at 120–150 atm. The product includes a carboxylic acid $C_6H_{12}O_2$, b. 190°–191°, and a ketone $C_9H_{12}O$, b. 114°–116°.

See also German Patent 492,427 (abs. **3925**) and United States Patent 1,798,288 (abs. **3927**).

1089. ——— (I. G. Farbenindustrie A. G.). [Oxygenated Organic Compounds.] German Patent 520,154, Dec. 1, 1927. Chem. Abs., vol. 25, 1931, p. 3664.

The method of German Patent 512,718 (abs. **1088**), for producing oxygenated organic compounds, that is, by the action of CO on aliphatic hydrocarbons under

pressure in the presence of $AlCl_3$, is extended to hydroaromatic hydrocarbons such as hexahydrotoluene, solvent naphtha, and cyclohexane. Gives examples.

1090. ——— (I. G. Farbenindustrie, A. G.). [Oxygenated Organic Compounds.] German Patent 535,254, Jan. 14, 1928. Chem. Abs., vol. 26, 1932, p. 3263.

The method of German Patent 512,718 (abs. **1088**) for oxygenating aliphatic or hydroaromatic hydrocarbons by the action thereon of CO under pressure is modified by carrying out the process in the presence of anhydrous $AlBr_3$, BF_3, $ZnCl_2$, $FeCl_3$, $TiCl_4$, $SnCl_4$, or $SbCl_5$ instead of anhydrous $AlCl_3$. Gives examples.

1091. Hori, S., and Others (Mansyū Kagakukōgyō K. K.). [Catalyst for Water-Gas Reaction.] Japanese Patent 132,543, Oct. 9, 1939. Chem. Abs., vol. 35, 1941, p. 3400.

Solution of $Fe(NO_3)_3$ and $Cr(NO_3)_3$ is obtained by mixing natural $Fe_2(CO_3)_3$ CrO_3, chromate, or dichromate and heating with HNO_3. The solution of nitrates is treated with alkali to form hydroxides, and these are filtered and dried.

1092. ——— (Mansyū Kagakukōgyō K. K.). [Catalyst for Water-Gas Reaction.] Japanese Patent 133,237, Nov. 14, 1939. Chem. Abs., vol. 35, 1941, p. 4166.

Natural $FeCO_3$ is crushed and heated above its temperature of decomposition 400°.

Horne, W. A. *See* abs. **2390, 2391, 2392.**

1093. Horne, W. A., and Crawford, V. L. (Gulf Research & Development Co.). Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,632,016, Mar. 17, 1953. Chem. Abs., vol. 47, 1953, p. 5666.

Hydrocarbons are produced from H_2 and CO in a fixed catalyst process in which a long catalyst life is obtained and the exothermic reaction is controlled. H_2, CO, in a mol. ratio of 15 : 1 to 30 : 1, and recycled gases are passed in contact with a series of synthesis catalyst beds, preferably an Fe catalyst, at synthesis temperature and superatmospheric pressure. A side stream of part of the partly reacted gases is removed from between the catalyst beds while the main stream of partly reacted gas is passed to the succeeding catalyst bed. The side stream is cooled and a makeup gas of CO is passed into it. Then the side stream is added to the main stream and passed to the next catalyst bed. The reacted gases are removed from the last bed and cooled to condense the liquid hydrocarbons. A portion of the remaining gas is then recycled with fresh feed gas into the reaction vessel. To obtain long catalyst life the temperature gradient across the catalyst beds is kept at 125°–165° F. The heat of the reaction is controlled by cooling the side stream from the discharge temperature of 610°–630° F. to at least 100° F.

Hottel, H. C. *See* abs. **2526.**

1094. Houdry, E. J. (Houdry Process Corp.). Catalytic Apparatus and Processes. British Patent 471,930, Sept. 13, 1937. Chem. Abs., vol. 32, 1938, p. 1144.

In effecting catalytic reactions in a converter having conduits for temperature-controlling fluid in indirect heat exchange with the catalyst, as described in British Patent 449,050 (abs. **1097**), the reactants are admitted at substantially reaction temperature and heat-conducting elements are disposed in all parts of the contact mass to convey heat to or from the said conduits. The invention is applicable to endothermic or exothermic reactions, for example, NH_3 synthesis, SO_3 production, and catalyst regeneration.

1095. ———. Preparation of a Multilayer Catalyst. United States Patent 2,643,980, June 30, 1953; appl. filed Sept. 23, 1950; Serial No. 186,503; 9 claims (*Cl. 252–455*).

301275°—55—PT. II——8

Claim 1. In a method for the manufacture of catalysts wherein the quantity of catalytically active material making up the catalyst is built up in a series of deposits produced by successive impregnations with a liquid solution containing said catalytic material, the improvement, which comprises applying to said successive deposits, between said successive impregnations, a protective film of an organic material that cannot be displaced or penetrated by said solution during said impregnations and is readily removable from said catalyst by oxidation.

1096. Houdry, E. J., and Prickett, T. B. (Houdry Process Corp.). Catalytic Apparatus and Processes. British Patent 471,931, Sept. 13, 1937. Chem. Abs., vol. 32, 1938, p. 1144.

In the use of catalytic converters, according to British Patent 449,050 (abs. **1097**), for a cycle of alternate endothermic and exothermic reactions, the fluids in each period of the cycle are admitted at such temperatures that the portion of the converter that is common to the reaction and manifolding zones is maintained at constant temperature. The invention is applicable to the heat treatment of hydrocarbons with subsequent regeneration of the catalyst with an oxydizing gas.

1097. Houdry Process Corp. Catalytic Apparatus. British Patent 449,050, June 19, 1936. Chem. Abs., vol. 30, 1936, p. 7395.

The temperature of a contact mass during endothermic or exothermic reactions is regulated by passing 1 or more streams of heating or cooling fluid through the mass, which is in the form of a deep and continuous bed, at such a speed that the change in temperature of the fluid is insufficient to cause any substantial difference in the rates of heat transfer along its path and keeping the fluid out of heat-conducting relation with the contact mass so that the heat exchange is effected mainly by radiation.

———. *See* abs. **1094, 1096, 3336.**

1098. Houtman, J. P. W., Engel, W. F., and Hoog, H. (N. V. de Bataafsche Petroleum Maatschappij). [Hydrocarbons, Alcohols, Aldehydes, by the Reaction of Carbon Monoxide and Hydrogen.] Netherlands Patent 64,719, Nov. 15, 1949. Chem. Abs., vol. 44, 1950, p. 1247.

In the synthesis of C-containing compounds from CO and H_2, as a rule, precautions are taken that the catalyst, Fe, Ni, or Co on a carrier, cannot be vitiated by silicates, for example originating from the diatomaceous earth used as a carrier, Netherlands Patent 50,858 (abs. **1677**). Now it has been found that, on the contrary the catalyst, a metal of the Fe group should contain silicates, for example, 5–30% of the metal being present as silicate. Improvements are: By varying the proportion of the silicates the properties of the catalyst can be varied; new carriers can be used, that allow the pressing of catalysts to pellets or the use of fluidized catalysts. According to an example, comparative experiments are made with (1) a catalyst consisting of Co oxide on kieselguhr, (2) Co oxide on α Al_2O_3 as a carrier, (3) Co silicate-containing catalyst made by precipitating $Co(NO_3)_2$ partly with Na_2CO_3 and partly with Na silicate. With H_2 about 60% of the CoO is reduced to metal. Hydrocarbons are synthesized from CO and H_2 1 : 2 at 185° and 1 atm., continuously led over the catalyst at a rate of 1 l. per hr. per 1 gm. catalyst. In experiment (I) the yield of fluid hydrocarbons was 124 gm. per $m.^3$ of gas, gradually diminishing to 116 gm.; in experiment (II) 70 gm., diminishing to 56 gm.; in experiment (III) a constant yield of 110 gm. was obtained during many hundreds of hours.

1099. ——— (N. V. de Bataafsche Petroleum Maatschappij). [Hydrocarbons and Their Oxygenated

Derivatives Particularly Aldehydes and Alcohols.] Swedish Patent 127,239, Jan. 24, 1950; appl. filed Fed. 20, 1948. Chem. Zentralb., 1951, I, p. 954.

Conversion of CO to hydrocarbons, aldehydes, or alcohols is carried out in the presence of catalysts consisting of metals of Group VIII of the periodic system 0.5–60%, preferably 5–30%, in the form of silicates. Further the catalysts should contain less than 2%, preferably less than 1%, alkali silicate. The catalysts are distinguished by a high degree of stability and long life. In addition to their use for the gasoline and Oxo syntheses, they can also be used for the removal of CO from gas by hydrogenation to CH_4.

1100. HOUTMAN, J. P. W., ENGEL, W. F., HOOG, H., AND VAN'T SPIJKER, P. (Shell Development Co.). Group VIII Silicate Catalyst on Nonsiliceous Support. United States Patent 2,548,159, Apr. 10, 1951; appl. filed Jan. 13, 1948, Serial No. 2,133, in the Netherlands Jan. 17, 1947; 11 claims (*Cl. 252–455*). Chem. Abs., vol. 45, 1951, p. 5910.

Fischer-Tropsch catalyst consists essentially of an inert silica-free support, a precipitated silicate of a metal of Group VIII, and a metal of Group VIII in intimate association therewith, the amount of metal of Group VIII present as a silicate being about 0.5% and 60% of the total amount of said metal, the total amount of the metal being 10–60% on the finished catalyst. 7 United States patents cited.

1101. HOWARD, F. A., AND PECK, E. B. (Standard Catalytic Co.). Synthesizing Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,274,064, Feb. 24, 1942; appl. filed Sept. 1, 1936, Serial No. 98,880; 4 claims (*Cl. 260–449*). Chem. Abs., vol. 36, 1942, p. 3936.

Process is employed in which the ratio H_2 : CO in the feed gas to the hydrocarbon synthesis reaction is adjusted to substantially 2 : 1, and which involves supplying a fresh gas mixture of H_2 and CO, re-forming at least a portion of the product gases leaving the synthesis reaction with an oxidizing gas selected from the class consisting of steam, CO_2, and O_2 in a proportion adjusted to produce a re-formed gas containing H_2 and CO in a ratio supplementing the ratio of H_2 : CO in the fresh gas, and mixing the re-formed gas with the fresh gas to obtain the feed gas of substantially a 2 : 1 ratio of H_2 : CO.

1102. HOWK, B. W. (E. I. du Pont de Nemours & Co.). Alloy-Skeleton Cobalt Catalyst Suitable for Use in Hydrogenation Reactions. United States Patent 2,257,800, Oct. 7, 1941; appl. filed Apr. 12, 1940, Serial No. 329,299; 7 claims (*Cl. 252–234*). Chem. Abs., vol. 36, 1942, p. 632.

Easily suspensible Co catalyst is made by preparing an alloy of Co and an alkali-soluble metal, such as Al, containing 25–35% Co, grinding the alloy to a fine powder, and extracting the alkali-soluble metallic component with a solution of caustic alkali.

1103. HOWK, B. W., AND HAGER, G. F. (E. I. du Pont de Nemours & Co.). Synthesis of Alcohols. United States Patent 2,549,470, Apr. 17, 1951. Chem. Abs., vol. 45, 1951, p. 8546.

Mixtures of primary straight-chain alcohols containing 3–50 C atoms are obtained from CO and H_2 in alcohols or H_2O above 200 atm. at 175°–225° in the presence of Ru, Ru carbonyl, or oxide; the molecular ratio of H_2 : O=1.5 : 1–10 : 1.

HUBBE, G. *See* abs. **638, 639, 640.**

HUBBE, H. *See* abs. **638, 639, 640.**

1104. HUBBE-FARENHOLTZ G. m. b. H. [Oxidation Products of High-Molecular Hydrocarbons.] German Patent Appl. H 145,293, no date (*Cl. IV d–12 o*). Auszüge deut. Patent Anmeldungen, vol. 6, p. 72.

Oxidation products of high-molecular hydrocarbons are obtained by passing a gas stream through a series of reaction vessels. Fatty acids or alcohols are produced.

1105. ———. [Process for Improving Synthetic Fatty Acids.] German Patent Appl. H 154,167, Dec. 27, 1937 (*Cl. 12 o–11*). FIAT Reel R–6, frames 5,212–5,218; PB 73,554.

This appears to correspond to French Patent 838,243 (abs. **3803**). In the purification or refining of synthetic fatty acids obtained by the oxidation of paraffin hydrocarbons, the carboxylic groups are blocked by conversion into esters or acid chlorides, and the material is then heated in the absence of H_2O or O_2 to temperatures preferably 220°–320°. The heat treatment is carried out in the presence of N_2, CO_2, CO, or steam and at atmospheric or lower pressure.

1106. ———. [Process for Obtaining and Improving Synthetic Fatty Acids.] German Patent Appl. H 152,778, Aug. 25, 1937 (*Cl. IV a–23 d*). FIAT Reel R–6, frames 4,911–4,928; PB 73,554.

In production and improvement of synthetic fatty acids, the acids, after saponification with alkali or earth alkali, are subjected in the absence of oxidizing gases and H_2 to a longer treatment at 280°–360°, preferably 290°–340°. An excess of at least 5% of the effective alkaline saponifying agent is used. Heating is carried out after the air has been driven off with steam, CO, CO_2, or N_2. The fatty acids are improved by heating to the melted condition with or without an excess of the saponifying agent or other effective alkaline compound at normal or subpressure. Powdered metallic soaps are first obtained, and these are heated with stirring or dispersion to 280°–360° in a high-boiling and neutral medium, and neutral gases such as steam, CO_2, or N_2 are passed through. The so pretreated and improved fatty acids in the form of their aqueous soda soaps are finally extracted with benzine to remove the unsaponifiable constituents or they are distilled.

1107. ———. [Producing Oxidation Products of High-Molecular Hydrocarbons.] German Patent 756,488, Oct. 11, 1935 (*Cl. IV d–12 o.*) FIAT Reel R–8, frames 7,306–7,313; PB 73,522.

Describes process and equipment for producing fatty acids or alcohols by the oxidation of high-molecular hydrocarbons such as those produced by the Fischer-Tropsch synthesis. Diagrams missing.

1108. HUBER, H. E., JR. (Standard Oil Co. of Indiana). Hydrocarbon Synthesis. United States Patent 2,417,164, Mar. 11, 1947; appl. filed Nov. 23, 1944, Serial No. 564,811; 4 claims (*Cl. 260–449.6*). Chem. Abs., vol. 41, 1947, p. 3603.

Gives 2-stage process for production of gasoline hydrocarbons from CO and H_2. A fluidized Fe catalyst is used in the 1st stage, and a precipitated Co or Ni type, either fluidized or in stationary bed, is used in the 2d stage. The synthesis gas charge consists of H_2 and CO in a ratio of 1 : 1 or 1.8 : 1. The proper ratio in the feed to the Fe system is necessary to produce the ideal feed for the Co system or 2 : 1 or 2.2 : 1 H_2 : CO ratio. The temperature range for the Fe system is 450°–650° F., pressure 100–350 p. s. i. and space velocity 1,000–10,000 vol. of gas per hr. per vol. of space occupied by the dense catalyst phase of the reactor. The temperature range for the Co is 340°–500° F., preferably <420° F., pressure not >50 p. s. i. and preferably atmospheric, space velocity 50–1,500 vol. of gas per hr. per vol. of space occupied by the dense catalyst phase. The reaction in the 1st stage is $3nH_2+3nCO \rightarrow 2(CH_2)_n+nH_2O+nCO_2$, and for the 2d stage, $2nH_2+nCO \rightarrow (CH_2)_n+nH_2O$. Total reaction

products are removed after each stage. 3 United States patents cited.

1109. HUDSON, T. B. (Phillips Petroleum Co.). Method of Catalyst Control in Organic Reactions. United States Patent 2,590,539, Mar. 25, 1952; appl. filed Oct. 14, 1947, Serial No. 779,786; 4 claims (*Cl. 260–449.6*).

Catalyzed exothermic organic conversions, such as those involved in the Fischer-Tropsch process, are effected by passing a fluid reaction mixture through a reaction zone under conditions so chosen that increase of temperature occurs in the direction of flow of the reaction mixture, owing to the exothermic heat of reaction. A solid mobile catalyst is introduced into the reaction zone at a number of points and passed countercurrently to the reaction mixture. The quantity and activity of the catalyst is so controlled as to provide a decreasing amount of catalyst activity in the direction of flow of the reactants as an inverse function of the temperature thus tending to equalize the extent of reaction throughout the reaction zone. In reducing CO with H_2 to form aliphatic organic compounds, enough heat of reaction is removed to limit the temperature rise to an amount avoiding undesired reactions.

1110. HUFF, L. C. (Universal Oil Products Co.). Reactor for Close Temperature Control. United States Patent 2,475,025, July 5, 1949; appl. filed Oct. 26, 1946, Serial No. 705,835; 3 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 7760.

Describes converter in which temperature control is provided by means of 2 different flow paths for cooling, or heating, heat-exchange medium. One heat-exchange medium flows internally within the path of each of the reactant fluid streams, whereas the other circulates externally around each of the tubular contacting zones. 2 different heat-exchange fluid mediums may be used within the converter, or it is possible to use the same medium in the inner and outer zones. The apparatus is adaptable for liquid to liquid or liquid to vapor heat exchange as well as for fluidized catalytic processes. 7 United States patents cited.

HUFFMAN, H. C. *See* abs. **2496.**

HUGHES, E. C. *See* abs. **279.**

HUGHES, W. B. *See* abs.

1111. HUGHES, W. B., AND NEWCOMBE, J. (Cities Service Oil Co.). Purification of Crude Alcohols. United States Patent 2,569,671, Oct. 2, 1951. Chem. Abs., vol. 46, 1952, p. 3062.

Crude alcohols are purified by catalytic hydrogenation in the presence of H_2O and acid to hydrolyze acetals. Crude alcohols (b. 58°–89° from controlled oxidation of natural gas) 500 ml., H_2SO_4 0.5, Cu chromite 8.35 gm., and H_2 at 1,500 p. s. i. were heated 5 hr. to 200° (2,600 p. s. i.). Impurities in the crude alcohols and in the product are, respectively: Aldehydes calculated as EtCHO 6.6, O; ketones calculated as Me_2CO 1.4, O; acetals calculated as $H_2C(OMe)_2$ 2, O; H_2O 8.9, 8.9%; unsaturation (mgm. Br per ml.) 162, 0. Crude alcohols from the Fischer-Tropsch process may be purified similarly; other catalysts containing Ni, Pt, Pd, may be used.

1112. HUJSAK, K. L., KRATZER, M. B., AND MUNGEN, R. (Stanolind Oil & Gas Co.). System for Synthesis From Hydrogen and Carbon Monoxide With Fluidized Catalyst. United States Patent 2,620,262, Dec. 2, 1952; appl. filed Aug. 26, 1949, Serial No. 112,554; 1 claim (*Cl. 22–288*).

Incoming synthesis gas is subjected first to reducing conditions and finally to oxidizing conditions within a single reaction zone. The reactor system is designed to prevent longitudinal mixing of the fluidized solids from the top to the bottom of the reactor. Geometrically spaced heat exchange tubes extend between a fixed coolant liquid header, that is at substantially the level of the distributor grid, and upper headers that are free to move up and down to take care of thermal expansion and contraction. Coacting vertical fins are secured to the walls of the heat exchange tubes. The system maintains a multiplicity of segregated flow channels in which the catalyst is retained. 10 United States patents cited.

HULTGREN, H. B. *See* abs. **3829, 3830, 3831.**

HULTGREN, N. F. *See* abs. **3827, 3828, 3829, 3830, 3831.**

1113. HUMPHREY, H. A. (Atmospheric Nitrogen Corp.). Combustible Gas Containing Hydrogen and Carbon Monoxide. United States Patent 1,794,232, Feb. 24, 1931. Chem. Abs., vol. 25, 1931, p. 2273.

In a continuous gas-producing process a mixture comprising steam and O_2, preheated to $>$ 1,000°, is passed into and through a gasification chamber and finely divided solid fuel is fed into the chamber to contact and react with the preheated mixture and to generate gas at such a high temperautre that CO and H_2 substantially free from CH_4 or other hydrocarbons and CO_2 are produced; the hot generated gas is led into and through a 2d preheating stage, and from the latter combustible gas is withdrawn. A reversal of flow of the mixture containing steam and O_2 is effected whenever its temperature, immediately before its contact with the fuel, tends to fall materially $<$1,000° and, irrespective of the direction of gas flow, the particles of solid fuel are maintained in suspension in a relatively large mass of enveloping gas in the reaction chamber. Describes apparatus.

1114. ——— (Imperial Chemical Industries, Ltd.). Production of Water Gas and Hydrogen. Canadian Patent 281,814, July 17, 1918. Chem. Abs., vol. 22, 1928, p. 4235.

In low temperature carbonization and gas manufacture, high coking coal is preheated in presence of O_2 to control its coking properties; the product is carbonized at $<$600° to produce lump semicoke; the semicoke is gasified with steam, and the gas is treated with steam at high temperature to decompose the CH_4. The gas is used for the synthesis of MeOH with the single passage of the gas over a catalyst, and the residual gas is used for NH_3 synthesis, after replacement by the CO by H_2, removal of CO and addition of N_2.

1115. HUMPHREY, H. A., AND SYNTHETIC AMMONIA & NITRATES, LTD. Water Gas, Methanol and Hydrogen. British Patent 282,573, Feb. 22, 1927. Chem. Abs., vol. 22, 1928, p. 3764.

Coal is dried at 200°–300° by hot combustion gases, to which air is added to effect partial oxidation and control the coking properties of the material, and is then further subjected to low-temperature carbonization at not above 600° to produce a semicoke for use in a water-gas generator. The water gas formed may be treated with steam at high temperature to convert the CH_4 into CO and H_2, or the semicoke may be heated to a higher temperature before use for generating water gas free from CH_4. The gas mixture is then passed over a catalyst containing finely divided Fe or other suitable metals at 200°–300° to produce higher paraffin hydrocarbons. After separation of paraffins and CH_4, if present, the residue from this treatment, or the original gas mixture, is compressed and passed over a catalyst such as basic Zn chromate for producing MeOH or may be treated with steam in the presence of an Fe oxide catalyst at about 500°, converting the CO into CO_2, which is then removed, leaving H_2, which may be mixed with N_2 for NH_3 synthesis.

HUMPHREYS & GLASGOW, LTD. *See* abs. **2636, 3940.**

1116. HUNTINGTON, R. L., AND REID, L. S. (Aluminum Co. of America). Gas Separation. United States Patent 2,642,955, June 23, 1953. Chem. Abs., vol. 47, 1953, p. 8996.

Continuous cyclic process for removing adsorbable components, such as H_2O, from a gas by use of a solid adsorbent, such as Al_2O_3, SiO_2, or C, in the form of particles involves adsorption followed by regeneration of the adsorbent. The countercurrent process is operable under high pressure, and a relatively small amount of adsorbent is required.

1117. HURTER, H. (Klöckner-Humboldt-Deutz. A. G.). [Gas Producer Operated With Solid Fuels, With Introduction of the Gasification Air Into the Free Surface of the Bed of the Fuels.] German Patent 817,010, Oct. 15, 1951 (*Cl. 24 e-3*$_{03}$). Chem. Abs., vol. 47, 1953, p. 1919.

1118. HÜTTNER, R., AND WIETZEL, G. (I. G. Farbenindustrie A. G.). Catalytic Production of Hydrogen From Hydrocarbons. United States Patent 2,038,566, Apr. 28, 1936; appl. filed Jan. 11, 1932. Chem. Abs., vol. 30, 1936, 3953.

Hydrocarbon of higher molecular weight than CH_4, such as a mixture of C_2H_6, C_3H_8 and C_4H_{10}, is brought into contact with a gas such as steam capable of converting C into CO, at 400°–1,000° and in the presence of a catalyst comprising an Fe-group metal or oxide, hydroxide or carbonate of such a metal distributed in set hydraulic cement.

1119. ——— (I. G. Farbenindustrie A. G.) [Mixtures of Hydrogen and Carbon Monoxide.] German Patent 552,446, Jan. 18, 1931. Chem. Abs., vol. 26, 1932, p. 4422.

Saturated or unsatured hydrocarbons other than CH_4 are treated with steam, CO_2, air and/or O_2 at a raised temperature in the presence of catalysts prepared by mixing compounds of metals of the Fe group with a hydraulic binder, for example, commercial cement, pasting the mixture with H_2O and allowing it to set. The catalysts so prepared hinder the formation of C. The compounds of metals of the Fe group are preferably used in association with activators, for example, oxides of Al, Mg, Ca, U, Cr, Mo, and V. Gives various details and examples. *See also* German Patent 538,012 (abs. **116**).

1120. HYDROCARBON RESEARCH, INC. Hydrocarbon Synthesis. British Patent 676,635, July 30, 1952. Chem. Abs., vol. 47, 1953, p. 5420.

Synthesis of hydrocarbons and oxygenated hydrocarbons from H_2, CO, and CO_2 over an Fe catalyst is improved by regulating the admission of feed gas so as to keep the catalyst in a fluidized state.

See also British Patent 671,652 (abs. **734**) and United States Patents 2,576,931 and 2,600,399 (abs. **770** and **733**).

1121. ———. Synthesis of Organic Compounds From Coal. British Patent 659,002, Oct. 17, 1951. Chem. Abs., vol. 46, 1952, p. 4201.

Bituminous coal, 2- to 10-mesh, is charged to a gasifier operated at 350 p. s. i. along with steam at 1,000° F. 7.7 vol., and O_2 of 95% purity 1 vol. The gaseous effluent is withdrawn, tar, oil, H_2O, and CO_2 are removed, and the residual gas is treated with O_2 at 2,300° F. and 575 p. s. i. The effluent from the re-former is contacted with Cr_2O_3–MgO–Fe oxide catalyst at 800° and 560 p. s. i. in a shift converter, the effluent is scrubbed with Et_2NH solution at 530 p. s. i. and atmospheric pressure, then passed over a bed of spongy Fe oxide at 770° F. and 550 p. s. i. The product has a composition of H_2, 62.8%; CO, 30.00%; CO_2, 0.5%; N_2, 6.5%; and H_2O, 0.2%. It is converted to hydrocarbons, oxygenated compounds, in contact with a fluidized Fe catalyst at 600° F. and 500 p. s. i. H_2O, hydrocarbons, and oxygenated compounds are condensed, gaseous hydrocarbons are absorbed in mineral seal oil, 20% of the dry gas is vented to a fuel system to prevent accumulation of N_2, and the remaining gas, after removal of CO_2, is passed to the re-former.

1122. ———. Synthetic Motor Fuel. British Patent 647,467, Dec. 13, 1950. Chem. Abs., vol. 45, 1951, p. 4429.

See United States Patent 2,470,216 (abs. **1818**).

———. *See* abs. **36, 168, 730, 731, 732, 733, 734, 735, 766, 767, 768, 769, 770, 771, 988, 1765, 1766, 1789, 1790, 1791, 1792, 1793, 1811, 1812, 1813, 1814, 1815, 1816, 1817, 1818, 1819, 1820, 1821, 1824, 2018, 2019, 2020, 2021, 2022, 2170, 2171, 2774, 2775, 2776, 2777, 3708, 3709.**

HYDROCARBON SYNTHESIS CORP. *See* abs. **12, 275, 647, 676, 689, 690, 949, 951, 2799, 2814, 2815, 2820, 3240.**

1123. "HYDROGEN" TOWAAZYSTWO WYZYSKANIA GAZU ZIEMNEGO I FABRYKA PRZETWORÓW CHEMICZNYCH SP. Z. OGR. ODP. [Carbon Monoxide and Hydrogen From Hydrocarbons.] Polish Patent 10,425, Sept. 25, 1929; appl. filed Apr. 28, 1928. Chem. Zentralb., 1930, II, p. 1641.

Heat required for the reaction is obtained by burning a part of the hydrocarbon with O_2; the reaction is performed in presence of steam or CO_2 in the catalyst chamber.

1124. HYDRO-NITRO SOCIÉTÉ ANON, Production of Hydrogen and Carbon Monoxide. British Patent 390,849, Oct. 5, 1931. British Chem. Abs., B, 1933, p. 534.

Mixture of CH_4 and H_2O is passed up through 1 and down through a 2d vertical chamber packed with refractory material, the latter having been heated by the combustion of gas in the chamber in such a manner as to heat the upper zones to 1,200°–1,500° and to give a falling temperature gradient down each chamber.

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1124a. IBING, G., AND SCHACHT, W. (Ruhroel G.m.b.H.). [High-Molecular Reaction Products From Olefins and Sulfur Dioxide.] German Patent Appl. —, no date. TOM Reel 8, items 3–7, 3 pp.

Example: 100 cc. primary gasoline from the Fischer-Tropsch synthesis is mixed at —20° with 100 cc. of liquid SO_2. Both gasoline and SO_2 are completely mutually soluble. To the solution are added 50 cc. of peroxidized ethylbenzene as catalyst. After standing for 2 hr., the SO_2 is evaporated and the gasoline and ethylbenzene distilled off. The polysulfones formed from the olefins of the gasoline are in the residue and can be freed from adhering gasoline at 40° in vacuum. From them can be obtained a white, shellac-like product.

1125. I. G. FARBENINDUSTRIE A. G. Alcohols. British Patent 278,777, June 10, 1926. Chem. Abs., vol. 22, 1928, p. 2753.

O-containing organic compounds obtained by the catalytic hydrogenation of C oxides by processes such as described in abs. **89, 91, 93,** and **75** are converted into colorless oils consisting of higher alcohols by catalytic treatment in the vapor phase with H_2 in the presence of a hydrogenation catalyst. The material may

be preliminarily purified by treatment with granular SiO_2 and then with NaOH. Ni, Co, Cu, or Pt may be used as catalyst and $Al(OH)_3$, Al phosphate or oxides of Th or W also may be present.

1126. ———. [Alcohols.] German Patent Appl. I 74,390, no date (*Cl. 12 o–5.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 210.

Alcohols are produced from carboxylic acids or their esters by catalytic reduction at elevated pressure and temperature, the low-boiling fractions of the reaction mixture being removed during the hydrogenation.

1127. ———. Alcohols by Catalytic Hydrogenation of Carbon Monoxide. British Patent 275,284, Mar. 4, 1926. Chem. Abs., vol. 22, 1928, p. 2171.

CO_2 formed in the reaction is removed continuously or periodically by absorption in solvents such as H_2O or by fixing it chemically under high pressures, for example, by H_2O containing a small quantity of NH_3. Gives several examples.

1128. ———. Aldehydes. British Patent 267,925, Mar. 19, 1926. Chem. Abs., vol. 22, 1928, p. 1163.

Carboxylic acids are treated in the presence of a heated catalyst (such as Fe, Co, Cr, or Ce catalysts) with CO or gases containing CO. Gives examples for the production of BzH from benzoic acid vapor and of AcH from HOAc.

1129. ———. Aliphatic Acids. British Patent 478,317, Jan. 14, 1938. Chem. Abs., vol. 32, 1938, p. 4609.

Paraffin hydrocarbons of high molecular weight are oxidized at not >115° in the presence of Mn compounds in which the Mn is contained in the anion and an alkali in the cation, for example, K, Na and NH_4 manganates, manganites, and permanganates, K Mn cyanide, with or without other catalysts, for example $(AcO)_2$, Mn, or alkaline substances, for example Na_2CO_3. Oxidation may be effected by O_2, air, or other gases containing O_2 and accelerating substances, for example N oxides may be present in small quantities. Describes apparatus.

1130. ———. Aliphatic Acids. British Patent 490,785, Aug. 22, 1938. Chem. Abs., vol. 33, 1939, p. 645.

In the oxidation of paraffin hydrocarbons of high molecular weight at not >115° in the presence of Mn compounds in which the Mn is contained in the anion and an alkali in the cation, as described in British Patent 478,317 (abs. **1129**), the Mn compound is added in solution in H_2O or an organic solvent, for example, Me_2CO, MeOH, EtOH, MeEtCO, acetonitrile, pyridine. After the catalyst solution is mixed with the hydrocarbon to be oxidized, the solvent is evaporated by gentle heating or removed by introduction of air or other gas; or when the mixing is effected in the reaction vessel the solvent may be removed by the action of the oxidizing gas. Examples describe the oxidation of brown coal paraffin and petroleum paraffin, respectively, with air or O_2 at 112°–114° with use of $KMnO_4$ in H_2O and Me_2CO, respectively.

1131. ———. Aliphatic Carboxylic Acids. British Patent 497,170, Dec. 14, 1938. Chem. Abs., vol. 33, 1939, p. 3397.

Acids are obtained by treating the saponified oxidation products of high-molecular aliphatic compounds with SO_2 or soluble bisulfites in the presence of H_2O. In examples, the saponified oxidation product of paraffin is treated with SO_2 and $NaHSO_3$, respectively; the saponified oxidation product of a paraffin obtained from CO and H_2 is treated with $NaHSO_3$; and a solid Ca soap of the oxidation product of hard paraffin that contains 70% H_2O is treated with a gas containing 6% SO_2.

1132. ———. [Antifoam Agent.] German Patent Appl. I 73,098, OZ 13,638, filed Aug. 31, 1942. TOM Reel 17, item 32, frames 894–897; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, chap. 93, 1948, p. 53; Auszüge deut. Patent-Anmeldungen, vol. 6, p. 189.

Mixture, consisting chiefly of alcohols obtained by the catalytic reduction of CO with H_2, especially at medium pressure and over catalysts of the Fe group, preferably Fe, and at synthesis temperature <250°, is especially suitable for preventing the foaming of liquids. Particular uses are in the evaporation of sugar and salt solutions in washing out of CO residues from H_2 with ammoniacal Cu salt solutions.

1133. ———. Antiknock Fuel. British Patent 503,602, Apr. 6, 1939; appl. filed Sept. 6, 1937. Chem. Zentralb., II, 1939, p. 2490; Chem. Abs., vol. 33, 1939, p. 7552.

Antiknock fuels are produced by cracking in the vapor phase at 400°–700° hydrocarbon oils consisting wholly or substantially of unsaturated hydrocarbons boiling at least for the greater part > the boiling point of benzines, whereas cyclic hydrocarbons, particularly mononuclear aromatic hydrocarbons, such as C_6H_6, toluene, and xylene, that are vaporous under the reaction conditions are added, the reaction being conducted in the absence of substantial amounts of H_2 or gases supplying H_2. Oil fractions rich in unsaturated hydrocarbons and boiling >200° for use as the initial materials are obtained by cracking mineral oils and tars, such as mineral oil or brown coal tar fractions containing wax; products of the destructive hydrogenation of coals, tars and oils; or oils produced by the reduction of CO. The reaction is preferably conducted in the presence of catalysts. Any low-boiling unsaturated products are polymerized in a further reaction zone filled with polymerizing catalysts. In an example, a fraction of boiling range 150°–300°, obtained by cracking brown-coal paraffin, is mixed with an equal amount of C_6H_6 and heated to 510° in a tubular reaction chamber under 150 atm. The product is distilled to separate a fraction b. 140°–200° that, after being refined with H_2SO_4 or bleaching earth, gives a good antiknock fuel with a flash point of 40°.

See also Belgian Patent 429,755 (abs. **1219**).

1134. ———. [Antiknock Fuel.] German Patent 720,928, Apr. 16, 1942 (*Cl. 23 b–1.04*). Chem. Abs., vol. 37, 1943, p. 2920.

This fuel is produced by catalytic cracking of heavy benzine or medium oils. The starting materials are passed through a reaction chamber in which the pressure and temperature gradually increase. The difference in pressure is at least approximately 5 atm. and in temperature at least approximately 10°.

See also British Patent 521,687 (abs. **1179**), and French Patent 857,177 (abs. **1597**).

1135. ———. [Antiknock Fuel.] German Patent 745,634, no date. Chem. Zentralb., 1944, I, p. 1458.

Oils that consist essentially or wholly of olefins, such as the cracked products of paraffin from the water gas synthesis, b. 150°–300°, are treated in the vapor phase over catalysts with the addition of mononuclear aromatic hydrocarbons. Highly antiknock motor fuels are obtained.

See also British Patent 503,602 (abs. **1133**) and Belgian Patent 429,755 (abs. **1219**).

1136. ———. [Antiknock Gasoline.] German Patent 764,394, no date; appl. J 62,358 (*Cl. 23 b–1.04*); Auszüge deut. Patent-Anmeldungen, vol. 6, p. 754.

Antiknock gasoline is obtained by the catalytic cracking of hydrocarbon oils, which were produced by the conversion of CO and H_2. The raw materials are cracked in mixture with paraffinic petroleum or fractions thereof.

1137. ———. [Antiknock Motor Fuel.] French Patent 681,345, Sept. 5, 1929. Chem. Zentralb., 1930, II, p. 2728; Chem. Abs., vol. 24, 1930, p. 4383.

The fuels are composed of any fuel mixed with hydrocarbons obtained by the catalytic reduction of natural or synthetic alcohols or aldehydes having more than 3 C atoms. Gives examples.

1138. ———. Apparatus for Ammonia Synthesis or Other Exothermic Gas Reactions. British Patent 306,054, Sept. 15, 1927. Chem. Abs., vol. 23, 1929, p. 5016.

Reaction chamber is cooled by the incoming mixture or other cooling fluid, which flows in a sinuous course around the walls. Describes various structural details.

1139. ———. Apparatus for Catalytic Exothermic Gas Reactions. British Patent 303,192, Sept. 23, 1927. Chem. Abs., vol. 23, 1929, p. 4380.

Catalyst is contained in a plurality of tubes closely packed together to form a bundle and the interspaces between the tubes are so restricted relative to the cross section of the tubes and to the density of the catalyst within the tubes that the incoming gas, which passes first on the outside of the tubes, travels at a higher velocity than it does within the tubes. Describes various structural details.

1140. ———. Apparatus for Catalytic Gas Reactions. British Patent 444,898, Mar. 30, 1936. Chem. Abs., vol. 30, 1936, p. 6245.

In apparatus for effecting exothermic catalytic gas reactions, the catalyst is arranged in a plurality of layers in a bundle of tubular reaction chambers around which the gases flow before entering the tubes, and a supplementary current of cool fresh gas is directed against the exterior of the tubes to cool the contents thereof at a point preceding that at which overheating would occur. The tubes are preferably free from catalyst at this point.

1141. ———. Apparatus for Effecting Reactions With Hydrogen Under Pressure. British Patent 341,153, Oct. 30, 1929. Chem. Abs., vol. 25, 1931, p. 3880.

Apparatus for reactions such as NH_3 synthesis, MeOH synthesis, or destructive hydrogenation of oil is formed of or coated with Zn alloys in those parts of the apparatus that come into contact with the hot reacting materials. Along with the Zn, the alloys may also contain Cu, Mn, Ni, Fe, Co, Al, or Ag. In destructive hydrogenations with raw materials high in S, enough H_2 should be used that the reaction mixture does not contain >2–3% by vol. of S compounds. Describes various structural details of apparatus.

1142. ———. Apparatus for Endothermic Catalytic Reactions. British Patent 327,025, Apr. 15, 1929. Chem. Age, 1930, p. 294; British Chem. Abs., 1930, B, p. 493; Chem. Abs., vol. 24, 1930, p. 4670.

In an apparatus suitable for catalytic conversion of CH_4 and steam into CO and H_2 or for the thermal decomposition of CH_4 or other organic compounds, the reaction or catalytic chambers are heated mainly by radiation. Describes various details of construction.

1143. ———. [Apparatus for Hydrocarbon Synthesis.] German Patent Appl. I 73,346, no date (*Cl. 12 g*). Auszüge deut. Patent-Anmeldungen, vol. 7, p. 206.

In the catalytic synthesis of hydrocarbons from CO and H_2, tube bundles for conveying the heat of reaction are used, which are closed at 1 end.

1144. ———. Apparatus for Pressure Reactions in Which Carbon Monoxide is Formed or Used. British Patent 247,217, Feb. 7, 1925. Chem. Abs., vol. 21, 1927, p. 515.

Portions of the apparatus exposed to temperatures not exceeding 150° may be formed of Fe, and portions of the apparatus that are subjected to higher temperatures may be formed of Cu, Ag, Al, or their alloys or special steels containing Cr, Mn, W, Mo, or V or may be lined with these metals or, if the temperature may be above 150° but not too high, may be lined with Zn, Sn, Pb, or alloys of these metals.

1145. ———. [Benzene by Catalytic Hydrogenation of Gases.] French Patent 621,550, May 12, 1927; appl. filed Sept. 15, 1926, in Germany Sept. 17, 1925. Chem. Zentralb., 1928, I, p. 621.

Gases containing CH_4, C_2H_6, unsaturated hydrocarbons, and higher homologs of the paraffin series are hydrogenated at 500°–900° under pressure up to 1,000 atm. and CO is added. The carbonates and other salts of the alkaline earths, mainly Mg and Be, their oxides or hydroxides, and Se, Te, Th compounds, active SiO_2, or C or mixtures of them are used as catalysts. Raw materials may be brown-coal gas, oil gas, coke-oven gas, low-temperature carbonization gas and natural gas. Benzol hydrocarbons are obtained.

1146. ———. Benzene Synthesis. British Patent 297,179, July 13, 1927. Chem. Abs., vol. 23, 1929, p. 2448.

C_6H_6 and its homologs are produced by treating mixtures of C oxide and H_2 at a temperature >300° with a catalyst comprising Fe and then heating the resulting olefins and CH_4 hydrocarbons to 600°–800° with or without a catalyst. A noble metal is preferably used with Fe in the 1st stage, and, in the 2d stage, substances that would cause deposition of C are avoided. Cu, Sn, Zn, or Cr may be used to line the apparatus or as catalysts.

1147. ———. [Carbon Monoxide and Hydrogen.] French Patent 701,003, Mar. 10, 1931; appl. filed Aug. 23, 1930. Chem. Abs., vol. 25, 1931, p. 3780.

CO and H_2 are obtained by the action of CH_4 or gases containing it on metal oxides capable of transformation to lower oxides, with the exclusion of oxides of metals of the Fe group. Gives examples of the use of TiO_2 and a mixture of Cr_2O_3 and MgO. The lower oxides are afterward oxidized to the higher oxide and used again.

See German Patent 488,502 (abs. **3920**).

1148. ———. [Carbon Monoxide-Hydrogen Mixtures for Synthesis.] German Patent Appl. I 62,832, OZ 11,118, filed Nov. 3, 1938; APC TC 1,153.

Hydrocarbons such as CH_4 are reacted with steam and CO_2, which are made, at least in part, by the reaction of hydrocarbons with a reducible metallic oxide such as Cu oxide or oxides of metals of the Fe group.

1149. ———. [Carboxylic Acids.] German Patent Appl. I 67,079, no date (*Cl. IV d—12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 130.

Carboxylic acids are obtained by converting CO with olefins and H_2O in the presence of a catalyst of Cu in an aqueous suspension, Cu salts being absent.

1150. ———. [Carboxylic Acids.] German Patent Appl. I 67,375, no date (*Cl. IV d—12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 132.

Carboxylic acids are obtained by converting olefins with CO and H_2O in the presence of a catalyst in the form of an aqueous Fe salt solution.

1151. ———. [Carboxylic Acids.] German Patent Appl. I 68,919, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 145.

Carboxylic acids are obtained by the action of H_2O and CO on high-molecular olefinic hydrocarbons in the presence of Ni– or Co–halogenides at elevated temperature.

1152. ———. [Carboxylic Acids.] German Patent Appl. I 69,045, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 146.

Carboxylic acids are made from oils containing unsaturated hydrocarbons by catalytic hydrogenation to saturated compounds followed by oxidation by means of O_2.

1153. ———. [Carboxylic Acids.] German Patent Appl. I 70,498, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 160.

Carboxylic acids are obtained by converting olefins with H_2O and CO with the use of V or metals forming metal carbonyls as catalysts. Addition to German Patent Appl. I 68,919 (abs. **1151**).

1154. ———. [Carboxylic Acids.] German Patent Appl. I 71,941, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 175.

Carboxylic acids are obtained by treating high-molecular olefinic hydrocarbons with H_2O and CO in the presence of metals of group 5 of the periodic system and of halogens at elevated temperature.

1155. ———. [Carboxylic Acids.] German Patent Appl. I 75,563, no date (*Cl. IV d–12 o*).

Carboxylic acids are obtained by the oxidation of synthesis products, which were produced by the reaction between CO and H_2 with olefins in the presence of catalysts, through treatment with O_2-containing or O_2-evolving gases.

1156. ———. [Carboxylic Acids and Anhydrides.] German Patent Appl. I 74,732, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 217.

Carboxylic acids and anhydrides are obtained by the reaction of CO and H_2O on olefins under pressure in the presence of halogen compounds together with carbonyl-forming metals as catalysts.

1157. ———. [Carboxylic Acids and Anhydrides.] German Patent Appl. I 74,733, no date (*Cl. 12 o–11*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 217.

Carboxylic acids and anhydrides are obtained by heating olefins with H_2O and CO under pressure in the presence of carbonyl-forming metals as promoters.

1158. ———. [Catalyst Chamber.] Italian Patent 385,693, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 161.

Tube bundles with inner heat exchange.

1159. ———. [Catalyst Chamber.] Swiss Patent 121,969, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 215.

See British Patent 247,217 (abs. **1144**), and German Patent 587,818 (abs. **2664**).

1160. ———. [Catalyst for Methanol Synthesis.] Austrian Patent 105,591, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 206; Chem. Zentralb., 1927, I, p. 3531.

See British Patent 229,715 (abs. **3289**), Canadian Patent 251,486 (abs. **3290**), French Patent 571,355 (abs. **3291**), and Swiss Patent 107,853 (abs. **3292**).

1161. ———. Catalyst for Methanol Synthesis. British Patent 317,807, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 207.

Cu (Ag, Au), Fe (Co, Ni) and difficultly oxidizable oxide (<5%), no Cd or Tl.

1162. ———. [Catalyst for Methanol Synthesis.] German Patent 408,811, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 206.

Alloys that break down under the working conditions.

1163. ———. [Catalyst for Methanol Synthesis.] German Patent 415,469, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 206.

Mixture of the oxides of Ti, V, Cr, Mn, Ce, Th, U, Mo, W, B.

1164. ———. [Catalyst for Methanol Synthesis.] Swiss Patent 91,562, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 207.

Thermal decomposition products of lithium formate. Acetone is produced as well as MeOH.

1165. ———. [Catalyst for Synthesis of Hydrocarbons From Water Gas.] German Patent Appl. I 63,257, OZ 11,220, filed Dec. 18, 1938; APC TC 1,190.

For the synthesis of hydrocarbons from CO and H_2 an Fe catalyst containing alkali borate is used. For example, Fe powder from the thermal decomposition of Fe carbonyl is treated with 1% Na borate, dissolved in H_2O, then dried, pelleted, and reduced with H_2 at 850° for 4 hr. Subsequent use of these sintered pellets in the Fischer-Tropsch synthesis with 1 CO : 1.2 H_2 gas at 330° C. and 15 atm. yields about 130 gm. of oil+wax per $m.^3$.

See also Italian Patent 379,250 (abs. **1686**).

1166. ———. [Catalyst for the Production of High Molecular Hydrocarbons by the Conversion of Carbon Monoxide.] German Patent Appl. I 74,790, OZ 14,131, filed Apr. 9, 1943 (*Cl. IV d–12 o*). FIAT Reel 171, frames 10,205–10,211; PB 25,615; FIAT Reel B–28, frames 38,367–38,373; PB 70,302; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 5, chap. 152, 1949, p. 24.

Fe or Fe compounds, capable of being converted to the oxide, are heated with 0.2–25% of metals of the 2d, 6th, or 7th group and with 0.5–15% of alkali metal compounds or salts of organic acids in a nonreducing atmosphere at 600° or more until sintering occurs and reduction is complete. Example: CO and H_2 in proportion of 5 : 4 is conducted at 20 atm. and 250° at a throughput of 250 l. per hr, over a catalyst produced by the decomposition products of Fe carbonyl, mixed with W oxide, K borate, and H_2O, pressed into pills, calcined for 4 hr. at 850° in presence of air, and reduced with H_2 at 450°.

1167. ———. [Catalyst Regeneration.] Swiss Patent 188,881, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 156.

See United States Patent 2,159,140 (abs. **595**).

1168. ———. Catalysts. British Patent 490,090, Aug. 9, 1938. Chem. Abs., vol. 33, 1939, p. 823.

Catalyst for the synthesis of hydrocarbons or their O derivatives from CO and H_2 is prepared by subjecting a metal of the Fe group, which has been obtained by decomposing a carbonyl compound to >500° and < the melting point until partial sintering takes place.

1169. ———. [Catalysts.] French Patent 901,970, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 152.

Catalysts reduced at 300°–500° and after cooling treated with O_2-containing gas.

1170. ———. [Catalysts.] French Patent 906,299, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 152.

Catalysts (Fe, Co, Ni) with a thin layer of Cu (Ag, Au).

1171. ———. [Catalysts.] German Patent Appl. I 64,187, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 118.

Conversion of CO with H_2 to hydrocarbons in the presence of Fe and Ni catalysts, which were obtained

by precipitation of reducible Fe and Ni compounds from their solutions by dropping into the alkaline precipitation agent and maintaining a precipitation period of more than 3 hr.

1172. ———. [Catalysts.] German Patent 756,725, Oct. 23, 1939; appl. I 65,845, OZ 11,841 (*Cl. 12 o–1.03*). FIAT Reel 164, frames 3,328–3,333; PB 75,220.

In a process of making catalysts for the conversion of CO with H_2, which contains Fe, Co, or Ni in metallic form, the reduced catalyst is provided with a thin, firmly adherent coating of Cu, Ag, or Au. This treatment enables the operation of conversion to be carried on at higher temperature without the disadvantage of C formation on the catalyst surface, thus prolonging the active life of the catalyst.

1173. ———. Catalysts and Catalytic Reactions. British Patent 379,335, Aug. 26, 1932. Chem. Abs., vol. 27, 1933, p. 4041.

Catalysts suitable for destructive hydrogenation of coals, tars, and mineral oils; cracking of liquid carbonaceous materials; purification of gases by treatment with H_2; preparation of MeOH or hydrocarbons from CO and H_2; purification, especially desulfurization, of carbonaceous materials with H_2; preparation of H_2S from H_2 and S; hydrogenation and dehydrogenation of hydrocarbons; and preparation of H_2 or polymerization products from the waste gases from destructive hydrogenation or cracking processes comprise metal sulfides (except of Fe), which are prepared from metals, especially from groups 5 and 6 of the periodic system, or their compounds under vigorously sulfidizing conditions, such as treatment with liquid or vaporous S or volatile compounds containing bivalent S, for example: H_2S, PhSH, mercaptans, CS_2, AcSH under conditions allowing an intensive reaction or by the thermal decomposition of thio salts, preferably with the exclusion of substances having an oxidizing effect during and after the preparation. Sulfides, such as commercial sulfides, oxides, hydroxides, carbonates, nitrates, chlorides, nitrides, or phosphides, may be treated. Gives details of the many methods of preparation.

1174. ———. Catalysts for Methanol Production. British Patent 286,284, Mar. 3, 1927. Chem. Abs., vol. 23, 1929, p. 155.

Catalysts of high mechanical stability, especially those of the metal oxide type, are obtained by adding H_2O soluble Mg salts such as the sulfate, chloride, or nitrate to the other components. Gives examples of the use of ZnO with $MgCl_2$ together to form a mass, which, after heating, is treated with chromic acid or alkali metal dichromate to form a catalyst suitable for MeOH production from CO and H_2 at 400°–450° under 200 atm. pressure.

1175. ———. [Catalysts for Synthesis of Alcohols.] German Patent Appl. I 76,545, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 236.

Catalysts for the synthesis of alcohols from CO and H_2 consist of Cr oxide and an excess of Zn oxide.

1176. ———. Catalytic Apparatus. British Patent 458,035, Dec. 11, 1936. Chem. Abs., vol. 31, 1937, p. 3343.

Conversion of oxides of C with H_2 into hydrocarbons or their O-containing derivatives is conducted in an apparatus, where the conversion is catalytically promoted by the internal surfaces of the apparatus itself, which at the parts coming into contact with the gas mixture comprises an etched metal, particularly Fe. Preferably, no other catalyst is present. Suitable metals include ingot steel, Fe, special steels, Ni, Co, Cu and their alloys, and metals coated with Zn, Ni, or Co; for example, by electrolysis, burning, or soldering. The surfaces may be etched with acid, for example, HNO_3, AcOH, lactic, formic, or picric, and compounds of U, alkali-metals, Cu, Ag, Mg, Hg, Mn, or Cr. especially $UO_2(NO_3)_2$, $Cu(NO_3)_2$, $Mg(NO_3)_2$, and KNO_3, may be added to the acids, as activators for the catalyst. Other materials may be used, such as alkalies or NH_4OH in the case of Zn and Fe; electrolysis; salts, for example, alkali nitrates, NH_4Cl, $CuSO_4$; gases, for example, HCl, oxides of N; or fused substances. In an example, the outer surface of a steel tubular spiral, made of Mannesmann–SII ingot steel and lined with Cu is etched with a solution of glacial AcOH, $UO_2(NO_3)_2$ and KNO_3, superheated steam at 200°–400° is passed through the spiral at 12 atm. as a heating and cooling medium and H_2 is 1st led through the reaction chamber past the spiral and then a mixture of equal parts of CO and H_2 at 100 atm. and 368°–412°. The product consists of oil and readily volatilizable hydrocarbons and a gas containing CH_4, C_2H_6, and homologs.

1177. ———. [Catalytic Conversion of Carbon Oxides With Hydrogen.] German Patent Appl. I 63,779, OZ 11,354, filed Feb. 10, 1939; APC TC 1,134.

Essentially horizontal reaction tubes are used for the synthesis of hydrocarbons from CO and H_2, with the object of giving more effective heat transfer to the surrounding coolant thus permitting operation at higher temperature without excessive CH_4 formation.

1178. ———. [Catalytic Cracking of Hydrocarbon Oils or Pressure Hydrogenation of Coal, Tar, or Mineral Oil.] French Patent 886,246, Oct. 8, 1943; appl. filed Sept. 29, 1942. Chem. Zentralb., I, 1944, p. 842.

Catalysts consist of natural or synthetic bleaching earths, which have been impregnated with metal-salts solutions of metals from groups 2–7. Such catalysts are very active and produce only small amounts of gaseous hydrocarbons as byproducts.

1179. ———. Catalytic Cracking of Hydrocarbons. British Patent 521,687, May 29, 1940. Chem. Abs., vol. 36, 1942, p. 1479.

Yield of nonknocking motor fuel is increased by passing the hydrocarbon oil in the liquid or vapor phase at a cracking temperature and at an initial pressure of 1–100 atm. through a reaction zone containing a cracking catalyst and increasing the pressure in the reaction zone continuously or stepwise by at least 5 atm., preferably 10 atm., while the catalyst is acting on the hydrocarbon oil without interruption of the process.

1180. ———. [Catalytic Cracking of Oils.] German Patent 711,316, Aug. 28, 1941 (*Cl. 23 b–1.04*). Chem. Abs., vol. 37, 1943, p. 4561.

Siliceous material is used as catalyst for cracking. This is produced by precipitating it from aqueous solutions with a H_2O-soluble metal salt and then partly leaching out the metal.

1181. ———. Catalytic Gas Reactions. British Patent 495,129, Nov. 8, 1938. Chem. Abs., vol. 33, 1939, p. 2777.

Reactions are effected under pressure in a number of cycles connected in parallel, each cycle comprising a pump, catalyst chamber, cooler, and separator. Foreign gases are eliminated by washing with the liquefied reaction product in a tower connected in parallel with the end cycle. Make-up gas is added to only a part of the cycles at the opposite end of the system. The invention is applicable to NH_3 synthesis, destructive hydrogenation, and MeOH synthesis.

1182. ———. [Catalytic Processes.] French Patent 688,927, Jan. 27, 1930. Chem. Abs., vol. 25, 1931, p. 1009.

In treating gases catalytically under pressure, mixtures of lubricating oil from the circulating pumps are

removed from the gases by solid absorption agents, such as active charcoal or SiO_2 before they reach the catalysts.

1183. ———. [Catalytic Production of Alcohols From Hydrogen and Carbon Monoxide.] German Patent Appl. I 64,683, OZ 11,561, no date (*Cl. 12 o–5.02*); APC TC 1,196.

In producing higher alcohols by catalytic reactions of H_2 and CO, the retarding effect of N_2 upon the desired reaction may be avoided by 1st treating the usual mixture of H_2, CO and N_2 to form MeOH and then treating the MeOH in the absence of N_2 in a 2d step for the production of higher alcohols.

1184. ———. Catalytic Production of Hydrocarbons. British Patent 271,452, May 22, 1926. Chem. Abs., vol. 22, 1928, p. 1594.

In producing hydrocarbons or their derivatives by reaction of C oxides with H_2 at ordinary, reduced, or increased pressure, metallic catalysts are used such as Fe, Co, Ni, and Mo, which are prepared by thermal decomposition of the corresponding metal carbonyl. Gives various details.

See also British Patent 267,554 (abs. **1321**).

1185. ———. Catalytic Production of Hydrocarbons. British Patent 279,347, May 30, 1927. Chem. Abs., vol. 22, 1928, p. 2754.

In producing CH_4 and other hydrocarbons from C oxides and H_2 or gases that split off H_2, the temperature is prevented from rising too high and the heat of reaction is utilized, by connecting the contact chamber with a generator of high-pressure steam, so that heat exchange is effected. Describes various structural features.

See also British Patent 271,452 (abs. **1184**).

1186. ———. Catalytic Production of Hydrocarbons. British Patent 312,717, Mar. 10, 1928. Chem. Abs., vol. 24, 1930, p. 954.

In producing hydrocarbons such as those of benzine from C oxides and H_2, a catalyst is used containing 1 or more metals of group 8 with an addition of an alkali compound in a quantity not exceeding 0.6% the quantity of the group 8 metal; for example, the catalyst may comprise Fe, 40; Co, 20; Ni, 10; and Na, 0.34 part.

1187. ———. [Catalytic Production of Hydrocarbons.] French Patent 631,882, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 215.

See British Patent 279,347 (abs. **1185**).

1188. ———. Catalytic Production of Hydrogen. British Patent 301,969, Sept. 15, 1927. Chem. Abs., vol. 23, 1929, p. 4307.

Catalytic conversion of mixtures of hydrocarbons with water vapor or CO_2 into H_2 and CO is effected in elongated chambers in which the catalyst is indirectly heated to 600°–1,000°. The reaction mixture is preferably preliminarily freed from S compounds by passing over heated metallic oxides. Describes an apparatus.

1189. ———. Catalytic Production of Olefins. British Patent 310,999, Feb. 6, 1928. Chem. Abs., vol. 24, 1930, p. 625.

In producing olefins from mixtures of H_2 and C oxides, the temperature is controlled by a fluid, which circulates in heat exchanging relation with the catalyst but not in contact with the reaction gases, for example, the temperature control fluid may be passed through bores in MN–Cu shelves on which the catalyst is placed. Describes apparatus.

1190. ———. [Catalytic Production of Organic Compounds.] French Patent 635,950, June 14, 1927. Chem. Zentralb., 1928, I, p. 2893; Chem. Abs., vol. 22, 1928, p. 4535.

Contact masses, which contain, apart from Cu, Ag, Au, Zn, or their mixtures or alloys, other elements, particularly those of the Fe group or their compounds, in small proportions and in the absence of supports that are poor conductors of heat, are used for the preparation of hydrocarbons and organic O compounds from H_2 and oxides of C. Catalysts containing Cd or Tl or their compounds or mixtures and 1 or more metals of the Fe group or their compounds may be used also. In examples, water gas is passed over a mixture of oxides of Cu and Co or over oxides of Cu, Fe, and Zr. CO and H_2 are passed over oxides of Cu, Ag and Co, and CrO_3. Water gas is passed over a dried precipitate of carbonates of Fe, Cd, and Cu or over ferrocyanides of Cd and Cu.

1191. ———. Catalytic Production of Oxygenated Organic Compounds. British Patent 280,522, Nov. 15, 1926. Chem. Zentralb., 1929, II, p. 519; Chem. Abs., vol. 22, 1928, p. 3169.

Oxides of C are passed with H_2 over an Fe catalyst containing small additions of alkalies and alkaline earths at a temperature below 300°, suitably about 200°, either under ordinary pressure or under reduced or slightly increased pressure. The products may comprise resinous, O–containing substances; paraffinic compounds; oily liquids; alcohol; and aqueous solution of organic acids.

See also Russian Patent 10,025 (abs. **1038**).

1192. ———. Catalytic Production of Oxygenated Organic Compounds From Oxides of Carbon and Hydrogen. British Patent 317,808, May 18, 1928. Chem. Abs., vol. 24, 1930, p. 2137.

Organic compounds such as MeOH, EtOH and higher alcohols, acids, esters, ketones, or fats are prepared by treating gaseous mixtures comprising C oxides and a quantity of H_2 or gas containing H_2 greater than that of the CO present at a pressure above 20 atm., with a catalyst comprising a mixture of an element from the 1st subgroup of the periodic system and a large quantity of an element from the 8th group of the periodic system and preferably from the Fe group (suitably with the further addition of <5% of a metal forming a difficulty reducible oxide) such, for example, as may be prepared by depositing $Fe(NO_3)_3$, $Cu(NO_3)_2$, and a small quantity of K_2CO_3 on pumice stone, calcining, and reducing with H_2. Gives other examples.

1193. ———. Catalytic Purification of Oxygen-Containing Hydrogenation Products of Carbon Oxides. British Patent 400,262, Oct. 23, 1933. Chem. Abs., vol. 28, 1934, p. 2136.

O-containing products obtained by the catalytic hydrogenation of oxides of C, particularly the fraction boiling above 110° and consisting largely of higher alcohols, are purified by catalytic hydrogenation at 100°–300° and pressures above 50 atm. in presence of sulfides or nonreducible oxides of metals of groups 1, 2, 4, 5, 6, or 8, metals of group 6 being especially suitable. The catalysts may be oxides, hydroxides, carbonates, and other salts from which the acid radical can be expelled by heat and complex salts of H_4SiO_4 or H_3PO_4 with H_2MoO_4 or H_2WO_4, such as NH_4 phosphomolybdate. Among examples an initial fraction boiling at 120°–180° is (1) trickled over a catalyst filling consisting of pieces of Ni and W sulfides made by treating Ni tungstate with H_2S at 200° and 200 atm. of H_2 and (2) vaporized in H_2 and passed over Cu chromite at 180° and 200 atm.

1194. ———. [Catalytic Reactions.] French Patent 652,595, Apr. 12, 1928. Chem. Abs., vol. 23, 1929, p. 3523.

In exothermic catalytic reactions the tubes containing the catalysts are assembled in groups so close together that the incoming gas has a greater linear speed than that in the tubes.

1195. ———. [Catalytic Reactions.] German Patent 685,371, Dec. 16, 1939 (*Cl. 12 g–4.01*). Chem. Abs., vol. 34, 1940, p. 4562.

Metal sulfides, which have been prepared by heating thio salts, are used as the catalysts. They find particular application in the preparation of hydrocarbons by pressure hydrogenation or the cracking of carbonaceous material. Thio salts of the metals of the 5th and 6th groups, as W, Mo, or V and other metals such as Cu and Re, are suitable. Addition to German Patent 682,018 (abs. **2060**).

1196. ———. [Catalytic Synthesis of Hydrocarbons.] French Patent 841,030, May 9, 1939. Chem. Abs., vol. 34, 1940, p. 1684.

Hydrocarbons with more than 1 C atom or of oxygenated derivatives of hydrocarbons, solid or liquid, are synthesized from CO and H_2 in a liquid medium, using as catalysts agglutinated heavy metals, particularly those of group 8 of the periodic table (Fe is preferred). The agglutinated metals are obtained, either by heating the metals themselves in powdery state at 600°–1,000° in presence of a nonoxidizing gas, such as N_2, or by heating reducible metallic compounds, such as oxides or hydroxides, at 600°–1,000° in presence of a reducing gas, such as H_2. Addition of Al_2O_3, SiO_2, infusorial earth, compounds of Cu, Ti, Mn, Cr, W, Th, Zr, Ce, and other rare earths increases the activity of the catalysts. As the liquid medium, a mineral oil or a tar oil is used.

1197. ———. [Chemical Compound.] German Patent Appl. I 74,495, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 212.

Patent application concerns the condensation of cyclic hydrocarbons with compounds obtained by the catalytic conversion of CO with H_2.

1198. ———. [Cleavage of Oils From the Hydrocarbon Synthesis.] Italian Patent 352,074, June 25, 1937. Chem. Zentralb., 1938, I, p. 2989.

See French Patent 823,262 (abs. **1221**).

1199. ———. [Compounds From Carbon Monoxide and Hydrogen.] French Patent 823,302, Jan. 18, 1938. Chem. Abs., vol. 32, 1938, p. 5409.

In making hydrocarbons or their derivatives containing O from CO and H_2 at a high temperature and in the presence of catalysts, there is introduced into the reaction space a mixture of H_2, CO, and an inert gas, the amount of H_2 being less than the amount of CO and the proportion of inert gas being 20–90%. The inert gas may be CO_2 or N_2.

See also British Patent 478,318 (abs. **1291**).

1200. ———. [Conducting Chemical Conversions.] German Patent Appl. —, OZ 13,717, filed Oct. 13, 1942. TOM Reel 17, item 32, frames 898–905; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, chap. 92, 1948, p. 49.

Describes apparatus for carrying out chemical reactions, such as synthesis of hydrocarbons from CO and H_2, which require special measures for the removal or introduction of heat, particularly those that must be maintained within a narrow temperature range. The apparatus is characterized by the arrangement of horizontal or slightly inclined tube bundles, which are filled with a heating or cooling fluid for the removal or addition of the heat of reaction. The reaction zone is located between the tubes and is filled with a catalyst. Aside from the tube walls it is traversed by no further heat transfer surfaces. Presents a formula for calculating the spacing of the cooling tubes, and shows a diagram of the apparatus.

1201. ———. [Conversion of Carbon Monoxide and Hydrogen Into Hydrocarbons.] Italian Patent 374,615, June 9, 1939. Chem. Zentralb., 1940, II, p. 2988.

See British Patent 516,160 (abs. **1207**).

1202. ———. [Conversion of Carbon Monoxide With Hydrogen.] German Patent Appl. —, OZ 14,622, filed Mar. 1, 1944. FIAT Reel 172, frames 595–599; PB 25,616.

In converting CO with H_2 to oxygenated organic compounds, particularly alcohols, in presence of Fe catalysts, the efficiency of conversion is greatly increased by adding varying amounts of ZrO_2 to the catalyst as a promoter. Other metals, such as those from groups 1 and 2 may be added. A typical catalyst has the following composition: Fe, 81.7; ZrO_2, 14.9; K_2CO_3, 1.5; Cu, 1.4; MgO, 0.5. The catalyst may be precipitated, sintered, or fused, the latter type being preferred. Reduction takes place at 400°–800°. The synthesis is preferably performed with this catalyst at 100–250 atm. and 280°–350° and with a synthesis gas containing 1.5–8 parts H_2 to 1 of CO.

1203. ———. [Conversion of Carbon Monoxide With Hydrogen.] German Patent Appl. I 63,658, OZ 11,324, filed Jan. 28, 1939; APC TC 1,142.

For the synthesis of hydrocarbons from CO and H_2, reaction tubes are arranged in rows with the tubes close together in each row but with the rows suitably spaced for circulation of coolant.

1204. ———. [Conversion of Carbon Monoxide With Hydrogen.] German Patent Appl. I 63,810, OZ 11,356, no date; APC TC 1,222.

In the synthesis of hydrocarbons from CO and H_2 in a plurality of stages, the fresh charge gas is contacted in the first stage with a catalyst that has suffered appreciable loss in activity by use in a succeeding stage.

1205. ———. [Conversion of Carbon Monoxide With Hydrogen.] German Patent Appl. I 73,177, OZ 13,668, filed Sept. 17, 1942 (*Cl. IV d–12 o*). FIAT Reel 170, frames 9,370–9,372; PB 64,236; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 7, chap. 192, 1950, p. 24.

Improvement of German Patent Appl. I 70,663 (abs. **2316**) is described; wherein the Fe carbonyl is passed in vapor form into an oil obtained in a previous operation by synthesis from CO and H_2 and in which K_2CO_3 is suspended, whereby it decomposes into finely suspended Fe until the suspension amounts to 50% by weight when it is removed and ground to 1- to 5-micron fineness. The synthesis process is then carried out with the catalyst suspended in oil and with foaming of the synthesis gas as in the original application. The gasoline yield is improved some.

1206. ———. [Conversion of Carbon Monoxide With Hydrogen.] German Patent Appl. I 75,440, OZ 14,294, filed July 10, 1943 (*Cl. IV d–12 o*). FIAT Reel 170, frames 9,735–9,737; PB 64,335; TOM Reel 26, item 11, frames 578–580.

In the conversion of CO and H_2, the catalyst described in German Patent Appl. I 68,608 (abs. **3261**), containing Fe, Cu, an alkali compound, and MgO on kieselguhr, the MgO is replaced with a F compound such as CaF_2 and, if desired, one or more difficultly reducible metallic oxides. With this catalyst and at the same temperatures as before, CO conversion and yields are increased, the products within the gasoline boiling range increasing at the expense of the higher boiling compounds.

1207. ———. Converting Carbon Monoxide and Hydrogen Into Hydrocarbons. British Patent 516,160, Dec. 22, 1939. Chem. Abs., vol. 35, 1941, p. 6094.

Process for regeneration of the catalyst in the conversion of CO and H_2 into hydrocarbons having more than 1 C atom, which comprises passing over the catalyst vapors of organic liquids in which the conversion products of high molecular weight deposited on the catalyst are soluble.

1208. ———. Converting Carbon Monoxide and Hydrogen Into Hydrocarbons. British Patent 516,352, Jan. 1, 1940. Chem. Abs., vol. 35, 1941, p. 6094.

Catalytic reaction in presence of a liquid medium can be advantageously effected by introducing the liquid medium into different zones of the reaction space through separate points of introduction adjacent to the zones. Describes apparatus.

See also British Patent 468,434 (abs. **1264**).

1209. ———. Converting Carbon Monoxide and Hydrogen Into Hydrocarbons. British Patent 516,403, Jan. 1, 1940. Chem. Abs., vol. 35, 1941, p. 6423.

Catalytic conversion of CO and H_2 in a liquid medium comprising considerable amounts of constituents, which are gaseous or vaporous under the reaction conditions, is advantageously carried out by first passing the liquid medium along the catalyst chamber in indirect heat exchange relation with the participants of the reaction and then passing it through the catalyst chamber in the same direction as the reaction participants. Preferably the liquid medium is passed along the reaction chamber countercurrent to the reaction participants, so that while the liquid medium is at its lowest temperature it comes into contact with the hottest part of the catalyst chamber, thus keeping the temperature of the chamber much more uniform. Describes an apparatus.

1210. ———. Converting Carbon Monoxide and Hydrogen Into Liquid Hydrocarbons. British Patent 518,605, Mar. 1, 1940; appl. filed July 15, 1938. Chem. Abs., vol. 35, 1941, p. 7687.

Formation of undesirable hydrocarbons of low molecular weight can be reduced considerably by adding cyclic hydrocarbons, which under the reaction conditions are at least partly vaporous, for example, C_6H_6 toluene, xylene, cyclohexane, and middle oils.

1211. ———. Cooling Gases. British Patent 474,191, Oct. 27, 1937. Chem. Abs., vol. 32, 1938, p. 2792.

Hot gases or vapors are cooled by injecting a liquid of a different chemical nature, preferably H_2O, in a finely divided state at a temperature that is (a) equal to or > its boiling point at the pressure of the gases to be cooled and (b) < the temperature of the gases. The complete evaporation of the injected H_2O thus insured is useful in process; for example, obtaining gases by roasting pyrites, where the presence of liquid H_2O is deleterious to the constructional materials of the apparatus. The invention is applicable to exothermic catalytic reactions in which the main part of the gases involved in converted by means of a 1st contact layer, the final conversion being effected by means of a 3d contact layer, and the gases being cooled between the 2 stages. Such processes are used, for example, for producing H_2 and CO from hydrocarbons and steam; for the oxidizing SO_2; in the synthesis of NH_3 from N_2 and H_2, liquefied NH_3 being preferably injected in this case between the contact layers for cooling the gas; or in the synthesis of hydrocarbons from CO and H_2, superheated hydrocarbons being injected between 2 or more contact layers. The invention is also useful when products formed are to be prevented from decomposing by being cooled rapidly, for example, in the production of oxides of N by combustion of NH_3 and in the production of unsaturated hydrocarbons by thermal decomposition.

1212. ———. Cracking and Hydrogenating Oils. British Patent 507,999, June 23, 1939; appl. filed Aug. 28, 1937. Chem. Abs., vol. 34, 1940, p. 613.

Nonknocking motor fuels are obtained by subjecting paraffin hydrocarbons together with C_6H_6 and/or its light-boiling homologs and/or light-boiling hydroaromatic hydrocarbons to a heat treatment at 300°–700°, preferably in the presence of a rigid catalyst having a splitting and advantageously polymerizing action and, if desired, in the presence of H_2. Light-boiling homologs of C_6H_6 and light-boiling hydroaromatic hydrocarbons are those boiling in the boiling range of benzines such as up to 225°. In an example, BuH, C_6H_6, and H_2, at 530° and <250 atm. pressure, are led over a splitting and polymerizing catalyst comprising H_2MoO_4, ZnO, and MgO to obtain a liquid product the fraction of which boiling up to 180° may be used to improve the nonknocking properties of motor fuels.

See also British Patent 503,602 (abs. **1133**) and United States Patent 2,245,157 (abs. **2661**).

1213. ———. Cracking and Refining Oils. British Patent 504,614, Apr. 24, 1939. Chem. Abs., vol. 33, 1939, p. 8002.

In the production of hydrocarbons or hydrocarbon oils by cracking, hydrogenation, refining, or desulfurization of carbonaceous material in the presence of catalysts, the catalysts comprise products obtained by mixing a solution of 1 or more salts of elements of the 3d and 4th groups of the periodic system, capable of forming mineral gels, with 1 or more metal salts, preferably in solution, precipitating the gel and separating and dryin it by heat. In a modification, the metal salts or solutions are mixed with the precipitated gel while still moist. The gel may be precipitated by standing, by heating, or by the use of precipitants. Precipitants for the metal radical may be added also, preferably after the gel precipitant. The catalyst may be prepared in the presence of bleaching earths, bauxite, etc., and may be mixed with carbonaceous material, such as, graphite and lignite small coke, shaped and heated to about 500°–600°. H_3BO_3 may be added. In cracking and hydrogenation processes, formation of gaseous products may be reduced by using the salt of a trivalent metal, for example, $FeCl_3$, and dissolving out of the metal compound. Among examples, middle oils are treated at 460° and atmospheric pressure with a catalyst comprising precipitated SiO_2 pasted with $Al(NO_3)_3$, or worked up with a solution of $Al(NO_3)_3$ before filtering.

See also Belgian Patent 429,626 (abs. **1214**).

1214. ———. [Cracking Catalysts.] Belgian Patent 429,626, Aug. 9, 1938. Chem. Zentralb. 1939, II, p. 2490.

The solution of 1 or more salts of the elements in groups 3 or 4 of the periodic system capable of forming gels is mixed with 1 or more metal salts and the mixture allowed to stand and form a gel. The gel is separated by heating or by precipitation, dried and heated to about 400°–800°, if desired, in presence of reducing gases. In this way catalysts are formed consisting of Si and Mg and Al and Mg together with compounds of Zn, Sn, Ti, V, Cr, Mo, W, Fe, Ni, or Co. The catalysts yield by the cracking of hydrocarbon oils from pressure hydrogenation only small amounts of gaseous products and can be regenerated without harm by heating to 800°. They are suitable also for cracking oils rich in H, such as those from the water-gas synthesis.

See also French Patent 841,898 (abs. **1605**) and British Patent 504,614 (abs. **1213**).

1215. ———. [Cracking Hydrocarbons.] French Patent 852,269, Jan. 27, 1940. Chem. Abs., vol. 36, 1942, p. 3036.

Hydrocarbons rich in H (containing 15 gm. H for 100 gm. C) are cracked in presence of known very active catalysts, the activity of which has been diminished by a previous cracking of hydrocarbons poor in H in liquid or vapor phase.

1216. ———. Cracking Hydrocarbons Such as Methane. British Patent 264,845, Jan. 20, 1926. Chem. Abs., vol. 22, 1928, p. 242.

Cracking of CH_4 to produce C_2H_2 or cracking of other gaseous or vaporous saturated hydrocarbons is effected by passage, alone or diluted with other gases, through a thin zone of high temperature, which extends across substantially the whole cross-sectional area of a tube, as in a special apparatus described. The reaction products may be rapidly cooled to separate the hydrocarbons or they may be directly subjected to other chemical treatment to produce other products such as C_6H_6 or AcH. Residual gases containing H_2 and CO may be converted catalytically into CH_4, which may be used to continue the process. A W wire gauze carrying platinized asbestos in a thin layer may be used as a catalyst, or a highly porous refractory material such as "Marquardt composition" may be used as a catalyst.

1217. ———. [Cracking of Synthesis Oil.] French Patent 855,815, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 184.

1218. ———. Cracking Oils. British Patent 480,442, Feb. 21, 1938. Chem. Abs., vol. 32, 1938, p. 6047.

Hydrocarbon mixtures b. >250° prepared by the reduction of CO with H_2 are purified before their subjection to cracking by (a) treatment with chemical refining agents, for example, H_2SO_4 or metal halides, for example, $AlCl_3$, $FeCl_3$, BF_3, $ZnCl_2$, $TiCl_4$; (b) treatment with selective solvents, for example, phenols, keto-acids, glycol acetate, liquid SO_2, or liquid NH_3; or (c) passage together with the residual gases from the CO reduction process, or with fresh H_2, over known hydrogenation catalysts, for example, compounds, particularly oxides or sulfides, of metals of the 5th–8th groups. The mixtures are preferably freed from low-boiling fractions and from paraffin before being refined. A mixture of CO and H_2 in the ratio 1 : 2 is led at 200° over a catalyst containing Co, Th, and bleaching earth, the fraction b.>320° is freed from paraffin and treated with 2% H_2SO_4 and subsequently with a bleaching earth, and the oil obtained is cracked at 550°–600° the products of high b. p. being returned; 72% of oil, consisting of benzine and middle oil 58%, gaseous hydrocarbons 27%, and coke 0.5%, is obtained.

1219. ———. [Cracking Process.] Belgian Patent 429,755, Aug. 17, 1938. Chem. Zentralb. 1939, II, p. 2490.

Oils that consist mainly or wholly of olefins, such as those obtained by the cracking of the paraffins from water gas synthesis b. 150°–300°, are treated in the vapor phase over catalysts in the presence of mononuclear aromatic hydrocarbons to produce highly antiknock motor fuels. To convert the existing low-boiling fractions into gasoline, either the reaction product is passed directly over a 2d polymerizing catalyst or a polymerizing catalyst is provided in step 1 in the vicinity of the exit for the reaction product.

See also British Patent 503,602 (abs. **1133**).

1220. ———. [Cracking Process.] French Patent 855,812, May 21, 1940; appl. filed June 6, 1939. Chem. Zentralb., 1940, II, p. 1818.

Hydrocarbons that have been synthesized from CO and H_2, are cracked to antiknock gasoline at 350° and at least 15 atm., preferably >20 atm., over catalysts of SiO_2 or silicates or containing these substances. Example: A gas oil synthesized from CO and H_2 at 460° and 30 atm. is cracked over bleaching earth at a throughput of 1 l. gas oil to 2 l. of catalyst per hr. The product contains 45% of gasoline b. up to 200° with octane number of 69.5, which can be raised to 84 by addition of 0.09 vol. % of tetraethyl lead.

1221. ———. [Decomposing Hydrocarbon Mixtures.] French Patent 823,262, Jan. 18, 1938. Chem. Abs., vol. 32, 1938, p. 5409.

Mixtures of hydrocarbons of relatively high boiling point formed during the hydrogenation of CO are treated, if necessary after removal of paraffin, with a known agent for purifying oils (H_2SO_4 and afterward decolorizing earth) and are then subjected to a pyrogenic decomposition.

See also Italian Patent 352,074 (abs. **1198**).

1222. ———. Dehydrogenated Hydrocarbons. British Patent 502,961, Mar. 27, 1939; appl. filed July 27, 1937. Chem. Abs., vol. 33, 1939, p. 7529.

Benzines obtained by reduction of CO are dehydrogenated and/or converted into aromatic hydrocarbons by treatment at 350°–500° in presence of a catalyst comprising alumina with a smaller proportion of a 6th group metal or compound. In an example, a mixture of alumina 3 and MoO_3 1 part is used, and the reaction temperature is 460°, the product having an octane no. of 60 and containing 35% of aromatic hydrocarbons.

1223. ———. Destructive Hydrogenation. British Patent 275.248, July 28, 1926. Chem. Abs., vol. 22, 1928, p. 2172.

Heat required for high-pressure reactions is supplied wholly or partly by injection of a preheated gas such as H_2 or gas containing H_2. The process may be applied to destructive hydrogenation of carbonaceous material or to the conversion of MeOH or EtOH into higher alcohols.

1224. ———. Destructive Hydrogenation. British Patent 277,273, Mar. 13, 1926. Chem. Age, vol. 17, 1927, p. 352; Chem. Zentralb., 1928, I, p. 616; Chem. Abs., vol. 22, 1928, p. 2456.

In producing liquid hydrocarbons by destructive hydrogenation of coal, tars, mineral oils, and like materials, both the hot and cold parts of the apparatus are made of metal not reacting with CO, as described in British Patent 247,217 (abs. **1144**) and British Patent 249,155 (abs. **1314**). For the cooler portions of the apparatus, metals of relatively low melting point may be used such as Sn, Zn, Cd, Pb, or their alloys; for the hotter portions, Cu, Ag, Al alloys, Cr, Mn, V, U or steel, or alloys of Ni or Co may be used containing about 20% or more of Mn, Ti, Cr, V, W, or Mo. Reducing gases other than those containing H_2 and CO may be used in the process.

1225. ———. Destructive Hydrogenations and Other Catalytic Reactions. British Patent 274,904, July 24, 1926. Chem. Abs., vol. 22, 1928, p. 2248.

Catalyst is brought into a state of suspension throughout the reaction space and whirled by a current of gas; for example, in destructive hydrogenation of a heavy oil with a Mo–Cr catalyst at 460° under 20 atm. pressure, or in synthesizing NH_3 or MeOH.

1226. ———. Desulfurizing Gases. British Patent 370,466, Nov. 6, 1930. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 214; Chem. Abs., vol. 27, 1933, p. 2564.

The S content of gases containing H_2S in excess of 7 gm. S per $m.^3$ is reduced before desulfurization by catalytic oxidation with active C by (1) dilution with gases free from or low in S, or (2) carrying out the oxidation in stages, the necessary amount of air being added before each stage. Alternatively all the O_2

needed may be added in 1 stage, the gas being cooled and moistened between stages.

1227. ———. [Diesel Fuel.] German Patent 730,897, Jan. 28, 1943; appl. filed Dec. 17, 1938. Oel u. Kohle, vol. 39, 1943, Sch. 212.

Mixture of H-poor oils and of hydrocarbon oils b. >200°, obtained by cracking the hydrogenation products of CO and a small amount of a solvent, is suitable for diesel fuel. The H-poor oils are those obtained by the low-temperature carbonization of solid carbonaceous materials, products of coal extraction with H-containing solvents, or products of the pressure hydrogenation of coal or of H-poor oils. The following solvents may be used; 0.5–5% of an aromatic or naphthenic oil such as heavy benzol or tetrahydronaphthalene.

1228. ———. [Diesel Oil From Synthetic Hydrocarbons.] German Patent Appl. I 72,919, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 187.

Hydrocarbon oils obtained by synthesis from C oxides and H_2 are converted into the diesel-oil fraction b. 200°–350° by oxidation in the liquid phase with O_2 or gases containing it in the presence of catalysts.

1229. ———. [Drying Oils and Plastics From Olefins.] Netherlands Patent 52,418, May 15, 1942; appl. filed June 3, 1938. Chem. Zentralb., 1942, II, p. 2320.

Hydrocarbons obtained by the reduction of CO and containing both paraffins and olefins are condensed with boron fluoride to produce drying oils and plastics.

1230. ———. [Emulsifying Agent.] French Patent 883,454, July 6, 1943; appl. filed June 23, 1942. Chem. Zentralb., 1944, I, p. 805.

An emulsifying agent is made by partial sulfochlorination of the synthetic paraffin b. 240°–320° and finally saponifying with an alkali solution.

1231. ———. [Esters.] German Patent Appl. I 72,970, no date (*Cl. 12 o–19.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 188.

Esters are formed from the alcoholic constituents and the organic acids obtained by the conversion of CO with H_2.

1232. ———. [Esters.] German Patent Appl. I 73,882, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 202.

Carboxylic acid esters are made from aliphatic alcohols and carboxylic acids by using such alcohols as are produced by the reaction between CO and H_2 and olefins with at least 4 C atoms in the molecule under pressure in presence of catalysts and finally by hydrogenation of the resulting oxo-compounds.

1233. ———. [Ethyl Alcohol.] French Patent 660,678, May 29, 1928. Chem. Abs., vol. 24, 1930, p. 130.

EtOH and other organic compounds are prepared by treating oxides of C and H_2 or hydrocarbons rich in H or both in the presence of catalysts containing elements of the 8th group of the periodic system, alone or mixed with other elements, at <320° and under pressure >20 atm. The content of oxides of C in the gaseous mixture is <25% of the H_2 or hydrocarbons present. When catalysts are used containing Cu, Ag, Au, Zn, or their mixtures or alloys, temperatures >320° may be used in the presence of supports that are poor heat conductors and using gaseous mixtures in which the contents of H_2 or hydrocarbons is greater than that of oxides of C.

1234. ———. Ethylene. British Patent 506,832, June 6, 1939. Chem. Abs., vol. 34, 1940, p. 452.

See United States Patent 2,154,676 (abs. **944**).

1235. ———. [Fluidized Catalyst and Its Regeneration.] German Patent Appl. —, OZ 14,803, filed June 15, 1944. FIAT Reel 172, frames 535–539; PB 25,616.

Fluidized catalysts, after utilization for cracking of hydrocarbons in the gas phase at normal or greatly increased pressure, are regenerated at higher pressure than the reaction pressure; for example, 20% higher than a reaction pressure of 20 atm. and 10% higher than a reaction pressure of >20 atm. The efficiency of regeneration is increased and the time required diminished.

1236. ———. Gas Comprising Hydrogen and Carbon Monoxide. British Patent 300,328, Aug. 24, 1927. Chem. Abs., vol. 23, 1929, p. 4030.

Describes apparatus for burning hydrocarbons with just enough O_2 to produce CO and H_2 at temperatures >1,000° without use of steam or catalysts.

1237. ———. Gas Purification. British Patent 571,285, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 166.

See United States Patent 1,766,763 (abs. **2685**).

1238. ———. [Gas Purification.] German Patent Appl. I 68,846, OZ 12,577, filed Feb. 7, 1941 (*Cl. IV b–26 d*). FIAT Reel 164, frames 3,376–3,380; PB 25,608; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 7, chap. 186, 1950, p. 11.

In removing organic S compounds and gum-forming substances from gases, the gas before desulfurization is cooled to such low temperatures, preferably —20° to —80°, that the gum-forming substances separate; or, the gas is washed at low temperature with liquids, such as low-molecular alcohols, which have the property of dissolving gum-forming substances.

1239. ———. [Gas Purification.] German Patent 411,389, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 214.

Continuous removal of S-compounds and carbonyls with steam over Fe_2O_3 then over active C or Cu oxide.

See British Patent 228,959 (abs. **90**) and United States Patent 1,766,763 (abs. **2685**).

1240. ———. [Gas Reactions.] French Patent 674,457, May 2, 1929. Chem. Abs., vol. 24, 1930, p. 2515.

In carrying out reactions at a high temperature with gases such as H_2, CO, or H_2S, which attack the metal of the apparatus, a small quantity of a substance, which is liquid at the temperature of reaction, is added to the gas so that the apparatus becomes covered with a film of liquid.

See French Patent 643,127.

1241. ———. Gaseous Catalytic Reactions. British Patent 500,366, Feb. 8, 1939. Chem. Abs., vol. 33, 1939, p. 5866.

Reactions are effected by moving the catalyst through the reaction zone and raising the temperature in the direction of movement so that the rate of reaction does not decrease to a substantial extent. The process is suitable for the dehydrogenation of hydrocarbons, the reduction of oxides of C, the incomplete combustion of hydrocarbons, the hydration of C_2H_2.

1242. ———. [Gaseous Catalytic Reactions.] French Patent 638,109, July 22, 1927. Chem. Abs., vol. 23, 1929, p. 247.

In catalytic reactions such as the synthesis of NH_3, the production of MeOH, and particularly the treatment of C by H_2 for the production of hydrocarbons, an irregular whirling movement is given to the contact materials by a current of gas entering the contact chamber.

1243. ———. [Gaseous Olefins.] French Patent 852,170, Jan. 25, 1940. Chem. Abs., vol. 36, 1942, p. 1945.

Gaseous olefins are obtained by decomposing normally liquid aliphatic hydrocarbons in vapor state

using O_2, the quantity of which is insufficient to burn the hydrocarbons completely. The operation is effected under reduced pressure at 750°–950°.

1244. ———. [Gaseous Olefins From Hydrogen and Carbon Oxides.] French Patent 660,560, July 12, 1929; appl. filed Sept. 18, 1928. Chem. Zentralb., 1930, I, p. 434; Chem. Abs., vol. 24, 1930, p. 127.

By using a catalyst of Fe and U oxide with a constant temperature of 360°–370° and a pressure of 120 atm. with a gas containing 2% CO_2, 23% CO, 71% H_2, 4% N_2, a yield of 3–4% C_2H_4, propylene, butylene, amylene, besides small amounts of C_2H_6 and C_3H_8, H_2O, and oil are obtained. No C was deposited on the catalyst over a period of 3 weeks.

1245. ———. [Halogenating Hydrocarbons.] French Patent 842,219, June 8, 1939. Chem. Abs., vol. 34, 1940, p. 5090.

Substances obtained for catalytic hydrogenation of CO, under normal or high pressure, or their dehydration products, or their polymerization products obtained after the hydrogenation, are treated with a halogen and a sulfurous, selenious or tellurious anhydride.

1246. ———. [Halosulfonylchlorides.] French Patent 52,993, no date. Kainer, p. 271. In addition to French Patent 865,251.

The reaction of French Patent 865,251 (abs. **1247**) and British Patent 516,214 (abs. **1359**) is carried out <0°, for instance at —20° to —30°.

1247. ———. [Halosulfonylchlorides.] French Patent 865,251, no date. Kainer, p. 271.

See British Patent 516,214 (abs. **1359**).

1248. ———. [Heat Control.] German Patent Appl. I 66,476, OZ 11,999, filed Feb. 8, 1940.

Converter is cooled by injecting the superheated product, instantaneous evaporation.

1249. ———. [Heat Removal.] French Patent 814,101, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 174.

Indirect heat exchange with wet steam.

See also British Patent 469,618 (abs. **1287**), French Patent 814,082 (abs. **1529**), German Patent 703,101 (abs. **2678**), and Italian Patent 346,769 (abs. **1541**).

1250. ———. [High Pressure Reactions.] French Patent 659,582, Aug. 28, 1928. Chem. Abs., vol. 23, 1929, p. 5253.

High-pressure reactions using high temperatures, particularly those operating in the presence of H_2, are carried out in double walled vessels, 1 or both walls being made of special steel such as V2A.

1251. ———. [Higher Alcohols.] German Patent 442,125, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 226.

1252. ———. [Higher Alcohols.] German Patent 442,840, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 226.

1253. ———. [Higher Alcohols.] German Patent 456,979, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 226.

1254. ———. Higher Alcohols From Products of Oxidation of Hydrocarbons. British Patent 352,537, Apr. 11, 1930. Chem. Abs., vol. 26, 1932, p. 3261.

Products obtained by the destructive oxidation of difficultly volatile hydrocarbon materials such as paraffin wax or paraffin oil are subjected to destructive hydrogenation under pressure, suitably at 100°–250° under pressures of 10–300 atm. in the presence of a Ni catalyst. Gives several examples with details of procedure.

1255. ———. [Hydrocarbon Synthesis.] Austrian Patent 160,901, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 174.

See United States Patent 2,248,099 (abs. **2055**).

1256. ———. Hydrocarbon Synthesis. British Patent 292,850, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 216.

Reaction gases are preheated.

1257. ———. Hydrocarbon Synthesis. British Patent 293,572, July 13, 1927. Chem. Abs., vol. 23, 1929, p. 1648.

Mixtures comprising C oxides and H_2 preferably under pressure at elevated temperatures, are passed over a catalyst containing Fe or Co, at a velocity less than that required for producing liquid hydrocarbons; olefinic gases may thus be formed. Examples are given of the use of Ni–Cr and Fe–Ag alloys as catalysts.

1258. ———. [Hydrocarbon Synthesis.] Netherlands Patent 47,123, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 174.

See United States Patent 2,248,099 (abs. **2055**).

1259. ———. [Hydrocarbon Synthesis Operation.] German Patent Appl. I 74,496, no date, (*Cl. 12 o–5.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 212.

CO and H_2 are reacted with olefins followed by hydrogenation in alternating operating catalyst zones.

1260. ———. Hydrocarbons. British Patent 449,274, June 24, 1936. Chem. Abs., vol. 30, 1936, p. 7835.

See French Patent 799, 058 (abs. **1272**).

1261. ———. Hydrocarbons. British Patent 457,934, Dec. 9, 1936. Chem. Abs., vol. 31, 1937, p. 2612.

In the production of solid paraffin hydrocarbons by thermal conversion of CO and H_2 at 1–50 atm. pressure, the catalyst is continuously passed through the reaction space, freed outside this space at least partly from hydrocarbons deposited thereon, and returned, if desired, after regeneration. Thus, it may be extracted with a suitable solvent, for example, middle oil, C_6H_6, pyridine, and treated at elevated temperature with H_2. Suitable catalysts are metals of group 8, for example, Fe, Ni, plus basic substances, for example, oxides, hydroxides, or carbonates of alkali or alkaline earth metals, if desired, together with other metals or metal oxides and carriers. Describes apparatus.

1262. ———. Hydrocarbons. British Patent 464,308, Apr. 15, 1937. Chem. Abs., vol. 31, 1937, p. 7243.

In the conversion of CO and H_2 into hydrocarbons in presence of a rigidly arranged catalyst, a liquid is caused to trickle over the catalyst while the formation of a body of liquid is avoided in the reaction space. The liquid is preferably a solvent for the reaction products, for example, alcohols, middle oils, heavy oils, paraffin oils, anthracene oils. The reaction products themselves may be used if liquid under the working conditions.

1263. ———. Hydrocarbons. British Patent 465,668, May 13, 1937. Chem. Abs., vol. 31, 1937, p. 7066.

Hydrocarbons, with or without oxygenated derivatives, are obtained by causing CO and H_2 to react in presence of a catalyst obtained by the reaction of previously fused Fe_3O_4 with a reducing gas at >300°. The catalyst may also contain compounds of Si, Ti, heavy metals, Ni, Co, and/or alkali metals. The reaction may be effected at 275°–425°.

1264. ———. Hydrocarbons. British Patent 468,434, June 29, 1937. Chem. Abs., vol. 32, 1938, p. 586.

Catalytic conversion of CO and H_2 into hydrocarbons and their O derivatives is effected in a liquid medium

consisting of oils obtained in a previous conversion under the same or similar conditions and containing at least 1%, usually 10–100%, of constituents that boil within the benzine range, which are vaporized under the prevailing conditions of temperature and pressure. The said medium may be prepared by leading the reaction products through a cooling zone; for example, a reflux condenser, so that the vapors are wholly or in part condensed and returned to the reaction zone. A foreign oil may be used for the commencement of the conversion, being gradually replaced by freshly formed reaction product. The invention includes working not only in liquid phase but in that state above the critical temperature of any or all the constituents of the medium in which the densities in the gaseous and liquid states show no appreciable difference. Temperatures may be 200°–420° and pressures >10, such as 50–250 atm. Lower pressures; that is 1 atm., may be used. Among examples Fe powder, obtained by the decomposition of Fe carbonyl, is mixed with Si powder, TiO_2, $KMnO_4$, and H_2O and fused in a stream of O_2, whereby it is oxidized to Fe_3O_4, the melt is cooled, comminuted, and treated with H_2 at 650°; this catalyst is arranged in layers in a tube, which is filled to above the top layer with an oil b. 65°–160°, a H_2O cooled reflux condenser at the upper end of the reaction zone, and a compensating vessel being provided; a CO–H_2 mixture is led upward into the tube in which the pressure is 100 atm. and temperature 360°–380°, the liquid products consisting of a hydrocarbon oil mainly b. 40°–300°; the gases leaving the tube contain paraffins and olefins:

See also French Patent 48,876 (abs. **1279**).

1265. ———. Hydrocarbons. British Patent 503,622, Apr. 12, 1939; appl. filed Oct. 13, 1937. Chem. Abs., vol. 33, 1939, p. 7528.

Products rich in unsaturated hydrocarbons are obtained by the catalytic conversion of CO and H_2 at atmospheric or slightly increased pressures with use of a gas that contains < 2 vol. of H_2 per vol. of CO, passing all the reaction participants and products through the whole reaction space and adding further H_2 during the reaction. In an example, purified water gas containing CO 42.7% and H_2 49.1% is led at 195° over a catalyst composed of Co and oxides of Th and Na applied to kieselguhr, gas containing 95% H_2 being added at 4 subsequent places in the reaction chamber in about equal proportions; the benzine fraction of the product b. up to 180° has an octane no. of 55.

1266. ———. [Hydrocarbons.] French Patent 49,333, Feb. 17, 1939. Chem. Abs., vol. 36, 1942, p. 2709.

Liquid hydrocarbons or O-containing derivatives of hydrocarbons from CO and H_2 are produced in presence of catalysts prepared by reducing compounds of metals belonging to the 8th group of the periodic system in presence of reducing gases at a temperature <500° and subjecting the compounds thus reduced to a thermal treatment at a temperature >500°, preferably >600°, in presence of nonoxidizing gases or in a vacuum to produce an agglutination of the catalysts.

See also French Patent 814,636 (abs. **1274**).

1267. ———. [Hydrocarbons.] French Patent 630,757, no date. Chem. Zentralb., 1931, I, p. 4177.

Liquid hydrocarbons at normal temperature are obtained by heating metal carbonyls (Fe, Co, Ni, Mo) in presence of H_2 or water gas or steam at a temperature (240°) effective to decompose the carbonyls with separation of metal.

See British Patent 270,705 (abs. **1325**).

1268. ———. [Hydrocarbons.] French Patent 648,946, Feb. 14, 1928. Chem. Abs., vol. 23, 1929, p. 2722.

See British Patent 293,572 (abs. **1257**).

1269. ———. [Hydrocarbons.] French Patent 660,133, Sept. 10, 1928. Chem. Abs., vol. 24, 1930, p. 127.

Hydrocarbons and other organic compounds are prepared by treating oxides of C with H_2 or gases containing it at a high temperature in the presence of catalysts that contain, besides metals of the 8th group of the periodic system, alkali metal compounds, the content of alkali metal (in the combined state) being <0.6% preferably 0.4–0.6 gm. per 100 gm. of metals of the 8th group. Gives examples.

See also French Patent 643,784 (abs. **1543**) and Czechoslovak Patent 33,469 (abs. **1296**).

1270. ———. [Hydrocarbons.] French Patent 664,420, Nov. 22, 1928. Chem. Abs., vol. 24, 1930, p. 860.

Liquid hydrocarbons with other organic compounds containing >1 C atom in the mol. are obtained by catalytic treatment of mixtures of CO and H_2, particularly water gas, by operating in a closed cycle and adding to the initial gases other gases such as CH_4 or allowing such other gases to accumulate so that the circulating gases contain at least 25%, preferably 40% or even more, of these gases.

1271. ———. [Hydrocarbons.] French Patent 680,619, Aug. 21, 1929. Chem. Abs., vol. 24, 1930, p. 3887.

In the preparation of hydrocarbons or their derivatives from tars, mineral oils, oxides of C, etc., by means of H_2 at a high temperature and pressure, fixation of substances of high molecular weight on the catalyst during the reaction is prevented by the presence of liquid solvents boiling at a high temperature, such as an anthracene or paraffin oil.

1272. ———. [Hydrocarbons.] French Patent 799,058, June 9, 1936. Chem. Abs., vol. 30, 1936, p. 7835.

Hydrocarbons of higher molecular weight than benzine, for example, paraffin waxes and lubricating oils, are obtained by the catalytic reaction of CO and H_2 at <375° and >20 atm. pressure in a hydrocarbon medium that remains liquid under the reaction conditions. The products may be separated from the medium by distillation or by extraction with SO_2 or other solvent. In an example, a mixture of CO with a large excess of H_2 is heated to 250° under 50 atm. pressure with anthracene oil in which a catalyst comprising ZnO, MgO,and Fe is suspended; a mixture of hydrocarbons, mainly paraffin wax and lubricating oil, is recovered from the product.

1273. ———. [Hydrocarbons.] French Patent 812,290, May 4, 1937. Chem. Abs., vol. 32, 1938, p. 950.

In making liquid and gaseous hydrocarbons and their derivatives from H_2 and CO, the reaction is carried out in the presence of a catalyst obtained by treating fused magnetic Fe oxide with a reducing gas, preferably H_2, at >300°. The catalyst may also contain Ti or Si or their compounds and activators, such as U, Mn, W, Cr, Mo, Cu, Ag, and their compounds or a small amount of Ni or Co or their compounds. Alkali or alkaline earth metal compounds may be added also.

1274. ———. [Hydrocarbons.] French Patent 814,636, June 26, 1937. Chem. Abs., vol. 32, 1938, p. 950.

Liquid, solid, and gaseous hydrocarbons and their derivatives are prepared by causing CO to react with H_2 in the presence of a catalyst prepared by decomposition of compounds of metals of the 8th group by heating to >500°, preferably >600°, but < the melting point of the compound or metal obtained and preferably in a current of H_2. Thus, Fe hydroxide containing 5% of $Al(OH)_3$ is reduced in this way and used.

1275. ———. [Hydrocarbons.] French Patent 814,853, July 1, 1937. Chem. Abs., vol. 32, 1938, p. 950.

CO and H_2 are passed through a catalytic mass at reaction temperature, the mass being sprayed by a fluid that is at least partly liquid under the conditions

considered and that dissolves the hydrocarbons formed. The products formed that remain liquid may be used for the spraying. Describes app.

See also British Patent 464,308 (abs. **1262**).

1276. ———. [Hydrocarbons.] French Patent 838,010, Feb. 24, 1939; appl. filed June 24, 1937. Chem. Abs., vol. 33, 1939, p. 7310.

Compounds relatively poor in H, for example, aromatic hydrocarbons, are obtained from compounds containing a higher content of H, for example, aliphatic hydrocarbons, by heating these, preferably at 350°–500°, in presence of mixtures of Al with a smaller proportion of a metal of group 6 or mixtures of compounds of these metals. A mixture of Al_2O_3 and Cr_2O_3, obtained by mixing ordinary hydrated alumina with H_2O-soluble Al_2O_3, heating to obtain active Al_2O_3, impregnating with chromic acid solution, drying and heating to 450°, may be used as catalyst for obtaining aromatic hydrocarbons from heptane. A mixture of Al_2O_3 and MoO_3 also may be used as catalyst.

1277. ———. [Hydrocarbons, Ammonia, and Methanol.] French Patent 684,181, Oct. 30, 1929. Chem. Abs., vol. 24, 1930, p. 5476.

Valuable hydrocarbons are made by hydrogenating under pressure coal, tars, and mineral oils with that fraction of the gases obtained by the distillation or gasification of coal or coke that is rich in H_2. That fraction of the gases rich in N_2 is used for the production of NH_3, and the waste gases resulting from the hydrogenation are used for the production of MeOH.

1278. ———. Hydrocarbons and Derivatives. Australian Patent 105,577, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgessell., Leipzig, 1950, p. 159; Chem. Zentralb., 1939, I, p. 5116.

See British Patent 503,247 (abs. **1289**), French Patent 48,876 (abs. **1279**), and United States Patent 2,207,581 (abs. **569**).

1279. ———. [Hydrocarbons and Derivatives.] French Patent 48,876, Sept. 19, 1938; appl. filed Oct. 2, 1937. Chem. Abs., vol. 33, 1939, p. 5001.

In the process of French Patent 812,598 (abs. **1305**), mixtures of CO and H_2 are used containing over 50% preferably 55–70%, by vol. of CO.

See also British Patent 468,434 (abs. **1264**).

1280. ———. [Hydrocarbons and Oxygen Derivatives.] French Patent 815,716, July 21, 1937. Chem. Abs., vol. 32, 1938, p. 1712.

See British Patent 469,959 (abs. **1281**).

1281. ———. Hydrocarbons and Oxygenated Compounds From Carbon Monoxide and Hydrogen. British Patent 469,959, Aug. 5, 1937. Chem. Abs., vol. 32, 1938, p. 1276.

Production of hydrocarbons and, if desired, derivatives containing O, such as MeOH or other alcohols, aldehydes, ketones, or carboxylic acids, from CO and H_2 is conducted with the addition of small amounts of volatile metal compounds that can be decomposed at up to 500°, either continuously or intermittently and during or after discontinuation of the conversion. The only other catalysts present may be etched metal apparatus surfaces, as described in British Patent 458,035 (abs. **1176**), in which case the volatile metal compounds serve to reactivate the etched surfaces. The reaction is conducted at increased pressures, especially >20 atm., and at 150°–500°. In an example, a mixture of CO 40% and H_2 60% is passed at 100 atm. and 330°–400° past the outside of a spiral Fe tube that has been previously etched with an aqueous solution of $Mg(NO_3)_2$, KNO_3, uranyl nitrate, and glacial AcOH, followed by treatment with H_2; the products are hydrocarbons, alcohols, esters, and acids, and the catalytic surface is reactivated by the repeated addition of small quantities; for example, 25–70 cc. of Fe carbonyl at intervals of several days; superheated steam is led through the interior of the pipe.

1282. ———. Hydrocarbons and Oxygenated Derivatives. British Patent 502,542, Mar. 20, 1939; appl. filed Sept. 20, 1937. Chem. Zentralb., 1940, I, p. 967; Chem. Abs., vol. 33, 1939, p. 7528.

Conversion of CO and H_2 into hydrocarbons of more than 1 C atom or O derivatives of hydrocarbons, for example, alcohols such as MeOH or iso-BuOH, ketones, aldehydes or acids, is effected in a liquid medium with a sintered metal of the Fe group as catalyst. The preparation of the catalysts is described in British Patents 474,448 (abs. **1288**), 490,090 (abs. **1168**) and 496,880 (abs. **1285**). The liquid medium may consist of liquid or fusible hydrocarbons. In an example, Fe powder obtained from the carbonyl is moistened with H_2O, pressed into pills, heated to 850° for 6 hr. in a current of H_2, and then charged into a vessel containing products of a prior conversion and consisting mainly of hydrocarbons b. 150°–350°; equal volumes of CO and H_2 are led upward through the vessel at 330° and 40 atm., the vapors pass to a separator at 100° where middle and heavy oils are condensed, enough being returned to maintain the liquid level; further cooling separates the benzines. The residual gas may be returned or caused to react in a 2d vessel after separation of CO_2 and of unsaturated hydrocarbons for conversion of polymer benzine.

See also French Patent 812,290 (abs. **1273**).

1283. ———. Hydrocarbons and Oxygenated Derivatives Thereof. British Patent 506,064, May 22, 1939; appl. filed Sept. 21, 1937. Chem. Abs., vol. 33, 1939, p. 9620.

Derivatives are prepared by reaction of CO and H_2 in the presence of a catalyst consisting wholly or mainly of a sintered metal of the Fe group to which is added an alkali compound that in aqueous solution has a neutral or acid reaction and is virtually undecomposed at up to 1,000°, such as, alkali halides KCl or KBr or NaCl or NaF, and phosphates such as NaH_2PO_4 or KH_2PO_4. Other activating substances, such as Al_2O_3, SiO_2 compounds of Cu, Ti, Mn, W. Mo, Cr. Th, Ce, Zr or other rare earth metals may be added in minor proportions. The products are mainly benzines, but middle and heavy oils, paraffin, gaseous hydrocarbons of more than 1 C atom, MeOH or higher alcohols, ketones, aldehydes, or acids are formed also. In an example, Fe powder obtained by the decomposition of $Fe(CO)_5$ is mixed with 5% of KCl and 5% of H_2O, heated, pressed into pills, and treated with H_2 for 4 hr. at 850°; a gas containing CO 35% and H_2 64% is converted at 330° and 15 atm., benzine being mainly formed.

1284. ———. [Hydrocarbons and Oxygen-Containing Derivatives.] Belgian Patent 427,233, no date.

See British Patent 496,880 (abs. **1285**).

1285. ———. Hydrocarbons and Oxygen-Containing Derivatives Thereof. British Patent 496,880, Dec. 5, 1938. Chem. Abs., vol. 33, 1939, p. 3389.

Hydrocarbons of more than 1 C atom and/or O-containing derivatives of hydrocarbons, for example, alcohols, ketones, esters, acids, and aldehydes, are obtained for bringing CO and H_2 into contact at a reacting temperature with a catalyst prepared, before the reaction, by reduction of a compound of an Fe group metal that is reducible to metal <500° with a reducing gas at <500° and treatment of the reduced substance in the absence of an oxidizing gas at such a temperature >500° but < the melting point and for such a time that at least a partial sintering occurs. In an example, precipitated $Fe(OH)_3$ mixed with $Al(OH)_3$ is reduced with H_2 at 450° and then heated for about 3 hr. at 850° with N_2; it is used for the conversion at

about 320° and 15 atm. of CO and H_2 in the ratio of 1 : 2 into mainly gaseous, liquid, and solid hydrocarbons.

See also British Patent 478,318 (abs. **1291**).

1286. ———. Hydrocarbons and Their Derivatives. British Patent 269,521, July 4, 1928; appl. filed Apr. 14, 1926. Chem. Age, vol. 17, 1927, p. 605; Chem. Abs., vol. 22, 1928, p. 1364.

H_2 and oxides of C are passed under pressures of 10–100 atm. or higher and at temperatures of 200°–600° over catalysts containing metal sulfide such as those of Co or Cu or Zn chromate or metal oxides that have been treated with H_2S. The apparatus should be free from Fe, especially the heated parts that come into contact with the reacting mixture. An Al-lined apparatus may be used.

1287. ———. Hydrocarbons and Their Oxygenated Derivatives. British Patent 469,618, July 29, 1937. Chem. Abs., vol. 32, 1938, p. 586.

In the conversion of oxides of C with H_2, particularly for the production of hydrocarbons or their oxygenated derivatives, wet steam is used as an indirect heat-exchange medium for regulating the temperature.

1288. ———. Hydrocarbons and Their Oxygen-Containing Derivatives. British Patent 474,448, Oct. 26, 1937. Chem. Abs., vol. 32, 1938, p. 3416.

In the thermal conversion of CO and H_2 into hydrocarbons having more than 1 C atom and/or their O-containing derivatives, the catalyst is prepared by adding to a previously precipitated reducible compound of a metal of the Fe group a compound of another metal that on heating yields an oxide not reducible by H_2<900°, and subsequently heating the mixture in a reducing gas to >500° so that a partial sintering of the catalyst takes place. The nonreducible ingredient may be a compound of an earth metal, for example, Al, Be, Mn, Zn, Th, Ce, or Zr. It may be added as a precipitate or an aqueous dispersion or solution, which last may be precipitated after admixture with the Fe metal compound. A 3d component, which is a compound forming a reducible metal oxide, for example $Cu(NO_3)_2$, may be incorporated in the mixture. In an example, moist precipitated $Fe(OH)_3$, is mixed with a suspension of $Al(OH)_3$, dried and reduced in H_2 at 850°.

1289. ———. Hydrocarbons and Their Oxygenated Derivatives. British Patent 503,247, Apr. 4, 1939. Chem. Abs., vol. 33, 1939, p. 7310.

See British Patent 468,434 (abs. **1264**) and French Patent 48,876 (abs. **1279**).

1290. ———. Hydrocarbons and Their Oxygenated Derivatives by Catalytic Hydrogenation of Carbonaceous Gases or Liquids. British Patent 328,586, Nov. 26, 1928. Chem. Abs., vol. 24, 1930, p. 5476.

In hydrogenations at elevated temperatures and under pressures >20 atm., deposition of substances of high molecular weight on the catalysts is prevented by adding a medium that is liquid under the working conditions and is inert to the reaction, such as anthracene oil. Catalysts are preferably used that are immune from S poisoning such as those comprising metals of the 6th group. Describes various details of procedure for production of alcohols.

1291. ———. Hydrocarbons and Their Oxygenated Derivatives From Carbon Monoxide and Hydrogen. British Patent 478,318, Jan. 14, 1938. Chem. Abs., vol. 32, 1938, p. 4606.

Hydrocarbons containing more than 2 C atoms or their liquid or solid O-containing derivatives, for example, alcohols, aldehydes, and acids, are obtained catalytically from a mixture of H_2, CO, and inert gas containing less H_2 than CO, the inert gas, which is essentially CO_2, comprising 40–90% of the mixture. Other inert gases, for example, CH_4, N_2, may be present. The process may be conducted at 150°–500°, preferably under increased pressure of 5–500 atm. or more. Preferred catalysts contain metals of the 8th group, particularly Fe.

See also French Patent 823,302, (abs. **1139**), and Italian Patent 351,714 (abs. **1528**).

1292. ———. [Hydrocarbons by Catalysis Under High Pressure.] French Patent 644,420, no date. Schmidt, J., Das Kohlenoxyd. Akad. Verlagsgesell., Leipzig, 1950, p. 216.
Addition to British Patent 266,405 (abs. **905**).

See also British Patent 313,467 (abs. **1593**).

1293. ———. [Hydrocarbons by Synthesis.] German Patent Appl. I 57,704, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 94.

Hydrocarbons are produced by the hydrogenation of CO in the presence of catalysts made in the described manner. Addition to German Patent Appl. I 53,767.

1294. ———. [Hydrocarbons by Synthesis.] German Patent Appl. I 57,907, filed May 5, 1937 (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 94.

Hydrocarbons are produced by converting CO with H_2 under the use of metals obtained by decomposition of carbonyls as catalysts. Addition to German Patent Appl. I 53,767.

1295. ———. Hydrocarbons from Carbon Monoxide and Hydrogen. British Patent 518,372, Feb. 26, 1940; appl. filed Aug. 22, 1938. Chem. Abs., vol. 35, 1941, p. 7687.

Method of effecting the synthesis of hydrocarbons with more than 1 C atom in the molecule comprises returning to the reaction space gases, which have already been subjected to the reaction. The volume of the gases returned is at least 20 times that of the fresh gas introduced in the same unit of time.

1296. ———. [Hydrocarbons From Carbon Monoxide and Hydrogen.] Czechoslovak Patent 33,469, Sept. 25, 1930; appl. filed, Dec. 12, 1928.

Catalysts are used that contain to each 100 parts of a metal of group VIII, 0.4–0.6 parts of alkali metal.

See also French Patent 660,133 (abs. **1269**).

1297. ———. [Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 49,424, Mar. 24, 1939. Chem. Abs., vol. 36, 1942, p. 2709.

See French Patent 814,636, (abs. **1274**), and British Patent 490,090 (abs. **1168**).

1298. ———. [Hydrocarbons From Carbon Monoxide and Hydrogen.] German Patent Appl. I 55,391, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 91.

Production of hydrocarbons from mixtures of CO and H_2 with a higher content of CO at temperatures up to 400° in the presence of Fe catalysts and at pressures of 50–500 atm. with introduction of a gas into the reactor containing over 20% CO_2, preferably >40%.

1299. ———. [Hydrocarbons From Carbon Monoxide and Hydrogen.] Italian Patent 345,471, Oct. 27, 1936.

See British Patent 468,434 (abs. **1264**) and French Patent 812,598 (abs. **1305**).

1300. ———. [Hydrocarbons From Carbon Monoxide and Hydrogen.] Italian Patent 345,513, Oct. 24, 1936.

See French Patent 812,290 (abs. **1273**) and British Patent 465,668 (abs. **1263**).

1301. ———. [Hydrocarbons From Carbon Monoxide and Hydrogen.] Italian Patent 345,671, Nov. 2, 1936.

See French Patent 814,636 (abs. **1274**).

1302. ———. Hydrocarbons From Carbon Monoxide and Hydrogen Catalysts. British Patent 473,932, Oct. 22, 1937; appl. filed Nov. 26, 1936. Chem. Abs., vol. 32, 1938, p. 2954.

Conversion of CO and H_2 into hydrocarbons or their O derivatives such as alcohols, is effected in the presence of a catalyst prepared, before the conversion, by thermal treatment of an Fe compound; for example, Fe_2O_3, $Fe(NO_3)_3$, $FeCO_3$, at >600° but below the melting or sublimation point of the compound or of the resulting Fe and by a treatment with reducing gases. The thermal treatment may be combined with the reducing treatment by effecting it in the presence of H_2 containing gases, or the Fe compound may be heated >600° in nonreducing gases, such as N_2 or air, and then treated with reducing gases at lower temperatures. The thermal treatment may be conducted in 1 or more stages at any pressure. Activating additions of Al_2O_3, $Al(OH)_3$, SiO_2, kieselguhr or compounds of Cu, Ti, Mn, W, Mo, Co, Th, Ce, Zr and other rare earths may be used. In an example, CO and H_2 in the ratio 1:2 is led at 220°–320° and 12 atm. over a catalyst formed by heating precipitated $Fe(OH)_3$ plus 5% of $Al(OH)_3$ to 850° in a current of H_2. Gaseous, liquid, and solid hydrocarbons are mainly formed.

1303. ———. Hydrocarbons From Carbon Oxides and Hydrogen. British Patent 322,284, Dec. 27, 1929; appl. filed Oct. 11, 1928. Chem. Abs., vol. 24, 1930, p. 2874.

Low-boiling-point and unsaturated hydrocarbons are obtained by treating gaseous mixtures of C oxides and H_2 at elevated temperature and pressure with catalysts that contain metals of the 8th group of the periodic system, together with alkali metal compounds and small quantities of S, Se, or Te in a free or combined state. Liquid products of olefinic character thus obtained can be used to prevent "knocking" in motor fuels for the manufacture of lubricating and insulating oils by condensation with use of $AlCl_3$, B fluoride, or the like, or for the production of benzene hydrocarbons, alcohols, glycols. Gives examples with details of procedure.

1304. ———. [Hydrocarbons From Oxides of Carbon and Hydrogen.] French Patent 636,882, July 1, 1927. Chem. Abs., vol. 23, 1929, p. 604.

Contact chamber is combined with a high-pressure steam generator so that heat is transmitted between them.

1305. ———. [Hydrocarbons or Derivatives.] French Patent 812,598, May 12, 1937. Chem. Abs., vol. 32, 1938, p. 950.

Oxides of C are caused to react with H_2 at a high temperature in the presence of catalysts, the reaction being carried out in a liquid medium composed of liquid products obtained by causing the starting materials to react under identical conditions, and containing appreciable amounts of constituents which are gaseous or vaporous under the conditions of temperature and pressure used. Describes apparatus.

1306. ———. [Hydrogen and Carbon Monoxide.] French Patent 644,147, Nov. 18, 1927. Chem. Abs., vol. 23, 1929, p. 1728.

Yield of H_2 and CO by the catalytic treatment of hydrocarbons is increased by removing organic as well as inorganic S compounds from the gases before treatment, for example, by passing them over a metallic mass, which will fix the S compounds or convert them into H_2S. In the conversion of the hydrocarbons elongated catalyst chambers made of Cr or Ni steel or alloys of Ni such as Cr–Ni are used, the walls of which are heated to <1,000°.

1307. ———. [Hydrogen and Carbon Monoxide.] French Patent 649,296, Nov. 14, 1927. Chem. Abs., vol. 23, 1929, p. 3059.

Mixture of H_2 and CO is obtained by introducing gaseous hydrocarbons or gases containing them tangentially into a vessel and adding O or gases containing it, preferably also tangentially to the circulating gases with a view to their partial combustion.

1308. ———. Hydrogen and Carbon Monoxide From Methane. British Patent 336,635, Apr. 8, 1929. Chem. Abs., vol. 25, 1931, p. 1956.

Gaseous hydrocarbons such as CH_4 or gas mixtures containing it, other than coke oven gases or other gases containing liquid hydrocarbons, are passed with H_2O vapor and, if desired, with further addition of air or O_2, through a water gas producer in which coke or other carbonaceous fuel is undergoing gasification, which is carried out without addition of CO_2, the coke having a temperature of at least 800°–1,000°. As starting material a natural gas or waste gases from NH_3 synthesis, hydrogenation of coal, and cracking may be used. Describes various details and modifications of procedure.

See also German Patent 507,917 (abs. **1310**).

1309. ———. Hydrogen and Carbon Monoxide From Methane. British Patent 336,944, Apr. 8, 1929. Chem. Abs., vol. 25, 1931, p. 1956.

Describes various details of a process generally similar to that of British Patent 336,635 (abs. **1308**).

1310. ———. [Hydrogen-Carbon Monoxide Mixtures.] German Patent 507,917, Dec. 5, 1926. Chem. Abs., vol. 25, 1931, p. 783.

A H_2–CO mixture free from, or containing, N_2 is obtained by the partial combustion of natural gaseous hydrocarbons with O_2 or air. Describes the apparatus in which the hydrocarbons are introduced tangentially into a reaction chamber through a number of inlets.

See also British Patent 300,328 (abs. **1236**).

1311. ———. Hydrogenation of Acetylene Compounds. British Patent 497,427, Dec. 16, 1938. Chem. Abs., vol. 33, 1939, p. 3810.

Compounds having acetylenic linkages are converted into compounds containing olefinic linkages by treatment with an aqueous suspension of Zn dust that has been activated by Cu and Cd. The Zn dust may be treated simultaneously or in turn with solutions of Cu and Cd salts; or a powdered alloy containing Zn, Cu, and Cd, with or without other metals, may be used. The reaction may be effected in the presence of a solvent and/or a dispersing agent. Among examples, Zn dust is treated in turn with solutions of $CuSO_4$ and $CdCl_2$, suspended in H_2O with the aid of the Na salt of oleic acid tauride and vinylacetylene passed through the suspension to produce butadiene.

1312. ———. [Hydrogenation Plant.] German Patent Appl. I 64,482, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 116.

Catalytic hydrogenation of CO is carried out in a plant consisting of several furnaces, with condensation of the vapors in each unit in separate condensers and with heat exchange of the condensate with a liquid in a common secondary boiler.

1313. ———. [Hydrogenation Reactions.] French Patent 697,539, June 17, 1930. Chem. Abs., vol. 25, 1931, p. 3153.

In reactions using H_2 at a high temperature, particularly in the hydrogenation of coal, tars, oils, the reaction vessels are protected against the destructive action of the H_2 by covering their surfaces with an alloy of Cu and Zn. Other metals such as Mn, Ni, Fe, Co, Al,

or Ag may be incorporated to increase the mechanical resistance.

See also British Patent 341,153 (abs. **1141**).

1314. ———. Hydrogenizing Coal, Oils, Tars. British Patent 249,155, Mar. 14, 1925. Chem. Abs., vol. 21, 1927, p. 1002.

In producing products such as oils by the action of reducing gases at high temperature and pressure upon coal, tars, mineral oils, and like materials, apparatus in contact with the gases is made of metal not reacting with CO, for example, Cu, Ag, Al or its alloys, Cr, Mn, V, U steels or corresponding alloys of Ni or Co containing Mn, Ti, Cr, W, V, or Mo. Sn, Zn, Cd, Pb, and their alloys may be used for the cooler portions of the apparatus.

1315. ———. [Improving Synthetic Fatty Acids.] German Patent Appl. I 72,249, OZ 13,426, filed May 11, 1942 (*Cl. IV a–23 d*). FIAT Reel 167, frames 6,474–6,476; PB 75,690.

Odor of fatty acids produced by the oxidation of nonaromatic hydrocarbons and intended for the manufacture of soap is improved by treating either or both the acid and the soap therefrom with formaldehyde or with such compounds as split off formaldehyde. Example: 5,000 parts of a soap and fatty acid mixture obtained by the oxidation of a brown coal paraffin is heated to 90°–100° and stirred slowly with 100 parts of paraformaldehyde. Stirring is continued until the odor of formaldehyde is no longer noticeable.

1316. ———. [Improving Synthetic Hydrocarbons.] German Patent Appl. I 73,210, no date (*Cl. IV d–23 b*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 760.

Products of the reduction of CO by H_2, which contain oxygenated compounds beside hydrocarbons, are improved by treatment with bisulfite solutions.

1317. ———. [Improving the Odor of Synthetic Fatty Acids.] German Patent Appl. I 75,662, OZ 14,356, filed Aug. 9, 1943 (*Cl. IV a–23 d*). FIAT Reel 170, frames 9,406–9,407; PB 64,246.

Odor of synthetic fatty acids can be improved by heating the crude acid obtained by the oxidation of nonaromatic hydrocarbons to 200°–250° for a short time under such pressure conditions (beginning with about 100 mm. and gradually decreasing it) that no appreciable amount of the fatty acids distill off. The fatty acids are then subjected in known manner to distillation under reduced pressure.

1318. ———. Incomplete Oxidation of Saturated Hydrocarbons. British Patent 265,234, Jan. 29, 1926. Chem. Abs., vol. 22, 1928, p. 243.

Gaseous or vaporous hydrocarbons, particularly saturated hydrocarbons such as CH_4, are subjected to incomplete combustion; for example, as a surface combustion in the presence of porous and refractory ceramic material, with pure O_2 or a gas containing at least 50% O_2, at temperatures above 850°, which may exceed 1,000°, to obtain unsaturated hydrocarbons such as C_2H_2 and its polymerization products and various other compounds. The C_2H_2 may be converted directly into other products, such as AcH or HOAc. The yield of C_2H_2 may be increased by heating the products to about 1,200° in an electric furnace.

1319. ———. [Iron Catalyst for the Synthesis Reaction.] German Patent Appl. I 70,230, filed Aug. 9, 1941; OZ 12,937 (*Cl. IV d–12 o*). FIAT Reel 172, frame 240; PB 25,616. Bureau of Mines Transl. T–433, January 1948.

Fe–Cu–Al salt solution is precipitated slowly over a period of 48 hr. by means of potash solution. The Fe precipitate is dried at 110° and reduced at 250° and ordinary pressure with a gas mixture consisting of 33% CO to 66% H_2 and at a rate of 1,000–5,000 l. per l. of catalyst per hr. After reduction, synthesis takes place at 193°, yielding 187 gm. of liquid and solid products, with 55% of the total product consisting of paraffin b.>320°. By carrying out the reduction under 7 atm. pressure, synthesis at 205° produces per $m.^3$ of reacting gas 175 gm. of liquid and solid products containing 70% paraffin.

1320. ———. [Iron Catalysts.] Italian Patent 383,206, May 31, 1940. Chem. Zentralb., 1942, I, p. 2914.

Catalysts suitable for the conversion of CO and H_2 to hydrocarbons and alcohol are made by treating Fe or metals of the Fe group, after mixing with activating substances, with H_2O vapor containing H_2 at high temperatures >600° and then reduced. Nascent H_2, produced by passing H_2O vapor over red-hot Fe, is especially suitable for use.

1321. ———. Iron for Catalyzing Ammonia Synthesis. British Patent 267,554, Mar. 13, 1926. Chem. Abs., vol. 22, 1928, p. 1221.

Fe obtained by decomposition of Fe carbonyl may be mixed with a small proportion of Al_2O_3, MgO, or ZrO_2 and a trace of KNO_3 and the mixture melted in a current of O_2 and the granular product reduced with H_2.

1322. ———. [Leather Treating Agent.] German Patent Appl. I 77,311, OZ 14,729, filed May 3, 1944 (*Cl. IV d–28 a*). FIAT Reel 171, frames 10,285–10,287; PB 25,615; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 43, 1949, p. 22.

In preparing leather treating agents, mixtures of solid nonaromatic hydrocarbons or nonaromatic hydrocarbons solidifying from melts in solid form and liquid nonaromatic hydrocarbons b.>200° are incompletely oxidized. The raw materials may consist of the gatsch residues from petroleum distillation or mixtures obtained by hydrogenating CO. Example: Such a material, containing, besides solid paraffinic and naphthenic hydrocarbons, about 22% liquid nonaromatic lubricating constituents, is oxidized at 110°–116° with air in the presence of Mn stearate up to a specific gravity of 0.875–0.890 at 70°. The melting point is about 45°. The products are melted with whale oil or chlorinated kogasin and used to treat leather.

1323. ———. Liquid Hydrocarbons. British Patent 519,613, Apr. 1, 1940. Chem. Abs., vol. 36, 1942, p. 251.

Formation of undesirable hydrocarbons of low molecular weight in the treatment of liquid CO reduction products (from cracking or destructive hydrogenation) can be considerably reduced by adding cyclic hydrocarbons boiling within the range of middle oils, which under the reaction conditions are at least partly vaporous. Naphthalene and its homologs or middle oils derived from the destructive hydrogenation of mineral coal are the most suitable addition products.

1324. ———. [Liquid Hydrocarbons.] French Patent 839,874, Apr. 13, 1939. Chem. Abs., vol. 33, 1939, p. 7814.

Liquid hydrocarbons are prepared by polymerizing gaseous olefins using catalysts of the Friedel-Crafts type, using gases that contain more than 30%, preferably 40%, of gaseous olefins and in which the olefins are composed for the greater part of butylenes and/or amylenes, and subjecting the products to a hydrogenation and a treatment with superheated steam in the presence of caustic alkalies.

1325. ———. Liquid Hydrocarbons From Gases Containing Hydrogen. British Patent 270,705, May 10, 1926. Chem. Age, vol. 17, 1927, p. 64; Chem. Abs., vol. 22, 1928, p. 1672.

Water gas or other gas containing H_2 is heated in the presence of metal carbonyls, such as those of Fe, Co, Ni, and Mo, to a temperature, suitably about 240°

with H_2 and Fe carbonyl, sufficient to decompose the carbonyl. Substances such as NH_3 may be added to facilitate the process. The liberated metal may be separated in dust chambers and the issuing gas treated with active silica to adsorb hydrocarbons.

1326. ———. Liquid Products From Carbonaceous Materials. British Patent 257,256, Aug. 20, 1925. Chem. Zentralb., 1927, I, p. 548; Chem. Abs., vol. 21, 1927, p. 3123.

Carbonaceous materials such as coal, lignite, peat, wood, animal or vegetable matter, tars, distillation residues, mineral oils, asphalts, bitumen schist oils, or resinous substances are treated with gases containing H_2 and C oxides or H_2O vapor under high pressure and temperature in the presence of catalysts, capable of forming MeOH by catalytic hydrogenation of C oxides. Benzines, other liquid hydrocarbons, and MeOH and higher O-containing organic compounds are obtained. Vanadic acid, Mn oxide, U oxide, titanic acid, chromic acid, ZnO or mixtures of ZnO with the other oxides or Pb oxide may be used as catalysts.

1327. ———. [Lubricants.] Belgian Patent 428,938, July 1, 1938; appl. filed in Germany July 5, 1937. Chem. Zentralb., 1940, I, p. 326.

Inorganic halogenides with acid reaction are used for the polymerization of compounds with double bonds to products of high molecular weight, together with cracked or dehydrogenated products of synthetic hydrocarbons.

1328. ———. [Lubricants.] German Patent Appl. I 70,108, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 156.

Lubricants are obtained by treating olefinic hydrocarbon mixtures with selective solvents through polymerization of the H_2-rich fractions obtained thereby using catalysts from the Friedel-Crafts reaction such as $AlCl_3$ or BF_3. The conversion products of CO and H_2 b. 250°–450° are passed over H_2O-splitting catalysts, treated with solvents, and polymerized.

1329. ———. [Lubricants.] Italian Patent 363,468, no date. Kainer, p. 255.

Unsaturated hydrocarbons occurring in the hydrogenation of CO can be polymerized together with other compounds showing a polymerizable double bond such as isobutylene or styrene. In this mixed polymerization in the presence of inorganic halogenides viscose compounds are obtained, which can be added to lubricating oils.

1330. ———. [Lubricants.] Italian Patent 381,194, Mar. 5, 1940. Chem. Zentralb., 1942, I, p. 2737.

Relatively light motor lubricants, for example, viscosity 11° E at 38° and 1.79° E at 99°, are blended with highly viscous products, which were obtained by polymerization of propylene or of mixtures of propylene and butylene, or better of fractions of hydrocarbons synthesized from CO and H_2 over Fe catalysts. Lubricants are thus obtained having a viscosity of at least 6° E at 99°.

1331. ———. Lubricating Oils. British Patent 485,478, May 20, 1938. Chem. Abs., vol. 32, 1938, p. 8129.

See French Patent 825,839 (abs. **1333**).

1332. ———. Lubricating Oils. British Patent 494,657, Oct. 28, 1938. Chem. Abs., vol. 33, 1939, p. 3137.

Lubricating oils are produced by polymerizing or condensing liquid or solid unsaturated hydrocarbons of the aliphatic, aromatic, and heterocyclic series by the aid of $AlCl_3$ in reaction vessels constructed of materials that do not exert an unfavorable catalytic influence on the reaction. Vessels of Cr-coated Fe, Cr, Cr-alloyed steels, or Cr–Ni-alloyed steels are preferred. $AlCl_3$ containing $< 5\%$ of unsublimable residue is also preferred.

1333. ———. [Lubricating Oils.] French Patent 825,839, Mar. 15, 1938. Chem. Abs., vol. 32, 1938, p. 6854.

Hydrocarbons are treated with silent electrical discharges, particularly high-frequency discharges, the hydrocarbons being composed of a mixture of pure hydrocarbons of a paraffin nature, b. 170°–250°, such as can be extracted from mineral oils of a paraffin basis or pressure hydrogenation products or products obtained by treating oxides of C with H_2.

1334. ———. [Lubricating Oils.] French Patent 866,256, July 21, 1941; appl. filed May 15, 1940. Chem. Zentralb., 1942, II, p. 126.

Example: A hydrocarbon mixture from the hydrogenation of CO containing 12–14 C atoms in the molecule is transformed into sulfochloride by treatment with Cl_2 and SO_2 and still contains 35% of unchanged hydrocarbons. The sulfamides produced with NH_3, after extraction in H_2O-soluble material such as NH_4Cl with high-molecular alcohols or H_2O, serves as lubricating oil.

1335. ———. [Making Solid Shaped Catalysts From Finely-Ground Material.] German Patent Appl. I 70,640, OZ 13043, filed Oct. 15, 1941 (*Cl. 12 g*). FIAT Reel 172, frame 255; PB 25,616; TOM Reel 20, item 161, frames 2,583–2,587.

Part of the (10–20%) is ground to colloidal fineness and mixed in moist condition with the less finely ground material (80% passing through a sieve with 10,000-mesh per $cm.^2$), and the mixture formed and heated. Such catalysts find use in the conversion of carbonaceous materials, as in the refining and aromatizing pressure hydrogenation of coal and the like, and in the synthesis of hydrocarbons from CO and H_2.

1336. ———. [Metal for Apparatus Not Attacked by Carbon Monoxide.] Austrian Patent 112,630, no date.

See British Patent 277,273 (abs. **1224**).

1337. ———. Methanol. British Patent 500,745, Feb. 15, 1939. Chem. Abs., vol. 33, 1939, p. 5869.

Synthetic MeOH is purified by treatment with a small quantity of chromic acid, which may be added in aqueous solution at a point in a distillation column at which the MeOH has a considerable H_2O content.

1338. ———. [Methanol.] French Patent 652,898, Apr. 16, 1928. Chem. Abs., vol. 23, 1929, p. 3716.

MeOH is produced from CO and H_2 at 100°–250° using catalysts having a basis of particularly active Cu. The Cu may contain oxides of metals from the 2d to the 7th group of the periodic system, precipitated from aqueous solutions of salts of the metals. In an example, a mixture of CuO and MgO obtained by precipitation at 20° of 2 mols. of $Cu(NO_3)_2$ and 1 mol. of $Mg(NO_3)_2$ by dilute aqueous NaOH, with washing and drying up to 250°, is reduced for 30 hr. by a mixture of N_2 and H_2 containing 5% of H_2 at 100°–250°. If a mixture of CO and H_2 containing 33% H_2 is directed on to this catalyst at 150°, a good yield of MeOH is obtained containing only traces of compounds reacting with Br.

1339. ———. [Methanol.] French Patent 791,729, Dec. 16, 1935. Chem. Abs., vol. 30, 1936, p. 4180.

Oily constituents in crude MeOH are removed by introducing the crude MeOH and H_2O into a rapidly turning centrifuge and, after an intimate mixture has been effected, separating the mixture into an oily layer and a MeOH layer.

See also United States Patent 2,115,553.

1340. ———. [Methanol and Other Oxygen-Containing Compounds.] French Patent 606,381, Nov. 19, 1925. Chem. Zentralb., 1928, I, p. 584.

See British Patent 266,410 (abs. **96**).

1341. ———. Methanol Synthesis. British Patent 308,181, Sept. 19, 1927. Chem. Abs., vol. 24, 1930, p. 130.

Catalytic hydrogenation of oxides of C is effected at ordinary or slightly raised pressure and at relatively low temperatures, suitably about 100°–250°, by using catalysts comprising Cu and 1 or more oxides of a metal of groups 2–7, obtained by precipitating aqueous solutions of the metal salts with alkalies at moderate temperatures, suitably <30°, and reducing the washed precipitate with H_2, CO, or their mixtures with inert gases. Gives various details and examples.

1342. ———. [Methanol Synthesis.] French Patent 612,505, Mar. 9, 1926. Chem. Zentralb., 1928, I, p. 584.

See British Patent 275,284 (abs. **1127**).

1343. ———. [Methanol Synthesis.] German Patent 600,625, no date. Schmidt, J., Das Kohlenoxyd. Akad. Verlagsgesell., Leipzig, 1950, p. 219.

See United States Patent 2,083,125 (abs. **3257**).

1344. ———. [Methanol Synthesis.] Italian Patent 334,877, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 219.

See United States Patent 2,115,553 (abs. **803**).

1345. ———. [Methanol Synthesis.] Italian Patent 376,947, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 227.

Raw product is extracted by addition of salt (pentane+NaCl). A very pure MeOH and H_2O-free isobutyl alcohol are obtained.

1346. ———. [Methanol Synthesis.] Netherlands Patent 34,085, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 219.

See United States Patent 2,059,495 (abs. **3352**).

1347. ———. Method for Converting Carbon Monoxide With Hydrogen. German Patent Appl. —, OZ 11,499, filed Apr. 28, 1939. TOM Reel 17, item 32, frames 848–854; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, chap. 98, 1948, p. 71.

In removing the heat formed in the catalytic conversion of CO with H_2 to hydrocarbons through direct heat exchange with a vaporizing cooling liquid, the vapor formed from the cooling liquid of the converter is condensed in a closed system, and the condensate is allowed to flow back into the cooling zone. In carrying out the reaction in several converters, the vapor formed in the cooling zone of each converter, after condensation in a special closed system, is returned again to this same zone, and the condensation in the individual closed systems is performed by heat exchange with a common secondary vaporizer. The temperature in the cooling zones of the converters is regulated by means of the vapor pressure in the condensation apparatus, preferably through automatic or manually operated valves in the lines between the cooling zones and the condensing apparatus. The method described is particularly advantageous if a liquid other than H_2O, diphenyl oxide, is used. Shows a sketch of the apparatus.

1348. ———. [Method for Producing Nitrogen-Free Synthesis Gas of Uniform Composition in Metallurgical Smelting Furnaces.] German Patent Appl. —, OZ 14,093, filed Mar. 22, 1943. TOM Reel 17, item 28, frames 636–639; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 3, chap. 111, 1948, p. 15.

N_2-free synthesis gas of uniform composition can be produced in a blast furnace or other metallurgical smelting furnace by the use of O_2 and other gasifying agents such as steam by preheating these gases together in a regenerator to 700°–1,400°, whereby the amount of O_2 during the preheating period is increased in about the same degree as the temperature of the regenerator decreases. The additional amount of O_2 necessary for equalizing the temperature change in the regenerator is about 5–10% of the total amount of O_2 used.

1349. ———. [Method for Production of Ammonia Synthesis Gas.] German Patent Appl. —, OZ 14,396, filed Sept. 10, 1943. TOM Reel 65, frames 119–127; Bureau of Mines Transl. T–188, 1946, 6 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 5, chap. 151, 1949, p. 20.

Residual gas from the Fischer-Tropsch process is cracked in presence of steam and/or O_2 or air at high temperatures and preferably in presence of catalysts such as Co–MgO–kieselguhr or Ni–Mg–kaolin, and the CO present is converted in the usual way with steam.

1350. ———. [Method for Reducing Powdered Catalysts.] German Patent Appl. I 72,695, OZ 13,542, filed July 10, 1942 (*Cl. IV b–12 g*). FIAT Reel 168, frames 6,870–6,875; PB 68,423; TOM Reel 134, item VII–8, 5 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 3, chap. 122, 1948, p. 52.

Re or Co catalysts in powdered form are reduced by being subjected, while in a suspended state in a closed and heated vessel, to a reducing gas such as H_2. Shows apparatus.

1351. ———. [Method of Separating Carboxylic Acids.] German Patent Appl. I 75,672, OZ 14,357, filed Aug. 9, 1943 (*Cl. IV d–12 o*). Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, chap. 20, 1948, p. 48.

In the separation of carboxylic acids the mixtures are continuously esterified, the esters separated from one another, suitably by fractional distillation, and then saponified.

1352. ———. Methyl Alcohol. British Patent 454,428, Sept. 29, 1936. Chem. Abs., vol. 31, 1937, p. 1045.

Interior of apparatus for reactions between CO and H_2, for example, for producing MeOH, is furnished with a coating of Zn or Cd or their alloys, produced by diffusion. The coating may be effected by subjecting the metal surface, for example, Fe, Fe alloy, to the action or Zn or Cd vapor, or it may be dipped in or sprayed with the molten metal and then heated to >500° to effect the diffusion.

1353. ———. [Methyl Alcohol.] German Patent Appl. B 108,556, no date (*Cl. 12 o–5*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 2.

MeOH and other O-containing organic compounds, such as alcohols, aldehydes and acids, are produced by the catalytic hydrogenation of the oxides of C under pressure. The catalysts contain metal oxides not reducible to the metals. Fe, Ni, and Co should not be present or only in small amounts.

1354. ———. Motor Fuels. British Patent 448,690, June 8, 1936. Chem. Abs., vol. 30, 1936, p. 7837.

For the production of nonknocking motor fuels, the mixture of isobutyl and higher alcohols obtained by the catalytic treatment of CO and H_2, such as described in British Patent 238,319 (abs. **75**), is freed from MeOH, converted into olefins, for example, by catalytic treatment with Al_2O_3 at 300°, and the mixed olefins, as a whole or after separation into 2 or more fractions, are at least in part polymerized. Thus, diisobutylene may be obtained by treating isobutylene with H_2SO_4 of 50–60% concentration, as described in British Patent 322,102, and triisobutylene by means of more concentrated acid, such as 70% and dimers and trimers of isoamylene, may be obtained similarly. When the separate fractions are polymerized, the polymers may be mixed with each other or with other fuels. Other antiknock agents as well as MeOH, higher alcohols from the MeOH synthesis, dyes, and substances that impart odor, may be added. In an example a mixture of CO and H_2 is passed at 200 atm. and 450°–500°

through a Cu-lined apparatus containing a catalyst prepared by adding ZnO to fused $K_2CR_2O_7$ and reducing with H_2. The reaction product is freed from MeOH and H_2O and converted to olefins, as described above, and the mixed olefins are treated with, for example, 55% H_2SO_4 at 100° to polymerize the lower olefins, particularly the isobutylene, to dimers and trimers or with 70% acid, which also polymerizes hexylene and heptylene to dimers. The products may be wholly or partly hydrogenated.

1355. ———. Motor Fuels. British Patent 454,389, Sept. 30, 1936. Chem. Abs., vol. 31, 1937, p. 1194.

Nonknocking motor fuels are made from the hydrocarbons formed by the catalytic conversion of CO with H_2 by treating the low-boiling constituents thereof or their fractions rich in olefins, preferably after separation of the higher boiling constituents, at an elevated temperature; for example, 20°–250°, with condensing agents under such conditions of time, temperature, and activity of catalyst that hydrocarbons boiling higher than, but not substantially above, the end boiling point of benzine are formed. In an example, a mixture of CO and H_2 is led at 190° over a catalyst consisting of Co, Mn, and kieselguhr, the product is cooled to remove constituents boiling >180°, the remaining gaseous mixture is compressed at 3, 8, and 24 atm., and the 2 latter fractions are treated at 235° with bleaching earth impregnated with H_3PO_4.

1356. ———. [Motor Fuels.] French Patent 790,873, Nov. 28, 1935. Chem. Abs., vol. 30, 1936, p. 3206.

Fuels stable to self-ignition are prepared by subjecting a mixture of CO and H_2 to a heat treatment under pressure under such conditions that besides MeOH there is formed principally iso-BuOH and other higher alcohols, removing the MeOH, submitting the higher alcohols to elimination of H_2O, and polymerizing wholly or in part the isoolefins thus obtained to form their di- or tri-isoolefins. The higher alcohols may be separated by fractionation before elimination of H_2O, in which case the polymers obtained are mixed. The products obtained may be completely or partly hydrogenated. In an example a temperature of 450°–500° and a pressure of 200 atm. is used with a catalyst obtained by introducing ZnO into $K_2Cr_2O_7$ and reducing by H_2.

1357. ———. [Motor Fuels.] German Patent 564,045, July 3, 1923. Chem. Abs., vol. 27, 1933, p. 1139.

Use is made of the liquid oxygenated products obtained from H_2 and oxides of C, as described in British Patent 238,319 (abs. **75**). The products may be used in admixture with MeOH or other fuel.

1358. ———. Olefins. British Patent 507,567, June 13, 1939. Chem. Abs., vol. 34, 1940, p. 452.

Gaseous olefins are obtained from the products of the catalytic hydrogenation of CO, the constituents of which contain more than 1 C atom and may or may not contain O, by leading them at elevated temperature with H_2 over a hydrogenation catalyst and cracking and/or dehydrogenating the resulting hydrocarbons. The initial products may be led with H_2 at 180°–200° and ordinary or elevated pressure over metals of groups 6–8 or their compounds; for example, Ni on carriers. The subsequent cracking is effected in known manner; that is, at >700°, with use of apparatus that inhibits C deposition, such as comprising coatings of Si or Ti or Cr steels, as described in British Patents 403,647 and 469,101. The products may be separated; liquid products are returned to the hydrogenation or constituents boiling at 80°–120°, mainly aromatic hydrocarbons, are removed. Gaseous products may be treated to remove acetylenic compounds, olefins then being separated with ammoniacal cuprous salts. C_2H_4 may be separated by pressure distillation and the higher olefins hydrogenated, as described in British Patent 506,832 (abs. **1234**), and wholly or in part subjected to cracking or dehydrogenation. In an example, an oil obtained from CO and H_2 is hydrogenated at 200° and 180 atm. with use of a Ni–Al catalyst and led with cracking gas through a packed tube of Cr steel at 750°, a gas containing C_2H_4, 35%; higher olefins, 20%; H_2, 10%; CH_4, 30%; CH_4 homologs, 5% and an oil containing C_6H_6 hydrocarbons being obtained.

1359. ———. Organic Halo Sulfonyl Chlorides. British Patent 516,214, Dec. 27, 1939. Chem. Abs., vol. 35, 1941, p. 5911.

These are obtained by causing mixtures of SO_2 and Cl to act in liquid phase on halo hydrocarbons containing in the molecule at least 1 C atom to which is attached 1 H atom but no halogen atom, in presence of short-wave irradiations. As initial materials are used 1– or 2–chloropropane, 1– or 2–chlorobutane and its isomers, 1,2–dichlorobutane, dichlorododecane, bromooctadecane, cyclohexyl chloride, and other cyclic halo hydrocarbons; also hydrocarbons from CO hydrogenation.

1360. ———. [Organic Oxygen Compounds.] French Patent 671,241, Oct. 23, 1928. Chem. Abs., vol. 24, 1930, p. 2137.

Organic O compounds are prepared by the action on aliphatic or hydroaromatic hydrocarbons or their derivatives of CO under pressure in the presence of catalysts such as $AlCl_3$, $AlBr_3$, $ZnCl_2$. Gives several examples.

1361. ———. [Organic Sulfur Compounds.] Belgian Patent 450,757, June 1943. Chem. Abs., vol. 42, 1948, p. 201.

Light yellow or colorless sulfonates are obtained by saponification of sulfonyl chlorides obtained by sulfochlorination of the products of the catalytic hydrogenation of C oxides. Saponification is carried out in the presence of, or is followed by the addition of reducing agents.

1362. ———. [Organic Sulfur Compounds.] Belgian Patent 450,758, June 1943. Chem. Abs., vol. 42, 1948, p. 201.

Mixtures obtained by the action of halogen and SO_2 on saturated paraffin hydrocarbons are treated under reduced pressure with superheated steam.

1363. ———. [Organic Sulfuric Acid Derivatives.] German Patent Appl. I 66,084, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 120.

High-molecular, unsaturated hydrocarbons obtained from the hydrogenation of CO are treated with sulfonating agents.

1364. ———. [Organic Sulfuric Acid Derivatives.] German Patent Appl. I 66,146, no date (*Cl. 12 o–23.01*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 120.

Saturated aliphatic hydrocarbons b.>200°, obtained by the hydrogenation of C oxides, are chlorinated, condensed with aromatic hydrocarbons (benzol, toluol, naphthalene), and the condensation product is sulfonated.

1365. ———. [Oxidation of Higher Molecular Weight Nonaromatic Hydrocarbons.] German Patent Appl. I 67,836, OZ 12,350, filed Sept. 12, 1940 (*Cl. IV d–12 o.*) FIAT Reel 164, frames 2,565–2,568; PB 25,608; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 49, 1949, p. 35.

In the preparation of oxidation products, such as fatty acids, by the oxidation of nonaromatic, higher molecular weight hydrocarbons in the liquid phase with O_2 or gases containing it in the presence of cata-

lysts, especially good results are obtained if at the beginning or during the oxidation, aldehydes besides metal-containing catalysts, are added to the hydrocarbons to be oxidized. It is especially advantageous to use the aldehydes that are obtained by the oxidation of paraffin hydrocarbons or which can be produced from the alcohols or acids resulting from oxidation or reduction. The effect of the aldehydes is made evident by a decrease of the oxidation time as well as the improvement of the properties of the oxidation products and in an increase in the yield of valuable products, especially of distillable fatty acids.

1366. ———. [Oxidation of High-Molecular Hydrocarbons.] German Patent Appl. I 59,123, OZ 10,224, filed Sept. 21, 1937 (*Cl. IV d–23 b*). FIAT Reel J 281, frame 2,757.

High-molecular hydrocarbons obtained by the catalytic reduction of CO with H_2 are purified before oxidation by heating them for a long time to temperatures 50°–150° and then separating the precipitated constituents.

1367. ———. Oxidation of Hydrocarbons. British Patent 482,954, Apr. 7, 1938. Chem. Abs., vol. 32, 1938, p. 6665.

Crude products containing solid paraffin hydrocarbons are dissolved in liquid aromatic nitrohydrocarbons or mixtures containing them and the solutions are cooled; solid paraffin hydrocarbons are deposited, and these are separated and oxidized with nitrogenous oxidizing agents. Suitable starting materials are brown coal tars or coal- or tar-hydrogenation products containing paraffin wax. The solution and cooling treatment may be repeated, with the same or another solvent of the above described type, before the oxidation of the paraffin hydrocarbons and the solvent adhering to the hydrocarbons may be separated or allowed to remain. Among examples, dehydrated brown coal tar is stirred with $PhNO_2$ at about 50°, the mixture cooled to 15°, and the deposited paraffin filtered and then treated at about 80° with HNO_3 of 45% concentration; the product separates in layers, 1 of which is a $PhNO_2$ solution of oxidation products, which are separated, treated with H_2O, and then freed from $PhNO_2$ by distillation, preferably under reduced pressure; the residual oxidation product is then worked up in known manner to yield fatty acids useful for making soaps; the oxidation product may include di- as well as mono-carboxylic acids.

1368. ———. Oxidation of Synthetic Wax. British Patent Appl. 28,989, filed 1938.

It is usual to employ a small proportion of a wax-soluble metallic compound, particularly a Mn compound, as a catalyst. The use of salts of metals of the 6th, 7th, and 8th groups is also specified.

1369. ———. [Oxidation Products of Carboxylic Acids.] German Patent Appl. I 67,944, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 136.

Oxidation products of carboxylic acids are obtained from the liquid olefinic hydrocarbons, which were obtained by the catalytic hydrogenation of CO with H_2 and oxidation with air in the presence of H_2O-splitting catalysts. Addition to German Patent Appl. I 66,643 (abs. **1496**).

1370. ———. [Oxidation Products of Carboxylic Acids.] German Patent Appl. I 67,948, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 137.

Oxidation products of carboxylic acids are obtained from olefins solid at ordinary temperatures and obtained by the catalytic hydrogenation of CO with H_2, by oxidation by means of air. Addition to German Patent Appl. I 66,643 (abs. **1496**).

1371. ———. [Oxidation Products of Synthetic Hydrocarbons.] German Patent Appl. I 75,423, no date (*Cl. 12 o–11*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 224.

Oxidation products containing carboxylic acids are obtained from high-molecular unsaturated solid hydrocarbon mixtures, which were produced by the catalytic hydrogenation of C oxides and by removing the low-boiling fractions by oxidation with air or other O_2-containing gases.

1372. ———. [Oxidation Products With Excellent Emulsifying Properties.] German Patent Appl. I 67,977, OZ 12,379, filed Oct. 4, 1940 (*Cl. IV d–12 o*). FIAT Reel 164, frames 2,688–2,671; PB 25,608; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 50, 1949, p. 37.

In preparing oxidation products with excellent emulsifying properties, hydrocarbons of very high molecular weight, resulting from the hydrogenation of the oxides of C, are partly oxidized up to an acid number that is appreciably lower than the number calculated from the assumption of only 1 carboxyl group for each average molecule of the raw material. Example: 250 kg. of a mixture of high-molecular-weight hydrocarbons, m. 98° and obtained by the hydrogenation of CO, is melted and introduced with 0.25 kg. $KMnO_4$ in a 5% aqueous solution into a tube provided with a gas distributing device. An air stream of 400 $m.^3$ per hr. is passed through the tube at 140° for 2 hr. giving a product with an acid number of 30. It is allowed to cool to about 100° and neutralized with potash. The product thus obtained has an excellent emulsifying property, especially for high-molecular-weight synthetic hydrocarbons.

1373. ———. [Oxygenated Aliphatic Compounds.] German Patent Appl. I 70,009, no date (*Cl. 12 o–5.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 155.

O-containing aliphatic compounds are obtained by the conversion of MeOH with CO at 100°–300° in the presence of carbonyl-forming metals and at 250 atm. and more.

1374. ———. [Oxygenated Compounds.] German Patent Appl. I 68,936, OZ 12,592, filed Feb. 22, 1941 (*Cl. IV d–12 o*). FIAT Reel 165, frames 4,337–4,342; PB 66,844; PB 25,609; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 7, chap. 196, 1950, p. 31.

Mixtures of oxygenated organic compounds with hydrocarbons obtained by the conversion of CO with H_2 are subjected before heating to 250° to an extraction with a volatile agent such as MeOH, which absorbs selectively the oxygenated compounds. Repeated extractions considerably increase the recovery of alcohols—17.8% of the total products as against only 12.9% by distillation.

1375. ———. [Oxygenated Compounds.] German Patent Appl. I 74,320, no date (*Cl. 12 o–5.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 209.

Production of organic oxygenated compounds from O-containing compounds, which have resulted from the reduction of CO with H_2 over catalysts of the Fe group by splitting off of H_2O under mild conditions.

1376. ———. Oxygenated Organic Compounds. British Patent 286,010, Aug. 18, 1926. Chem. Abs., vol. 23, 1929, p. 154.

In producing alcohols and other oxygenated organic compounds by interaction of CO with vaporized aliphatic alcohols or esters, as described in British Patent 254,819 (abs. **78**), the presence of free Fe, Ni, or Co or volatile compounds of these metals is excluded from the inner parts of the apparatus, the catalysts, and the reaction gases.

1377. ———. [Oxygenated Organic Compounds.] German Patent 559,892, Apr. 6, 1923. Chem. Abs., vol. 27, 1933, p. 730.

In the manufacture of oxygenated organic compounds by the catalytic interaction of CO and H_2 at high temperature and under high pressure, the parts of the apparatus that come into contact with CO are made of or lined with steel containing a considerable proportion of Cr, W, V, or Mo.

1378. ———. [Oxygenated Organic Compounds From Carbon Monoxide and Hydrogen.] German Patent 548,434, Mar. 20, 1923. Chem. Abs., vol. 26, 1932, p. 3513.

Reaction vessel is made of or lined with Al or its alloys.

See also German Patent 490,248 (abs. **2679**).

1379. ———. [Oxygenated Organic Compounds From Carbon Monoxide and Hydrogen.] German Patent 612,229, Apr. 16, 1935 (*Cl. 12 o-5.01*). Chem. Abs., vol. 29, 1935, p. 4771.

Parts of the apparatus having a temperature of 180°–200°, and preferably also the parts having a temperature of 150°–180° or 200°–250°, are made of or lined with material with which CO does not react to yield $Fe(CO)_4$. The parts at temperatures $>$ or $<$ the limits specified may be made of Fe, since $Fe(CO)_4$ is not produced at temperatures beyond those limits. The preliminary heating and aftercooling of the apparatus are preferably effected in the absence of CO. Addition to abs. **1377, 1378, 1996, 2664, 2672, 2679.**

1380. ———. [Oxygenated Organic Compounds From Oxides of Carbon by Reduction.] German Patent 462,837, June 28, 1928. Chem. Abs., vol. 22, 1928, p. 4128.

In the catalytic preparation of oxygenated organic compounds, for example, MeOH, by reduction of oxides of C by H_2 or hydrocarbons or both at high temperatures and pressures, the mixture of gases entering the reaction is completely freed from catalyst poisons, not only S compounds, especially organic ones, but also from volatile Fe compounds, preferably by using active C.

1381. ———. [Oxygen-Containing Organic Compounds.] French Patent 593,942, Feb. 4, 1925. Chem. Zentralb., 1928, I, p. 583.

See United States Patent 1,841,910 (abs. **2684**).

1382. ———. [Paraffin Hydrocarbons From Carbon Monoxide and Hydrogen.] Norwegian Patent 57,461, Jan. 11, 1937; appl. filed Feb. 29, 1936. Chem. Zentralb., 1937, I, p. 3548.

The operation is performed in the presence of solid catalysts under normal pressure and in the gas phase. During the conversion the catalyst is continuously passed through the reaction space. On removal it is wholly or partly freed from the deposited paraffin and returned to the reactor. The excess reaction heat is conducted off by means of cooled surfaces.

1383. ———. [Paraffinic Hydrocarbons.] French Patent 802,208, Aug. 31, 1936. Chem. Abs., vol. 31, 1937, p. 1426.

Hydrocarbons are made from CO and H_2 in the presence of solid catalysts and working under ordinary pressure in the gaseous phase. The catalyst is passed continuously through the reaction chamber and recycled, if necessary, after a complementary regeneration. Excess heat is dissipated by the use of cooled surfaces, such as by using plate furnaces or rotary tubular furnaces. Describes apparatus.

1384. ———. [Photochemical Reactions.] French Patent 647,730, Nov. 14, 1927. Chem. Abs., vol. 23, 1929, p. 2369.

Photochemical reactions are produced in gases or vapors by resonance radiations, the maximum intensity of irradiation in the reaction chamber being obtained by arranging the apparatus so that the metallic vapor, which emits the radiations, surrounds the gases on all sides or the reaction chamber surrounds the source of the radiations. A relatively high intensity of the narrow resonance ray is obtained by the addition of indifferent gases, such as He, or the use of high-frequency vibrations. Gives examples of the production of aldehydes from mixtures of CO and H_2.

1385. ———. [Photochemical Reactions.] French Patent 649,295, Nov. 14, 1927. Chem. Abs., vol. 23, 1929, p. 3408.

Yields in photochemical gaseous reactions are increased by passing the gas or gaseous mixture charged with metallic vapor in permanent circulation near the source of resonance radiations so that the products are formed in relatively feeble concentration, preferably $<2\%$, and are continually removed from circulation by solvents. Gives examples of the preparation of CH_2O and glyoxal from CO and H_2, H_2O from O_2 and H_2, aldehydes from water gas, and aldehydes and H_2O_2 from CH_4 and air.

See also United States Patent 1,788,170 (abs. **2674**) and French Patent 647,730 (abs. **1384**).

1386. ———. [Polymer Gasoline From Synthetic Gasol Hydrocarbons.] French Patent 892,365, no date. Kainer, p. 251.

Synthetic gasol hydrocarbons, containing olefins with 3–4 C atoms in the molecule, into hydrocarbons boiling approximately 80° and an octane No. of 81–98 is converted at temperatures of 190°–210° and pressure of 100 atm. in presence of a catalyst composed of water glass and Na aluminate.

1387. ———. Polymerized Hydrocarbons. British Patent 502,730, Mar. 20, 1939. Chem. Abs., vol. 33, 1939, p. 7546.

Polymerization products are prepared by treating with BF_3 or $AlCl_3$, styrene or styrene admixed with isobutylene, and a liquid hydrocarbon mixture containing unsaturated constituents obtained either by cracking or dehydrogenating hydrocarbons or synthetically from CO and H_2. The polymerization may be effected in solution, such as in hydrocarbons or halohydrodrocarbons, and may be conducted at ordinary, increased, or reduced temperature. The plastic or oily polymers may be added to hydrocarbon oils, for example, lubricating or gear oils, to improve the viscosity.

1388. ———. Polymerizing Olefins. British Patent 498,526, Jan. 10, 1939. Chem. Abs., vol. 33, 1939, p. 4351.

Gases containing more than 30% and preferably 40% or more of olefins with up to 5 C atoms, mainly butylenes or amylenes or both, are polymerized with catalysts of the Friedel-Crafts type, the product being subjected to hydrogenation and a treatment with superheated steam in the presence of caustic alkali. Gases containing butylenes and propylene are especially suitable; they may be obtained by hydrogenation of C oxides. Suitable catalysts are B halides, or chlorides of Al, Zn, and Fe, or their double compounds. Polymerization may be conducted in the gas phase, or in the liquid phase under pressure or in the presence of an inert diluent. The catalyst is preferably decomposed, as soon as a polymer of desired viscosity is obtained, by treatment with H_2O or dilute caustic alkali. The oils may then be fractionated. The crude products, or their fractions, are preferably 1st hydrogenated, using increased temperature and pressure and Ni catalysts, up to 5% of caustic alkali is added, and the products distilled

with superheated steam. A subsequent distillation in vacuo may be effected. Products suitable as insulating oils are obtained, in addition to lower boiling fractions that can be used as benzine or diesel oils.

1389. ———. [Polymerizing Olefins.] French Patent 845,108, Aug. 1, 1939. Chem. Abs., vol. 34, 1940, p. 8115.

Polymerization products of high molecular weight are obtained from volatile gaseous or liquid olefins by converting first the initial products into liquids whose boiling point is not >300° using moderately active polymerization catalysts and continuing the polymerization of these products by means of highly active catalysts. In the first phase of polymerization H_2SO_4, H_3PO_4, decolorizing earth, or AlF_3 are used as catalysts, and in the second phase $AlCl_3$, $AlBr_3$, $FeCl_3$, BF_3, $ZnCl_2$, or $SnCl_4$.

1390. ———. [Preparation of Aluminum Soaps.] German Patent Appl. I 76,149, OZ 14,448, filed Oct. 30, 1943 (*Cl. IV d–12 o*). FIAT Reel 170, frames 9,729–9,730; PB 25,614; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 40, 1949, p. 18.

Al soaps can be prepared by heating soap-forming fatty acids with the Al salts of lower fatty acids such as Al formate or acetate at temperatures > the boiling points of the corresponding acids such as formic or acetic acids. Temperatures of about 140°–250° are suitable. It is advantageous to work under vacuum especially toward the end of the reaction, as the soap-forming fatty acids paraffin oxidation products are suitable.

1391. ———. [Preparation of Dicarboxylic Acids.] German Patent Appl. I 78,338, OZ 14,975, filed Oct. 9, 1944 (*Cl IV d–12 o*). FIAT Reel 171, frames 10,869–10,874; PB 25,615; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 46, 1949, p. 27.

Dicarboxylic acids with 5 or more C atoms in the molecule are made from saturated aliphatic hydrocarbons with 5 or more C atoms in the molecule, such as the paraffin obtained by CO hydrogenation and b. 240°–260°, by oxidation with HNO_3, with the addition, if necessary, of nitrous gases and perhaps O_2 or gases containing it. The concentration of the HNO_3 is maintained >60% by weight (preferably >75%), based on the total amount of H_2O present in the reaction mixture, the oxidation being carried out at temperatures <100° (preferably <70°). The operation may be carried out under raised pressure in the presence of catalysts and solvents.

1392. ———. [Preparation of Drying Oils.] German Patent Appl. I 78,619, OZ 14, 954, filed Sept. 18, 1944 (*Cl. IV d–12 o*). FIAT Reel 171, frames 10,826–10,827; PB 25,615; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 45, 1949, p. 26.

Drying oils are prepared by heating to 300°–390° the residues obtained by distillation up to 280° under 1–10 mm. pressure of fatty acid mixtures obtained by the oxidation of nonaromatic hydrocarbons. Suitable initial materials for the process are the distillation residues of fatty acid mixtures resulting from the oxidation of high molecular weight paraffins such as are obtained in the processing of lignites and petroleum or their hydrogenation. The resulting oils are readily soluble in the usual lacquer solvents and on evaporation of the solvent give a drying, very glossy coating.

1393. ———. [Preparation of Esters.] German Patent Appl. I 73,701, OZ 13,810, filed Nov. 27, 1942 (*Cl. IV d–12 o*). FIAT Reel 170, frames 9,617–9,620; PB 25,614; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 39, 1949, p. 16.

In preparing esters from the unsaponifiable portions of the oxidation products of higher molecular, nonaromatic hydrocarbons, such as lignite paraffins or the hydrogenation products of CO, the fractions of the unsaponifiable constituents b. <300° under ordinary pressure are esterified in known manner with dicarboxylic acids and the unsaponified constituents are separated. Before esterification it is often advantageous to hydrogenate the starting material so as to convert the hydroxy compounds into alcohols. The unesterified constituents are removed from the esterification mixture by steam distillation.

1394. ———. [Preparation of Hydrocarbons.] German Patent Appl. I 67,903, OZ 12,365, filed Sept. 26, 1940 (*Cl. IV d–12 o*). FIAT Reel 169, frames 8,026–8,032; PB 25,613; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 7, chap. 189, 1950, p. 17.

To form hydrocarbons with more than 1 C atom in the molecule by catalytically reacting CO with H_2, the operation is carried out in the presence of mixtures of different catalysts, which have been prepared separately and whose individual grains contain only 1 catalyst of the same method of preparation. Thus, mixtures of Co or Ni catalysts with Fe catalysts may be used, 1 being prepared by precipitation, the other by fusion.

1395. ———. [Preparation of Organic Oxygenated Compounds.] German Patent Appl. I 74,440, OZ 14,020, filed Feb. 25, 1943 (*Cl. 12 o–5.02*). FIAT Reel 169, frames 8,465–8,467; PB 25,613; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 7, chap. 199, 1950, p. 40.

Alkylene oxides, for example, ethylene or propylene oxides, are reacted with oxygenated products, which have been obtained by the reduction of CO with H_2 under elevated pressures and at temperatures <250° over catalysts containing metals of the Fe group.

1396. ———. [Preparation of Paraffin Oxidation Products.] German Patent I 74,630, OZ 14,082, filed Mar. 20, 1943 (*Cl. IV d–23 b*). FIAT Reel 169, frames 8,650–8,652; PB 25,613; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 54, 1949, p. 45.

Paraffin oxidation products are prepared from high-boiling paraffins by subjecting them before oxidation to a refining pressure hydrogenation in which there occurs simultaneously a mild cracking to form paraffins b. about 170°–325° under 5 mm. vacuum. The catalyst consists of active alumina together with sulfides of metals of group 6 of the periodic table and Ni or Co sulfides. Example: Paraffin, which has been obtained by extraction with synthesis gasoline of a Co–MgO–kieselguhr catalyst used in CO conversion, m. 96° and b. >325° under 5 mm. pressure, is heated under a pressure of 250 atm. with 3 $m.^3$ of H_2 per kg. paraffin and passed at 400° through the reaction zone. A catalyst is used consisting of 70 parts active alumina, 25 W oxide and 6 Ni oxide, the W and Ni oxides being treated with S. The throughput is 1 kg. of charge per l. of catalyst per hr. A product is obtained containing about 50% of a paraffin b. 170°–325° under 5 mm. vacuum and 5% constituents boiling up to 340°. The constituents b. >325° under vacuum are separated by high-pressure H_2O distillation and recycled.

1397. ———. [Preparation of Plasticizers.] German Patent Appl. I 75,541, OZ 14,317, filed July 17, 1943 (*Cl. IV d–23 c*). FIAT Reel 170, frames 9,299–9,300; PB 25,614; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 37, 1949, p. 13.

In the preparation of plasticizers (Gleitmittel), such as are required in the production and processing of synthetic resins or plastics, the acidic constituents in oxidation products obtained by the oxidation of aliphatic hydrocarbons melting >40° and containing from 30–70% of acidic constituents, are converted into salts of multivalent metals without separation of the nonacidic constituents. Example: 80 parts ZnO is added with stirring at 150° to 1,000 parts of a hydro-

carbon mixture melting at 80°, which has been produced by the hydrogenation of CO and then oxidized to an acid number of 70. The temperature is then gradually increased to 200° and an additional 35 parts of ZnO added. The reaction is complete within 3 hr. or more and can be recognized by the transparent appearance of the mass. The cooled mass can be ground without difficulty.

1398. ———. [Preparation of Salts of Fatty Acids.] German Patent Appl. I 73,290, OZ 13,699, filed Sept. 30, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 7,442–7,444; PB 25,612; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 34, 1949, p. 7.

In preparing the metal soaps of the fatty acids of paraffin oxidation, difficulty is often found in obtaining a product that is dry and suitable for grinding. The defect can be remedied by carrying out the reaction of these fatty acids with metal compounds in the presence of montanic acid or similar high molecular weight acids of natural origin.

1399. ———. [Preparation of Sulfuric Acid Esters.] German Patent Appl. I 76,953, OZ 14,635, filed Mar. 4, 1944 (*Cl. IV d–12 o*). FIAT Reel 171, frame 10,027; PB 25,615; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 41, 1949, p. 19.

In preparing H_2SO_4 esters, the residue resulting from the steam distillation of fatty acid mixtures obtained by the oxidation of higher molecular weight aliphatic hydrocarbons is treated with sulfonating agents after first being hydrogenated. By this means the so-called residues are converted into compounds containing hydroxyl groups, which are easily sulfonated. The alkali salts of the esters are suitable as plasticizers for rayon and artificial silk.

1400. ———. [Preparation of Waxy Substances.] German Patent Appl. I 74,553, OZ 14,060, filed Mar. 10, 1943 (*Cl. IV d–12 o*). FIAT Reel 169, frames 8,601–8,604; PB 25,613; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 53, 1949, p. 43.

Fatty acid mixtures or fractions thereof, b. > about 240° under 1 mm. pressure and obtained by the oxidation of high molecular weight aliphatic hydrocarbons, are esterified with high molecular weight alcohols, which have been obtained by the hydrogenation of this acid mixture or of the constituents b. about 160°–240° under 1 mm. pressure. Example: 1,000 parts of a hydrocarbon mixture, prepared by hydrogenation of CO and having a m. p. of 95°, is oxidized with air at 115° in presence of 0.2% Mn stearate up to an acid number of 50. The product is saponified with NaOH solution; the unsaponifiable portions being extracted from the soap solution with benzine and returned to the oxidation zone. H_2SO_4 is added to the soap solution and the resulting acid mixture distilled under 1 mm. pressure with the addition of small amounts of steam. The fractions b. >240° are separated and ½ is converted into alcohols by hydrogenation under pressure. Acids and alcohols are then mixed and heated to 150° with the addition of 40 parts xylene. The esterification is complete after 6 hr., giving 580 parts of a wax with drop point of 93°.

1401. ———. [Preparation of Waxy Substances.] German Patent Appl. I 75,540, OZ 14,316, filed July 17, 1943 (*Cl. IV d–12 o*). FIAT Reel 170, frames 9,296–9,298; PB 25,614; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 36, 1949, p. 11.

Process covered by German Patent Appl. I 74,553 (abs. **1400**) for the preparation of waxy substances is improved by making use of all or part of the initial materials without removal of the hydrocarbons accompanying them. Example: 1,000 parts of a mixture of hydrocarbons m. 100° obtained by the catalytic hydrogenation of CO is oxidized by air at 115° after addition of 0.15% $KMnO_4$ to an acid number of 45. The fraction (800 parts) b. >240° under 1 mm. pressure is distilled with addition of small amounts of steam from the oxidation product. ½ of this fraction is treated with H_2 under pressure with reduction of the acids to alcohols. The product is esterified with the nonhydrogenated fatty acid-containing fraction with the addition of 80 parts of toluene by heating for several hr. at 120° and driving off the toluene, which entrains the H_2O formed. The waxy material with a yield of 792 parts has a drop point of 95°.

1402. ———. [Preparation of Waxy Substances.] German Patent Appl. I 77,177, OZ 14.684, filed Apr. 1, 1944 (*Cl. IV d–12 o*). FIAT Reel 171, frames 10,134–10,135; PB 25,615; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 42, 1949, p. 20.

Process of German Patent Appl. I 74,553 (abs. **1400**) and I 75,540 (abs. **1206**) is improved by adding to the waxy substances obtained by the oxidation of a 100° melting-point paraffin the salts of multivalent metals with products, which have been obtained by oxidizing aliphatic hydrocarbons melting >35° and containing at least 30% acidic constituents. The resulting products have the properties of hard wax and are suitable for making shoe polish, treating leather, preparing varnish, and processing synthetic resins.

1403. ———. [Preparing Carboxylic Acids.] German Patent Appl. I 73,147, OZ 13,660, filed Sept. 11, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 7,352–7,359; PB 25,612; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 7, chap. 188, 1950, p. 14.

In preparing carboxylic acids from alcohols by oxidation or by addition of CO, alcohols that have been obtained at temperatures <250° by reduction of CO with H_2 under medium pressure and over catalysts of the Fe group are used as starting materials.

1404. ———. Preventing Gas Diffusion Through Copper Apparatus. British Patent 260,888, June 2, 1926. Chem. Abs., vol. 21, 1927, p. 3405.

To prevent diffusion of reducing gases through Cu by reason of the possible reduction of small quantities of oxide present in the Cu, the walls of apparatus are protected from direct contact with reducing gases by a layer of nonreducing gases such as N_2 or CO_2. Apparatus for use in synthesis of MeOH may be constructed for operation in this manner.

1405. ———. [Process for Carrying Out Hydrogenation Reactions.] German Patent Appl. I 74,060, OZ 13,912, filed Jan. 12, 1943 (*Cl. IV b–12 g*). FIAT Reel 169, frames 8,078–8,085; PB 25,613; TOM Reel 17, item 39, frames 1,133–1,140; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 3, chap. 114, 1948, p. 22.

In carrying out catalytic hydrogenation reactions, such as ammonia synthesis, hydrogenation of organic compounds, and conversion of CO with H_2, catalysts are used that are obtained by reduction with H_2 of compounds of metals of the Fe group at 300°–500°, treatment of the cooled reduction products with weakly oxygenated gases until O_2 adsorption slackens or ceases, and renewed reduction at a temperature (150°–250°) below that of the 1st reduction step. Catalysts produced in this manner are said to maintain their efficiency over longer periods of operation and are immune to the action of air.

1406. ———. [Process for Catalytically Reacting Liquid Substances.] German Patent Appl. —, OZ 13,965, filed Jan. 29, 1943. TOM Reel 17, item 40, frames 1,197–1,200; Meyer Transl. PC–S–V, Oxo Process, vol. 2, chap. 32, 1949, p. 5.

In reacting liquids in the presence of finely divided solid catalyst with recycling of the catalyst separated from the reaction product, the finest catalyst particles are continuously or periodically separated from the

liquid reaction product or a part thereof, and only the coarser particles are recycled to the reactor. The centrifuge described in OZ 13,955 (abs. **1451**) is specifically applied to the situation in which olefins are reacted with CO and H_2 in presence of a catalyst consisting of Co, 33%; MgO, 2%; and ThO_2, 2% in a slurry of kieselguhr.

1407. ———. [Process for Conversion of Carbon Monoxide With Hydrogen.] German Patent Appl. I 72,850, OZ 13,581, filed Aug. 1, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 7,023–7,025; PB 68,463 and PB 25,612; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 7, chap. 187, 1950, p. 13.

In preparing Fe catalysts, the treatment of compact Fe with oxidizing gases is specified in German Patent 756,609 (abs. **1580**), whereas in German Patent Appl. I 70,918 (abs. **2325**) the oxidation of the Fe is promoted by addition of 30–70% of H_2O vapor to the oxidizing gases. It has now been found that porous Fe, such as used Fe catalysts, can be employed and the oxidation be performed in the presence of oxidizing gases to which H_2O vapor is added. These catalysts are said to have the same efficiency as the original catalyst.

1408. ———. [Process for Converting Carbon Monoxide With Hydrogen.] German Patent Appl. I 67,099, OZ 12,177, filed May 31, 1940 (*Cl. IV d–12 o*). APC TC 1,188; FIAT Reel 165, frames 3,505–3,510; PB 66,676; PB 25,609; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 7, chap. 190, 1950, p. 20.

For the synthesis of hydrocarbons from CO and H_2, a Co catalyst is supported on alumina, which has been heated for 6 hr. at 850°–1,000° C. to convert it to the α form. This form of alumina is not attacked by alkali. Using a catalyst containing 1 part by weight of Co, 1–2 parts of α alumina and 0.1–0.15 part Zn oxide, a yield of 135 gm. of oil per $m.^3$ of synthesis gas is obtained. 70% of this oil b. >320° C. If ordinary Al_2O_3 is used, however, the yield is only 30 gm. of oil per $m.^3$, of which only 50% b. >320° C.

1409. ———. [Process for Converting Carbon Monoxide With Hydrogen to Hydrocarbons.] German Patent Appl. I 66,711, OZ 12,064, filed Mar. 18, 1940 (*Cl. 12 o*). FIAT Reel 163, frames 1,456–1,461; PB 25,607; Meyer Transl. PC-S-II, Fischer-Tropsch, vol. 6, chap. 165, 1949, p. 6.

Owing to sudden or even extreme fluctuations in the gas flow to the catalyst, the undesired presence of S in the feed, or sudden changes in operating temperature, the activity of the catalyst is curtailed by stoppage of the pores with soot or by decomposition of the body of the catalyst itself. It is suggested in this connection that normal operation be maintained and severe fluctuations be detected or avoided by the installation of sensitive electrically operated devices, which would correct automatically any undesired changes in operating conditions.

1410. ———. [Process for Dehydrogenating Paraffin.] French Patent 863,503, Apr. 3, 1941. Chem. Abs., vol. 43, 1949, p. 660.

Paraffin with or without olefins is treated with a H halide at temperatures >500° to give a mixture of the paraffin and an increased amount of olefin. Butane (500 gm.) mixed with 1500 gm. dry HCl is passed each hr. through a steel tube, 2 m. x 60 mm. dimensions, heated at 650°. Washing and freezing gives 80% butane and 20% butylene.

1411. ———. [Process for Improving the Products Derived From the Carbon Monoxide-Hydrogen Conversion.] German Patent Appl. I 70,190, OZ 12,933, filed Aug. 7, 1941 (*Cl. IV d–12 o*). FIAT Reel 166, frames 4,772–4,775; PB 68,677.

Mixtures of hydrocarbons and O-containing compounds, obtained by the conversion of CO with H_2 particularly at medium pressures in the presence of Fe catalysts, are improved in odor by heating them with highly basic substances such as caustic soda or potash at 100° or higher, but under the reaction temperature of the alcohols in the mixtures. By this means, not only is the odor improved, but the content of alcohol is increased.

1412. ———. [Process for Improving the Products From Reduction of Carbon Monoxide.] German Patent Appl. —, OZ 13,686, filed Sept. 22, 1942. TOM Reel 15, bag 3,043, item 18, frames 2,414–2,418; Meyer Transl. PC-S-II, Fischer-Tropsch, vol. 2, chap. 103, 1948, p. 88.

Products obtained from the conversion of CO with H_2, which contain oxygenated compounds in addition to hydrocarbons, especially those obtained at medium pressure in the presence of Fe catalysts, have their odor improved by treatment with bisulfite solution. Example: A fraction of the above products b.>200° is obtained by distillation and treated in a stirring vessel for 5 min. with about ⅛ its volume of a nearly saturated solution of sodium bisulfite. After the operation is finished, the gasoline layer is separated and subjected to distillation. A glass-dish gum test of 100 cc. of the untreated gasoline showed 12.2 mg. as compared with only 2.0 mg. with the treated sample. The odor of the product was greatly improved also.

1413. ———. [Process for Making Salt-Containing Colloidal Solutions of Metal Hydroxides.] German Patent Appl. I 62,993, OZ 11,158, no date; APC TC 1,204.

Describes preparation of trivalent or tetravalent metal hydroxide gels as catalyst carriers. Mentioned (but not described) as being particularly useful for the production of liquid hydrocarbons from CO and H_2 are Co catalysts containing Th.

1414. ———. [Process for Obtaining a Hydrogen-Carbon Monoxide Gas Mixture From Hydrocarbons.] German Patent Appl. I 67,460, OZ 12,258, filed July 19, 1940 (*Cl. 26 a*). FIAT Reel 163, frames 2,199–2,202; PB 25,607; TOM Reel 26, item 11, frames 625–628; Meyer Transl. PC-S-II, Fischer-Tropsch, vol. 1, chap. 73, 1948, p. 184.

H_2–CO mixture is obtained by the incomplete combustion of gaseous hydrocarbons with O_2 or gases containing it in the presence of solid catalysts and steam by thoroughly saturating the raw gas before it comes into contact with the catalyst with vapors of metals of the Fe group. Example: Coke oven gas is burned with O_2 and steam in a furnace filled with a Ni–Mg catalyst. Into the furnace are introduced steadily 4 gm. per hr. of Fe in the form of Fe carbonyl, which vaporizes at once. At a temperature of 990° at the exit of the furnace, a mixture of H_2 and CO is obtained containing only 0.25% of CH_4. By operating in this fashion the furnace is not stopped even in long periods of operation.

1415. ———. [Process for Obtaining High-Molecular Fatty Acids.] German Patent Appl. I 77,898, OZ 14,882, filed July 25, 1944 (*Cl. IV d–12 o*). FIAT Reel 171, frames 10,663–10,665; PB 25,615; Meyer Transl. PC-S-IV, Wax Oxidation, vol. 3, chap. 44, 1949, p. 24.

Residues from the distillation of the fatty acid mixtures obtained by oxidation of paraffin are treated with acid and then further distilled under diminished pressure. Example: 100 parts of the residue from the distillation of the fatty acid mixture obtained by oxidation of brown-coal paraffin and containing 14% of unsaponifiable material was stirred for ½ hr. at 95° with 100 parts of 25% H_2SO_4, washed free from acid with hot H_2O, and then dried. The steam distillation of the treated residue at 1 mm. pressure yielded up to 340°, nearly 40% of a distillate with a

content of about 80% fatty acids with the saponification number of 176.

1416. ———. [Process for Obtaining Paraffin.] German Patent Appl. —, OZ 13,344, filed Mar. 27, 1942. TOM Reel 17, item 36, frames 1,016–1,019.

In obtaining paraffin from oils containing it by adding solvents and then cooling, better results are obtained without noticeable increase in the asphalt content or separations by producing polymerizates in the oil under treatment through careful aging. Example: A paraffin-containing oil fraction from the pressure hydrogenation of brown-coal tar is distilled, and a fraction b. 345°–450° is mixed with 0.3% of a condensation product of chlorinated paraffin and naphthalene as a filter aid and the mixture twice treated with propane at about —40°. The paraffin thus obtained has a m. p. of 49.5° and contains 4.7% of oil. Before working up to fatty acids the paraffin is distilled to separate the filter aid. Should the oil fraction be carefully aged for several weeks in a steam-heated holder with exclusion of air, the double propane treatment gives an oil of m. p. 49.4° with 4.2% of oil. The paraffin is ready for working up into fatty acids.

1417. ———. [Process for Obtaining Synthesis Gas From Hydrocarbons.] German Patent Appl. —, filed June 13, 1940. TOM Reel 26, item 11, frames 592–595. Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 66, 1948, p. 169.

In obtaining synthesis gas from hydrocarbons by their incomplete combustion with air or O_2, if desired in the presence of steam and solid catalysts, a catalyst in vapor form is used consisting of a saturated vapor of a metal of the Fe group. Example: 176 m.³ of a S-containing manufactured gas were reacted with 40 m.³ of O_2 and steam in a reactor filled with a Ni–Mg catalyst. At the entrance to the reactor were added per hr. 4 gm. Fe in the form of Fe carbonyl. At a temperature of 990° at the outlet of the reactor, a gas mixture was obtained composed essentially of $CO+H_2$ with only 0.25% of CH_4. There was no stoppage owing to C deposition with these quantities of Fe, O_2, and steam.

1418. ———. [Process for Producing Acetaldehyde.] German Patent Appl. —, OZ 12,693, filed Apr. 2, 1941. TOM Reel 26, item 11, frames 607–612; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 69, 1948, p. 176.

CO and H_2 are caused to react with MeOH or dimethylether at a temperature <200° and under increased pressure, preferably at 150–300 atm., in the presence of catalysts consisting of metals of group 8 or their compounds capable of forming carbonyls. The $CO:H_2$ ratio can vary in wide limits. Conversion may take place either in the gas or liquid phase.

1419. ———. [Process for Producing Aldehydes and Ketones.] German Patent Appl. I 70,739, OZ 13,059, filed Oct. 25, 1941 (*Cl. IV d–12 o*). FIAT Reel 166, frames 5,200–5,205; PB 68,774; TOM Reel 17, item 32, frames 866–871; TOM Reel 36, bag 3,454, item 21; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 11, 1948, p. 28.

In a process for producing aldehydes and ketones, compounds with olefinic double bonds are caused to react with CO and H_2 at increased temperature and pressure in presence of catalysts that contain as the active constituent metals of the 8th group, particularly Co, and substances that depress the hydrogenating effect of the catalyst. Metalloids of the 5th and 6th groups, particularly S or its compounds in which the metalloid atom is not directly combined with O, may be used. Example: 60 parts of a catalyst (Co, 34%; Th, 2.2%; MgO, 1.4%; kieselguhr, 62%), made by precipitating the metal as the carbonate in the presence of kieselguhr and reducing with H_2 at 400°, are added to 800 parts of an olefin-paraffin mixture, obtained by cracking and b. 250°–260°, and 2 parts of CS_2. The mixture is stirred at 140° with an equal amount of a mixture of CO and H_2 under 200 atm. pressure until no more water gas is absorbed. Then the $CO+H_2$ mixture is substituted by H_2 and heated for 15 min. at 180° and 200 atm. pressure. Thus, a mixture of aldehydes and paraffins is obtained having a carbonyl number of 110 and a hydroxyl number of 0.0 that is free from Co carbonyl. The conversion is about 90%.

1420. ———. [Process for Producing Aliphatic and Cycloaliphatic Nitrohydrocarbons.] German Patent Appl. —, OZ 14,924, filed Aug. 21, 1944. TOM Reel 17, item 33, frames 971–974.

Aliphatic and cycloaliphatic nitrohydrocarbons are produced by treating aliphatic or cycloaliphatic hydrocarbons with N_2O_4 without the addition of H_2O and at increased temperature and pressure. The reaction is carried out in homogeneous liquid phase. Suitable raw materials are hexane, isooctane, cyclopentane, decahydronaphthalene and mixed saturated aliphatic and cycloaliphatic hydrocarbons. The raw materials may be obtained through the hydrogenation of CO or through the hydrogenation of brown or bituminous coal, or from aromatic-free petroleum oils.

1421. ———. [Process for Producing Antiknock Gasoline.] German Patent Appl. I 69,074, OZ 12,621, filed Mar. 7, 1941 (*Cl. IV d–23 b*). FIAT Reel 165, frames 3,585–3,586; PB 66,693.

In an improvement of the process of the main German Patent Appl. I 62,611 for the production of antiknock gasoline from the gasolines produced from gas mixtures containing CO and H_2 with Fe catalysts by passing them in vapor state over alumina or magnesia or Zn oxide or Al phosphate at temperatures 300°–400°, the temperatures are raised 400°–450°, suitably up to 440°. Similar results are obtained as in the main patent.

1422. ———. [Process for Producing Antiknock Motor Fuels.] German Patent Appl. I 69,041, OZ 12,610, filed Mar. 4, 1941 (*Cl. IV d–23 b*). FIAT Reel 165, frames 3,546–3,550; PB 66,685.

Improvement in the process of German Patent Appl. I 65,742 (abs. **1434**), whereby rather than 2 m.³ of H_2-containing end gases, 4 m.³ is recirculated per kg. of raw material.

1423. ———. [Process for Producing Branched Aliphatic Compounds.] German Patent Appl. I 73,190, OZ 13,669, filed Sept. 17, 1942 (*Cl. IV d–12 o*). TOM Reel 36, bag 3,454, item 21, 4 pp.; Meyer Transl. PC-S-V, Oxo, vol. 1, chap. 24, 1948, p. 60.

Branched aliphatic compounds are obtained through the interaction of olefins with CO and H_2 under elevated pressure and temperature in presence of catalysts and with hydrogenation, if desired, of the products. It has now been found that the reaction of CO and H_2 at the olefinic double bond occurs in only 1 direction if such olefinic compounds are used as the raw material for the process in which 1 double bond C atom has no H atom, whereas the other has at least 1. With such olefinic compounds, the formyl group adds only to the C atom having at least 1 H atom, whereas an H atom adds to the C atom that previously had no H atom. There arises by the use of such raw material not a mixture of 2 structural isomers, but an individual product. It is illustrated by the following example:

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C{=}CH_2 + CO + H_2 \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH{-}CH_2{-}CHO.$$

1424. ———. [Process for Producing Condensation Products.] German Patent Appl. —, OZ 14,046,

filed Mar. 3, 1943. TOM Reel 17, item 32, frames 920–927.

Cyclic hydrocarbons or their derivatives are condensed with the synthesis products containing olefins and alcohols obtained by the catalytic reduction of CO with H_2<250° and at medium pressure in the presence of catalysts of the Fe group, especially Fe. Substances that create H_2O solubility are introduced into the condensation products. Example: 200 parts of the synthesis product are mixed with an equal amount of phenol and 100 parts of ZnCl and the mixture heated with stirring under reflux for 12 hr. at 180°. The condensation product is washed with H_2O and the oily layer distilled under reduced pressure. The major part goes over at 15 mm. pressure at 190°–240° as a light-yellow oil, which is made H_2O soluble and can be used as emulsifier, wetting agent, and detergent.

1425. ———. [Process for Producing Ethers.] German Patent Appl. —, OZ 13,969, filed Feb. 1, 1943. TOM Reel 17, item 32, frames 911–915.

Ethers are produced by reacting organic hydroxyl compounds with compounds of organic hydroxyl compounds and metals whose hydroxides do not form alkaline solutions with H_2O. Example: An Al alcoholate, obtained by the reaction of 5, 5–dimethyl–3–methylhexanol–1 with Al, is caused to react with the like alcohol. 1,000 parts of the alcoholate are used with 950 parts of the pure alcohol. The liquid alcoholate is miscible with the alcohol. The liquid mixture is heated for 12 hr. under pressure to 320°. After cooling the mixture is treated with HCl, and the oily layer is washed with H_2O, dried, and distilled under reduced pressure. 870 parts of ether, or 50% of the calculated amount, are obtained. It b. 290°–300°. The O content is 5.5%. Besides ether, 410 parts of olefins with 9 C atoms and 90 parts with 18 C atoms are obtained. The remainder, 450 parts, consists of unchanged raw alcohol, which can be returned to the process. By heating Al alcoholate, made from Synol and Oxo alcohols C_6–C_{13}, with the same free alcohol, the corresponding ethers can be obtained in relatively good yield.

1426. ———. [Process for Producing Fatty Acids or Salts of Fatty Acids.] German Patent Appl. I 69,044, OZ 12.614, filed Mar. 5, 1941 (*Cl. IV d-12 o*). FIAT Reel 165, frames 3,561–3,565; PB 66,689.

In a process for producing fatty acids or salts of fatty acids, a mixture of paraffinic and olefinic hydrocarbons obtained by cracking of natural or synthetic paraffins or by the catalytic hydrogenation of CO in presence of Co or Fe catalysts is treated in the presence of catalysts with CO and alcohol. The esters of fatty acids contained in the conversion mixture are saponified and the fatty acids or the salts of fatty acids are recovered. The catalysts may consist preferably of carbonyl-forming metals, particularly Ni and Co, or Fe, W, and Mo, their compounds or mixtures, or Cu. Example: 1,500 parts of a diesel oil with I number 50, b. 72°–170° under 16 mm. pressure, hydroxyl number 25 and the carbonyl number 20, and obtained by the hydrogenation of CO, are heated with 300 parts EtOH in presence of 30 parts of CuI and 20 of Raney Ni for 24 hr. to 270°, with the simultaneous injection of CO under 180–200 atm. pressure. When no more CO is absorbed, the unused alcohol is driven off and the remainder heated with 3,000 parts 50% alcohol and 400 parts KOH for 6 hr. to b. p.. The unconverted portion comes to the surface and is removed. The soap solution is extracted with ligroin, then freed from alcohol by steaming and acidified with H_2SO_4. The fatty acids then separate out. The unconverted portion amounts in total to 973 parts or 64%. By distilling the fatty acids there are obtained in 17% yield a fraction b. 80°–160° under 26 mm. pressure, in 43% yield a fraction b. 125°–150° under 0.5 mm. pressure, and in 40% yield a fraction b. 150°–200° under 0.5 mm. pressure. The acid number falls with increasing b. p about 300–230.

1427. ———. [Process for Producing High-Molecular Alcohols.] German Patent Appl. I 68,563, OZ 12,523, filed Dec. 30, 1940 (*Cl. IV d–12 o*). FIAT Reel 164, frames 3,161–3,167; PB 75,184.

In a process for making high-molecular alcohols, the hydrocarbons b. >200° containing unsaturated constituents, which were obtained by the hydrogenation of CO, are sulfonated and the sulfonated products hydrolyzed.

1428. ———. [Process for Producing High-Molecular Alcohols.] German Patent Appl. I 71,524, OZ 13,199, filed Jan. 12, 1942 (*Cl. IV d–12 o*). FIAT Reel 166, frames 5,628–5,632; PB 68,877.

In a process for producing high-molecular alcohols by the catalytic hydrogenation of free fatty acids or fatty acid mixtures with H_2 under increased pressure and temperature (200 atm. and 225°–265°), the reduction is performed continuously in apparatus, which, so far as it is in contact with the fatty acids, is built of Cu or its alloys. The catalyst of the reaction consists of Cu or Cr or their oxides and if desired activated with Ba or Al oxides. The raw material for the process may be either fatty acids obtained from natural fats and oils or those obtained by the oxidation of synthetic paraffins.

1429. ———. [Process for Producing High Molecular Hydrocarbons.] German Patent Appl. I 66,644, OZ 12,053, filed Mar. 7, 1940 (*Cl. 12 o*). FIAT Reel 163, frames 1,396–1,404; PB 25,607; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 6, chap. 164, 1949, p. 3.

In obtaining high-molecular hydrocarbons with at least 10 atoms in the molecule from the conversion of CO with H_2, mixtures of these gases are passed through the converter at an hourly speed of at least 1,000 times the unit volume of the catalyst space. Before recirculation of the gases or before their further treatment the desired high-molecular fractions are separated. This method of operation not only increased the formation of high-molecular hydrocarbons in the product but also the total yield, since CH_4 formation is reduced. The usual catalysts used for CO conversion are suitable for this process. If Co catalysts are used, the best temperature is 200°–225°, with Fe catalysts, 240°–420°. Normal or medium pressures may be used, preferably 3–25 atm. The synthesis gas should have a ratio of CO–H_2 of about 1–1.1 or 1.3.

1430. ———. [Process for Producing Hydrocarbons.] German Patent Appl. I 65,560, OZ 11,757, filed Sept. 5, 1939 (*Cl. IV d–12 o*). FIAT Reel 162, frames 251–254; PB 68,931; FIAT Reel B–196, frames 360–363; PB 83,253; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 7, 1950, chap. 193, p. 26.

In a process for the production of hydrocarbons with >1 C atom in the molecule from CO and H_2 in a converter in which the heat of conversion with maintenance of a constant or nearly constant temperature is conducted through the walls of the converter into a cooling liquid, the gases leaving the converter are recirculated in an amount several times that of the entering fresh gas without removal of the conversion products and without intermediate cooling.

1431. ———. [Process for Producing Hydrocarbons.] German Patent Appl. I 67,690, OZ 12,316, filed Aug. 21, 1940 (*Cl. IV d–12 o*). FIAT Reel 165, frames 3,511–3,515; PB 66,677; PB 25,609; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 7, chap. 191, 1950, p. 22.

In a process for producing hydrocarbons from CO and H_2 at increased temperature in presence of Fe catalysts, temperature-resistant fibrous material, such

as asbestos, is added to the catalyst to about 10% by weight of the Fe, or enough to produce a mass of high mechanical stability. The best operating conditions for the synthesis appear to be 20 atm. pressure and 250° with a synthesis gas composition of 60% or more CO. The reaction product consists of paraffin and middle oil with some gasoline.

1432. ———. [Process for Producing Liquid Hydrocarbons.] German Patent Appl. —, filed Apr. 2, 1943. TOM Reel 26, item 11, frames 603–606; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 68, 1948, p. 174.

In producing liquid hydrocarbons with > 1 C atom in the molecule by the reduction of CO with H_2 in the presence of catalysts like those described in German Patent Appl. I 68,608 (abs. **3261**), which contain Fe, Cu, alkali beside large amounts of MgO and kieselguhr, 1 or more of the components is wholly or partly replaced by fluorine compounds or these are additionally incorporated therein. Example: A catalyst of Fe, Cu, K, and MgO on kieselguhr has the MgO replaced by CaF_2. With the same throughput, synthesis gas, and temperature, the CO conversion and the yield per $m.^3$ of gas were both increased and the product contained a greater proportion of high-boiling constituents.

1433. ———. [Process for Producing Low-Boiling Aromatic Hydrocarbons.] German Patent Appl. —, OZ 14,248, filed June 18, 1943. TOM Reel 15, bag 3,043, frames 2,423–2,425, item 18.

Low-boiling aromatic hydrocarbons are obtained from high-boiling aromatics by catalytic pressure hydrogenation of the latter in the vapor state by passing them together with H_2 under a pressure of 200–700 atm. at 390°–440° over an artificially produced catalyst consisting of Al and/or Mg silicates with 0.2–10% of Mo oxide. The gasoline produced contains 40% boiling up to 100° and 60% aromatics with I number 1.5.

1434. ———. [Process for Producing Motor Fuels.] German Patent Appl. I 65,742, OZ 11,807, filed Oct. 4, 1939 (*Cl. IV d–23 b*). FIAT Reel 162, frames 426–431; PB 68,971.

In a process for producing antiknock motor fuels from aliphatic hydrocarbon mixtures, such as the middle oil from the Fischer-Tropsch synthesis, by catalytic cracking at temperatures 420°–560° in presence of H_2, the raw material in vapor state, together with H_2 is passed, under a total pressure of 3–25 atm. and a H_2-partial pressure of not > ½ but at least 25% of the total pressure, over oxides of the metals of groups 2–6 (particularly V, Cr, Mo, or W on active alumina), the H_2-containing gases leaving the converter being recirculated without addition of fresh H_2 in an amount of about 0.3–2 $m.^3$ per kg. of raw material. Example: In addition to 16.5% of gaseous hydrocarbons, a liquid product is obtained containing 44% gasoline and 56% middle oil. The gasoline has an octane number 64 and 40% boils up to 100°, its aromatic content is 29% and olefins only 1.5%. The middle oil b. 200°–343° and, as its aniline point of 45° shows, is highly aromatized in comparison with the original oil.

1435. ———. [Process for Producing Organic Oxygen-Containing Compounds.] German Patent Appl. —, OZ 13,983, filed Feb. 8, 1943. TOM Reel 17, item 32, frames 916–919; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, chap. 91, 1948, p. 47.

Organic, O-containing compounds are obtained by reducing CO with H_2 over catalysts containing metals of the Fe group at medium pressure and at temperatures < 250°. The resulting oxygenated compounds, with the addition, if desired, of compounds containing hydroxyl or aldehyde groups is subjected to a mild H_2O-splitting treatment. The products are useful as solvents, softeners, and plasticizers.

1436. ———. [Process for Producing Organic Oxygen-Containing Compounds.] German Patent Appl. I 69,072, OZ 12,616, filed Mar. 6, 1941 (*Cl. IV d–12 o*). FIAT Reel 165, frames 3,574–3,579; PB 66,691.

In a process for the production of organic O-containing compounds, acetals are treated with a mixture of CO and H_2 (1 : 2) in the presence of catalysts consisting of metals capable of forming carbonyls such as Co and Ni, with additions, if desired, of other metals such as Cu or metal oxides of Al, Mg, or Th deposited on carriers such as active C or kieselguhr and under increased pressure (75–250 atm.) and temperature (100°–300°). If desired the products can be treated with H_2 in the presence of hydrogenating catalysts. They resemble glycols in their properties and appearance.

1437. ———. [Process for Producing Oxygenated Compounds.] German Patent Appl. I 72,009, OZ 13,373, filed Apr. 10, 1942 (*Cl. IV d–12 o*). TOM Reel 36, bag 3,454, item 21, 5 pp.; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 15, 1948, p. 38.

In preparing oxygenated organic compounds by the interaction of CO and H_2 with olefins with double bonds at raised temperature and pressure, the catalysts consist of the oxides of the catalyst metals, particularly Fe, Co, or Ni. Example: In preparing the catalyst there is added to a solution of 120 parts of crystallized Co $(NO_3)_2$ in 400 parts of H_2O at 25° a solution of 75 parts of $(NH_4)_2MoO_4$ $(3(NH_4)_20.7\ MoO_3.4\ H_2O)$. After addition of 300 parts of 20% NH_3 the solution is evaporated to dryness. The dry residue is heated by slow stages to 300° and maintained at this temperature for about 20 minutes.

1438. ———. [Process for Producing Oxygen-Containing Organic Compounds.] German Patent Appl. I 68,296, OZ 12,449, filed Nov. 25, 1940 (*Cl. IV d–12 o*). FIAT Reel 164, frames 2,884–2,891; PB 75,130; TOM Reel 36, item 21, bag 3,454, 8 pp.; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 9, 1948, p. 20.

In a process for producing O-containing organic compounds, particularly aldehydes and ketones also alcohols, CO and H_2 are caused to react with olefin compounds with double bonds at increased temperatures (100°–180°) and under increased pressure (150–250 atm.) in the presence of catalysts, the active constituents of which consist of Co together with excess amounts of 1 or more easily reducible oxides of metals that do not form carbonyls, for example: 10% Cu : 1% Co : 89% silica gel. The catalyst may be used in the solid fixed form or as a suspension in the reacting gases. It is preferable that the gas mixture contain an excess of $CO+H_2$ over the olefinic portion. The conversion reaction should take about 1–2 hr. for completion. The product normally amounts to about 95%, calculated on the olefins processed, with 80% of aldehydes.

1439. ———. [Process for Producing Oxygen-Containing Organic Compounds.] German Patent Appl. I 68,642, OZ 12,538, filed Jan. 13, 1941 (*Cl. IV d–12 o*). FIAT Reel 164, frames 3,210–3,221; PB 75,194; TOM Reel 36, item 21, bag 3,454, 12 pp.; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 10, 1948, p. 23.

In a process for producing O-containing compounds, especially aldehydes and ketones also alcohols, CO and H_2 are caused to react with olefin compounds with double bonds at increased temperature and under increased pressure in presence of technical catalysts. The reacting gases have been thoroughly freed from CO_2. The operating details are virtually identical with German Patent Appl. I 68,296 (abs. **1438**).

1440. ———. [Process for Producing Valuable Hydrocarbons.] German Patent Appl. —, OZ 12,147, filed May 6, 1940. TOM Reel 17, item 30, frames 774–779.

Valuable hydrocarbons are produced by conducting an equimolar mixture of aromatic hydrocarbons, such as benzol and the higher boiling alcoholic products of the MeOH synthesis, in the vapor state over condensation catalysts consisting of phosphoric acid on a silicate carrier, preferably asbestos. The alcohols have 5–10 C atoms, an average mol. wt. of 112, and an end b. p. of 189°. The pressure is 50 atm., and the temperature is 322°. The product, particularly the main fraction b. 90°–200°, is subjected to mild hydrogenation at 200 atm. and 190° in presence of a Ni–WS_2 catalyst whereby only the olefins are hydrogenated. An olefin product is obtained with an octane No. of about 115, C. F. R. method.

1441. ———. [Process for Producing Valuable Oils.] German Patent Appl. —, OZ 11,761, filed Sept. 6, 1939. TOM Reel 17, item 34, frames 992–1,001.

Valuable oils can be produced by esterifying aliphatic hydrocarbons with at least 3 C atoms, containing 2 or more primary alcohol groups, with fatty acids with at least 6 C atoms. A mixture of fatty acids with straight chains and fatty acids with branched chains can be used as the esterifying agent. Lubricants can be obtained by using the esters of fatty acids with at least 6 C atoms and aliphatic hydrocarbons with at least 3 C atoms, which contain 2 or more primary alcohol groups, either alone or in mixture with each other or with other lubricating agents particularly natural or synthetic hydrocarbon oils. The mixture of alcohols and the fatty acids obtained through the conversion of CO with H_2 may supply the raw materials for the process.

1442. ———. [Process for Producing Water Gas or Synthesis Gas.] German Patent Appl. I 74,150, OZ 13,939, Jan. 20, 1943 (*Cl. V–24 e*). FIAT Reel 169, frames 8,162–8,165; PB 25,613.

In making water gas or synthesis gas from carbonaceous material by gasification of solid fuels or by partial combustion of carbonaceous gases in presence of pure O_2 or O_2-enriched air, the necessary O_2 is obtained in a known air separation plant with low- and high-pressure stages and the high-pressure air is cooled in an absorption refrigerating machine, which is operated by making use of the waste heat from the produced gas. Example: Brown coal, low-temperature coke is gasified in a Winkler generator in the presence of 10,000 $m.^3$ of O_2 per hr. The resulting 40,000 $ft.^3$ of water gas leaves the generator at 900° and is cooled in a waste-heat boiler and a heat exchanger to 120°. At this temperature it enters an absorption refrigerating plant and is further cooled to 75° while giving up 600,000 heat units. About ⅓ of the refrigerating capacity obtained thereby is sufficient to produce the necessary 10,000 $m.^3$ of O_2 for cooling the high-pressure air.

1443. ———. [Process for Reducing Carbon Monoxide With Hydrogen.] German Patent Appl. —, filed Mar. 23, 1944. TOM Reel 26, item 11, frames 596–602. Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 67, 1948, p. 171.

Describes a process for producing high-molecular hydrocarbons, especially paraffins, by reduction of CO with H_2 in presence of Fe catalysts. Fe, Fe oxide, or Fe compounds or substances containing them, convertible into the oxide at increased temperatures, are heated in the presence of metals of groups 2, 3, 6, or 7. Their oxides or compounds are converted into the oxides in nonreducing, preferably oxidizing atmosphere >600°, but below the melting point of the metals or metal compounds themselves, until sintering takes place and the material is eventually reduced. To the basic catalyst mass is added a metal such as Ag or Cu capable of facilitating the reduction. Such catalysts have the advantage of being active at temperature <220° and produce high-boiling paraffins. Furthermore they have a high mechanical stability.

1444. ———. [Process for Refining Organic Oxygenated Products.] German Patent Appl. I 71,756, OZ 13,299; filed Mar. 10, 1942 (*Cl. IV d–12 o*). TOM Reel 36, bag 3,454, item 21, 3 pp.; Meyer Transl. PC-S-V, Oxo, vol. 1, chap. 13, 1948, p. 33.

In separating the organic oxygenated products obtained by the reaction of CO and H_2 with olefins from the catalyst metals or metal compounds dissolved therein, the compounds are treated in the presence of such materials as active C. kieselguhr, pumice, or the like, and at elevated temperature and pressure with H_2. Example: An oxygenated product containing 0.11% of dissolved Co is heated with 10% of its weight of granulated active C for 3 hr. at 120° in the presence of H_2 at 200 atm. pressure. The Co content is reduced to 0.005%.

1445. ———. [Process for Removing Foreign Gas Constituents From Gas Mixtures Under Pressure.] German Patent Appl. —, filed Dec. 27, 1944. TOM Reel 17, item 28, frames 652–658.

Undesirable gaseous constituents are removed from gas mixtures under pressure, especially from the recycle gases of high-pressure synthesis, by washing with a washing agent in which the gas constitutents to be removed have a specifically high dissolving power. The washing agent saturated with the gases is treated in counterstream with the gas mixture set free by the regeneration of the washing medium, and the gas mixture resulting from this treatment is added to the synthesis gas at some suitable spot. The washing agent is regenerated by flashing or by heating, and the gas mixture set free is compressed, if desired, to the pressure at which the process is carried out. Gives diagram of the apparatus.

1446. ———. [Process for Removing Paraffin From Hydrocarbon Oils.] German Patent Appl. I 75,994, OZ 14,425, filed Oct. 9, 1945 (*Cl. IV d–12 o*). TOM Reel 17, item 36, frames 1,020–1,028.

In the deparaffining of hydrocarbon oils using selective solvents and separation of the crystallized paraffin at low temperature by filtration, use is made of wire sieves as filter material instead of cloth filters. The method is said to be at least 3–5 times faster than when using cloth filters. Sieves of Cu or stainless steel are suitable with 400–2,500 mesh per $cm.^2$. Not >0.5–1% of paraffin will be found in the filtrate, and this can be easily recovered by means of a cloth filter or by centrifuging.

1447. ———. [Process for Removing Paraffin From Oils.] German Patent Appl. —, OZ 14,705, filed Apr. 6, 1944. TOM Reel 17, item 36, frames 1,035–1,037.

Oils are first extracted with a selective solvent after which the raffinate phase, without being freed from the solvent, is deparaffined by means of tetrahydrofuran and, if desired, further amounts of selective or other solvents. Addition to German Patent Appl. I 76,558 (abs. **1449**).

1448. ———. [Process for Removing Paraffin From Oils.] German Patent Appl. —, OZ 14,820, filed June 22, 1944. TOM Reel 17, item 36, frames 1,038–1,048.

Describes method and apparatus for removing paraffins from oils by means of solution, cooling to lower than usual temperatures, and inducing the formation of layers with oil precipitants.

1449. ———. [Process for Removing Paraffin From Oils.] German Patent Appl. I 76,558, OZ 14,554, filed Jan. 10, 1944 (*Cl. IV d–23 b*). TOM Reel 17, item 36, frames 1,029–1,034.

In deparaffining oils by cooling in presence of solvents, use is made of tetrahydrofuran together with other solvents that favor the crystallization of the

paraffin but have a low washing ability. Such solvents are acetone, acetonitrile, methanol, dichlorethane, and aliphatic alcohols, whereas benzol and methylenechloride have the opposite action.

1450. ———. (Ammoniakwerk Merseburg G. m. b. H.). [Process for Separating Alcohols From Nonaqueous Liquids.] German Patent Appl. —, filed Apr. 7, 1941. TOM Reel 134, item II–22, 11 pp., 1 fig.

Alcohols, such as those obtained from the hydrogenation of CO with H_2 are separated from the nonaqueous hydrocarbon liquids with which they are mixed by forming their boric acid esters, splitting these with H_2O, and then saponifying. Saponification of the boric acid esters is performed at elevated temperature with an aqueous solution of boric acid. On standing the mixture separates the alcohol is removed, and the boric acid is allowed to crystallize and is used again in the process. The alcohol, after separation from the mixture, is washed thoroughly with H_2O to remove the last traces of boric acid. Operation described by aid of a diagram.

1451. ———. [Process for Separating Catalysts From Liquids and Remixing With Fresh Charge Stock.] German Patent Appl. —, OZ 13,955, filed Jan. 26, 1943. TOM Reel 17, item 40, frames 1,193–1,196; Meyer Transl. PC–S–V, Oxo, vol. 2, chap. 31, 1949, p. 3.

In separating catalysts from liquids and mixing them again with fresh charge stock, both operations are carried out in a centrifuge in which 2 liquid layers form, the inner of which, free of catalyst or coarse catalyst particles, is removed, whereas the other layer containing the catalyst is mixed in the centrifuge with fresh charge.

1452. ———. [Process for Separating Mixtures of Alcohols and Hydrocarbons.] German Patent Appl. —, filed Oct. 6, 1942. TOM Reel 19, item 141, frames 1,656–1,660.

In separating high-molecular alcohols from mixtures with hydrocarbons in accordance with the main patent, the mixture is dissolved in a liquid solvent, such as petroleum ether, and the solution then allowed to flow over a substance such as silica gel, which adsorbs the alcohols that are recovered by means of steam, preferably superheated, or hot gases. Addition to German Appl. I 72,811, OZ 13,570.

1453. ———. [Process for Separating Mixtures of Alcohols and Hydrocarbons.] German Patent Appl. I 73,795, OZ 13,831, filed Dec. 8, 1942 (*Cl. IV d–12 o*). TOM Reel 17, item 37, frames 1,054–1,057; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 3, chap 112, p. 17.

In separating higher molecular weight alcohols, liquid mixtures or mixtures of alcohols and hydrocarbons, liquefied by heating, are treated without the use of a solvent. Example: A mixture of alcohols and hydrocarbons, obtained from CO and H_2 synthesis at medium pressure and at temperatures $<250°$ in the presence of Fe catalyst, is fractionated. 5 parts of the fraction 300°–350°, containing 60% of higher alcohols, are contacted with 2.5 parts of wide-pored silica gel for about 30 min. After separation of the hydrocarbon-rich portion not retained by the gel, the latter is treated with a mixture from the same source b. 60°–100° containing 60% MeOH, ethanol, and acetone. On distilling the liquid there are obtained 1.3 parts by weight of a residue containing up to 95% of higher alcohols. Instead of using the mixture mentioned, the alcohols retained can be removed with H_2 at 280°. Addition to German Patent Appl. I 72,813 and I 73,572 (abs. **1564** and **1554**).

1454. ———. [Process for Separating Mixtures of Alcohols and Hydrocarbons by Means of Adsorption Agents.] German Patent Appl. —, filed Oct. 5, 1942. TOM Reel 19, item 141, frames 1,661–1,664.

The mixture is broken down into fractions, which consist of alcohols and hydrocarbons of about the same molar magnitude, and each of these fractions are contacted with adsorbent materials, which adsorb the alcohols. These are then recovered by means of solvents or if desired by superheated steam or hot gases. A fraction of higher boiling range may be brought into contact with the adsorbing material retaining the alcohols, and the adsorbed higher-molecular alcohols are removed from the adsorbent with a lower boiling fraction of the alcohol-hydrocarbon mixture.

1455. ———. [Process for Shifting the Double Bond in Olefinic Hydrocarbons.] German Patent Appl. I 73,149, OZ 13,662, filed Sept. 12, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 7,363–7,367; PB 68,533; TOM Reel 17, item 31, frames 820–824; TOM Reel 134, item VII–9, 5 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 3, chap. 123, 1948, p. 54.

Olefinic hydrocarbons with at least 4 C atoms in a straight chain may have their double bonds shifted to middle positions by subjecting the hydrocarbon to the action of a metal carbonyl under such conditions of temperature and pressure that the hydrocarbon is changed to the isomeric form. Example: A Fischer-Tropsch product b. 100°–160°, is heated for 2 hr. at 150° and under 70 atm. pressure in the presence of CO and about 3% of Co on kieselguhr. After the treatment there is noted a considerable increase in octane number of the gasoline but no other change in the properties.

1456. ———. [Process for the Catalytic Reduction of the Oxides of Carbon with Hydrogen.] German Patent Appl. —, OZ 14,259, filed June 23, 1943. TOM Reel 134, item II–5, 7 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 3, chap. 121, 1948, p. 48.

In the catalytic conversion of C oxides with H_2 in the presence of catalysts containing Fe and/or Ni, preferably under elevated pressure, the gas is converted only to a slight extent, the H_2O in the mixture leaving the catalyst space is extensively removed, and the remaining gas further converted. In the intermediate separation the H_2O is removed so that the ratio of the partial pressure of steam to the pressure of the gases under conversion is < 0.05, preferably < 0.1. By this procedure the formation of CO_2 is greatly reduced, and a much better utilization of the synthesis gas is realized. Example: An hourly feed of 350 m.^{3} of fresh synthesis gas ($CO : H_2 = 1 : 1.4$) per m.^{3} of catalyst is passed at 25 atm. gage over a fused Fe catalyst. The synthesis gas is then recycled with 15 times the recycle, based on the amount of fresh feed. The gas leaving the reactor is cooled to 20°, after separation of the reaction H_2O, and brought again to the synthesis temperature in a preheater and then returned to the reactor where the reaction occurs at 183° with a conversion of 150 m.^{3} of gas per hr. A yield of 160 gm. of liquid product per m.^{3} of processed gas, with a total content of about 65% alcohols is obtained. The reacted O is present in the form of H_2O to the extent of 92%, and in the form of CO_2, only 8%.

1457. ———. [Process for the Catalytic Reduction of the Oxides of Carbon With Hydrogen.] German Patent Appl. I 76,934, OZ 14,626, filed Mar. 1, 1944 (*Cl. IV d–12 o*). FIAT Reel 171, frames 10,005–10,011; PB 25,615; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 5, chap. 154, 1949, p. 29.

In the conversion of CO with H_2 to hydrocarbons in the presence of Fe or Ni catalysts under pressure, the formation of CO_2 can be greatly restricted and H_2O obtained instead. This can be removed from the process and the residual gas recirculated and converted, by regulating the conversion of the original gas mixture

to so limited an extent that the uncooled gas mixture leaving the catalyst space exhibits a partial-pressure ratio of H_2O vapor to CO and $H_2 < 0.1$ and preferably < 0.05. By this means the formation of CO_2 can be reduced to 1/10 or even less and the troublesome enrichment of the synthesis gas in CO_2 greatly restricted and a more efficient use of the synthesis gas made possible. This is contrary to the previously stated opinion as to the effect of Fe catalysts on the course of the conversion.

1458. ———. [Process for the Conversion of Carbon Monoxide With Hydrogen.] German Patent Appl. I 65,518, Aug. 28, 1939: OZ 11,747 (*Cl. IV d–12 o*). FIAT Reel 162, frames 208–215; PB 68,923.

In a process for producing hydrocarbons with > 1 C atom in the molecule from CO and H_2 in a converter in which the heat of conversion is conducted through the walls of the catalyst space into a cooling liquid, the CO and H_2 gas passes through the converter at a linear flow velocity of > 0.1 m. per sec., preferably > 0.6 m. per sec. The ratio of the space velocity of the synthesis gas in l. per hr. and per catalyst space to the depth of the catalyst layer in meters is maintained at not over 100. The synthesis gas is circulated in a continuous cycle through the converter in such a way that the amount of cycle gas is at least 4–5 times that of the fresh gas.

1459. ———. [Process for the Conversion of Carbon Monoxide With Hydrogen.] German Patent Appl. I 70,050, filed July 11, 1941; OZ 12,887 (*Cl. IV d–12 o*). FIAT Reel 165, frames 4,603–4,608; PB 66,902.

In a process for producing branched hydrocarbons from CO and H_2 by the use of catalyst having carriers of active silicates, the highest yields are obtained when the total pore volume of the carrier consists of at least 30%, preferably 60–85%, of pores having diameters < 2 millimicrons, or at least 15%, preferably 30–60%, of < 1 millimicron diameter. Describes preparation of the catalyst.

1460. ———. [Process for the Conversion of Carbon Monoxide With Hydrogen.] German Patent Appl. I 70,366, filed Aug. 30, 1941; OZ 12,964 (*Cl. IV d–12 o*). FIAT Reel 166, frames 4,893–4,898; PB 68,703.

Product of the conversion is cooled on emerging from the converter by being brought into indirect heat exchange with a cooler gas such as fresh synthesis gas. After the condensate is removed, the remaining gaseous and vaporous product is further cooled by indirect heat exchange with the cool liquid product obtained by the conversion of CO with H_2.

1461. ———. [Process for the Conversion of Carbon Monoxide With Hydrogen.] German Patent Appl. I 70,367, filed Aug. 30, 1941; OZ 12,963 (*Cl. IV d–12 o*). FIAT Reel 166, frames 4,887–4,891; PB 68,702.

In a process for converting CO with H_2 to branched hydrocarbons and, if desired, to liquid and solid O-containing organic compounds at increased temperature, and, if desired, under pressure in presence of catalysts containing metals of the Fe group, the products emerging from the catalyst space are brought for the purpose of cooling into immediate heat-exchange relation with the colder liquid product likewise obtained from the conversion of CO with H_2. Reference to a diagram is essential for understanding the method.

1462. ———. [Process for the Conversion of Carbon Monoxide With Hydrogen.] German Patent Appl. I 70,455, filed Sept. 16, 1941; OZ 12,989 (*Cl. IV d–12 o*). FIAT Reel 166, frames 4,975–4,980; PB 68,722.

In a process for converting CO with H_2 into liquid and solid O-containing organic and branched hydrocarbons in several steps, after each individual step the CO_2 is washed from the residual gas by H_2O under pressure down to about 4%, the wash H_2O being then expanded and the CO_2 content reduced to equilibrium with the washed gas. By such a means, according to an example, the yield of O-containing organic compounds and branched hydrocarbons can be raised to 148 gm. per $m.^3$ of raw gas and 10 gm. gasol, as compared with 139 and 6 gm., respectively, with an unregenerated wash H_2O.

1463. ———. [Process for the Preparation of Olefins From Gaseous or Vaporized Saturated Hydrocarbons.] German Patent Appl. I 52,516, OZ 8,906, filed June 7, 1935 (*Cl. IV d–12 o*), Meyer Transl. PC–S–II, Fischer- Tropsch, vol 1, chap. 70, 1948, p. 178.

In preparing olefins from gaseous or vaporized saturated hydrocarbons (except CH_4) by addition of O_2 to the separately preheated hydrocarbons, the O_2 on contacting the hydrocarbons is so greatly diluted by introducing at least 1 of the gases with high rate of flow, or by mixing the gases under reduced pressure, that the formation of flame or local overheating does not occur. Example: Vapors of 3.1 kg. per hr. of middle oil from the hydrogenation of CO are introduced into the central line of a mixer of the type of a H_2O-jet pump, while through the jacket of the mixer, 530 l. of O_2 are passed per hr. The oil vapor is preheated to 600°–650° and the O_2 to 500°. After passing through the apparatus heated to 820°, the reaction product is cooled, the liquid constituents separated, and the gases drawn off by a vacuum pump. 3 $m.^3$ of gas are obtained hourly containing 33% by volume of C_2H_4 and 20% higher olefins consisting almost entirely of propylene and butylene. Based on the oil charged and 1 pass, about 75% by weight of olefins is obtained.

1464. ———. [Process for the Production of a Hydrogen-Carbon Monoxide Mixture Suitable for Synthesis Gas.] German Patent Appl. I 75,218, OZ 14,223, filed June 7, 1943 (*Cl. IV b–26 a*). FIAT Reel 170, frames 9,053–9,058; PB 64,147.

Process with diagram of the apparatus and operation thereof is described for producing synthesis gas by the complete gasification of coal in a slagging generator with the help of O_2 and steam. The coal is first distilled at low temperature in the upper part of the producer, part of the resulting gas is burned with O_2, the remainder together with steam, tar, and dust is injected into the bottom of the producer. The slag is drawn off at the bottom.

1465. ———. [Process for the Production of Alcohols.] German Patent Appl. I 75,247, OZ 14,226, filed June 9, 1943 (*Cl. IV d–12 o*). FIAT Reel 170, frames 9,064–9,070; PB 64,150.

Process is given such as described in German Patent Appl. I 70,009 (abs. **1373**) and I 75,246 (abs. **1467**) for the production of alcohols by the conversion of other alcohols of lower C number using CO and H_2 at increased temperature and pressure. The temperature and pressure conditions are maintained under which conversion takes place in the liquid phase. The catalysts are made up of carbonyl-forming metals of the 8th group or compounds of them and are activated by additions of heavy metals of group 1 or their compounds, preferably with metals of groups 5 or 6, their salts, or oxides. Particularly advantageous are halogenides of groups 1, 5, or 6. The object of the invention is to produce the greatest quantity of the lower alcohol with exclusion of the higher alcohols, acids, esters, and the like. Gives 5 examples.

1466. ———. [Process for the Production of Antiknock, Storage-Stable Gasoline.] German Patent Appl. ––, OZ 12,069, filed Mar. 19, 1940. TOM Reel 17, item 38, frames 1,070–1,076; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 3, chap. 113, 1948, p. 19.

To improve unstable gasolines, particularly those obtained by cracking hydrocarbons or by catalytically

hydrogenating CO, the material to be improved is brought together with a mixture of H_2 and CO suitable for conversion to hydrocarbons at such temperatures and pressures and in the presence of such known catalysts that stable hydrocarbons are formed from CO and H_2. Example: CO and H_2 are reacted at about 190° in 2 steps in tubular converters provided with a Co catalyst. The gas remaining in the 1st step after the removal of the liquid hydrocarbons has the following composition: CO_2, 0.6%; H_2, 60.2%; CO, 19.8%; CH_4, 11.0%; N_2, 8.4%. It serves as synthesis gas for the 2d step. Daily in this step there is sprayed, per l. of catalyst, 2 l. of a gasoline produced by cracking a gasoline obtained by the reduction of CO by the Fischer process and having an olefin content of 41%, an octane number 68, and a bomb test of 33. The end product, which contains about 10% of the synthetic gasoline, after distilling off the constituents b. >200°, gives a gasoline with olefin content 39%, octane number 66, and a bomb test of O. The loss by evaporation is virtually nil. The synthesis of stable hydrocarbons is not appreciably affected by the introduction of the cracked gasoline. The yield decreases only to about 95% of normal.

1467. ———. [Process for the Production of Oxygen-Containing Aliphatic Compounds.] German Patent Appl. I 75,246, OZ 14,225, filed July 9, 1943 (*Cl. IV d–12 o*). FIAT Reel 170, frames 9,062–9,063; PB 64,149.

In a further development of the process for producing O-containing aliphatic compounds in accordance with German Patent Appl. I 70,009 (abs. **1373**), MeOH may be substituted by 1 of its homologs in the liquid phase at temperatures >100°, but < the critical temperature of the alcohol being used at the time, and at a pressure >300 atm. The conversion is carried out with CO and H_2 in presence of a catalyst consisting of a carbonyl-forming metal of the 8th group or its compounds. An example describes the use of ethyl alcohol as the raw material.

1468. ———. [Process for the Production of Oxygen-Containing Compounds.] German Patent Appl. I 75,063, OZ 14,189, filed May 19, 1943 (*Cl. IV d–12 o*). FIAT Reel 170, frames 8,949–8,953; PB 64,120.

In carrying out the Oxo reaction, trouble has been experienced in the formation of carbonyl from the Co catalyst, the solution of this carbonyl in the products of reaction and its removal from the process thus robbing the catalyst. This phenomenon of carbonyl formation takes place whether the catalyst is in the solid fixed state, suspension, or slurry form. According to the main patent application, the reaction is performed in 2 steps, each in separate vessels and on identical catalysts. The carbonyl formed in the 1st stage is carried over to the 2d stage, becomes reconverted to the metal by action of H_2, and is deposited on the catalyst carrier. After about 24 hr. the flow is reversed, and the depleted catalyst in the 1st vessel is renewed. This patent application specifies that the catalyst be in the fixed and solid form. Addition to German Patent Appl. I 74,496 (abs. **1259**).

1469. ———. [Process for Working up the Products Obtained by Conversion of Carbon Monoxide With Hydrogen.] German Patent Appl. I 73,342, OZ 13,711, filed Oct. 10, 1942 (*Cl. IV d–12 o*). FIAT Reel 169, frames 8,728–8,732; PB 25,613; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 7, chap. 200, 1950, p. 41.

Describes a method for distilling and fractionating the high-molecular products obtained by the reduction of CO with H_2.

1470. ———. [Producing Oxygenated Compounds.] German Patent Appl. I 73,818, OZ 13,835; filed Dec. 11, 1942 (*Cl. 12 o–5.02*). FIAT Reel 169, frames 7,887–7,890; PB 25,613; TOM Reel 36, bag 3,454, items 17, 21, and 32, frames 906–910; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 26, 1948, p. 64.

When CO and H_2 are added to olefinic compounds with double bonds in presence of Co catalysts for the purpose of producing oxygenated compounds, difficulty is experienced in the formation of metal carbonyls and their solution in the liquid products. In the further hydrogenation of these liquid oxo-products to oxy-products, the carbonyls tend to break down, and the resulting CO interferes with the hydrogenation. Furthermore, the carbonyls are entrained in the hydrogenating gas thus wasting the catalyst and causing stoppages in the H_2 lines. These difficulties are prevented in accordance with this present invention by passing the liquid material to be hydrogenated into the liquid-filled part of the converter about 1 m. below the point where, under the conversion conditions, the separation of gas and liquid takes place. Example: 97 parts of a mixture of olefinic hydrocarbons, b. 200°–250°, and 3 parts of a Co catalyst activated with ThO_2 and MgO and deposited on kieselguhr are mixed to form a slurry and are continuously treated at 150° and 220 atm. with H_2. The liquid slurry coming from the converter contains 0.2% Co in the form of dissolved carbonyl. It is passed continuously, countercurrent to the H_2, into a vertical converter (described in German Patent Appl. I 73,072, abs. **1474**) of 200 mm. diameter and 8 m. tall, 1 m. below the liquid surface maintained at 7-m. level, at 185° and 200 atm. The gas leaving the converter contains no Co carbonyl.

1471. ———. [Producing Oxygenated Compounds.] German Patent Appl. I 74,142, OZ 13,947, filed Jan. 23, 1943 (*Cl. IV d–12 o*). FIAT Reel 169, frames 8,186–8,190; PB 25,613; TOM Reel 36, item 21, bag 3,454, 5 pp.; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 28, 1948, p. 68.

In producing oxygenated compounds by the reaction between CO, H_2, and olefinic compounds with double bonds in presence of catalysts containing metals of the 8th group, the conversion is performed in a tube coil in such a manner that the raw materials pass through in the same direction as the catalyst. Example: A slurry, consisting of 97 parts of an olefinic hydrocarbon mixture, b. 215°–235° with I number 70, and 3 parts of a catalyst containing 35% Co and some ThO_2 as promoter, is continuously pumped into a high-pressure pipe coil consisting of 3 parts, 2 parts of 24 mm. inside diameter and 1 of 45 mm., each section being 10 in. long. The separate parts are joined by pipes 60 mm. i. d., and these carry the gas-inlet nozzle. For the 1st 2 sections, which are maintained at temperatures of 128° and 138°, boiling H_2O circulating around the outside serves as the cooling medium, and the last section is kept at 150° by being immersed in a bath of tricresylphosphate. Into the 1st coil are injected hourly 6 $m.^3$ of water gas and into each of the other 2 coils 7.5 $m.^3$. Through the coils are pumped 100 l. of slurry per hr., thus giving a contact time of about 14 min. In spite of this short contact time more than 96% conversion of the charge into oxygenated compounds is attained.

1472. ———. [Producing Oxygenated Organic Compounds.] German Patent Appl. I 71,966, OZ 13,366, filed Apr. 4, 1942 (*Cl. IV d–12 o*). FIAT Reel 167, frames 6,262–6,268; PB 75,639; TOM Reel 36, item 21, bag 3,454, 7 pp.; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 14, 1948, p. 35.

Oxygenated compounds, such as aldehydes, ketones, and alcohols, are obtained by the interaction of CO and H_2 on olefins with double bonds at raised temperature and pressure in presence of catalysts and with the addition of enough H_2O to create a liquid condition in the reactor. Example: A pressure vessel is packed

with a catalyst of Co on silica gel, and a 1:1:1 mixture of C_2H_4, CO, and H_2 is passed over it at 200° and 200 atm. at a rate of 25 l. per hr. During the same time 10 l. of H_2O are trickled over it. The product of the reaction is an aqueous liquid with admixture of oily substances. After repeated fractionation at reduced pressure considerable propionaldehyde is obtained, with smaller amounts of higher boiling compounds, mainly ethylmethylacrolein.

1473. ———. [Producing Oxygenated Organic Compounds.] German Patent Appl. I 72,925, OZ 13,596, filed Aug. 10, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 7,071–7,077; PB 68,477; TOM Reel 36, 3,454, item 21; Meyer Transl. PC-S-V, Oxo, vol. 1, chap. 17, 1948, p. 42.

In the production of oxygenated organic compounds by treating olefinic compounds with CO and H_2 in the liquid phase under high pressure and high temperature in presence of catalysts, preferably with hydrogenation of the products, the liquid raw materials together with CO and H_2 are passed in parallel flow or counterflow through the pressure vessel in such a way that the entering material does not become mixed with the products leaving the reactor. If desired, an excess of CO–H_2 mixture can be used as a circulation gas, in which case the conversion products are not expanded until after the circulation gas is separated. In a pressure vessel 8 m. long and 200 mm. diameter, an hourly charge of 95 parts middle oil and 5 parts of catalyst (33% Co, 2% ThO_2, 2% MgO, and 63% kieselguhr) is maintained at 140°. Water gas (52% H_2, 41% CO, 2% N_2, and 5% CO_2) is admitted at the lower end at such a velocity that only 1/30 is chemically combined by the olefins in the liquid mixture. It acts mainly as a circulation gas to keep the mixture in suspension. After withdrawal of the reacted material, expansion takes place, and the liquid portion is hydrogenated at 180° and 200 atm., separated from the catalyst, and fractionated. A yield of mainly C_{16} and C_{17} alcohols, b. 315°–345°, amounting to 92% of the 95% converted olefins, is obtained.

1474. ———. [Producing Oxygenated Organic Compounds.] German Patent Appl. I 73,072, OZ 13,634, filed Aug. 31, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 7,221–7,227; PB 68,507; TOM Reel 36, bag 3,454, item 21, 6 pp.; Meyer Transl. PC-S-V, Oxo, vol. 1, chap. 23, 1948, p. 57.

In effecting the reaction of CO and H_2 on olefins for the production of oxygenated compounds, it has been found that the best temperature range for the reaction lies 80°–150°. To control most favorably the heat of reaction, it is found best to begin the conversion near the lower part of the temperature range and increase the temperature gradually toward the end of the reaction. In this manner the speed of conversion is maintained at a normal rate, and the yield of conversion products is improved. Gives diagram of an apparatus with 2 converters suitable for controlling the temperature of the process as suggested.

1475. ———. [Producing Oxygenated Organic Compounds.] German Patent Appl. I 73,291, OZ 13,705, filed Oct. 5, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 7,464–7,468; PB 68,561; TOM Reel 36, bag 3,454, item 21; Meyer Transl. PC-S-V, Oxo, vol. 1, chap. 25, 1948, p. 62.

When oxygenated compounds are obtained by the interaction of CO and H_2 on olefins, considerable quantities of the Co catalyst is lost by solution and otherwise. It is now proposed to recover and make use of this catalyst material by passing through the converter space at increased temperature and pressure CO, together with a solvent of the organic compounds of the catalyst metal as well as an organic acid suitable for the formation of a soluble metal salt. The solution thus obtained is added to the olefinic raw material. Example: Through the synthesis converter provided with a Co catalyst is passed, at 160° and 200 atm. with injection of CO and H_2 in proportion of 1:1, at the rate of 700 cc. per hr., a mixture of 97.25 wt. % of a synthetic gasoline having a 65% olefin content, 2% of a synthetic alcohol obtained by synthesis from CO and H_2 serving as a solvent for the catalyst, and 0.75% of the Co salt of a so-called first-run fatty acid from paraffin oxidation. The crude liquor contains about 0.12% of Co; the conversion mixture leaving the reactor space an average of only 0.006% Co. There is formed then from the metal precipitated in the reactor space and from the acid under the influence of the CO the metal salt corresponding to that dissolved in the solvent utilized. After all the metal has been recovered, the solution is added to the original catalyst. Addition to German Patent Appl. I 71,700 (abs. **1504**).

1476. ———. [Producing Oxygenated Organic Compounds.] German Patent Appl. I 74,240, OZ 13,972, filed Feb. 2, 1943 (*Cl. IV d–12 o*). TOM Reel 36, bag, 3,454, item 21, 7 pp.; Meyer Transl. PC–S–V, Oxo, vol. 2, chap. 33, 1949, p. 7.

In producing oxygenated compounds by adding CO and H_2 to hydrocarbons with at least 4 C-atoms in a straight chain and with olefinic double bonds, the raw material, before contact with CO and H_2, is exposed to Co carbonyl or to Co or other Co compounds and CO under pressure and at slightly raised temperature, preferably >100°. Example: 100 parts of a dodecylene with terminal double bonds is treated with 4 parts of a catalyst (30 Co: 2 ThO_2: 2 MgO: 66% kieselguhr) in a pressure vessel for 15 min. and with CO at 160° and 100 atm. After cooling and expanding, CO and H_2 are added at 135°. The alcohol mixture obtained by subsequent hydrogenation at 190° with H_2 at 200 atm. is a highly branched alcohol mixture.

1477. ———. [Producing Oxygenated Organic Compounds From Carbon Monoxide and Hydrogen.] German Patent Appl. —, OZ 14,718, filed Apr. 25, 1944. FIAT Reel 172, frames 640–643; PB 25,616; Meyer Transl. PC–S–II, Fischer-Tropsch vol. 2, 1938, chap. 90, p. 44.

In producing oxygenated organic compounds besides hydrocarbons by the hydrogenation of CO in the presence of Fe catalysts at medium pressure and temperatures, the yield of higher alcohols can be greatly increased by using Fe catalysts, which contain 0.1–0.7% K or an equivalent amount of another alkali metal calculated on the dry catalyst. Gives directions for preparing such precipitated and fused catalysts.

1478. ———. [Producing Oxygen-Containing Organic Compounds.] German Patent Appl. I 75,412, OZ 14,274, filed July 1, 1943 (*Cl. IV d–12 o*). FIAT Reel 170, frames 9,204–9,205; PB 64,185.

In producing oxygenated organic compounds by the conversion of compounds containing at least 1 olefinic double bond and in presence of catalysts containing O with H_2O_2 or with compounds yielding this under the conversion conditions, the reaction is carried out in an acid medium. Example: Into 100 parts of a 0.5% aqueous solution of Os tetroxide, with a pH concentration of 3–4, is stirred at 30° a mixture of 720 parts of a 70% aqueous solution of allyl alcohol and 870 parts of a 36% aqueous solution of H_2O_2, the pH being maintained at 3.5–3.75 by simultaneous addition of an aqueous KOH solution. The conversion begins at once and occurs rapidly yielding, after the usual workup, 90% of the calculated amount of glycerin. At pH concentrations > or <3–4, the yields fall greatly.

1479. ———. [Producing Unsaturated Hydrocarbons.] French Patent 843,844, July 11, 1939. Chem. Abs., vol. 34, 1940, p. 7091.

Mixture of hydrocarbons rich in unsaturated constituents is obtained from a mixture of CO and H_2 by using for the catalytic reaction a gas containing less than 2 parts by volume of H_2 for every part by volume of CO and adding new quantities of H_2 in the course of the reaction. As catalysts are used Co or Ni on appropriate supports, mixtures of Fe and Cu, the Fe obtained by reduction of ferrous-ferric oxide in presence of silicic acid, Ti oxide or alumina, and metals of the Fe group with Mn and Cu or with Al or with Th oxide. Thus, a gas containing 0.9–1.5 parts H_2 for every part CO is caused to pass, under atmospheric pressure and at a temperature ranging 160°–350°, over 1 of the above mentioned catalysts; the ratio of H_2 : CO is maintained during the reaction by adding new quantities of H_2. The contents in olefins of the more volatile fractions of the final products amount to 50–80%.

1480. ———. [Production of Aliphatic Chlorhydrocarbons.] Italian Patent 390,187, July 31, 1941. Chem. Zentralb., 1942, II, p. 2849.

Mixture of monosulfochlorides produced by the action of SO_2 and Cl_2 on hydrocarbons obtained from CO hydrogenation b. 230°–320° and freed from unsaturated and oxygenated compounds, is dissolved in xylol and heated (138°–140°) until evolution of SO_2 ceases. After distilling off the xylol monochlorhydrocarbons are obtained containing 15% Cl.

1481. ———. [Production of Antiknock Gasoline.] German Patent Appl. I 74,059, OZ 13,904, filed Jan. 11, 1943 (*Cl. IV d–23 b*). FIAT Reel 169, frames 8,066–8,069; PB 25,613.

In the process for producing gasoline by cracking hydrocarbons and alkylating isobutane, petroleum oils and CO reduction products are cracked separately. The isobutane separated from the cracking gases from the petroleum products is alkylized with the olefinic cracking products from the CO reduction products. The cracked gasoline and the alkylation gasoline are mixed. Only so much olefinic cracked products are made from the CO reduction products as are necessary for the alkylation of the isobutane obtained from the petroleum. Gasolines of high octane no. are obtained.

1482. ———. [Production of Antiknock Gasoline.] German Patent Appl. I 75,051, OZ 14,190, filed May 20, 1943 (*Cl. 12 o*). FIAT Reel 172, frame 387; PB 25,616.

Aldehydes, other than those produced by the reaction of olefins with CO and H_2, and ketones, which in neighboring position to the carbonyl group contain a methyl or a methylene group, are used as raw materials for the conversion with formaldehyde into unsaturated aldehydes or ketones, which are easily reduced to hydrocarbons. Addition to German Patent Appl. I 67,516 (abs. **1484**).

1483. ———. [Production of Antiknock Gasoline from the High Boiling Oils of Carbon Monoxide Hydrogenation.] Italian Patent 385,590, Oct. 25, 1940. Chem. Zentralb., 1942, II, p. 1202.

These oils are first passed at 200°–450° without essential cracking over dehydrogenating and isomerizing catalysts. For this purpose catalysts are advantageously used that have already served for the cracking of previously treated products. As cracking catalysts natural or artificial bleaching earths are preferably used.

1484. ———. [Production of Antiknock Motor Fuel From Olefins.] German Patent Appl. I 67,516, OZ 12,277, filed July 30, 1940 (*Cl. 12 o*). FIAT Reel 172, frame 140; PB 25,616.

Olefins, such as propylene, isobutylene, and the like, are converted with CO and H_2 in known manner at temperatures 50°–200° and pressures of 10–200 atm. or more in the presence of catalysts into aldehydes. These are condensed with CH_2O in presence of secondary or tertiary amines, which are partly in the form of their salts with carboxylic acids. The high molecular aldehydes thus obtained are reduced in known manner to hydrocarbons. The participants in the reaction are so chosen that the hydrocarbons are branched and have 5–11 C atoms. Suitable raw materials are both straight- and branched-chain olefins, which can be produced in any number of ways, for example, by the dehydration of alcohols, the splitting of chlor paraffins, or the conversion of CO with H_2. Suitable catalysts for the 1st step are those containing Co or Ni, the chromates of Mg, Cu or Hg, with carriers of pumice, bleaching earth, or alumina. The aldehydes are reduced preferably with H_2 under increased pressure (10–100 atm. or more) at 230°–350° with hydrogenating catalysts such as sulfides of the 6th or of the Fe group.

1485. ———. [Production of Diesel Oil.] German Patent Appl. I 63,192, OZ 11,209, no date; APC TC 1,156.

Diesel fuel is made by blending oil deficient in H, such as obtained by mild hydrogenation of coal, with hydrocarbons b. > about 200° C. obtained by cracking the product of the hydrogenation of CO. This cracked oil, preferably from catalytic cracking, is stated to be relatively rich in H and yet will not allow separation of asphaltic matter from the blended fuel.

1486. ———. [Production of Dispersing Agents.] German Patent Appl. I 73,176, OZ 13,666, filed Sept. 15, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 7,368–7,370; PB 68,534.

Mixture of high-molecular hydrocarbons melting at 98° obtained from the hydrogenation of CO is oxidized with addition of 0.15% K permanganate in aqueous solution by a stream of air of 20 $m.^3$ per hr. at 130° to an acid number of 22. To 4,000 kg. of the melted product are added 50 kg. of a fatty acid mixture b. 240°–300° at 1 mm. pressure obtained from the oxidation of paraffin. The acid number rises to 24. The saponified product is quite hard and is a good dispersion agent. Addition to German Patent Appl. I 67,977 (abs. **1372**).

1487. ———. [Production of Edible Fats and Oils.] German Patent Appl. I 68,798, OZ 12,569, filed Feb. 3, 1941 (*Cl. IV a–53 h*). FIAT Reel 164, frames 3,343–3,348; PB 25,608; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 52, 1949, p. 41.

In preparing edible fats and oils by esterification of fatty acid mixtures, which have been prepared by the oxidation of paraffin hydrocarbons and extensively freed of nonacidic constituents, fatty acid mixtures are used, which are as free as possible of dicarboxylic acid and branched chain fatty acids. It is also best to remove any fatty acids that contain O besides the carbonyl group. Example: Paraffin gatsch, obtained by the catalytic hydrogenation of CO, is oxidized with air and the oxidation products saponified. The soaps are heated to 300° and the unsaponified constituents distilled off. The soaps are then split with mineral acid and the mixture of the free fatty acids distilled. The C_{10}–C_{22} fraction of the fatty acids is then freed of the dicarboxylic acids and a part of the hydroxy and keto acids by washing with dilute NaOH and then by H_2O. The refined fatty acids are then freed of the branched-chain fatty acids by the method of German Patent 744,136 (abs. **1847**). An edible fat, harmless to the human organism, is obtained from the refined fatty acid mixture by esterification with glycerin.

1488. ———. [Production of High-Molecular-Weight Alcohols.] German Patent Appl. I 74,465, OZ 14,033, filed Mar. 2, 1943 (*Cl. IV d–12 o*). FIAT Reel 169. frames 8,514–8,517; PB 25,613; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 55, 1949, p. 47.

High molecular weight alcohols are produced from the fatty acid residues or the high boiling fractions and residues of the distillation of synthetic fatty acids obtained by the oxidation of paraffin by dissolving the starting material in a solvent, which is not easily altered by hydrogenation, such as alcohols of medium chain lengths of 4–10 C atoms, freeing the solution of inorganic impurities, and then treating with H_2 in the presence of fixed catalysts and at elevated temperature and pressure (230°–270° and 100–500 atm.). Suitable catalysts consist of Cu-Cr promoted by additions of Zn, Ba, and precipitated on silica gel, kieselguhr, or alumina. Different types of alcohol mixtures are obtained, depending upon the nature of the raw material.

1489. ———. [Production of Liquid Hydrocarbons and Their Derivatives.] French Patent 632,011, Dec. 30, 1927; appl. filed Apr. 4, 1927. Chem. Zentralb., 1928, I p. 1738.

Gas mixtures containing CO and H_2 are passed at raised temperatures and at any pressure over catalysts consisting wholly or partly of metal sulfides. Example: Water gas at about 20 atm. pressure is passed through an Al-lined pressure vessel at 270° over a catalyst of CoS. A petroleumlike oil is obtained by cooling the exit gases.

1490. ———. [Production of Low-Boiling Liquid Hydrocarbons.] German Patent Appl. I 63,778, OZ 11,353, filed Feb. 11, 1932 (*Cl. 12 o–1.03*). FIAT Reel K 30, 7,620–7,623; PB 73,587.

Catalysts are produced by gradual precipitation from Co salt solutions over a precipitation time of >3 hr.

1491. ———. [Production of Methanol and Other Oxygenated Organic Compounds.] Austrian Patent 116,601, Apr. 10, 1930; appl. filed Sept. 26, 1923, in Germany July 23, 1923. Chem. Zentralb. 1930, II, p. 852.

See French Patent 571,356 (abs. **2369**).

1492. ———. [Production of Multibranched Alcohols.] German Patent Appl. I 75,762, OZ 14,379, filed Aug. 28, 1943 (*Cl. IV d–12 o*). FIAT Reel 1770, frames 9,456–9,458; PB 64,261.

This application appears to be an addition to German Patent Appl. I 75,412 (abs. **1478**). As catalysts are specified compounds of heavy metals of groups 1 and 2, such as Cu, Ag, Zn, Cd, or Hg, or metallic elements of group 5, such as As, Sb, or Bi.

1493. ———. [Production of Non-Knocking Motor Fuels by Conversion of Hydrocarbons.] British Patent 532,424, Aug. 30, 1939. British Chem. Abs., 1941, B, p. 134.

Formation of gaseous and low boiling products, which normally occurs during the catalytic cracking of hydrocarbons formed by reduction of CO with H_2, is suppressed if such cracking is effected in presence of a paraffinic base petroleum (10–50%.)

1494. ———. [Production of Organic Sulfur Compounds.] German Patent Appl. I 58,987, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 97.

Organic S compounds with easily saponifiable halogens are made by treating hydrogenated olefins with halogens and SO_2.

1495. ———. [Production of Organic Sulfur Compounds.] German Patent Appl. I 58,988, no date (*Cl. IV d. 12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 97.

Organic S compounds are made by treating with halogen and SO_2 the hydrocarbons obtained from the catalytic hydrogenation of CO. Addition to German Patent Appl. I 58,987 (abs. **1494**).

1496. ———. [Production of Oxidation Products of Carboxylic Acids.] German Patent Appl. I 66,643, OZ 12,052, filed Mar. 7, 1940 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 658–665; PB 83,253.

In producing oxygenated products of carboxylic acids by the catalytic oxidation of hydrocarbons, the liquid, olefinic hydrocarbons obtained through the catalytic hydrogenation of CO by H_2, preferably under pressure and in presence of Fe catalysts, are subjected to oxidation by air of other O_2-containing gases. Such hydrocarbon mixtures are very rich in olefins (up to 70–80%), particularly when they are produced from a synthesis gas containing <2 vol. H_2–1 CO. Suitable catalysts for the oxidation are those consisting of Mn, Cu, Pb, Co, or alkali- and alkaline-earth compounds. The best temperature is 70°–140°. For the lower-boiling fractions pressure is often necessary (up to 200 atm.) and a higher temperature (up to 180°). The oxygenated products have good lubricating properties; are solvents for natural and synthetic resins; and are useful as solvents and thinners in the paint and dye industries, as softeners in the linoleum, oilcloth, patent leather, and plastic fields, and as an assistant in the finishing of textiles and leather as a substitute for fatty oils.

1497. ———. [Production of Oxidation Products of Solid Hydrocarbons.] German Patent Appl. I 63,487, OZ 11,285, filed Jan. 13, 1939 (*Cl. IV d–12 o*). FIAT Reel J–281, frame 2,758.

In preparing oxidation products from solid hydrocarbon mixtures or their solid constituents obtained by the catalytic reduction of CO with H_2, the hydrocarbon mixtures are freed from the branched-chain hydrocarbons contained therein by treatment with solvents or with condensing, polymerizing, or oxidizing agents or by sweating or pressing and then oxidized.

1498. ———. [Production of Oxygenated Compounds.] German Patent Appl. I 72,531, OZ 13,498, filed June 19, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 6,707–6,712; PB 68,381; TOM Reel 36, item 21, bag 3,454, 6 pp.; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 16, 1948, p. 40.

Describes method for the recovery and utilization of dissolved Co metal in the liquid mixture of oxygenated compounds, obtained by the action of CO and H_2 on olefins. The liquid is allowed to trickle over pumice or other filling material under 25 atm. pressure and 100° in the presence of H_2. A part of the Co becomes deposited on the filler, which then is treated with CO at 200 atm. and then at 150° with the CO–H_2–olefin mixture used for making the oxygenated compounds. The Co goes into solution as the carbonyl, leaves the converter in the outgoing liquid, and can be used again as catalyst in the conversion of CO with H_2.

1499. ———. [Production of Oxygenated Compounds.] German Patent Appl. I 73,059, OZ 13,631, filed Aug. 28, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 7,209–7,216; PB 68,505; TOM Reel 36, bag 3,454, item 21; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 22, 1948, p. 54.

In the production of oxygenated organic compounds by reacting CO and H_2 with olefins at increased temperature and pressure in presence of catalysts with subsequent hydrogenation under increased pressure, it has been found that yields of alcohols can be increased by performing the hydrogenation in presence of a circulating stream of H_2. The CO content in this cycle gas is kept as low as possible, preferably under 0.1%. The CO can be removed from the H_2 cycle by catalytically converting it with H_2 under pressure. Also, previous to hydrogenation, the dissolved CO is removed from the conversion products produced during the 1st step of the process. Describes other methods and gives examples of operation.

1500. ———. [Production of Oxygenated Compounds.] German Patent Appl. I 73,820, OZ 13,837, filed Dec. 12, 1942 (*Cl. IV d–12 o*). FIAT Reel 169, frames 7,891–7,894; PB 25,613; TOM Reel 36, item 21, bag 3,454, 4 pp.; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 27, 1948, p. 66.

In producing oxygenated compounds by the catalytic reaction of CO and H_2 with olefins with double bonds under raised temperature and pressure and in presence of Co catalysts, the formation of metal carbonyls is greatly suppressed by causing the reaction between the CO, H_2, and olefins to take place more rapidly than carbonyl can be formed. This may be accomplished by increasing the active surface of contact between the reactants by various described means. By such means conversion takes place very rapidly. Example: A slurry consisting of 97 parts of a cracked Fischer-Tropsch paraffin and 3 parts of a Co catalyst containing 35% Co and 65% kieselguhr is treated with lively stirring at 140°–155° with water gas for an average period of contact of 7 min.; the amount of gas being 180 $m.^3$ per $m.^3$ of liquid. Olefin conversion is 97%. The material from the converter is then hydrogenated at 190°. The resulting alcohol is separated from the catalyst and the unreacted material by distillation. The product, m. 14°, is of higher grade than that, m. 5°, which is obtained at a contact time of 30 min.

1501. ———. [Production of Oxygenated Compounds, Particularly Alcohols.] German Patent Appl. I 73,384, OZ 13,725, filed Oct. 16, 1942 (*Cl. IV d–12 o*). FIAT Reel 169, frames 8,733–8,742; PB 25,613; TOM Reel 134, item II–3, 10 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 3, chap. 120, 1948, p. 44.

Describes process for the production of oxygenated compounds and multibranched hydrocarbons by the conversion of C oxides with H_2 in presence of Fe catalysts at medium pressures and at temperatures lower than those usually considered suitable for the formation of branched hydrocarbons. Example: A water gas ($CO:H_2=1:0.75$) is passed at 195° and 19 atm. over a catalyst consisting of Fe with Al_2O_3 and K_2O and reduced at 500° in H_2. The product yield is 160 gm. per $m.^3$ of converted gas, with an average alcohol content of 51 and 11% of other O-containing compounds. The alcohol contents of the various fractions were: Up to 200°, 48%; 200°–230°, 51%; 230°–350°, 58%; >350°, 33%.

1502. ———. [Production of Oxygenated Compounds Particularly Aldehydes or Ketones.] German Patent Appl. I 72,741, OZ 13,552, filed July 15, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 6,908–6,911; PB 68,437.

Olefins, such as ethylene or isobutylene, are reacted at raised temperature (100°–400°) and pressure (50–350 atm.), with CO and H_2O in presence of catalysts consisting of carbonyl-forming metals such as Ni, Co, W, or Mo on a carrier. A mixture, for example, of equal part of C_2H_4 and CO, and 50 cc. H_2O to each l. of catalyst, is passed over a Co catalyst (15% Co) on silica gel. By distillation of the liquid conversion products, diethylketone is obtained beside alcohols and aldehydes.

1503. ———. [Production of Oxygenated Organic Compounds.] French Patent 605,349, Oct. 12, 1925. Chem. Zentralb., 1928, I, p. 584.

See British Patent 266,405 (abs. **95**).

1504. ———. [Production of Oxygenated Organic Compounds.] German Patent Appl. I 71,700, OZ 13,284, filed Mar. 4, 1942 (*Cl. IV d–12 o*). FIAT Reel 167, frames 5,950–5,955; PB 75,563; TOM Reel 36, bag 3,454, item 21, 6 pp.; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 12, 1948, p. 31.

In producing aldehydes, ketones, and alcohols by treating olefin compounds with double bonds at increased temperature and pressure with CO and H_2 in presence of catalysts, the catalysts specified here are the organic compounds of the catalyst metal soluble in organic solvents. Especially suitable for this purpose are the Co, Ni, or Fe salts of high-molecular fatty acids, of the wholly or partly hydrogenated aromatic carboxylic acids, such as hexahydrobenzoic acid, and of other cyclic acids, such as naphthenic acid. The saturated hydrocarbons or ethers, especially the raw material supplied for the conversion, as for example, diisobutylene, are mentioned as inert solvents.

1505. ———. [Production of Oxygenated Organic Compounds.] German Patent Appl. I 72,605, OZ 13,521, filed June 26, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 6,765–6,769; PB 68,397.

Ethers or esters derived from alcohols with at least 2 C atoms, such as diethylether, tetrahydrofuran, also lactones such as butyrolactone, are reacted with CO and H_2 at raised pressure and temperatures (100–250 atm. and 100°–250°) in presence of metals of group 8 or other carbonyl-forming metals or their compounds on kieselguhr or the like with activators such as compounds of Mn, Th, Zn, or Cu. The products thus obtained are hydrogenated.

1506. ———. [Production of Oxygenated Organic Compounds.] German Patent Appl. I 72,947, OZ 13,597, filed Aug. 11, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 7,078–7,081; PB 68,478; TOM Reel 36, bag 3,454, item 21; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 18, 1948, p. 45.

In producing oxygenated organic compounds by reacting CO and H_2 with olefins at raised temperature and pressure (180°–250° and 250 atm.), in the presence of catalysts with subsequent hydrogenation of the products, use is made of raw materials, which are contaminated with S, and of metals of group 8 as catalysts. For the subsequent hydrogenation, S-resistant catalysts such as Ni–W sulfides are used at about 160°–250° and 200–220 atm.

1507. ———. [Production of Oxygenated Organic Compounds.] German Patent Appl. I 72,948, OZ 13,599, filed Aug. 11, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 7,084–7,090; PB 68,480; TOM Reel 36, bag 3,454, item 21; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 19, 1948, p. 47.

In producing oxygenated organic compounds, especially aldehydes or ketones or their hydrogenation products, through the reaction of CO and H_2 with olefins in presence of metals of group 8, the gas mixture, and desirably also the liquid reaction products, are freed from compounds of the catalyst metal by washing the gases leaving the reactor with liquids that are solvents for metal carbonyls, such as the liquid olefinic raw materials of the process. The washing may be done at 0°–30° and 5–25 atm. pressure. Also, it may be done in 2 steps; 1st, with the fresh olefinic raw material and then by adsorption with dilute HNO_3 or other oxidizing agents. After washing, the washing liquid as well as the washed gas are used in the process.

1508. ———. [Production of Oxygenated Organic Compounds.] German Patent Appl. I 72,975, OZ 13,604, filed Aug. 15, 1942 (*Cl. 12 o–5.02*). FIAT Reel 168, frames 7,116–7,120; PB 68,485; TOM Reel 36, bag 3,454, item 21; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 20, 1948, p. 50.

In the process for producing oxygenated organic compounds by reacting CO and H_2 with olefins at raised temperature and pressure in presence of catalysts and with subsequent hydrogenation, a raw material is used that has been thoroughly freed from organic S compounds (various methods are specified), and the con-

version and the subsequent hydrogenation are carried out in the presence of metals of group 8. The conversion process is performed at 80°–150° and at least 50 atm. for 1 hr., with an excess of S-free water gas so that the catalyst is kept suspended. After hydrogenation and separation by filtration and distillation of the filtrate, a yield of 60% of C_{15}–C_{19} alcohols, calculated on the olefins converted, is obtained.

1509. ———. [Production of Oxygenated Organic Compounds.] German Patent Appl. I 72,982, OZ 13,610, filed Aug. 19, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 7,149–7,151; PB 68,491; TOM Reel 36, bag 3,454, item 21, 3 pp.; Meyer Transl. PC-S-V, Oxo, vol. 1, chap. 21, 1948, p. 52.

Crude primary products of the hydrocarbon synthesis from CO- and H_2-containing oxygenated compounds are hydrogenated under such conditions as are the most suitable for the conversion of carboxylic acid esters into alcohols. Example: A primary product of hydrocarbon synthesis from CO and H_2 is treated with CO and H_2 in proportion of 1:1 in presence of a Co catalyst at 150° and 200 atm. until no more of the CO–H_2 mixture is taken up. The conversion mixture is trickled at 200°, at the rate of 8 l. per hr. through a high-pressure tube of 25 l. capacity filled with a Cu catalyst on silica gel activated by Cr and Ba, into which H_2 is passed at 200 atm. pressure. The product issuing from the tube is colorless and consists mainly of alcohols, which can easily be sulfonated to alcohol sulfonates.

1510. ———. [Production of Sulfonic Acids and Esters.] Belgian Patent 443,658, Dec. 9, 1941. Chem. Zentralb., 1943, I, p. 2142.

Saturated, nonaromatic hydrocarbons, alcohols, carboxylic acids or their derivatives are simultaneously reacted with SO_2, O_2, and photoactive rays.

1511. ———. [Production of Unsaturated Fatty Acids.] German Patent Appl. I 77,488, OZ 14,752, filed May 20, 1944 (*Cl. 12 o*). FIAT Reel 171, frames 10,333–10,334; PB 25,615.

Unsaturated fatty acids are produced, for example, from the primary alcohols obtained by oxidation of paraffins from the conversion of CO with H_2, by the conversion of halogenated fatty acids with alkaline agents at raised temperature and pressure. The operation is carried out in the presence of liquid H_2O instead of, as previously used, only that amount that would remain in the vapor form under the pressure used. The product is suitable as a substitute for oleic acid in soap manufacture or for the production of softeners, lacquers, dye bases.

1512. ———. Protecting Apparatus Used for Gas Reactions. British Patent 317,996, Aug. 29, 1928. Chem. Age, 1929, p. 294; Chem. Abs., vol. 24, 1930, p. 2015.

In carrying out reactions with gases such as H_2, CO, or H_2S, which attack the material of the apparatus, a small quantity of an inert material that remains liquid (such as paraffin added to a middle oil to be hydrogenated) is introduced so that it forms a protective film on the surface of the apparatus. The process may be applied to the synthesis of alcohol.

1513. ———. Purification of Methanol. British Patent 448,898, no date. Chem. Zentralb., 1936, II, p. 4768.

See United States Patent 2,115,553 (abs. **803**).

1514. ———. [Purification of Synthesis Hydrocarbons.] German Patent Appl. I 72,047, no date (*Cl. IV d–23 b*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 759.

Hydrocarbon mixtures obtained by the hydrogenation of CO are purified by passing them in vapor state at temperatures <350° over Mo oxide. This is an addition to German Patent 750,072 (abs. **1555**).

1515. ———. [Purification of Synthesis Products.] German Patent Appl. I 74,594, no date (*Cl. 12 o–5.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 213.

Reaction mixtures from the conversion of CO with H_2 are purified by the use of compounds from the resulting mixture, which are suitable as wash liquids.

1516. ———. Purification of Synthetic Methanol. British Patent 444,019, Sept. 7, 1934. Chem. Zentralb., 1936, II, p. 2446.

See United States Patent 2,083,125 (abs. **3257**).

1517. ———. [Purification of Synthetic Products.] French Patent 650,543, Mar. 7, 1928. Chem. Abs., vol. 23, 1929, p. 3236.

Synthetic substances such as MeOH, iso-BuOH, are purified by treatment with oxidizing agents, for example $KMnO_4$, if necessary with the addition of alkalies or organic bases and metal halides, with or without treatment with active purifying agents.

1518. ———. Purifying Alcohols. British Patent 494,985, Nov. 4, 1938. Chem. Abs., vol. 33, 1939, p. 2533.

Pure alcohols are obtained from aqueous solutions or mixtures of aliphatic alcohols containing carbonyl compounds as impurities by treatment with primary amines in the liquid phase under increased pressure at a temperature appreciably > the boiling point of the alcohols to be purified. Isohexylamine, isoheptylamine, isooctylamine, and dodecylamine may be used. Gives examples of the preparation of pure MeOH and PrOH from the crude products obtained synthetically from CO.

1519. ———. Purifying Hydrocarbons From Destructive Distillation. British Patent 257,270, Aug. 18, 1926; appl. filed Aug. 20, 1925. Chem. Zentralb., 1927, I, p. 1066; Chem Abs., vol. 21, 1927, p. 3123.

Products from the hydrogenation of carbonaceous materials are freed from tarry, O-containing substances by means of a low aliphatic alcohol (methyl, ethyl, and propyl alcohols), which has been obtained by the catalytic hydrogenation of CO under pressure.

1520. ———. [Purifying Organic Compounds.] French Patent 746,640, June 2, 1933. Chem. Abs., vol. 27, 1933, p. 4538.

MeOH and other products of higher boiling point containing O, produced by the catalytic treatment of oxides of C with H_2, are purified by heating them to 100°–300° under a pressure >50 atm. in the presence of O-containing compounds, which are not reduced to the metallic state under the conditions of working, or S-containing compounds of heavy metals of the 1st, 2d, 4th, 5th, 6th, or 8th group, or a mixture of such compounds.

1521. ———. [Purifying Organic Liquids.] German Patent 542,616, Oct. 16, 1923. Chem. Abs., vol. 26, 1932, p. 3261.

Organic liquids prepared catalytically from oxides of C and H_2 and containing impurities other than or as well as, MeOH, are purified by treatment with bases. Thus, the fractions going over at 105°–110° from crude oil obtained catalytically from H_2 and oxides of C, which is rich in terpenes is purified by distilling over burned lime. Gives further examples.

1522. ———. [Purifying Oxygenated Organic Compounds.] French Patent 614,127, Dec. 7, 1926; appl. filed Apr. 7, 1926. Chem. Zentralb., 1928, I, p. 617.

Oxygenated compounds obtained by the catalysis of CO and H_2 are catalytically hydrogenated in the vapor state after they have been treated with purifying agents. By means of hydrogenation the substances,

such as aldehydes and ketones, that are discolored or have an unpleasant odor are converted into colorless and nonodorous oils.

1523. ———. [Purifying Products of Methanol Synthesis.] Swiss Patent 122,810, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 218.

Products are hydrogenated with Ni as catalyst.

See British Patent 278,777 (abs. **1125**) and United States Patent 1,684,640 (abs. **3295**).

1524. ———. [Purifying Products of Methanol Synthesis.] Swiss Patent 136,373, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 218.

Purification with oxidizing agents such as H_2O_2, NaOCl, $KMnO_4$, with addition of nonvolatile alkalies or organic bases and of halogen salts.

See German Patent 508,953 (abs. **2379**) and United States Patent 1,744,180 (abs. **3760**).

1525. ———. [Purifying Synthetic Alcohols.] British Patent 311,468, Feb. 16, 1928. Chem. Abs., vol. 24, 1930, p. 861.

Alcohols such as methyl or iso-Bu alcohol obtained catalytically from H_2 and C oxides are purified by use of oxidizing agents such as $KMnO_4$, H_2O_2, persulfates, percarbonates, or hypohalites, followed by distillation. Organic bases or fixing agents such as $ZnCl_2$ may be added in small quantities, and auxiliary purifying agents may also be used such as NaOH, $NaHSO_3$, or oxalic acid.

1526. ———. [Purifying Synthetic Methanol.] French Patent 842,463, June 13, 1939. Chem. Abs., vol. 34, 1940, p. 5467.

See British Patent 500,745 (abs. **1337**).

1527. ———. [Reaction Between Carbon Monoxide and Hydrogen.] Belgian Patent 418,492, Apr. 30, 1937; appl. filed Nov. 19, 1936. Chem. Zentralb., 1937, II, p. 4101.

Fixed reaction temperature is maintained by removing the excess heat by indirect heat exchange with wet steam whose saturation point lies at 60–80%.

1528. ———. [Reaction of Carbon Monoxide With Hydrogen.] Italian Patent 351,714, June 14, 1937. Chem. Zentralb., 1938, I, p. 3693.

See British Patent 478,318 (abs. **1291**).

1529. ———. [Reaction of Hydrogen With Oxides of Carbon.] French Patent 814,082, June 14, 1937. Chem. Abs., vol. 32, 1938, p. 1060.

In the reaction of H_2 with oxides of C at a raised temperature and atmosphere or raised pressure, the excess reaction heat is absorbed by indirect exchange of heat with H_2O vapor having a humidity of 60%–80%. The H_2O vapor is used at such a pressure that the temperature of the saturated vapor is only slightly $<$ the desired reaction temperature.

See also British Patent 469,618 and Italian Patent 346,769 (abs. **1287** and **1541**).

1530. ———. [Reactions With Carbon Monoxide.] French Patent 799,270, June 10, 1936. Chem. Abs., vol. 30, 1936, p. 7396.

Surface of the apparatus coming in contact with hot CO, for example, in making MeOH from CO and H_2, is covered by an alloy obtained by diffusing Zn or Cd into Fe or steel.

1531. ———. [Recovering Volatile Substances.] French Patent 651,406, no date.

Liquid product b. $>200°$ obtained by the synthesis of MeOH from CO and H_2 is used as the wash oil.

See British Patent 302,297 (abs. **1538**).

1532. ———. [Recovery of Alcohols From Mixtures.] German Patent Appl. I 70,527, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 161.

High-molecular alcohols are recovered from their mixtures with nonalcoholic compounds of similar boiling range by forming the boric, arsenic, or phosphoric acid esters, separating the products by distillation with steam under reduced pressure, and finally hydrolyzing the esters.

1533. ———. [Recovery of Higher Molecular-Weight Carboxylic Acids or Their Salts.] German Patent Appl. I 67,224, OZ 12,205, filed June 19, 1940 (*Cl. IV d–12 o*). FIAT Reel 163, frames 2,005–2,009; PB 25,607; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 32, 1949, p. 3.

In recovering higher molecular weight carboxylic acids or their salts from mixtures containing unsaponifiable or unsaponified organic substances, such as the oxidation products of paraffins, middle oils, the hydrogenation products of CO, coal, and tar, the saponified mixture is extracted with fat solvents (gasoline or other liquid hydrocarbons) with the addition of such monovalent alcohols, ethers or esters thereof, or ketones with 3–6 C atoms in the molecule (propyl alcohol, acetone and methylethylketone), which are highly miscible with the fat solvents employed. By means of this process crude fatty acids are obtained that have a content of only 0.1–0.3% unsaponifiable constituents.

1534. ———. [Recovery of High-Grade Motor Fuels.] German Patent Appl. I 74,591, OZ 14,084, filed Mar. 22, 1943 (*Cl. 46 a*). FIAT Reel 172, frame 372; PB 25,616.

Propylene is converted together with CO and H_2 at raised pressure and temperature to aldehydes, which are reduced to alcohols and these to n– and i–butylene by splitting off H_2O. The latter are then converted to motor fuels by dimerization, alkylation with isoparaffins, and hydrogenation. The alcohols higher than n–butyl are subjected to a cracking hydrogenation with a MoS_2 catalyst at 400°–450° to produce an antiknock gasoline when mixed with that produced in the 1st step.

1535. ———. [Recovery of Hydrogenation Gas.] Austrian Patent 118,058, June 10, 1930; appl. filed June 11, 1926. Chem. Zentralb., 1930, II, p. 1313.

Hydrocarbon-containing gases, after addition of the necessary amount of O_2 or O_2-containing gas for complete combustion, are burned in the presence of catalysts with or without the presence of steam or CO_2, and the CO formed is wholly or partly removed from the reaction mixture. In this manner the waste gases of hydrogenation are made useful.

1536. ———. [Recovery of Low-Molecular-Weight Organic Oxygenated Products in the Oxidation of Nonaromatic Hydrocarbons.] German Patent Appl. I 68,657, OZ 12,543, filed Jan. 15, 1941 (*Cl. IV d–12 o*). FIAT Reel 164, frames 3,244–3,248; PB 25,608; Meyer Transl. PC-S-IV, Wax Oxidation, vol. 3, chap. 51, 1949, p. 39.

In the oxidation of higher molecular-weight nonaromatic hydrocarbons with O_2 or gases containing it, there are formed, besides higher molecular weight carboxylic acids, hydroxy acids, esters, aldehydes and ketones, considerable amounts of low-molecular-weight oxygenated compounds, chiefly lower fatty acids, which contain up to about 10 C atoms in the molecule, besides hydroxy acids and lactones of the same molecular size. They are obtained in the form of an aqueous condensate containing up to 40% of these compounds. It has been found that these low molecular weight oxidation products can be recovered in pure and

H_2O-free condition if the aqueous portion is extracted with a solvent mixture consisting of methyl-ethyl ketone and an ether or hydrocarbon b.<100° and, with H_2O, forms an azeotrope with a minimum boiling point. A mixture of methyl-ethyl ketone and benzene in proportions of 70:30 is a satisfactory mixture.

1537. ———. [Recovery of Organic Acids.] German Patent Appl. I 75,006, OZ 14,172, filed May 12, 1943 (*Cl. IV d–12 o*). FIAT Reel 170, frames 8,907–8,910; PB 25,614; Meyer Transl. PC-S-IV, Wax Oxidation, vol. 3, chap. 35, 1949, p. 9.

Describes process for recovering H_2O-soluble organic acids from acid mixtures, which have been obtained by the oxidation of nonaromatic hydrocarbons, saponification, separation of the unsaponifiable portions, and splitting of the crude soap with mineral acid. To recover the lower volatile H_2O-soluble acids the crude fatty-acid mixture is first subjected to distillation up to about 140° under a pressure of 25 mm., and then the less volatile, H_2O-soluble acids are treated with H_2O or aqueous solutions. The crude fatty-acid mixture obtained in accordance with the process of German Patent 707,227 (abs. **2081**) is a suitable charging stock.

1538. ———. [Recovery of Volatile Solvents.] British Patent 302,297, Sept. 12, 1927. Chem. Zentralb., 1929, I, p. 1645; Chem. Abs., vol. 23, 1929, p. 4282.

Products having a b. p.>200° obtained as byproducts in the catalytic hydrogenation of C oxides to form MeOH are used for washing gases and vapors such as result in the production of lacquers, artificial silk, or in cleaning fabrics.

1539. ———. [Reducing Oxides of Carbon.] French Patent 805,696, Nov. 26, 1936. Chem. Abs., vol. 31, 1937, p. 4461.

In catalytic treatment of oxides of C and H_2, the catalysts are formed of metal parts of apparatus, the surface of which entering in contact with the reacting gases is cleaned, preferably in the presence of activators, these parts being at the same time swept interiorly or exteriorly by a heating or cooling medium.

1540. ———. [Reduction of Carbon Monoxide With Hydrogen.] German Patent Appl. I 63,572, OZ 11,312, filed Jan. 21, 1939; APC TC 1,136.

For the synthesis of predominantly solid paraffins from CO and H_2, the catalyst is made by precipitating a compound of a metal of the Fe group on Al_2O_3 and immediately reducing the precipitate.

1541. ———. [Reduction of Carbon Monoxide With Hydrogen to Form Hydrocarbons.] Italian Patent 346,769, Dec. 1, 1936. Chem. Zentralb., 1938, I, p. 430.

See French Patent 814,082 (abs. **1529**).

1542. ———. [Reduction of Iron Catalysts.] German Patent Appl. I 70,151, OZ 12,930, filed Aug. 4, 1941 (*Cl. IV d–12 o*). FIAT Reel 168, frames 6,803–6,808; PB 68,406; Auszüge deut. Patent-Anmeldungen, vol. 6, p. 156; Meyer Transl. PC-S-II, Fischer-Tropsch, vol. 6, chap. 180, 1949, p. 48.

It has been discovered that the hydrocarbon synthesis process can be performed at lower temperatures with a considerably greater yield of oxygenated products, if reduction of the Fe catalyst is carried out at a very much higher rate of throughput of H_2 per hr. A rate of >800 $m.^3$ per $m.^3$ of catalyst per hr. is specified.

1543. ———. [Reduction of Oxides of Carbon.] French Patent 643,784, Nov. 12, 1927. Chem. Abs., vol. 23, 1929, p. 1648.

Organic O_2 compounds, alone or mixed with hydrocarbons, are obtained by reducing oxides of C under reduced, ordinary, or slightly raised pressure at a temperature <300° and using as catalyst Fe to which small quantities of alkalies or alkaline earths or their compounds are added. Examples are given in which Fe oxide wetted with KOH or NaOH solution is reduced with H_2 and a mixture of CO and H_2 containing 40% of H_2 is passed over it at 200°. A brownish yellow oily liquid containing 10% of O_2 and an aqueous solution having an acid reaction are obtained.

1544. ———. [Refining the Oxygenated Products of Carbon Monoxide Reduction.] German Patent Appl. I 72,407, OZ 13,475, filed June 3, 1942 (*Cl. IV d–23 b*). FIAT Reel 167, frames 6,641–6,644; PB 75,733.

Mixtures of hydrocarbons and oxygenated compounds, particularly alcohols, obtained by the conversion of CO with H_2 in presence of Fe catalysts, often are contaminated with Fe compounds, which become troublesome. The trouble can be alleviated by heating the mixture with a strong acid such as HCl, H_2SO_4, and, if desired after the addition of H_2O, separating the aqueous layer from the purified product. The Fe compounds go into solution in the H_2O and are extracted thereby. The color of the mixture also is improved thereby. The Fe content of the purified product is reduced from 0.1% to not >0.005%.

1545. ———. [Regenerating Catalysts.] German Patent Appl. I 71,558, OZ 13,255, filed Feb. 11, 1942 (*Cl. IV b–12 g*). TOM Reel 20, item 162, frames 2,588–2,594.

Describes process and an apparatus for removing the C deposits from catalysts in shaft furnaces, wherein the shaft furnace is divided into several successive zones, each provided with the essential O_2-containing gases. The regeneration takes place by steps.

1546. ———. [Regenerating Catalysts.] German Patent Appl. I 72,810, OZ 13,565, filed July 22, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 6,956–6,959; PB 68,444; TOM Reel 17, item 32, frames 890–893; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, chap. 94, 1948, p. 55.

In rebuilding used, so-called fused Fe catalysts, preferably after the removal of conversion products still held by them, by treatment with a solvent or at raised temperature with H_2 they are exposed to small amounts of O_2 or to another oxidizing gas until they no longer become heated in air and then are fused in a stream of O_2.

1547. ———. [Regeneration of Catalyst.] French Patent 857,174, no date.

See British Patent 516,160 (abs. **1207**).

1548. ———. [Regeneration of Catalysts.] German Patent Appl. I 73,366, Oct. 16, 1942, OZ 13,723 (*Cl. IV b–12 g*). FIAT Reel 170, frames 9,186–9,193; PB 64,182; TOM Reel 17, item 39, frames 1,109–1,117.

In regenerating catalysts that have become coated with C deposition by burning off the coke in the presence of O_2-containing gases without injuring the catalyst by excessive heat, the temperature of the catalyst at the beginning of the regeneration is kept lower and that of the gases higher than the ignition temperature of the coke deposit. Both temperatures are kept only high enough to maintain combustion of the coke without rising to undesirable heights. Specifies various ways for accomplishing this.

1549. ———. [Regeneration of Catalysts by Treatment With Oxygen-Containing Gases at Raised Temperature.] Italian Patent 386,631, June 1, 1940. Chem. Zentralb., 1942, II, p. 2626.

Gas is passed through the catalyst at such increased velocity that it carries away the heat so that undesired increase in temperature does not occur. It is best to begin with gases with low O_2 content, such as air, then continue with recirculation of the gas whereby it is cooled before its entrance into the catalyst to the

catalyst temperature and gradually increase the O_2-content. The method thus avoids temperature increases without retarding the regeneration. The process is especially suitable for the regeneration of catalysts used in the conversion of carbonaceous substances, such as the cracking of hydrocarbons, pressure hydrogenation, and the production of hydrocarbons by the conversion of CO with H_2.

1550. ———. [Removing Carbon Monoxide From Gases.] German Patent Appl. —, OZ 13,919, filed Jan. 14, 1943. TOM Reel 17, item 28, frames 625–629; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 109, 1948, p. 10.

In removing CO from gases obtained by the gasification of brown coal, using a cuprous oxide salt solution under pressure, there are added to the solution small amounts of synthetic alcohols with more than 12 C atoms in the molecule or mixtures containing them, particularly such as are obtained by the action of CO and H_2 on olefins and hydrogenation of the products, or by reduction of CO with H_2 at medium pressures in the presence of catalysts of the Fe group at temp. < 250°. The alcohols are used in the form of an aqueous emulsion, the emulsifying agent being prepared by the introduction of ethylene oxide into the alcohols themselves.

1551. ———. [Separating Alcohols and the Like From Mixtures With Hydrocarbons.] German Patent Appl. I 78,911, no date (*Cl. 12 o–5.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 248.

Alcohols, ketones, esters, and amines are separated from their mixture with hydrocarbons, particularly from those obtained by hydrogenation of CO, by adsorption on active gel by treating the gel after the adsorption operation with limited amounts of a H_2O-soluble organic solvent in which the adsorbed compounds are soluble and then displacing them in the gel by means of H_2O or a mixture of H_2O and an organic liquid in which the adsorbed substance is insoluble.

1552. ———. [Separating Alcohols From Mixtures.] German Patent Appl. I 74,834, no date (*Cl. 12 o–5.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 218.

High-molecular alcohols in mixture with hydrocarbons are separated by extraction 1st with dilute aqueous solutions of organic O-containing material, then with the concentrated solvent. Both extracts are then combined.

1553. ———. [Separating Liquids From Vapors.] German Patent Appl. I 73,619, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 198.

Separation of liquids from vapors, especially those obtained by condensation of the liquid hydrocarbons produced in the conversion of CO with H_2 in the presence of Fe catalysts.

1554. ———. [Separating Mixtures of Alcohols and Hydrocarbons.] German Patent Appl. I 73,572, OZ 13,783, filed Nov. 11, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 7,707–7,709; PB 68,623; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 6, chap. 178, 1949, p. 44.

In separating the high-molecular alcohols from their mixtures with hydrocarbons, obtained in the conversion of CO with H_2 on Fe catalysts at medium pressure, the mixture is dissolved in a solvent such as petroleum ether or light benzine. The solution is then caused to flow over an adsorbent material, such as silica gel or alumina, that has an affinity for the alcohols. The absorbent is washed with some of the solvent and the alcohols removed by treatment with superheated steam or with hot gases. A raw material containing 48% alcohols and 52% saturated and unsaturated hydrocarbons, contained after treatment only 4% alcohols. Addition to German Patent Appl. I 72,813 (abs. **1564**).

1555. ———. [Separating Oxygenated Compounds.] German Patent 750,072, no date; appl. I 69,940 (*Cl. 23 b–1.05*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 758.

Organic oxygenated compounds are removed from virtually S-free hydrocarbon mixtures obtained by the hydrogenation of CO by passing them <350° over oxides of W or V.

1556. ———. [Separating the Products of the Fischer-Tropsch Synthesis.] German Patent Appl. I 73,500, OZ 13,757; filed Nov. 3, 1942 (*Cl. IV d–12 o*). FIAT Reel 168, frames 7,615–7,625; PB 68,600; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 6, chap. 171, 1949, p. 21.

Describes process and apparatus for the stepwise cooling of the reaction gases and the separation of the condensible products. The temperature is so regulated in successive tube coolers that the liquid hydrocarbon products are removed in order of their molecular weights, the final low-boiling constituents being adsorbed on charcoal in the last vessel. It is specified that in at least 1 of the cooling steps the gas is passed in the direction opposite to the flow of the outgoing liquid products, preferably in intimate contact with them, and the temperature of the liquid products leaving the cooling step is kept considerably higher than that of the gas.

1557. ———. [Separating the Unsaponifiable Components From Sulfochlorinated Mixtures.] French Patent 52,734, May 17, 1945; appl. filed Jan. 26, 1943, in Germany Jan. 3, 1942; addition to French Patent 879,513. Chem. Zentralb., 1949, II, E, p. 90.

The method of the main patent, wherein liquid SO_2 is used to separate the unsaponifiable constituents, is improved by the subsequent or simultaneous application of a volatile or liquid hydrocarbon. Example: A hydrocarbon b. 240°–360° obtained by the hydrogenation of CO is sulfochlorinated. The product contains 4.5% of hydrolyzable Cl. After adding about 3.7 times amount of liquid SO_2, stratification takes place. The lower layer after evaporation of the SO_2 contains 12.5% of saponifiable and 5.7% of unsaponifiable constituents. After renewed treatment with 1.5 times the amount of liquid butane at —20° and subsequent stratification, the lower layer contains a product with only 0.8% unsaponifiables and 14.9% of hydrolyzable Cl.

See also German Patent 715,323 (abs. **1561**).

1558. ———. [Separation of Alcohols From Mixtures.] German Patent Appl. I 70,064, OZ 12,895, filed July 1, 1941 (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 155.

Alcohols are recovered from mixtures with non-alcoholic compounds by means of the boric acid esters and by saponification of the ester with aqueous boric acid solution introduced in a cycle. On cooling, the boric acid separates.

1559. ———. [Separation of Alcohols From Their Mixtures With Hydrocarbons.] German Patent Appl. I 77,004, OZ 14,653, filed Mar. 13, 1944 (*Cl. 12 o*). FIAT Reel 172, frames 611–614; PB 25,616.

Oxygenated organic compounds, particularly alcohols, in mixtures with hydrocarbons produced by the conversion of CO with H_2, are separated therefrom by adding H_2O-free MeOH to the mixture in amounts of ⅕–⅓ of the volume and then sufficient H_2O to cause a separation into 2 layers, 1 of which consists almost entirely of the hydrocarbons and the other of oxygenated compounds. In general, the amount of H_2O required is about 15–25% of the volume of MeOH added.

1560. ———. [Separation of Crude Synthesis Product.] Swiss Patent 141,673, no date. Schmidt, J., Das Kohlenoxyd. Akad. Verlagsgesell., Leipzig, 1950, p. 227.

See Norwegian Patent 63,409 (abs. **3438**).

1561. ———. [Separation of Hydrocarbons.] German Patent 715,323, Dec. 19, 1941; appl. filed Sept. 23, 1939. Chem. Zentralb., 1942, I, p. 1826.

Liquid SO_2 is used for separating mixtures of hydrocarbons obtained when high-boiling saturated hydrocarbons containing paraffins are treated with SO_2 and halogen.

1562. ———. [Separation of Hydrogenation Products.] German Patent Appl. I 62,342, no date (*Cl. 12 o–5.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 105.

Higher O-containing compounds obtained by the catalytic hydrogenation of CO are separated by treatment with selectively acting solvents.

1563. ———. [Separation of Hydrogenation Products.] German Patent Appl. I 62,807, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 108.

Higher O-containing compounds obtained by the catalytic hydrogenation of CO are recovered by treatment with selectively acting solvents with addition of K_2CO_3 solution. Addition to German Patent Appl. I 62,342 (abs. **1562**).

1564. ———. [Separation of Mixtures of Alcohols and Hydrocarbons.] German Patent Appl. I 72,813, OZ 13,570, filed July 23, 1942 (*Cl. 12 o–5.02*). FIAT Reel 168, frames 6,978–6,981; PB 68,450; TOM Reel 17, item 37, frames 1,050–1,053; Auszüge deut. Patent-Anmeldungen, vol. 6, p. 186; Meyer Transl. PC-S-IV, Wax Oxidation, vol. 2, chap. 22, 1948, p. 15.

In separating high-molecular alcohols b. 200°–320° admixed with hydrocarbons, the mixture is 1st dissolved in a liquid solvent such as pentane and then allowed to flow over silica gel, which adsorbs the alcohols. The pentane is distilled to recover the hydrocarbons and the silica gel is extracted with MeOH to obtain the alcohols.

1565. ———. Soap. British Patent 487,317, June 13, 1938. Chem. Abs., vol. 32, 1938, p. 9539.

Saponified oxidation products of nonaromatic hydrocarbons of high molecular weight are freed from unsaponifiable constituents by introducing such saponaceous mixture containing at least 25% of H_2O into a tubular vaporizing plant at 100 atm. or higher pressure and releasing the pressure to atmospheric within the tube system, the temperature in the tubes being such, for example, 310°–350°, as to maintain the soap liquid. The pressure may be reduced in stages, and a vacuum pump may be arranged beyond the condenser for the steam and unsaponifiables to insure that the pressure falls to atmospheric in the tube system. Before saponification, the oxidation products may be freed from readily soluble and strongly acid products by H_2O, acids, dilute alkali, or organic solvents. The saponification may be effected in presence of H_2O, alcohols, ketones, or hydrocarbon solvents and by the saponification equivalent or more or less of alkali. Before treatment in the vaporizer, the saponified mixture is preferably (1) freed from any unsaponifiables separating as an upper layer, (2) maintained >220° for some time to convert lactones, hydroxy acids, into ordinary fatty acids and improve the color and odor; the preheat treatment may be in presence of hydrogenating agents, for example, H_2 or Zn dust. Describes apparatus.

1566. ———. Soaps; Fatty Acids. British Patent 482,277, Mar. 21, 1938. Chem. Abs., vol. 32, 1938, p. 7297.

Soaps, or fatty acids therefrom, freed from unpleasant odor, are obtained from nonaromatic hydrocarbons oxidized by air or other gas containing O_2 by treating the saponified oxidation products with steam at a temperature < that at which the unsaponifiables distill off and until the unpleasant odor is removed. The unsaponifiables may be removed before or after, for example, by solvents, or by treatment with steam at the higher temperatures necessary but for a time too short to remove much of the malodorous substances. Before saponification the oxidized products may be freed from readily soluble oxidation products of low boiling point by H_2O, acids, or organic solvents. The odor-free soaps may be bleached by H_2O_2 or NaClO. In an example, a mixture of crude scale wax with unsaponifiables from a previous oxidation is oxidized at 115° with air presence of $KMnO_4$, saponified at 230° under pressure with a 15% NaOH solution, diluted to a 20% soap solution with H_2O and EtOH, and extracted with benzine to remove unsaponifiables, the soap solution being then forced by a pump through a preheater under pressure and sprayed at 250°–300° into the tower; the H_2O, solvents, and malodorous substances evaporated pass to a condenser, and the soap solution, now at about 150°, flows over Raschig rings against a current of steam from a pipe and is withdrawn through another pipe.

1567. ———. [Softeners From Synthetic Fatty Acids.] French Patent 889,079, no date. Kainer, p. 287.

1568. ———. [Softening Agents for High-Polymer Substances.] French Patent 882,450, June 2, 1943; appl. filed May 29, 1942. Chem. Zentralb., 1944, I, p. 605.

Chlorination products of saturated or unsaturated, aliphatic or cycloaliphatic hydrocarbons with straight or slightly branched chain containing at least 8 C atoms are used. They may be obtained by the hydrogenation of coal or C oxides.

1569. ———. [Softening Agents for Polyvinyl Compounds.] Danish Patent 60,971, May 31, 1943; appl. filed Jan. 3, 1942. Chem. Zentralb., 1944, I, p. 605.

See Norwegian Patent 66,363 (abs. **1570**).

1570. ———. [Softening Agents for Polyvinyl Compounds.] Norwegian Patent 66,363, June 21, 1943; appl. filed Dec. 31, 1941. Chem. Zentralb., 1944, I, p. 605.

Esters are used that are obtained from the first-runnings of fatty acids with 5–14 C atoms in the molecule and at least a trivalent alcohol.

1571. ———. [Softening Agents for Polyvinyl Compounds.] Swiss Patent 223,963, no date.

See Norwegian Patent 66,363 (abs. **1570**).

1572. ———. [Stabilizing Fischer-Tropsch Liquid Fuels.] French Patent 800,956, July 23, 1936. Chem. Abs., vol. 31, 1937, p. 242.

Volatile hydrocarbons formed by the catalytic reaction of H_2 and CO are rendered stable to spontaneous combustion by treating them at high temperature with agents having a condensing action, such as decolorizing earth impregnated with H_3PO_4, $AlCl_3$, $ZnCl_2$, $SnCl_2$, or B fluoride.

1573. ———. [Stable Chlorinated Hydrocarbons.] German Patent Appl. I 72,625, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 183.

Stable chlorhydrocarbons are obtained by chlorinating the hydrocarbons with at least 6 C atoms occurring in the catalytic hydrogenation of CO.

1574. ———. [Stuffing-Box Packing for High-Pressure Pumps.] German Patent Appl. __, OZ 14,794, filed June 10, 1944. TOM Reel 17, frames 1,204–1,207, item 40.

Describes stuffing-box packing for the plunger and piston rods of high-pressure pumps. Each packing element consists of 2 rings resting on conical surfaces. The wood used for the 2 rings, or especially for the 1 which touches the piston rod or the plunger is of such porosity that a satisfactory lubrication and cooling of the sliding surfaces is attained by means of the material being pumped. Suitable woods for the purpose are acacia, maple, or elm. The wooden rings are subjected to pretreatment with liquids at normal or raised temperatures, preferably under pressure, vacuum, or both.

1575. ———. [Substitutes for Fats and Waxes.] German Patent Appl. J 74,972, no date (*Cl. IV c–22 g*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 616.

The compounds consist of H_2O-insoluble urethane containing at least 1 aliphatic or cycloaliphatic part with at least 6 C atoms. Alcohols, obtained by the catalytic hydrogenation of CO or by the conversion of olefins with CO and H_2, are used for producing urethane.

1576. ———. [Sulfochlorination of Liquid Synthetic Hydrocarbons.] French Patent 892,978, no date, Kainer, p. 272.

1577. ———. [Sulfo-Oxidation.] French Patent 52,-826, Aug. 10, 1945; appl. filed Apr. 8, 1943. French Patent 53,324, Oct. 16, 1945; appl. filed Jan. 27, 1944. French Patent 53,821, Sept. 9, 1946; appl. filed July 18, 1944. Chem. Zentralb., 1949, No. 1, p. E 14.

Sulfo-oxidation of aliphatic or cycloaliphatic hydrocarbons, such as the products of CO hydrogenation that are free from olefins and aromatics, with a mixture of SO_2 and O_2 or air, is catalyzed by radiation with photoactive light. The reaction is promoted and a more pure product is obtained in the presence of anhydrides or chlorides of some lower aliphatic acids or ketenes such as the anhydrides of acetic or propionic acids.

See also French Patent 877,672 (abs. **1578**).

1578. ———. [Sulfo-Oxidation.] French Patent 877,-672. Chem. Zentralb., 1943, I, p. 2764.

See Belgian Patent 443,658 (abs. **1510**).

1579. ———. [Synthesis Catalysts.] German Patent 686,456, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 150.

Sulfides treated with S or with O-free volatile S compounds.

1580. ———. [Synthesis Catalysts.] German Patent 756,609, Dec. 21, 1938; appl. I 63,254 (*Cl. 12 o–1.03*). Aüszuge deut. Patent-Anmeldungen, vol. 6, p. 110.

In the conversion of CO to hydrocarbons with more than 1 C atom in the molecule, a catalyst is used that is made by oxidizing Fe pieces or foil with oxidizing gases and then reducing.

1581. ———. [Synthesis Catalysts.] Italian Patent 364,488, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 151.

See United States Patent 2,183,146 (abs. **2330**).

1582. ———. [Synthesis Gas.] French Patent 892,974, May 25, 1944; appl. filed Mar. 30, 1943. Chem. Zentralb., 1945, I, p. 1093.

Gases such as coke oven gas are burned in the presence of catalysts such as Ni or Mg, and if desired with addition of H_2O vapor. Before the flame touches the catalyst, it is coated with metal vapor such as metals of the Fe group. For instance, Fe carbonyl, which decomposes when a temperature of about 1,000° is reached, is used. The gas mixture, leaving the furnace at about 600°, contains only about 0.25% of CH_4.

1583. ———. [Synthesis of Higher Alcohols.] Swiss Patent 110,740, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 227.

See United States Patent 1,889,251 (abs. **1947**).

1584. ———. [Synthesis of Hydrocarbons.] German Patent Appl. I 54,112, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 90.

Hydrocarbons and their oxygenated derivatives are produced from CO and H_2 while feeding small amounts of such metal compounds as are decomposed at the operating temperature with formation of metals.

1585. ———. [Synthesis of Hydrocarbons.] German Patent Appl. I 58,926, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 97.

Hydrocarbons are produced by converting CO with H_2 in presence of sintered metals of group 8 of the periodic system as catalysts.

1586. ———. [Synthesis of Hydrocarbons.] German Patent 764,766, no date; appl. I 63,452 (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 110.

CO and H_2 used for the conversion into hydrocarbons are passed at a velocity of 200–600 $m.^3$ per hr. per $m.^3$ of catalyst space.

1587. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Austrian Patent 160,564, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 159.

See United States Patent 2,207,581 (abs. **569**).

1588. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 855,515, May 14, 1940; appl. filed May 31, 1939. Chem. Zentralb., 1940, II, p. 2988.

See British Patent 516,352 (abs. **1208**).

1589. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] German Patent Appl. —, no date. German Patent Abridgments, vol. 64, 1943, p. 936; British Coal Utilisation and Research Assoc., Monthly Bull., vol. 8, 1944, abs. 8,306.

Reaction is preferably carried out in narrow tubes, with the catalyst occupying substantially the center of the tubes.

1590. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Italian Patent 361,595, Apr. 8, 1938.

Addition to Italian Patent 345,671 (abs. **1301**).

See also British Patent 496,880 (abs. **1285**) and French Patent 49,333 (abs. **1266**).

1591. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Italian Patent 374,321, May 11, 1939. Chem. Zentralb., 1940, II, p. 2988.

See British Patent 516,352 (abs. **1208**).

1592. ———. [Synthesis of Hydrocarbons From Hydrogen and Oxides of Carbon.] British Patent 293,185, June 9, 1927. Chem. Abs., vol. 23, 1929, p. 1415.

Reaction of C oxides with H_2 or gases rich in H_2, such as CH_4, or steam, is catalyzed by contact masses that contain Cu, Ag, or Au or their oxides or Zn together with elements of the 8th periodic group or their compounds. Mn, Ce, Cr, Mo, W, Ti, Sb, Bi, and Zr or their compounds may be added. The products are mainly unsaturated hydrocarbons, but some MeOH may also be formed.

See United States Patent 1,698,602 (abs. **2373**).

1593. ———. Synthesis of Organic Compounds From Carbon Monoxide and Hydrogen. British Patent 313,467, July 11, 1929; appl. filed Feb. 9, 1928. Chem. Abs., vol. 24, 1930, p. 1118.

In the production of hydrocarbons and O-containing compounds containing a plurality of C atoms from CO and H_2 by pressure catalytic reactions, the operation is effected in a circulatory system with a gas mixture containing only the reactants in requisite proportion for the reaction and extraneous gases such as CH_4, C_2H_6, N_2, or rare gases to the extent of at least 40% by volume. The process is especially suitable for the production of liquid hydrocarbons with catalysts containing Fe and Co, and to the manufacture of acids, esters, alcohols and ketones by use of catalysts containing Fe, Cd, and Cu, or K, Zn, and Cr, or Zn, Cr, and Mn. The reacting gases are preferably freed from CO_2, S compounds, and Fe carbonyl.

1594. ———. [Synthesis Process With Suspended Catalyst.] German Patent 630,828, no date. Kainer, p. 201.

1595. ———. [Synthetic Alcohols.] German Patent Appl. I 64,693, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 117.

Production of alcohols from gas mixtures containing CO and H_2 in the ratio of at least 3 : 1 by catalytic pressure treatment in the presence of chiefly MeOH-forming catalysts and the conversion of the MeOH formed into higher alcohols.

1596. ———. [Synthetic Gasoline.] French Patent 855,122, no date. Kainer, p. 261.

Hydrocarbon oils from the hydrogenation of CO are profitably cracked to antiknock gasoline by treatment at temperatures >350° and at pressures of at least 15 atm., preferably >20 atm., and in presence of catalysts of silicic acid or silicates. Example: Gasol obtained by synthesis from CO and H_2 is cracked at 460° and 30 atm. over bleaching earth at the rate of 1 l. gasol per 2 l. catalyst per hr. The cracked product contains 45% of gasoline boiling up to 200° with an octane number of 69.5, which can be raised to 84 by adding 0.09 vol. % of tetraethyl Pb.

1597. ———. [Synthetic Gasoline.] French Patent 857,177, no date. Kainer, p. 261.

See British Patent 521,687 (abs. **1179**).

1598. ———. [Synthetic Gasoline.] French Patent 859,121, no date. Kainer, p. 264.

Cracking of higher boiling hydrocarbons to high-grade gasolines is accomplished in the presence of paraffin-base petroleums or fractions thereof in the vapor phase over catalysts composed of natural or artificial silicates. Through the mutual cracking of the hydrocarbon oils, the formation of gaseous cracked products are reduced and high antiknock gasolines obtained.

1599. ———. [Synthetic Hydrocarbons.] French Patent 48,739, June 21, 1938. Chem. Abs., vol. 33, 1939, p. 5001.

In converting CO and H_2 to hydrocarbons or their derivatives containing O, the catalysts used are prepared by precipitating metals of the Fe group as compounds reducible to metals by heating with H_2, adding compounds that are difficult to reduce to metals, treating the mixture preferably in the presence of reducing gases to a temperature at which at least partial concretion takes place. Thus Fe hydroxide is precipitated, mixed with a mud of Al_2O_3, the mixture is dried and heated in H_2 to 850°.

See also French Patent 814,636 (abs. **1274**).

1600. ———. [Synthetic Hydrocarbons.] German Patent 763,689, no date; appl. I 62,978 (*Cl. 12 o–1.03*). Auszüge deut. Patent–Anmeldungen, vol. 6, p. 108.

CO and H_2 are passed at a velocity of >200 $m.^3$ per hr. per $m.^3$ catalyst space through 3 or more reaction vessels with separation of the liquid hydrocarbons formed after each vessel. The hydrocarbons contain >1 C atom in the molecule. Higher velocities than that mentioned above do not give any higher yields of products.

1601. ———. Synthetic Oxygenated Organic Compounds by Catalytic Hydrogenation of Carbon Oxides. British Patent 300,294, July 7, 1927. Chem. Abs., vol. 23, 1929, p. 3933.

Various compounds such as alcohols, esters, and acids are made by passing C oxides and H_2 at an elevated temperature, suitably 250°–350°, and either under ordinary or under elevated pressure, which may be up to 1,000 atm., over catalysts comprising a mixture of considerable amounts of Fe, Co, Ni, Pt, Pd, or other metal of the 8th periodic group with Cd or Tl, with or without other materials such as Cu, Au, Ag, Ce, Zr, Al, V, U, Cr, Mo, W, Mn, alkali or alkaline-earth metals of their compounds. Gives numerous details.

1602. ———. [Synthetic Production of Methanol.] Hungarian Patent 96,253, Nov. 2, 1929; appl. filed Dec. 14, 1923. Chem. Zentralb., 1931, I, p. 1708.

See abs. 89, 90, 91, 92, 94.

1603. ———. [Synthetic Products From Industrial Gases.] French Patent 690,091, Feb. 17, 1930. Chem. Zentralb., 1931, I, p. 1,554; Chem. Abs., vol. 25, 1931, p. 1062.

In the manufacture of synthetic products such as alcohols, aldehydes, acids, or NH_3 from industrial gases containing CO, excess CO in the gas not required for the synthesis is removed by using it for the preparation of Fe carbonyl.

1604. ———. [Transforming Carbon Monoxide Into Hydrocarbons.] French Patent 842,507, June 14, 1939. Chem. Abs., vol. 34, 1940, p. 5459.

Method of transforming CO by means of H_2 into hydrocarbons containing more than 1 C atom and/or into liquid oxygenated derivatives of hydrocarbons, such as alcohols, ketones, aldehydes, or acids, consists in using as catalysts heavy metals, preferably Fe, to which an alkaline compound has been added.

1605. ———. [Treating Carbonaceous Matter.] French Patent 841,898, May 31, 1939. Chem. Abs., vol. 34, 1940, p. 4544.

Particularly good results are obtained in the treatment of carbonaceous matter by using mixed catalysts prepared by precipitating metallic compounds from corresponding salt solutions, which have been previously mixed with substances analogous to gels obtained by treating salt solutions containing Si, Ti, Zr, Ce, Th, or Al with an appropriate precipitating agent. Thus, the gel of silicic acid obtained by the addition of an acid to a water-glass solution or alumina gel obtained by the addition of NH_4OH to Al nitrate is mixed with a solution of 1 or more salts of metals belonging to the groups 2–8 of the periodic, table and the mixture is treated with an appropriate precipitating agent such as NH_3, $(NH_4)_2CO_3$, $(NH_4)_2S$, or an aqueous solution of a caustic alkali. As metallic constituents, Mg, Sn, Zn, Fe, Cr, Ni, Co, and Al are particularly indicated. Among examples, a solution of 50 cc. Na silicate, of 1.35 d., in 3 l. H_2O, is treated with 160 cc. HCl, mixed with a solution of 2,750 gm. $Al(NO_3)_3 \cdot 9\,H_2O$ in 8 l. H_2O and treated with NH_4OH. The precipitate obtained containing 66% Al_2O_3 and 34% SiO_2 is used as a catalyst in the cracking of paraffin oils, at 460°, with the resulting yield of 30% motor spirit.

See also Belgian Patent 429,626 (abs. **1214**).

1606. ———. [Treatment of Sulfonate Solutions.] French Patent 899,332, May 28, 1945; appl. filed Oct 30, 1943; in Germany Aug. 8, 1942. Chem. Zentralb., 1949, I, p. E 14.

Describes method for working up the mixtures obtained by the saponification of the sulfochlorinated products of Fischer-Tropsch hydrocarbons b. 230°–320° and the separation of the sulfonates from the unsaponified and other impurities. A recovery of 98% of the crude sulfonates as a pure product is reported.

1607. ———. [Unsaturated Hydrocarbons.] French Patent 677,973, July 6, 1929. Chem. Abs., vol. 24, 1930, p. 3247.

Unsaturated hydrocarbons boiling at a low temperature and other organic compounds free from O are prepared by treating CO with H_2 at a high temperature in the presence of catalysts containing metals of the 8th group (100 parts), alkali compounds (0.3–0.6 parts of alkali metal), and S (0.15–0.4 parts). The S may be replaced by Te or Se.

See also French Patent 666,161.

1608. ———. [Unsaturated Hydrocarbons and Hydrogen.] British Patent 269,547, Apr. 15, 1926. Chem. Abs., vol. 22, 1928, p. 1364.

CH_4 or other saturated hydrocarbons are subjected to a treatment suitable for producing unsaturated hydrocarbons, and the residual gases are converted into a mixture containing CO and H_2 by treatment with steam or O_2 or both with or without a catalyst. In the first stage of the process an electric arc or incomplete combustion may be employed as described in British Patent 264,845 (abs. **1216**) and British Patent 265,234 (abs. **1318**). C_2H_2 may be produced from CH_4 and H_2 in an electric arc, the C_2H_2 may be absorbed in C, and the residual gas may be brought to a temperature of about 1,100° by preheating and partial combustion and then passed with steam over a catalyst containing Ni and Al_2O_3 to obtain C oxides and CH_4. CH_4 may be subjected to incomplete combustion and the product containing C_2H_2, passed at 700° over SiO_2 coated with graphite to produce C_6H_6; residual gases are saturated with H_2O vapor, preheated, subjected to partial combustion, and passed together with steam over a catalyst of Ni and MgO to obtain an impure mixture of CO and H_2, which may be freed from CO_2 and H_2S and then used to make MeOH.

1609. ———. Use of Purified Iron for Apparatus for Use at High Temperatures and Pressures. British Patent 293,077, Mar. 3, 1927. Chem. Abs., vol. 23, 1929, p. 1317.

Apparatus suitable for use with materials comprising H_2, O_2, or S may be made of iron such as that prepared from mild steel by treatment with H_2 at 900° or with a weakly oxidizing mixture of H_2 and H_2O vapor at 550°–600° and 150 atm. pressure. The apparatus may be coated with Cr, W, U, Mn, Al, Ag, Cu, or enamel.

1610. ———. [Wax for Polishing Agents.] German Patent Appl. J 75,504, no date (*Cl. IV c–22 g*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 616.

Esters of the carboxyl groups containing very high molecular hydrocarbons from the hydrogenation of CO, as well as free carboxyl groups, are used as waxes.

1611. ———. [Waxy Substances.] German Patent 733,401, Feb. 25, 1943 (*Cl. 12 o–10*). Chem. Abs., vol. 38, 1944, p. 1136.

Natural or synthetic esterlike waxes are ketonized with the aid of catalysts that promote the splitting off of CO_2. Waxes mixed with fats, fatty oils, and/or fatty acids are used as starting materials.

1612. ———. [Working Up Mixtures of Oxygen-Containing Compounds With Hydrocarbons Obtained Through Conversion of Carbon Monoxide With Hydrogen.] German Patent Appl. I 69,189, OZ 12,656, filed Mar. 20, 1941 (*Cl. IV d–12 o*). FIAT Reel 165, frames 4,346–4,350; PB 66,846; PB 25,609; FIAT Reel B–196, frames 183–187; PB 83,253; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 7, chap. 195, 1950, p. 29.

In a process for working up mixtures of liquid and/or solid hydrocarbons with O-containing compounds obtained in the conversion of CO with H_2, these mixtures or portions of them are treated, before any noteworthy heating takes place, with solid inorganic acid-binding substances, preferably at slightly increased temperature. Example: To 100 kg. of such a mixture as above are added with stirring 2 kg. of powdered Ca $(OH)_2$; the mixture is then heated with further stirring to 80°. Reaction is complete in 5 minutes. The liquid is poured off, the salt washed with liquid pentane, and the total liquid fractionated. The yield of alcohols is greatly increased and that of esters and fatty acids greatly diminished over that obtained without the pretreatment.

1613. ———. [Working Up the Higher Compounds Obtained by the Catalytic Hydrogenation of Carbon Oxides.] French Patent 628,107, Oct. 19, 1927; appl. filed Jan. 26, 1927. Chem. Zentralb., 1928, I, p. 752.

Three methods are available: (1) Oxidation of the higher alcohols to aldehydes, treating with bisulfite, separating the aldehydes and reducing to alcohols or by further oxidation to acids; (2) separating by means of H_2O-free $MgCl_2$, $CaCl_2$ as molecular compounds, separating with benzine and decomposing with H_2O; (3) treating with dilute H_2SO_4 or HCl. Gives examples of each method.

1614. ———. [Working Up the Products of a Carbon Monoxide-Hydrogen Conversion.] German Patent Appl. I 73,341, OZ 13,710, filed Oct. 10, 1942 (*Cl. IV d–12 o.*) FIAT Reel 170, frames 9,177–9,185; PB 64,181; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 6, chap. 177, 1949, p. 40.

In a process for working up the conversion products of CO and H_2, especially those that contain both multibranched and liquid or solid oxygenated hydrocarbons, the products are separated into fractions of different boiling points by a series of distillations, the 1st at normal pressure, the next at diminished pressure, and the 3rd a steam distillation under diminished pressure. The material is kept in brisk circulation and in at least 1 spot in the evaporation is introduced in a very thin layer or in a state of fine division. Vacuum distillation may not be introduced until the distillate has a drop point of at least 50° and preferably 70°.

1615. ———. [Working Up the Products of Hydrogenation.] German Patent Appl. I 66,305, OZ 11,960, filed Jan. 18, 1940 (*Cl. 23 b*). FIAT Reel 172, frames 97–98; PB 25,616.

Hydrocarbon oils obtained by the pressure hydrogenation or extraction of coal or by synthesis from CO and H_2 are converted into high-grade fuels suitable for aviation gasoline by hydrogenation cracking or reforming at temperatures of 400°–500° and pressures of 15–100 atm. in the presence of catalysts consisting of the oxides or sulfides of metals of groups 6 and 8 such as Ni and W sulfides at a throughput of about 1 l. per l. of catalyst per hr.

1616. ———. Working With Gases Containing Carbon Monoxide at High Temperatures. British Patent 314,129, July 18, 1929; appl. filed Dec. 30, 1927. Chem. Zentralb., 1929, II, p. 2852.

Apparatus for carrying out processes involving the use of gases containing CO at high temperatures and pressures is constructed of Fe in all parts except those maintained at temperatures 150°–250°. These are constructed or coated with metals such as Cu, Al, or special steels, which do not form metal carbonyls under the working conditions. CO is excluded from the apparatus and is preferably replaced by H_2 while it is being heated or cooled.

———. *See* abs. **77, 85, 108, 116, 117, 118, 119, 120, 155, 156, 157, 170, 249, 351, 364, 430, 453, 455, 456, 494, 568, 569, 570, 571, 573, 574, 605, 646, 736, 742, 781, 783, 788, 802, 803, 804, 805, 808, 809, 839, 840, 944, 944a, 945, 946, 989, 1035, 1036, 1037, 1038, 1040, 1041, 1042, 1064, 1088, 1089, 1090, 1118, 1119, 1761, 1762, 1764, 1778, 1806, 1807, 1842, 1843, 1844, 1845, 1846, 1847, 1887, 1888, 1889, 1944, 1945, 1946, 1947, 1996, 2050, 2051, 2054, 2056, 2057, 2080, 2081, 2082, 2083, 2084, 2085, 2086, 2087, 2088, 2315, 2316, 2318, 2319, 2320, 2321, 2322, 2323, 2324, 2325, 2326, 2328, 2329, 2330, 2334, 2351, 2352, 2353, 2354, 2355, 2363, 2364, 2367, 2372, 2373, 2374, 2379, 2428, 2429, 2430, 2431, 2433, 2532, 2633, 2646, 2647, 2648, 2650, 2651, 2652, 2654, 2657, 2659, 2662, 2664, 2665, 2666, 2672, 2674, 2676, 2677, 2678, 2679, 2680, 2681, 2682, 2683, 2684, 2685, 2726, 2727, 2728, 2763, 2842, 3222, 3223, 3225, 3257, 3258, 3261, 3265, 3274, 3286, 3287, 3288, 3293, 3295, 3299, 3306, 3308, 3352, 3353, 3354, 3436, 3438, 3451, 3519, 3568, 3655, 3656, 3760, 3761, 3765, 3839, 3890, 3896, 3899, 3900, 3901, 3902, 3903, 3904, 3905, 3914, 3915, 3917, 3918, 3919, 3920, 3921, 3923, 3924, 3925, 3926, 3927, 3928, 3937, 3946, 3947, 3948, 3949, 3950, 3952, 3959.**

1617. I. G. Farbenindustrie A. G., and International Hydrocarbon Synthesis Co. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 854,617, Apr. 19, 1940; appl. filed May 11, 1939. Chem. Zentralb., 1940, II, p. 2988.

See British Patent 516,403 (abs. **1209**).

1618. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Italian Patent 373,277, Apr. 26, 1939. Chem. Zentralb., 1940, II, p. 2988.

See Britsih Patent 516,403 (abs. **1209**).

1619. Iijima, T. (Kawaguchi Chemical Industries Co.). [Catalyst for Hydrogenation.] Japanese Patent 2224 (1951), May 8, 1952. Chem. Abs., vol. 47, 1953, p. 2519.

$NiCO_3 \cdot 2Ni(OH)_2$-kieselguhr (25 gm.) is reduced in H_2 at 400°, the product poured into 100 ml. 0.01 *N* H_2O_2, let stand 1 hr., and dried to make a catalyst stable in air.

1620. Ikawa, K. (Mitsui Kôzan K. K.). [Catalyzers.] Japanese Patent 91,310, May 6, 1931. Chem. Abs., vol. 26, 1932, p. 1730.

Small grains are made from a mixture of 1 or more powdered metallic oxides, metals, and oxidizing agents, with or without diluents. By burning of the grains after applying heat, rough and hard catalyzers are prepared. For example, dried grains prepared from Fe_2O_3, Zn, Fe, Mg, BaO_2, and $K_2Cr_2O_7$ are heated in a muffle furnace at 200°–300°. After part of the grains are ignited, combustion continues of itself to produce black coarse grains, which are used for the manufacture of H_2 from CO and H_2O. Grains prepared from a mixture of ZnO, Zn, $(NH_4)_2Cr_2O_7$, and feldspar (containing no Fe) give by the same treatment a grayish white catalyzer, which is used in the synthesis of MeOH.

1621. Imhausen, A. [Edible Fats.] German Patent Appl. __, filed Oct. 24, 1940; APC 362,684.

Starting materials are fatty acids produced by oxidation from petroleum paraffins from which aromatics have been removed, hydrogenated low-burning paraffin, hydrogenation products of C oxides, and the like. Fatty acids from C_4–C_{22} b. 150°–280° C., 2–5 mm. vacuum, are used. The product after refining is a light, solid, odorless, and agreeable tasting fat adapted for human consumption.

1622. Imhausen, A., and Staennings, C. Aliphatic Carboxylic Acids. British Patent 491,927, Sept. 9, 1938. British Chem. Abs., 1938, B, p. 1389; Chem. Abs., vol. 33, 1939, p. 1347.

Aliphatic carboxylic acids are produced by the oxidation by means of oxidizing gases of hydrocarbons that have been produced by hydrogenation of oxides of C, for example, by the Fischer process. The oxidation may be effected in the presence of catalysts, such as heavy metal salts of unsaturated acids of the type $C_nH_{2n-x}O_2$, in which n is >15 and x is >5. In an example, the initial hydrocarbon has a b. p. >250°, and the oxidation is effected at 115° by means of air in the presence of a catalyst; the product contains stearic, palmitic, myristic, lauric, and capric acids.

1623. Imperial Chemical Industries, Ltd. [Apparatus for Carrying Out Catalytic Exothermic Reactions.] German Patent 523,032, Sept. 18, 1928. Chem. Abs., vol. 25, 1931, p. 4153.

Addition to German patent 482,925 (abs. **1624**).

1624. ———. [Apparatus for Carrying Out Catalytic Exothermic Reactions Under Pressure.] German Patent 482,925, Apr. 13, 1926. Chem. Abs., vol. 24, 1930, p. 532.

Apparatus is primarily intended for NH_3 synthesis and consists of a catalytic chamber for the gases, surrounded by heating tubes embedded in nonconducting material, and the whole enclosed in pressure-resisting walls.

1625. ———. [Catalysts for the Production of Alcohols.] French Patent 672,797, Apr. 8, 1929. Chem. Abs., vol. 24, 1930, p. 2140.

Catalysts for the production of MeOH or higher alcohols are prepared by heating metal carbonates to form the oxides and making them into the form of balls.

1626. ———. [Catalysts for the Production of Methanol.] French Patent 642,318, Sept. 5, 1927. Chem. Abs., vol. 23, 1929, p. 1227.

Catalysts for the production of MeOH and other compounds from CO and H_2 are prepared by heating a mixture of $ZnCO_3$ or basic $ZnCO_3$ and a Cr compound which may be $ZnCrO_4$ or basic $ZnCrO_4$, in which case the heating takes place in the presence of H_2 or the reacting gases. Examples are given in which (1) $ZnSO_4$ is boiled with Na_2CO_3 and the washed precipitate is digested with Cr acid; (2) aqueous solutions of $ZnSO_4$, Na_2CO_3, and $Na_2Cr_2O_7$ are heated together, and the precipitate is washed.

1627. ———. [Catalysts for the Production of Methanol.] French Patent 644,189, Nov. 21, 1927. Chem. Abs., vol. 23, 1929, p. 1651.

Catalysts for the production of CH_3OH and other alcohols are prepared by heating a mixture of basic Zn and Cr carbonates. The mixture may be obtained by precipitation of a solution of Zn and Cr salts. The catalyst is preferably used as pellets. If alkali salts are present in the catalyst, they are useful for producing higher alcohols.

See also French Patent 642,318, (abs. **1626**).

1628. ———. [Chemical Reactions.] French Patent 783,732, July 18, 1935. Chem. Abs., vol. 29, 1935, p. 8175.

In carrying out reactions with circulating gases, such as in the synthesis of NH_3, a part of 1 or more of the constituents is removed by causing the gases of a part of them to pass rapidly in the same direction as an appropriate liquid absorbent. The absorption may take place in a long tube or worm under high pressure.

1629. ———. [Methanol.] French Patent 689,757, May 9, 1927. Chem. Abs., vol. 25, 1931, p. 972.

MeOH is prepared by passing a mixture of CO and H_2 over a catalyst composed of 4 $ZnO.CrO_3$ at 300°–400°

and under high pressure. The catalyst is prepared by suspending ZnO or $Zn(OH)_2$ in H_2O and treating it at ordinary temperature with a slight excess of CrO_3. If the catalyst contains alkali salts, higher alcohols are formed.

1630. ———. Production of Higher Alcohols. British Patent 371,804, May 26, 1932; appl. filed Oct. 23, 1930. Chem. Zentralb., 1933, I, p. 1683.

Mixtures of H_2 and CO, containing at most 10 vol. % of the latter and in which <1 vol. of CO is present to 5 vol. of H_2, are passed at temperatures >300° and at pressures of at least 100 atm. over alcohol-forming catalysts at such a speed that in the reaction gases after the catalysis the content of CO does not exceed 8 vol. % and amounts preferably to not more than 2–4 vol. %. Suitable catalysts are those that consist of 1 or more metal oxides difficult to reduce and a relatively small amount of an alkali metal oxide; the best results are obtained with catalysts that contain Mn oxide.

1631. ———. Purification of Methanol. British Patent 346,648, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 219.

Synthetic MeOH is purified by refining with halogen and then washing with alkali.

———. *See* abs. **27, 28, 38, 277, 278, 466, 645, 738, 739, 823, 824, 1070, 1114, 1986, 2074, 2075, 2076, 2580, 2581, 2823, 3358, 3731, 3732, 3733, 3866.**

IN SITU GASES, INC. *See* abs. **843.**

INLAND STEEL CO. *See* abs. **1794.**

1632. INSTITUTION OF GAS ENGINEERS. Combustible Gas. British Patent 528,338, Oct. 28, 1940. Chem. Abs., vol. 35, 1941, p. 7689.

Carbonaceous fuel is gasified by the action of O_2 and steam under pressure with a high rate of gasification so as to produce a gas consisting mainly of H_2 and CO. CO and H_2, thus produced, are caused to react to form CH_4 while the gas is still under pressure. Heat evolved by this reaction is used to preheat steam under pressure to be used for the gasification.

1633. INTERNATIONAL CATALYTIC OIL PROCESSES CORP. Catalytic Reaction of Oxides of Carbon With Hydrogen. British Patent 559,044, Feb. 2, 1944. Chem. Abs., vol. 40, 1946, p. 444.

Process and apparatus are described for the production of liquid hydrocarbons by the hydrogenation of oxides of C in the presence of a catalyst. Powdered catalyst is suspended in a gaseous mixture of CO and H_2, and the suspension is passed upward through 1 or more externally cooled stationary reaction tubes 1.5–5.0 in. in diameter. The tubes are arranged parallel within a chamber in which a cooling medium is circulated.

1634. ———. Contacting Gases and Solids; Catalytic Apparatus. British Patent 596,870, Mar. 1, 1945.

In gas-phase operations carried out in presence of solid contact material that is regenerated after use, the contact material of a size retained on a 100-mesh screen, but having particles not larger than about 15 mm. in diameter, is moved as a descending compact bed through both the reaction and regeneration zones while being raised from a lower to a higher level. The process may be used for the catalytic conversion of hydrocarbons in presence of activated clays or synthetic gels, which may be in the form of pellets or spheres. Synthesis of hydrocarbons from CO and H_2 is effected at 390° F., using an Fe group metal on kieselguhr catalyst activated with Th or Mg; wax is removed from the catalyst in the regeneration zone by treatment with a hydrocarbon gas or vapor.

1635. INTERNATIONAL HYDROCARBON SYNTHESIS CO. Apparatus for Conversion of Carbon Monoxide. British Patent 536,169, May 6, 1941; appl. filed Sept. 30, 1939. Chem. Abs., vol. 36, 1942, p. 1468.

In the production of hydrocarbons above C_1 the temperature in a number of converters is controlled by providing each of the converters with a closed cooling system in which a high boiling liquid is vaporized; the vapors are condensed by heat exchange in a common secondary vaporizing system employing H_2O.

1636. ———. [Carbon Monoxide—Hydrogen Synthesis.] French Patent 860,360, Jan. 13, 1941; appl. filed Sept. 23, 1939. Oel u. Kohle, vol. 39, 1943, Sch. 6.

In conducting the synthesis of hydrocarbons from CO and H_2 the reaction products are passed at a temperature of 295° from the converter, packed with the catalyst into a heated dephlegmator, in which the fractions boiling essentially above 300° are separated. The residue, after passing through a heat exchanger and a cooler, is led into a separator kept at 120° from which a part of the liquid product is drawn off from below and after passing through the heat exchanger and being heated to about 200° is returned to the converter where the reaction proceeds in the liquid phase. The gases and vapors leaving the separator are then cooled and separated on the one hand in to H_2O and benzine and on the other into residual gas.

1637. ———. [Carbon Monoxide—Hydrogen Synthesis.] French Patent 860,383, Jan. 13, 1941; appl. filed Sept. 25, 1939; in Germany, Oct. 8, 1938. Oel u. Kohle, vol. 39, 1943, Sch. 6.

Products obtained by the hydrogenation of CO on Fe catalysts and boiling in the gasoline range can be freed from troublesome, acid-containing compounds by passing them in the vapor state at temperatures 200°–600°, preferably 300°–500°, over water-splitting catalysts such as alumina, bauxite, Al phosphate, magnesia, ZnO. Sometimes it is expedient to add a dehydrogenating catalyst, such as CrO, to the water-splitting catalyst.

1638. ———. [Carbon Monoxide—Hydrogen Synthesis.] Italian Patent 387,038, Dec. 30, 1940. Oel u. Kohle, vol. 39, 1943, Sch. 178; Chem. Zentralb., 1943, I, p. 589.

To cool the catalyst space in the synthesis of hydrocarbons from CO and H_2, a synthetic oil b. 200°–320° is used as the cooling agent. Because of its purity this oil is very stable to temperature.

1639. ———. [Catalyst.] Italian Patent 380,542, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 153.

See French Patent 862,870 (abs. **1653**).

1640. ———. [Catalyst.] Norwegian Patent 63,361, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 153.

See French Patent 862,870 (abs. **1653**).

1641. ———. [Catalyst.] Norwegian Patent 64,995, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 153.

Co catalysts with >200 gm. Co per liter and 5–25% Mn+alkali.

See Netherlands Patent 57,692 (abs. **1691**) and United States Patent 2,339,927 (abs. **949**).

1642. ———. [Catalyst Chamber.] Italian Patent 391,251, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 163.

Catalyst chamber with catalyst tubes longer than 5 m.

See British Patent 567,609 (abs. **2712**) and French Patent 870,213 (abs. **1664**).

1643. ———. [Catalyst for Converting Carbon Monoxide and Hydrogen Into Hydrocarbons.] Nether-

lands Patent 53,611, Dec. 15, 1942. Chem. Abs., vol. 41, 1947, p. 3604.

Compact sheet Fe, 1.5 mm., Raschig rings are converted into Fe oxide by air at 700° in 24 hr. The Fe oxide is reduced to Fe by H_2 at 600° and treated with a borax solution, 1% borax in prepared catalysts. A gas mixture of $CO:H_2=4:5$ is passed over this catalyst at 320° at 20 atm., converting 80% of the gas into hydrocarbons with boiling point of gasoline.

1644. ———. [Catalyst for Hydrocarbon Synthesis.] Belgian Patent 440,411, Nov. 29, 1941; appl. filed Jan. 28, 1941; in Germany, Dec. 9, 1939. Chem. Zentralb., 1942, I, p. 2736.

Fe catalysts are used, which, calculated on the Fe content, contain at least 5% of Ca in the form of O-containing compounds. They are produced by precipitating Fe- and Ca-salt solutions with alkali hydroxides.

1645. ———. [Catalyst for the Hydrogenation of Carbon Monoxide.] French Patent 863,311, Mar. 29, 1941. Chem. Abs., vol. 42, 1948, p. 9124.

In preparing a reducible compound of Co, the Co salt solution is added slowly, for example, over 50 hr., to the precipitating liquid or vice versa. The Co salt solution may contain Fe and/or Ni salts, and oxides of Th, Mg, or Al can be added as activators. Usually, 3–8% of Co is present in the Fe–Ni–Co mixture. The precipitation can be effected on diatomaceous earth. By reducing the precipitants the catalyst is obtained. Several examples given.

1646. ———. [Catalyst Regeneration.] Italian Patent 378,812, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 156.

See French Patent 861,745 (abs. **1703**) and German Patent 748,374 (abs. **2819**).

1647. ———. [Catalyst Regeneration.] Norwegian Patent 62,581, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 156.

See French Patent 853,302 (abs. **1661**) and Netherlands Patent 53,095 (abs. **1673**).

1648. ———. [Catalyst Regeneration.] Swedish Patent 99,689, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 156.

See French Patent 853,302 (abs. **1661**).

1649. ———. [Catalyst Support.] French Patent 896,955, no date. Schmidt, J., Das Kohlenoxyd. Akad. Verlagsgesell., Leipzig, 1950, p. 154.
Silica gel with very fine pores.

1650. ———. [Catalytic Conversion of Hydrogen With Carbon Monoxide to Polybranched Hydrocarbons.] French Patent 53,200, Sept. 20, 1945; appl. filed Nov. 11, 1943; in Germany, Nov. 20, 1941. Chem. Zentralb., 1948, II, p. 549.

Process for producing Fe catalysts by calcining of compact Fe or Fe oxide, while retaining the outer form followed by reduction, is improved by changing the form by grinding, not compact Fe, but powdery materials such as used catalysts. The oxidative calcining is carried out in an atmosphere that contains 30–70% steam. The catalyst gives a very high conversion of 80–82% CO to gasoline. Addition to French Patent 862,870 (abs. **1653**).

1651. ———. [Catalytic Hydrogenation of Carbon Monoxide.] French Patent 862,171, Feb. 28, 1941. Chem. Abs., vol. 42, 1948, p. 6091.

Co and H_2 are circulated at 150°–350° over a catalyst of Fe, Ni, Co, and Th on silica gel or the like, the reaction being carried out in stages and liquid products being removed at each stage. The speed of circulation per $m.^3$ of catalyst per hr. is 400 $m.^3$, whereas formerly a speed of 110 $m.^3$ was used.

1652. ———. [Catalytic Hydrogenation of Carbon Monoxide.] French Patent 862,536, Mar. 8, 1941; appl. filed Dec. 23, 1939. Chem. Abs., vol. 42, 1948, p. 9124.

In the formation of liquid hydrocarbon from CO and H_2, using Co, Th, and diatomaceous earth catalysts, the process is carried out in several stages, the fresh gases first passing 150°–350° over a catalyst previously used. Describes apparatus.

1653. ———. [Catalytic Hydrogenation of Carbon Monoxide.] French Patent 862,870, Mar. 18, 1941. Chem. Zentralb., 1941, II, p. 2279; Chem. Abs., vol. 42, 1948, p. 9124.

Small pieces of Fe having 2 dimensions above 1–2 mm., preferably about 5 mm., and the 3d dimension 0.1 mm. are heated in an oxidizing atmosphere at 700°–800° and then heated at 500° in a reducing atmosphere. This material is an improved catalyst for hydrogenation of CO. Halides, phosphates, and borates of Na, Li, K, or Cs (0.1–10%), Al_2O_3, SiO_2, compounds of Cu, Ti, Mn, W, Mo, Cr, Th, etc. may be added.

1654. ———. [Catalytic Hydrogenation of Carbon Monoxide.] French Patent 863,473, Apr. 2, 1941. Chem. Abs., vol. 42, 1948, p. 9124.

In preparing the Fe and Ni catalysts, reducible compounds of these metals are slowly precipitated at a temperature <40°, the *p*H of the solution being kept at 8. The suspended precipitant is then boiled for a few minutes, filtered and washed, and dried and reduced. Activators such as Al_2O_3 or Ag may be added.

1655. ———. [Catalytic Hydrogenation of Carbon Monoxide.] French Patent 863,687, Apr. 7, 1941. Chem. Abs., vol. 42, 1948, p. 9124.

Catalysts for use in obtaining liquid products from H_2 and CO at pressures below 20 atm. and temperature of 190° are made by precipitating a Co and Ag salt on an active earth and reducing by H_2 at 220°. The amount of Ag present is about 8% of the Co.

1656. ———. [Catalytic Hydrogenation of Carbon Monoxide.] French Patent 864,161, Apr. 21, 1941. Chem. Abs., vol. 43, 1949, p. 1172.

Exothermic reaction is controlled by having a refrigerating liquid circulating in a closed circuit several places in the apparatus.

1657. ———. [Catalytic Hydrogenation of Carbon Monoxide.] French Patent 870,211, Mar. 5, 1942. Chem. Abs., vol. 43, 1949, p. 4836.

Fe catalysts having CaO, with or without Ni, Co, or Cu adjuvants, are impregnated with alkali-metal hydroxides. They give a higher yield and have a longer life in treating H_2 and CO under temperature and pressure to give liquid hydrocarbons.

1658. ———. [Cobalt-Thorium Oxide-Kieselguhr Catalysts.] French Patent 859,198, no date. Kainer, p. 39.

1659. ———. Conversion of Carbon Monoxide and Hydrogen Into Hydrocarbons. British Patent 528,617, Nov. 1, 1940; appl. filed May 11, 1939. Chem. Abs., vol. 35, 1941, p. 8259.

Conversion is carried out in narrow tubes, bathed in a cooling medium, and containing the catalyst in such a manner that the reacting gases can stream along the walls of the reaction space through a narrow passageway, which is not or only little obstructed by catalyst. In the middle of the tube no or only little space remains unfilled by catalyst. The tube may be filled with pieces in the form of tablets or pellets having a diameter only a little smaller than the tube width. The process may be carried out either in the gaseous or the liquid phase. In an example, the catalyst consists of 85 parts of Co and 15 parts of ThO on 85 parts of kieselguhr.

1660. ———. Conversion of Carbon Monoxide With Hydrogen Into Hydrocarbons. British Patent 538,225, July 25, 1941; appl. filed Nov. 6, 1939. Chem. Abs., vol. 36, 1942, p. 2119.

Conversion of CO and H_2 into liquid, solid, or gaseous hydrocarbons is carried out in the presence of Fe catalysts. Compact Fe is treated with oxidizing gases at 700°–900° and for such a long time that the Fe is substantially completely converted into Fe oxide without melting of the Fe or the Fe oxide formed, and, subsequently, the Fe oxide is reduced to metal by treatment with reducing gases to secure the catalyst for the process. The temperature of the aforesaid reduction is 500°. Additions of alkali metal compounds increase the activity of the catalyst. This catalyst may also be used for high-pressure hydrogenation of oil.

1661. ———. [Converting Carbon Monoxide Into Hydrocarbons.] French Patent 853,302, Mar. 15, 1940. Chem. Abs., vol. 36, 1942, p. 2393.

CO is converted by H_2 into hydrocarbons with more than 1 C atom, by using a gaseous mixture containing at least 2 parts of H_2 for each part CO and alternately, by intermittence, a gaseous mixture containing at least 2.5 parts of H_2 for each part of CO.

1662. ———. [Diatomaceous Earth as Catalyst Support.] Netherlands Patent 52,657, June 1942. Chem. Abs., vol. 41, 1947, p. 3934.

To render calcining possible without sintering, the diatomaceous earth is first treated with acids b. 120° or < and then calcined at 500°–550° instead of >600° as was usual for the synthesis of hydrocarbons from CO and H_2.

1663. ———. [High-Molecular Paraffins From Carbon Monoxide and Hydrogen.] Italian Patent 378,208, Aug. 24, 1939. Chem. Zentralb., 1942, I, p. 2843.

Catalysts are used in the synthesis of hydrocarbons from CO and H_2, which were obtained by precipitation from compounds of the Fe group on alumina and finally reduced. These catalysts can be activated by additions of the oxides of Zn, Th, Mn in amounts up to 20%. Example: The catalyst is obtained by precipitation from Co- or Zn-nitrate as the carbonate on alumina. Gas is passed over it at 180° consisting of $CO : H_2 = 1 : 2$ with 15% of inerts. 146 gm. of hydrocarbons are obtained per $m.^3$ of gas. At 1 atm. 76% paraffin is obtained, 92% at 6 atm. and almost wholly paraffin at 10 atm. It is 70% soluble in benzol, m. p. 83°, 11% in toluol, m. p. 100°, and 13% in xylol, m. p. 108°, the insoluble residue m. p. 138°.

1664. ———. [Hydrocarbon Synthesis.] French Patent 870,213, Mar. 5, 1942; appl. filed Feb. 21, 1941. Chem. Zentralb., 1942, II, p. 1086.

Synthesis takes place in tubes 5 m. or more in length, preferably 6–10 m. With a greater throughput, the same comparative rate of yield is obtained as with the shorter tubes previously used.

1665. ———. [Hydrocarbon Synthesis.] German Patent 750,581, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 154.

Hydrocarbon synthesis in presence of carbonyl vapors on etched metal surfaces.

1666. ———. [Hydrocarbon Synthesis.] Italian Patent 381,315, Mar. 14, 1940; in Germany, April 29, 1939. Chem. Zentralb., 1942, I, p. 2736.

In the synthesis of hydrocarbons from CO and H_2 the heat of reaction is removed from the reactor by means of a cooling liquid flowing in a closed circuit. Outside the reactor the warm liquid gives up its heat indirectly to H_2O contained in the tubes of a boiler.

1667. ———. [Hydrocarbon Synthesis.] Italian Patent 382,962, Feb. 28, 1940. Chem. Zentralb., 1942, II, p. 243.

Fe-Ni catalysts are used that were obtained by precipitation at temperatures <40° and at a *p*H value of <8 during the precipitation. Precipitation should take at least 1 hr., preferably 3–12 hr. or more. It can also be performed stepwise. Simultaneously, alumina or Ag_2O is precipitated as activators. The catalysts are distinguished by a very long life.

1668. ———. [Hydrocarbon Synthesis.] Swiss Patent 211,489, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 176.

See British Patent 518,372 (abs. **1295**) and French Patent 855,136 (abs. **1710**).

1669. ———. [Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen.] Italian Patent 379,797, Dec. 20, 1939. Chem. Zentralb., 1942, II, p. 1086.

Synthesis is conducted in several steps, with separation of the reaction products between steps at so great gas velocity, that at further increased throughput the space-time yield does not increase any further. In general, the throughput amounts to 200–600 $m.^3$ gas per l. of catalyst per hr. The high throughputs are attained through stepwise gas addition to the individual reaction zones or through recirculation of the reaction gases. By this method high yields of hydrocarbons are obtained.

1670. ———. [Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen.] Italian Patent 380,045, Jan. 11, 1940. Chem. Zentralb., 1942, II, p. 1086.

Synthesis is conducted in catalyst tubes outside cooled and horizontally laid or slightly inclined, whereby the reaction gases pass through in a horizontal or nearly horizontal direction. In this way an especially good conduction of heat is obtained with less CH_4.

1671. ———. [Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen.] Italian Patent 381,276, Feb. 6, 1940; in Germany, Feb. 11, 1939. Chem. Zentralb., 1942, I, p. 2736.

Synthesis is carried out with Co catalysts, obtained by stepwise precipitation of Co salts extended over at least 3 and preferably >12 hr. Then by carrying out the synthesis under increased pressure in known manner high yields of solid paraffin are obtained.

1672. ———. [Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen.] Italian Patent 390,152, July 30, 1941. Oel u. Kohle, vol. 39, 1943, Sch. 192. Chem. Zentralb., 1943, I, p. 589.

Operation is carried out in the presence of Fe or Co catalysts suspended in a liquid medium. The synthesis gas is a CO-rich water gas, which is recycled through the converter, ratio of fresh gas to recycle gas 1 : 2 or 1 : 3. Following are the reaction conditions: Catalyst, 100 parts Fe, 5 Cu, 10 CaO, 100 kieselguhr; temperature, 240°–250°; pressure, 10 atm.; throughput, 1,000 l. fresh gas and 2,500 recycle gas per hr.; 10 l. 50% catalyst suspension; fresh gas, 38% CO and 48% H_2; 100–120 gm. hydrocarbons per $m.^3$ fresh gas are obtained. The hydrocarbons consist of 20% benzine, 50–65% soluble in H_2SO_4, 50% middle oil, b. 200°–320°, and 20% b. above 320°, of which 40–50% is olefins.

1673. ———. [Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen.] Netherlands Patent 53,095, Sept. 15, 1942. Chem. Abs., vol. 41, 1947, p. 3942.

Pressure is kept <50 atm., temperature at 180°; the Co catalyzer contains 18% Th oxide, with a gas having $CO : H_2 = 1 : 2$. If after 28 days the activity is much reduced, the catalyzer is regenerated by using a gas having $CO : H_2 = 1 : 4$. Activity is restored in 2 days.

1674. ———. Hydrocarbons. British Patent 534,357, Mar. 5, 1941; appl. filed Feb. 5, 1940. Chem. Abs., vol. 36, 1942, p. 1468.

Conversion of CO and H_2 into solid and liquid hydrocarbons is effected in presence of Fe- and Ni-containing catalysts, which have been prepared by gradually precipitating reducible Fe and Ni compounds by gradual addition to a solution maintained at a *p*H value of not less than 8 of a mixed solution of the salt of the metals at a temperature not exceeding 40°.

1675. ———. Hydrocarbons. British Patent 534,367, Mar. 5, 1941; appl. filed Feb. 8, 1940. Chem. Abs., vol. 36, 1942, p. 1468.

Conversion of CO and H_2 into hydrocarbons with more than 1 C atom in the molecule is effected in presence of catalysts, which contain Co together with 0.2–8%, calculated with reference to the Co, of Ag as such or in form of a compound. The catalysts are subjected, before use, to a treatment with reducing gases at a temperature not exceeding 250°.

1676. ———. Hydrocarbons. British Patent 536,912, May 30, 1941; appl. filed Jan. 24, 1940. Chem. Abs., vol. 36, 1942, p. 1759.

Hydrogenation of CO is effected in presence of catalysts produced by gradually precipitating a reducible Co compound from a solution of a Co salt during a period of at least 3 hr.

1677. ———. [Hydrocarbons by Conversion of Carbon Monoxide With Hydrogen in the Presence of Catalysts.] Netherlands Patent 50,858, Sept. 15, 1941. Chem. Abs., vol. 36, 1942, p. 5337.

To prevent attack of the siliceous carrier, such as kieselguhr, asbestos, meerschaum firebrick, by the alkali used in coprecipitation of metals, Fe, Co, Ni, for use as catalyst in the synthesis of hydrocarbons, the carrier is pretreated with alkali, the soluble material made insoluble by heating, or the precipitation performed in a minimum time. Drying the kieselguhr at 600°–700° and calcining it at 1,000°–1,100° reduced the solubility to 1/5.

1678. ———. Hydrocarbons Containing More Than One Carbon Atom. British Patent 536,767, May 27, 1941; appl. filed Nov. 22, 1939. Chem. Abs., vol. 36, 1942, p. 1759.

Hydrogenation of CO is effected in presence of catalysts comprising diatomaceous earth as a carrier. The latter is obtained by leaching crude diatomaceous earth with acids which b. 120° or below, washing, drying, and freeing the diatomaceous earth from organic substances by calcination at temperatures at which a sintering of the earth does not yet take place.

1679. ———. [Hydrocarbons From Carbon Monoxide.] Netherlands Patent 58,695, Dec. 16, 1946. Chem. Abs., vol. 41, 1947, p. 4910.

Since Fe catalysts and, for example, Co catalysts give different results, a mixture of separately precipitated and granulated catalysts was tried; for example, a Co catalyst of Co 46 and ThO_2 3 and MgO 5 gm., precipitated from the nitrates with K_2CO_3 on diatomaceous earth, is granulated (3–5 mm.) and reduced. 10 vol. thereof are mixed with 90 vol. of a granulated and reduced molten Fe catalyst with additions of 6% $SiO_2+Al_2O_3+Mn_3O_4$. The yield in hydrocarbons was 114 gm. liquid and solid hydrocarbons for a normal $m.^3$ gas in 1 stage and 15 gm. C_3 and C_4 hydrocarbons. The temperature of reaction is about 200°. An Fe catalyst requires 300° and under similar circumstances gives only 70 gm. liquid and solid hydrocarbons.

1680. ———. Hydrocarbons From Carbon Monoxide and Hydrogen. British Patent 536,843, May 29, 1941; appl. filed Dec. 21, 1939. Chem. Abs., vol. 36, 1942, p. 1759.

Throughput of the initial gas per $m.^3$ of catalyst is maintained substantially the same in each of the stages and is such that further increase in the throughput does not give a substantial increase in the amount of the hydrocarbons produced per vol. of catalyst per hr.

1681. ———. [Hydrocarbons From Carbon Monoxide and Hydrogen.] Italian Patent 384,545, Aug. 1, 1940. Chem. Zentralb., 1942, II, p. 243.

Fe catalysts are used, which were obtained from granulated or compact Fe, if desired, with activation and with the use of carriers such as Al, Zn, or Ag. Good yields of benzine are obtained without destructive soot formation.

1682. ———. [Hydrocarbons From Carbon Monoxide and Hydrogen.] Netherlands Patent 55,196, Sept. 15, 1943. Chem. Abs., vol. 41, 1947, p. 3603.

Catalyzers are prepared from a solution containing Fe and Ni salts by precipitating gradually at 40° or less and *p*H not under 8 while the solution is added to the precipitating liquid. The precipitate is then reduced. In an example, 9 l. of a solution in H_2O of 725 gm. $Fe(NO_3)_3 \cdot 9H_2O$ and 480 gm. $Ni(NO_3)_2 \cdot 6H_2O$, and 268 gm. $Al(NO_3)_3 \cdot 9H_2O$ is trickled in 48 hr. into 9 l. aqueous solution of 1010 gm. K_2CO_3. The liquid and precipitate are boiled for 5 min., filtered, washed with H_2O, and dried in air at 110°. Then 50 cc. unreduced catalyst, containing 5.6 gm. Fe and Ni is reduced by H_2 for 5 hr. at 350°. This catalyst loses only 10% activity in 6 weeks. Precipitating in the inverse way or quickly gives much heavier catalyzers, of which more is needed to fill the same reaction space.

1683. ———. [Hydrocarbons From Carbon Monoxide and Hydrogen by Catalysis.] Netherlands Patent 53,262, Oct. 15, 1942. Chem. Abs., vol. 41, 1947, pp. 3942–3943.

Large volume of gases that have reacted is cooled and recirculated with fresh gas mixture to repress heat development. It may be 100 times the fresh gas. A small fraction of the reacted gas is strongly cooled to obtain reaction products. Thus 700 $m.^3$ per hr. at 20 atm. was introduced and 70,000 $m.^3$ recirculated. Temperature was 320° at the entrance and 330° at the outlet. 96 kg. solid, liquid, and gaseous products were obtained: 17 kg. CH_4 and ethane, 20 kg. ethene and C_3–C_4 alkenes, 42 kg. gasoline b. 200°, 10 kg. middle oil, 1 kg. solid paraffin, 6 kg. ethanol.

1684. ———. [Hydrocarbons From Carbon Monoxide by Hydrogenation With a Catalyst.] Netherlands Patent 55,360, Oct. 15, 1943. Chem. Abs., vol. 41, 1947, p. 3280.

Catalyst is prepared by precipitating a solution of Fe and Ca salts with alkali hydroxide; the Ca content, calculated as CaO or $Ca(OH)_2$, is at least 5% of the Fe content; for example, Fe 259 gm. in form of $Fe(NO_3)_3 \cdot 9H_2O$ and CaO 10 gm. as $Ca(NO_3)_2$ were dissolved in 600 gm. H_2O and heated to boiling. To this solution is added 425 cc. 40% NaOH, specific gravity 1.438, at least at 50°. After stirring and filtering, the residue was washed 2 times with 350 cc. H_2O at 80°–90° until the nitrate content was under 1.5%. The hydroxides were dried and reduced with the synthesis gas or with H. They can be impregnated with alkali solution and 2–5% Cu or Ni may be added.

1685. ———. [Hydrocarbons From Gases Containing More Carbon Monoxide Than Hydrogen.] Netherlands Patent 52,257, Apr. 15, 1942. Chem. Abs., vol. 41, 1947, p. 3942.

Solid, liquid, and volatile hydrocarbons are synthesized, with Fe as a catalyzer, at temperatures $<320°$ and pressure 2–100 atm. The catalyzer is activated for hours and days at 240°–250° by CO or CO-containing gases under a lower pressure than the one of synthesis.

1686. ———. [Hydrocarbons From Water Gas.] Italian Patent 379,250, Dec. 14, 1939; in Germany, Dec. 22, 1938. Oel u. Kohle, vol. 39, 1943, Sch. 185.

Synthesis of hydrocarbons from water gas is performed by acid of Fe catalyst, especially of sintered Fe, containing 1–15% of alkali borate. There is obtained from a synthesis gas with 45% CO, 54% H_2, and 1% N_2 at 330° and 15 atm. 130 gm. of product per $m.^3$, consisting under normal conditions of low-boiling, gaseous hydrocarbons besides small amounts of O-containing compounds.

1687. ———. [Iron Catalyst.] Italian Patent 382,921, no date. Kainer, p. 18.

See French Patent 863,473 (abs. **1654**).

1688. ———. [Kieselguhr Catalysts.] Norwegian Patent 63,292, no date. Kainer, p. 33.

See French Patent 862,105 (abs. **1706**).

1689. ———. [Liquid Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 855,378, May 9, 1940; appl. filed May 26, 1939. Chem. Zentralb., 1941, I, p. 607.

As catalysts for the process, metals such as Fe, Ni, Co, Cr, Mo, W, and Ru are used in the form of a colloidal suspension in an inert liquid such as a high-boiling hydrocarbon oil; the suspension is obtained by decomposing the corresponding carbonyl in the liquid at raised temperature. CO is passed at 25°–120° over the metal and the gaseous carbonyl passed into the liquid and decomposed therein at the synthesis temperature of 175°–230°. It is then ready for passage of the synthesis gas therethrough.

1690. ———. [Motor Fuel.] French Patent 912,759, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 185.

Antiknock motor fuel from synthetic hydrocarbons.

1691. ———. [Paraffins Boiling Above 320° Synthesized From Carbon Monoxide and Hydrogen.] Netherlands Patent 57,692, June 15, 1946. Chem. Abs., vol. 41, 1947, p. 4634.

Catalyst is the main point. It contains at least 200 gm. per l. of Co (200 gm. of Co per l. of finished catalyst), generally 40–80% by wt. of all the catalyst and MnO as an activator, namely 5–25% of the Co. It is made by precipitation of a solution containing Co and Mn. In an example, 25 gm. Co and 3.75 gm. Mn were dissolved as nitrates in 500 cc. H_2O; this was heated to boiling and vigorously stirring added to a boiling solution of 61 gm. Na_2CO_3 in 750 cc. H_2O. Immediately after precipitation 3.5 gm. diatomaceous earth, washed with acid and calcined, was stirred in. The precipitate was sucked off and washed with 3 l. hot H_2O, then dried in air, reduced at 400° 1 hr. with a H_2–N_2 mixture, and put into use at 160° and 10 atm. The intake was 10 l. synthetic gas per 100 cc. catalyst per hr. If 75% CO was converted, 120 gm. paraffins per $m.^3$ gas was produced. In the course of 5 mo. the gasoline yield (to 200°) decreased 21–12.9%; the diesel oil 20.5–15.1%; the solid paraffin increased 58.5–72% of the total yield. This decreased from 140 gm. hydrocarbons per $m.^3$ synthetic gas in the 1st mo. to 100 gm. in the 5th.

1692. ———. [Preparing Hydrocarbons From Carbon Monoxide and Hydrogen.] Netherlands Patent 60,033, Oct. 15, 1947. Chem. Abs., vol. 42, 1948, p. 347.

Reduction occurs in a space kept at constant temperature by cooling with a liquid. A part of the gases leaving the reaction chamber is recirculated. The conversion products are not removed from this gas, and it is not cooled before recirculation. This increases the yields by 40%. Example: A synthesis gas of about 28% CO and 65% H_2, the rest being inert gases, is passed over a Co–Th catalyst in a cooled 15 mm. diameter tube. A portion 5 times as great as the quantity of fresh gas is admixed and passed through hot tubes to the catalyst again. The velocity in the oven is 60 m. per sec. From the rest of the gas the liquid and solid components are removed to yield 138 gm. per $m.^3$ of ideal gas ($CO+2H_2$). (100 gm. if circulating only once.)

1693. ———. [Process and Converter for Producing Hydrocarbons With More Than One Carbon Atom in the Molecule by Catalytic Hydrogenation of Carbon Monoxide.] French Patent 870,212, Mar. 5, 1942; appl. filed February 21, 1941. Chem. Zentralb., 1942, II, p. 1,086.

Gives directions for filling and emptying a catalyst furnace for the synthesis of hydrocarbons from CO and H_2.

1694. ———. [Process for Converting Carbon Monoxide by Means of Hydrogen.] French Patent 896,627, Feb. 27, 1945; appl. filed July 20, 1943. Chim. et ind., vol. 56, 1946, p. 213.

CO is converted to hydrocarbons by H_2 in presence of a catalyst prepared by fusing Fe and alkali in a stream of O_2 and by reducing the magnetic oxide thus formed by H_2. The activity of the catalyst can be increased by adding AS or Sb thereto.

1695. ———. [Process for Producing Hydrocarbons.] French Patent 897,240, Mar. 15, 1945; appl. filed Aug. 13, 1943.

For producing hydrocarbons, whose molecules contain more than 1 C atom, by the catalytic reaction of CO with H_2, mixed catalysts are used, each part of which is prepared separately and in individual grains, 1 part at least having an Fe base and the others a Co or Ni base.

1696. ———. [Production of Diesel Oil by Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen.] French Patent 873,645, July 15, 1942; appl. filed July 4, 1941.

See Italian Patent 389,201 (abs. **1697**).

1697. ———. [Production of Diesel Oil by Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen.] Italian Patent 389,201, June 24, 1941. Chem. Zentralb., 1943, I, p. 590.

Synthesis is carried out in a liquid medium, a part of which is withdrawn and freed from the organic acids which have formed by washing with alkali solution such as KOH, and then returned to the process. By this means a substantially larger proportion of diesel oil is obtained. Example: The synthesis is carried out over a catalyst of Co, ThO_2, MgO, and kieselguhr under 11 atm. pressure and at 190°, with a throughput of 1–4 $m.^3$ of gas per kg. Co per hr. The reaction product contains about 80% of diesel oil.

1698. ———. [Recovering Used Thorium Catalysts.] Italian Patent 374,226, June 16, 1939. Chem. Zentralb., 1940, II, p. 2987.

Catalysts are dissolved in HNO_3, precipitated by Na_2CO_3 solution in such amounts and so slowly at 60°–70° that Co and Ni remain in solution, but the $Th(CO_3)_2$ is precipitated. The Fe-containing precipitate is dissolved in H_2SO_4, and by addition of solution of K_2SO_4 and Na_2SO_4 the double salt $Th(SO_4)_3K_2$ is precipitated. This is converted by boiling with a concentrated solution of alkali- or NH_4-carbonate into insoluble basic Th carbonate. The double sulfate can also be treated with excess alkali- or NH_4-carbonate solution so that $Th(CO_3)_2$ is dissolved, the solution heated, and basic Th carbonate precipitated by means of H_2SO_4 or HCl. The recovered Th is pure enough for making fresh catalysts.

1699. ———. [Regenerating a Catalyst.] Netherlands Patent 53,451, Nov. 16, 1942. Chem. Abs., vol. 41, 1947, p. 3604.

Catalyst for converting CO with H_2 are precipitated on $MgCO_3$. This is dissolved in carbonated H_2O and precipitated again by heating. The catalyst proper is dissolved in acid and precipitated with an alkaline lye on the regenerated $MgCO_3$.

1700. ———. [Regenerating Catalyzers From The Conversion of Carbon Monoxide and Hydrogen to Hydrocarbons.] Netherlands Patent 53,298, Oct. 15, 1942. Chem. Abs., vol. 41, 1947, p. 3943.

Full regeneration is possible in 2 phases, the 1st with H_2 at 350° or more to remove high-molecular compounds, the 2d at about 450° until activity is restored. The method is meant for Co catalyst, also for Ni or Fe, possibly activated with Th, Mn, U, Ce, or Mg oxide.

1701. ———. Regeneration of Catalysts for the Hydrogenation of Carbon Monoxide. British Patent 533,459, Feb. 13, 1941. Chem. Abs., vol. 36, 1942, p. 1168.

After a treatment with solvents, the catalyst is treated with H_2 at 400°–450° for such a period of time until the catalyst has again attained the activity of a freshly prepared catalyst. This time is generally 2–4 hr. A velocity of 1,000 $m.^3$ of cross section of the passageway is particularly advantageous. Temperature is preferably increased gradually.

1702. ———. [Regeneration of Exhausted Cobalt Catalysts.] Norwegian Patent 62,414, April 29, 1940; appl. filed Sept. 16, 1938. Chem. Zentralb., 1940, II, p. 1973.

Exhausted Co catalysts from the synthesis of hydrocarbons from CO and H_2 are regenerated by dissolving in HNO_3 and reprecipitating the dissolved constituents. Separation of the salts from the undissolved kieselguhr is accomplished satisfactorily if dilute HNO_3 of 20% concentration, preferably 3–5%, is used. The treatment with HNO_3 is performed at 70°–90° when only moderate stirring is needed. The paraffin deposited on the catalyst melts, is removed with the solution, and separates on cooling. By this method an HNO_3 already containing Co salts can be used and then a concentrated $Co(NO_3)_2$ solution is directly obtained.

1703. ———. [Regeneration of Metallic Catalysts Used in Preparing Hydrocarbons From Hydrogen and Carbon Monoxide.] French Patent 861,745, Feb. 15, 1941; appl. filed Nov. 18, 1939. Chem. Abs., vol. 42, 1948, p. 6091.

Metals, such as Mn, U, Ce, Mg, Ni, and Fe, deposited in kieselguhr, are regenerated after use in the catalytic preparation of hydrocarbons by heating in a stream of H_2 at 350°–450°; the speed of the gas is 500–1,000 $m.^3$ per hr. for each $m.^2$ of the passage and the gas having less than 2.5 gm. of CO and 1 gm. H_2O per $m.^3$ The temperature may be attained gradually. The used catalyst may, before this treatment, be treated with O_2 or an O_2-yielding gas.

1704. ———. Regeneration of Spent Catalysts in the Synthesis of Hydrocarbons. British Patent 530,036, Dec. 3, 1940; appl. filed June 15, 1939. Chem. Abs., vol. 35, 1941, p. 8226.

Spent catalyst containing Th is treated with a mineral acid to dissolve the Th and, if desired, the other catalyst constituents. A sludge is precipitated by Na_2CO_3 from the acid solution obtained. This sludge contains a large amount of Th. The sludge is dissolved in H_2SO_4. The Th is precipitated by K_2SO_4 from the H_2SO_4 solution obtained as Th–K sulfate, which in turn is separated from the solution. An insoluble $Th(CO_3)_2$ is prepared from the sulfate and the carbonate is recovered.

1705. ———. [Regeneration of Thorium Catalysts.] French Patent 856,933, Aug. 16, 1940; appl. filed June 27, 1939. Chem. Zentralb. 1941, I, p. 3036.

The catalyst used in the hydrogenation of CO, included with other constituents such as Ni or Co, can be dissolved in H_2SO_4 and precipated at 60°–70° with an alkaline carbonate solution. The precipitate is essentially Th, and the other constituents remain in solution. The precipitate is dissolved in H_2SO_4 and a solution of K_2SO_4 or a mixture of K_2SO_4 and Na_2SO_4 or KCl and Na_2SO_4 or KCl and H_2SO_4 is added. The precipitated double salt of Th–K–sulfate will be separated from the solution and changed into insoluble Th carbonate, which results through heating with a concentrated solution of alkali or ammonium carbonate. One uses an excess of carbonate and heats the solution to 90° to precipiate the Fe present in the form of colloidal hydroxide which is filtered off. The Th carbonate is precipitated with H_2SO_4 or HCl. This is washed with warm H_2O and dissolved in 60% HNO_3. This solution is then ready for the production of fresh catalyst.

1706. ———. [Support for Catalyst for Hydrogenation of Carbon Monoxide.] French Patent 862,105, Feb. 27, 1941; appl. filed Dec. 5, 1939. Chem. Abs., vol. 42, 1948, p. 6091.

Diatomaceous earth is leached with a dilute acid, such as HNO_3 or HCl, washed, dried, and calcined at 500°–550°. The usual Co and Th catalysts are then supported on this earth, an increase in liquid hydrocarbons being obtained from the CO–H_2 reaction.

1707. ———. [Synthesis Catalyst.] Italian Patent 382,942, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 153.

Fe or Ni catalysts are slowly precipitated, 1 hr. or more, at $<40°$.

See French Patent 863,473 (abs. **1654**) and Netherlands Patent 55,196 (abs. **1682**).

1708. ———. [Synthesis in Liquid Medium.] French Patent 905,913, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 160.

Liquid medium is rotated in the reaction vessel, and fresh gas is passed through the cone-shaped center.

1709. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 854,402, April 15, 1940; appl. filed May 6, 1939. Chem. Zentralb., 1940, II, p. 2987.

Life of catalysts can be prolonged by heating the synthesis gas beforehand $>800°$, preferably 1,000°–1,250° for 0.5–1 sec., and at the same time freeing it from H_2S formed by the decomposition of the organic S compounds. Harmful resins are destroyed at the same time. The heating takes place in heat exchangers with CaO, dolomite, or bauxite packing. The synthesis gas consists of gas from the gasification of brown coal or from the transformation of natural or refinery gases with steam.

1710. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 855,136, May 3, 1940; appl. filed May 22, 1939. Chem. Zentralb., 1940, II, p. 2987.

Gases leaving the reactor are recycled at least with 20 times (better 50–500) the amount of fresh gas. By this means the heat of reaction is almost wholly removed and the reactor temperature regulated without harmful increase. The reaction gases are cooled and mixed with the fresh gas until they are at the right temperature for the synthesis. A part of the reaction gas is drawn off and the reaction products recovered while the remainder is recycled to the reactor. The temperature rise in the reactor should not exceed 50°. The flow velocity is so regulated that at each passage the gases remain in the reactor 0.1–5 sec.

1711. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent

855,270, May 7, 1940; appl. filed May 25, 1939. Chem. Zentralb., 1940, II, p. 2987.

Catalyst is so arranged in narrow tubes surrounded by cooling liquid that the reacting gases are able to move along the walls without hindrance through the catalyst, while in the axial space of the tube no room is left that is not filled with catalyst. The catalyst pieces have a somewhat smaller cross section than the tube itself so that a free space of about 0.2–2 mm. is left. A very even temperature is maintained throughout the whole reaction space.

1712. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 871,909, May 22, 1942, appl. filed May 5, 1941. Oel u. Kohle, vol. 39, 1943, Sch. 192.

Paraffin is chiefly obtained whenever the synthesis is performed under pressures of 5–50 atm. and on a catalyst of Co activated with 5–25% of Mn. The catalyst should contain at least 200–300 gm. of Co per l. of catalyst mass. At 165°–180° about 120 gm. of hydrocarbons are obtained per $m.^3$ of pure gas, of which about 80% is solid paraffin.

1713. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Italian Patent 374,024, April 15, 1939. Chem. Zentralb., 1940, II, p. 2987.

See French Patent 854,402 (abs. **1709**).

1714. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Italian Patent 374,071, Mar. 31, 1939. Chem. Zentralb., 1940, II, p. 2987.

Synthesis gas made from brown coal or hard coal, after desulfurization, is washed with an organic liquid at 15° or up to 200°, preferably under pressure, with alcohols, ethers, esters, ketones, hydrocarbons, halogen compounds, amines, and pyridine. Through this gas purification the yield and the life of the catalyst are increased. The wash liquid can be regenerated by distillation or by H_2SO_4.

1715. ———. [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen.] Italian Patent 374,244, May 20, 1939. Chem. Zentralb., 1940, II, p. 2987.

See French Patent 855,136 (abs. **1710**).

1716. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Italian Patent 374,322, May 16, 1939. Chem. Zentralb., 1940, II, p. 2987.

See French Patent 855,270 (abs. **1711**).

1717. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Italian Patent 390,547, May 5, 1941. Chem. Zentralb., 1943, II, p. 1254.

Part of the reaction gases is recycled through the reaction zone, and fresh gas is introduced into the cycle by means of an injector instead of the previously used blast. The recycle gas may thereby contain some of the reaction products and hence does not especially need to be cooled.

1718. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Swedish Patent 104,113, Mar. 31, 1942; appl. filed June 18, 1941; in Germany, July 5, 1940. Oel u. Kohle, vol. 39, 1943, Sch. 193.

Operation is conducted in a liquid medium with recycling of the catalyst contained therein. The catalyst may however be packed solid in the reaction space. The liquid medium is freed from fatty acids outside the reaction space by washing with alkali. In obtaining diesel fuel as the main product, a Co catalyst is used at 180°–220° and 7–15 atm., with a synthesis gas having a CO : H_2 ratio from 2.5 : 1–1 : 1. About 170 gm. of hydrocarbons are obtained per $m.^3$ of pure gas, of which 80% is diesel fuel. The amount of benzine obtained is about 20%, of which 5% is gas oil. The alkali wash tends to keep down the formation of paraffin.

1719. ———. [Synthesis of Hydrocarbons With More Than One Carbon Atom From Carbon Monoxide and Hydrogen.] Netherlands Patent 60,321, Dec. 15, 1947. Chem. Abs., vol. 42, 1948, p. 1724.

Velocity of the gases over the catalyst had to be increased to raise production. In a reaction vessel a catalyst containing 46% Co, 8% ThO_2, and 46% diatomaceous earth is used in tubes of 15 mm. diameter, cooled by H_2O. A gas of 85 vol. CO and H_2 and 15 vol. inert gases is led through the catalyst at linear velocity of 0.56 m. per sec. at 195° and normal pressure. Space velocity is 400, and its proportion to the vessel's height is 80. Under these conditions 1,500 kgm. hydrocarbons, solid, liquid, and gaseous, of more than 1 C atom are obtained per $m.^3$ catalyst per day. The liquid yield (48%) was a gasoline fraction b. under 155°, having an octane value of 60. In comparison with a vessel 2 m. high, with the same catalyst vol. in similar tubes and a space velocity of 100 with linear velocity 0.056 m. per sec. at a temperature 185° and normal pressure, only 200 kg. hydrocarbons were obtained. 35% of the liquid boiled under 155° and had an octane value of 45.

1720. ———. [Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen.] Italian Patent 373,532, April 13, 1939. Chem. Zentralb., 1940, II, p. 2708.

See French Patent 853,302 (abs. **1661**).

1721. ———. [Synthesis of Paraffins.] Belgian Patent 440,888, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 153.

See United States Patent 2,339,927 (abs. **949**).

1722. ———. [Synthetic Diesel Oil From Water Gas.] Netherlands Patent 58,224, Sept. 16, 1946. Chem. Abs., vol. 41, 1947, p. 4634.

Yield of the 200°–320° fraction is increased by alkali washing, once in 8 hr., of the filtrate from the catalyst, which is used in suspension in a liquid medium. For example, into a reaction vessel of 40 l. a synthetic gas containing 58 vol. % H_2 and 29 vol. % CO is fed at 11 atm. pressure at a rate of 1.5 $m.^3$, normal temperature and pressure, per hr. The vessel contains a suspension of 2 kg. reduced Co catalyst in 25 l. diesel oil. The catalyst had Co 33, MgO 1.5, ThO_2 1.5, and diatomaceous earth 64%. Temperature was kept at about 190°. About 1.25 l. oil with catalyst per hr. was filtered and washed well with about 10% by volume of a 5% NaOH solution and with H_2O after that. Reaction products were distilled off and the rest returned to the reaction vessel.

1723. ———. [Tube Furnace for Converting Carbon Monoxide With Hydrogen to Hydrocarbons.] French Patent 858,330 no date. Kainer, p. 166.

See German Patent 741,826 (abs. **3952**).

———. *See* abs. **953, 954, 1617, 1618, 1826, 2712, 3954.**

INTERNATIONAL HYDROGENATION ENGINEERING & CHEMICAL CO. *See* abs. **2495.**

1724. INTERNATIONAL HYDROGENATION PATENTS CO., LTD. Catalysts. British Patent 489,551, July 28, 1938. Chem. Abs., vol. 33, 1939, p. 823.

See French Patent 818,078 (abs. **1725**).

1725. ———. [Catalytic Compositions.] French Patent 818,078, Sept. 17, 1937. Chem. Abs., vol. 32, 1938, p. 2304.

Powdered composition consisting of or containing a catalytic material is formed into separate pieces by strong compression, and the pieces are heated to 850° or above, preferably to > 920°, to yield products of high mechanical strength suitable for use at temperatures > about 480°. The powdered starting material must have a melting point > the temperature used in the subsequent heating, or must be converted during the

heating stage into a substance having such a melting point. Preferably a powdered catalyst, such as a mixture of a metal of the Fe group with a difficultly reducible basic oxide, is heated with a minor proportion of a substance; for example, an acidic oxide with which it reacts to form a compound of high melting point, and the mixture is heated, crushed, and treated, as described above. Gives examples and numerous details. The process may be applied in the preparation of catalysts for use in reactions such as the destructive hydrogenation of carbonaceous materials, the manufacturer of MeOH from CO and H_2 and the dehydrogenation of hydrocarbons.

1726. ———. [Catalytic Hydrogenation of Hydrocarbons in the Vapor Phase.] Italian Patent 349,685, 1938.

Material to be hydrogenated is led with the hydrogenating gas downwards through an assembly of tubes filled with catalyst. In order that each tube be fed uniformly an orifice plate is inserted at the entry of the tubes. This causes a pressure drop, which is about 2–10 times as great as that arising in the usual catalyst tube. This method also can be used with advantage in the hydrogenation of phenols or C oxides to liquid hydrocarbons or even to MeOH.

1727. ———. Destructive Hydrogenation. British Patent 597,053, May 28, 1945; in United States, May 26, 1944. British Abs., 1948, B, I, p. 292.

To produce a gasoline of improved octane rating, a hydrocarbon oil synthesized from CO and H_2 is subjected to destructive hydrogenation in presence of H_2 and a hydrogenation catalyst such as WS_2, preferably supported on a cracking clay such as acid-washed bentonite. The best results are obtained by hydrogenating a Fischer-Tropsch product b. in the gas oil range, 370°–400°, pressure 1,500 p. s. i., and feed rates of 4–8 vol. of liquid charge per vol. of catalyst per hr.

1728. ———. [Gases Containing Carbon Monoxide and Hydrogen From Gaseous Hydrocarbons and Steam With Added Carbon Dioxide.] Netherlands Patent 51,930, Feb. 16, 1942. Chem. Abs., vol. 41, 1947, p. 3604.

This conversion at 700°–900° results in a gas with $CO : H_2$ ratio 2 : 1–1 : 3, if enough CO_2 is used so that the reaction product contains at least ⅓, preferably ½, of the original amount of CO_2.

1729. ———. [Hydrocarbons From Gases Containing Carbon Monoxide and Hydrogen.] Netherlands Patent 52,326, Apr. 15, 1942. Chem. Abs., vol. 41, 1947, p. 3942.

Raw material is obtained by oxidizing gaseous hydrocarbons, for example, CH_4, with CO_2 and steam. After the synthesis, part of the gaseous hydrocarbons is burned to CO_2; this is separated and used again for converting hydrocarbons into CO and H_2. Describes an apparatus.

1730. ———. [Hydrogen and Carbon Monoxide.] French Patent 845,361, Aug. 25, 1939. Chem. Abs., vol. 35, 1941, p. 1194.

Lower hydrocarbons, such as CH_4 and C_2H_6 are converted into H_2 and CO according to $3CH_4+CO_2+2H_2O = 4CO+8H_2$ with alternating blowing and production periods. During the blowing period a carbonaceous material is burned in air by heating 980°–1,200°, and during the production period the catalytic transformation of a gaseous hydrocarbon mixture, water gas and CO_2 occurs at 1,200°–980°. Describes apparatus.

1731. ———. Hydrogenation of Synthetic Oils. British Patent 579,053, Jan. 16, 1948. Chem. Abs., vol. 42, 1948, p. 4334.

Fischer-Tropsch products are hydrogenated at high temperatures and low contact times with common hydrogenation catalysts. High yields of gasoline are obtained. The following optimum operating conditions are recommended: Temperatures of 700°–750° F., pressures of 1,500 p. s. i., feed rates of 4–8 vol. of liquid charge per volume of catalyst per hr., and 1,000–8,000 $ft.^3$ of H_2 per bbl. of oil feed.

1732. ———. [Mixtures of Carbon Monoxide and Hydrogen Suitable for the Synthetic Reactions.] French Patent 845,492, Aug. 24, 1939. Chem. Abs., vol. 35, 1941, p. 1194.

In a mixture produced by the reaction of gaseous hydrocarbons, such as CH_4, C_2H_6, or C_3H_8, with H_2O vapor, the ratio of CO to H_2 is increased by adding to the starting components CO_2 in suitable proportion. The reaction is effected at 700°–900° in the presence of a Ni catalyst.

1733. ———. [Production of Motor Fuel.] French Patent 854,962, Apr. 29, 1940; appl. filed May 19, 1939, in United States May 20, 1938. Chem. Zentralb., 1941, I, p. 3175.

Production of synthesis gas from natural, cracked, low-temperature carbonization gas, etc., and its conversion at 150°–343° and 200 atm. pressure over Ni, Co, or Fe catalysts into hydrocarbons. The end gas is treated and recycled; the hydrocarbons obtained in the 2 steps being subjected to cracking at 370°–510° on Si-containing catalysts activated with metal oxides to produce a motor fuel.

1734. ———. Regeneration of Catalysts. French Patent 854,439, Apr. 15, 1940; appl. filed May 8, 1939. Chem. Zentralb., 1940, II, p. 1817.

Catalysts that have been used for cracking, hydrogenation, and reduction of CO are regenerated by oxidation with O_2-poor gases. Regeneration is begun with a O_2 content in the gas of 2–6%, which is gradually raised to about 20%.

1735. ———. [Synthesis Gas.] French Patent 845,962, no date. Kainer, p. 132.

Gaseous hydrocarbons such as natural gas, cracked gas, low-temperature carbonization gas, and the like after desulfurizing are mixed with CO_2 and steam and passed over Ni or Co catalysts at >650°.

1736. ———. [Synthesis of Hydrocarbons.] French Patent 854,903, Apr. 27, 1940; appl. filed May 17, 1939, in United States May 18, 1938. Chem. Zentralb., 1941, I, p. 3175.

Gives treatment of the end gases from the synthesis process and their reutilization.

1737. ———. [Synthetic Gasoline.] French Patent 855,381, no date. Kainer, p. 262.

Synthetic oils from CO hydrogenation are catalytically cracked as high pressures, >400 atm., in presence of catalysts poor in heavy metals such as bleaching earth, natural or artificial silicates, especially Al silicate, or active C from brown-coal coke or coke from coal extracts.

1738. ———. Synthetic Hydrocarbons From Synthetic Gas Mixture and Hydrogen. British Patent 528,826, Nov. 7, 1940. Chem. Abs., vol. 36, 1942, p. 1468.

CH_4–CO_2 mixture is converted to CO and H_2 in the ratio 1 : 1 in the presence of Ni deposited upon clay such as fire clay. This gas mixture is passed into a reactor held >200° containing a catalyst mixture such as Co–Th–kieselguhr, Ni–Mn, Al_2O_3–kieselguhr or Co–Th–Cu–kieselguhr. The products are discharged into a separator wherein unreacted gases are removed by an overhead line. The unreacted gases CO and H_2 in part are subjected to oxidation to convert the CO to CO_2. The CO is extracted and recycled to the conversion of gaseous hydrocarbons.

INTERNATIONAL NICKEL CO. OF CANADA, LTD. *See* abs. **3862.**

ISII TEKKOZIO K. K. *See* abs. **3989.**

1739. IVANNIKOV, P. Y., AND TELEGIN, V. G. [Catalyst for Synthesis of Ammonia.] Russian Patent 52,907, Mar. 31, 1938. Chem. Abs., vol. 34, 1940, p. 5608.

Mixture of Fe hydroxide and activator is pressed at normal temperature under 3,000 kg. per cm.^{2} and then reduced.

JACOB, P. *See* abs. **2680, 2681.**

1740. JACOBSON, R. A. (E. I. du Pont de Nemours & Co.). Mixture of Polyethylene With Hydrocarbon Obtained by Hydrogenation of Carbon Monoxide. Canadian Patent 481,962, Mar. 25, 1952; appl. filed Sept. 5, 1946, Serial No. 547,508; 2 claims.

Composition of matter comprising a blend of an ethylene polymer melting 85°–120° and a paraffin hydrocarbon obtained by the catalytic hydrogenation of CO melting > 120°. The blend consists of 80–60% ethylene polymer and 20–40% paraffin hydrocarbon.

1741. ——— (E. I. du Pont de Nemours & Co.). Mixture of Polyethylene With Hydrocarbon Obtained by Hydrogenation of Carbon Monoxide. United States Patent 2,499,756, Mar. 7, 1950. Chem. Abs., vol. 44, 1950, p. 4719.

Properties of polyethylene films are improved by addition of various quantities of paraffin hydrocarbons having a melting point > 120° and obtained from CO by hydrogenation.

1742. JACOLEV, L., AND GERMAN, I. F. (The Texas Co.). Preparation of Synthesis Gas. United States Patent 2,591,700, Apr. 8, 1952; appl. filed May 28, 1948, Serial No. 29,866; 8 claims (*Cl. 48–196*).

Method contemplates the reaction of CH_4 and O_2 in the proportion of about 1 : 1 in an enclosed, unobstructed reaction zone, the incoming stream of reactants being passed longitudinally through the central portion of the reaction zone at about 2,000° and 200 p. s. i., the direction then being reversed and directed into a spirally moving flow surrounding the central stream of incoming gases. In this way the 2 streams flow in countercurrent heat-exchange relationship whereby the reaction is materially promoted and maximum yields of CO and H_2 are realized. Also, the overall reaction is carried out in a relatively limited reaction space, which contributes materially to economy of size and investment required for large-scale operation.

JAECKH, W. *See* abs. **2329, 2330, 2331, 2332, 2333, 2334, 2677.**

1743. JAEGER, A. O. (Selden Co.). Apparatus for Exothermic Catalytic Gas Reactions. British Patent 331,468, Dec. 22, 1928. Chem. Abs., vol. 25, 1931, p. 177.

Various structural details.

1744. ——— (Selden Co.). Apparatus for Exothermic Vapor-Phase Catalytic Reactions Such As Production of Phthalic Anhydride From Napthalene. United States Patent 1,945,812, Feb. 6, 1934. Chem. Abs., vol. 28, 1934, p. 2223.

Describes various details of construction and operation of a converter having vertical catalyst tubes surrounded by a liquid bath such as molten $NaNO_3$ and $NaNO_2$ in which are immersed vertical heat-exchange elements through which a gaseous cooling medium such as air may be passed.

1745. ——— (Selden Co.). Catalytic Reduction of Carbonyl Compounds. Canadian Patent 310,207, Apr. 7, 1931. Chem. Abs., vol. 25, 1931, p. 3135.

Carbonyl compounds are catalytically reduced by reaction with reducing gases in the presence of a contact mass containing a diluted permutogenetic body.

1746. ——— (Selden Co.). [Catalytic Reduction of Carbonyl Compounds.] French Patent 669,872, Feb. 19, 1929. Chem. Abs., vol. 24, 1930, p. 1944.

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See British Patent 306,471 (abs. **1749**) and United States Patent 1,925,389 (abs. **1747**).

1747. ——— (Selden Co.). Catalytic Reduction of Carbonyl Compounds. United States Patent 1,925,389, Sept. 5, 1933; appl. filed Apr. 6, 1929, Serial No. 353,270 (*Cl. 260–169*). Chem. Abs., vol. 27, 1933, p. 5518.

Reductions such as the production of motor-fuel hydrocarbons from purified water gas are effected in the presence of a catalyst containing a permutogenetic material.

1748. ——— (Selden Co.). Catalytic Reduction of Carbonyl Compounds Such as Carbon Oxide Mixtures. United States Patent 1,834,621, Dec. 1, 1931; appl. filed Feb. 21, 1928, Serial No. 256,065. Chem. Abs., vol. 26, 1932, p. 1076.

See Canadian Patent 310,207 (abs. **1745**).

1749. ——— (Selden Co.). Catalytic Reduction of Organic Compounds. British Patent 306,471, Feb. 21, 1928. Chem. Abs., vol. 23, 1929, p. 4949.

Catalysts such as those used for reduction and hydrogenation of organic nitrogen compounds are used for the reduction of oxides of C or organic compounds containing O such at ketones, aldehydes, acids, esters, alcohols, or ether. Oxides of C may be reduced to CH_2O, MeOH, or CH_4, or, in the presence of alkaline stabilizers, which cause condensation, to higher alcohols, ketones, acids such as propionic, and butyric acids and hydrocarbons of a petroleum character. Ketones may be reduced to secondary alcohols and aldehydes to primary alcohols. Describes various other reductions also, and the reducing gas may be H_2 or various hydrocarbons.

1750. ——— (Selden Co.). Cooling Apparatus Used for Exothermic Catalytic Reactions. British Patent 310,956, May 4, 1928. Chem. Abs., vol. 24, 1930, p. 532.

Catalyst tubes are cooled by a surrounding liquid bath, Hg or an Hg alloy. The liquid is allowed to boil only after it is withdrawn from the bath itself to a region of lower pressure.

1751. ——— (Selden Co.). Exothermic Catalytic Reactions. United States Patent 1,972,937, Sept. 11, 1934. Chem. Abs., vol. 28, 1934, p. 6881.

In effecting catalytic reactions in which more heat is produced than that required for preheating the reaction gases from atmospheric temperature, a gas is passed in heat-exchange relation with a catalyst, and a portion only of the gas is brought into heat-exchange relation with at least 1 component of the reaction mixture, and the reaction mixture is subsequently passed over the catalyst at reaction temperature. Describes apparatus.

1752. ——— (Selden Co.). Exothermic Vapor-Phase Catalytic Reactions. United States Patent 1,900,715, Mar. 7, 1933. Chem. Abs., vol. 27, 1933, p. 3017.

In effecting reactions such as oxidations of aromatic hydrocarbons, the reaction gases are passed through at least 1 catalyst zone and the exothermic heat of reaction is absorbed by a nonboiling liquid in heat-exchange relation to the reacting gases; the liquid is removed from the catalytic zone, its pressure is reduced to permit a part at least of the exothermic heat absorbed to be given off as latent heat of vaporization, the vapors are condensed, and the condensate and unboiled liquid are returned to the catalytic zone at the pressure there existing.

1753. ——— (Selden Co.). Formaldehyde by Catalytic Reaction of Carbon Dioxide With Hydrogen. United States Patent 1,831,179, Nov. 10, 1931; appl. filed Aug. 28, 1925, Serial No. 53,203. Chem. Abs., vol. 26, 1932, p. 737.

CO_2 and H_2 are caused to react in the presence of catalysts favoring only the formation of CO, and the CO thus formed, without separation from the gas stream, is caused to react with H_2 in the presence of mild reduction catalysts associated with an excess of oxidation catalysts. Gives numerous examples.

1754. ——— (Selden Co.). Methanol Synthesis. United States Patent 1,824,896, Sept. 29, 1931; appl. filed Sept. 9, 1925, Serial No. 55,393. Chem. Abs., vol. 26, 1932, p. 156.

Reaction between CO and H_2 is effected in the presence of catalysts favoring only the production of formaldehyde and the formaldehyde thus produced, without separation from the gas stream and in a separate stage, is caused to react further with H_2 in the presence of mild reduction catalysts and oxidation catalysts with the reduction catalysts in such excess as to favor only the production of MeOH. Gives numerous details and examples.

1755. ——— (Selden Co.). Reduction of Carbon Monoxide. United States Patent 1,741,306, Dec. 31, 1929; appl. filed Nov. 8, 1927, Serial No. 232,003. Chem. Abs., vol. 24, 1930, p. 1125.

CO or a gas containing CO is caused to react with a H_2 containing gas in successive stages to form CH_2O, MeOH, and then CH_4, without isolating intermediate products formed, and at least 1 of the 1st 2 stages of the reaction is effected in the presence of mild reduction catalysts such as Cu, Mn, Cd, Zn, Pb, Sn, Mg, Ag, Au, or Pt associated with oxidation catalysts such as compounds of Cr, V, Ti, Mo, W, Ce, Th, U, or Zr, both of which are incorporated in porous carriers such as pumice or kieselguhr of not more than slight catalytic activity; the stage producing CH_4 from MeOH is effected in the presence of strong reduction catalysts such as Fe, Ni, Co, or Pd.

1756. ——— (Selden Co.). Reduction of Carbon Monoxide. United States Patent 1,741,307, Dec. 31, 1929; appl. filed Nov. 9, 1927, Serial No. 232,202. Chem. Abs., vol. 24, 1930, p. 1125.

In a process similar to United States Patent 1,741,306 (abs. **1755**), the oxidation catalyst serves as a carrier for the mild reduction catalyst in at least 1 of the 1st 2 stages.

1757. ——— (Selden Co.). Reduction of Carbon Monoxide. United States Patent 1,741,308, Dec. 31, 1929; appl. filed Nov. 9, 1927. Chem. Abs., vol. 24, 1930, p. 1125.

Specifies the admixture together of the catalysts for the different successive stages of the process described in United States Patent 1,741,306 (abs. **1755**).

1758. ——— (Selden Co.). Reduction Products of Carbon Dioxide by Hydrogen. United States Patent 1,735,925, Nov. 19, 1929; appl. filed Mar. 9, 1928, Serial No. 260,553. Chem. Abs., vol. 24, 1930, p. 695.

CO_2 is caused to react with H_2-containing gases in stages forming successively CO, CH_2O, MeOH, and CH_4, without isolation of the intermediate stage products. The process may be carried out by using various specified catalysts in different stages. Gives numerous details.

1759. JAEGER, E. [Substitute for Wash Oil, Spindle Oil and Solvents for Resins and Bitumen.] German Patent Appl. J 71,277, no date (*Cl. 22 g–14*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 614.

Unsaponified residues from the manufacture of synthetic fatty acids by the Fischer-Tropsch method.

1760. JAHNIG, C. E. (Standard Oil Development Co.). Process and Apparatus for Contacting Finely Divided Solids and Gases. United States Patent 2,518,693, Aug. 15, 1950; appl. filed July 24, 1941, Serial No. 403,829; 7 claims (*Cl. 196–52*).

Major portion of the catalyst particles is removed from the bottom of the reaction zone so that less catalyst passes overhead with the vapors and gases, thus reducing the number of separation units needed. The process may be applied to the Fischer-Tropsch synthesis. 2 foreign and 31 United States patents cited.

———. *See* abs. **884.**

JAHRSTORFER, M. *See* abs. **3308.**

1761. JAHRSTORFER, M., AND SCHWARTE, G. (I. G. Farbenindustrie A. G.). [High-Molecular Waxlike Substances.] German Patent 695,860, Aug. 8, 1940; appl. I 45,780, filed Nov. 18, 1932 (*Cl. 12 o–1.01*). FIAT Reel AA–90, frames 1,379–1,380; PB 70,275; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 47, 1949, p. 30; Chem. Abs., vol. 35, 1941, p. 5604.

High-molecular oxidation products of aliphatic hydrocarbons, fatty acids or oils, which contain a carbonyl group, are treated catalytically so as to split off CO_2, and the resulting product is hydrogenated. These substances are good for dressing and impregnating of all kinds of fiber and paper. Being neutral they also can be used for lubrication.

1762. ——— (I. G. Farbenindustrie A. G.). [Process for Producing High-Molecular Waxy Substances.] German Patent 732,957, Mar. 19, 1943; appl. I 62,522, filed June 19, 1935 (*Cl. 12 o–1.02*). FIAT Reel AA88, frames 3,463–3,464; PB 70,273; Chem. Abs., vol. 38, 1944, p. 886.

Waxlike substances, consisting mainly of secondary aliphatic alcohols or of aliphatic hydrocarbons or both, are prepared by the catalytic treatment of materials that contain free or esterified carboxyl groups. The raw materials specified are the products arising from the oxidation of the residues from the distillation of fatty acids. The material is passed over an Fe catalyst for 8 hours at 290°. The product is then hydrogenated over a Ni–kieselguhr catalyst at 300° and 200 atm. pressure for about 10 hr.

JAKOB, W. *See* abs. **1048.**

1763. JAMM, W. (Mannesmannrohren-Werke). [Cooler Assembly for Synthetic Production of Benzine at Low Pressure.] German Patent 719,652, Apr. 13, 1942; appl. M 136,915, filed Jan. 20, 1937 (*Cl. 12 o–1.03*). Chem. Zentralb., 1942, II, p. 2227; Chem. Abs., vol. 37, 1943, p. 2164.

Apparatus allows for efficient cooling of the catalytic reaction. The sheet metal supports for the catalyst bodies are arranged in the form of a series of superimposed truncated cones surrounded by wire netting. The cooling liquid is circulated in a number of vertical pipes distributed throughout the device, which is constructed along the principle of an automobile radiator.

1764. JANNEK, J. (I. G. Farbenindustrie A. G.). Purifying Gases, United States Patent 1,631,823, June 7, 1927; appl. filed June 8, 1925, Serial No. 35,781, in Germany June 16, 1924. Chem. Abs., vol. 21, 1927, p. 2517.

To remove Fe carbonyl vapors from water gas or other gases, the gases are passed over active absorbing material such as active C or SiO_2 gel, and the latter is acted on with a substance such as O_2, Cl, HCl or phosgene chemically reacting on Fe carbonyl until the absorbing mass is substantially saturated with the reaction product. The mass is then regenerated, for example, by leaching with dilute acids or H_2O and drying.

JASCO, INC. *See* abs. **2702.**

JASION, L. Z. *See* abs. **2205.**

1765. JENNY, F. J., AND RIBLETT, E. W. (Hydrocarbon Research, Inc.). Process for Synthesizing Hydrocarbons. Canadian Patent 479,511, Dec. 18, 1951; appl. filed Sept. 10, 1945, Serial No. 531,403, in United States Sept. 12, 1944; 5 claims.

Catalytic hydrogenation of CO is effected by passing a mixture of CO and H_2 upward through a mass of fluidized powdered Fe catalyst, the velocity of fluidization being low enough that there is relatively little entrainment of the powdered catalyst in the effluent gases. The reactants are continuously introduced into the lower part of the reaction zone at a predetermined rate and pass upward at 600° F. and 250 lb. pressure, converting gaseous reactants into hydrocarbons with substantial volume contraction. An effluent stream of normally liquid hydrocarbons is continuously removed from the reaction zone, and the liquid hydrocarbons vaporizable under the prevailing conditions in the reaction zone are separated and injected into the reaction mixture at a number of points along the direction of travel through the catalyst mass, the amount injected being such as to compensate for the contraction in volume of the reactant gases and to maintain substantial fluidization of the catalyst along the vertical dimension of the reaction zone.

1766. ——— (Hydrocarbon Research Inc.). Process for Synthesizing Hydrocarbons. United States Patent 2,474,845, July 5, 1949; appl. filed Sept. 12, 1944; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 7213.

Synthesis gas is passed under reacting and fluidizing conditions through powdered Fe catalyst, preferably Fe itself. The reaction gases are withdrawn and cooled to separate a liquid fraction that is injected into the catalyst mass at a number of succeeding points spaced apart in the direction of reactant travel. This maintains good fluidization and effects close temperature control. The reaction gases remain uncondensed at the stage where the liquid fraction is taken for recycling to the reactor and go to a recovery plant where the products are collected by fractionation.

JEWELL, J. W. *See* abs. **2202.**

1767. JEWELL, J. W., AND JOHNSON, W. B. (M. W. Kellogg Co.). Method for Synthesis of Organic Compounds. United States Patent 2,543,974, Mar. 6, 1951; appl. filed July 21, 1947, Serial No. 762,250; 15 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 5392.

Mixture of H_2 and CO containing finely divided hydrogenation catalyst is passed through the reaction zone at a sufficiently high velocity under conditions such that even the heaviest catalyst particles are carried through the reaction zone with the gaseous mixture. Preferably the velocity is above 10 ft. per sec. and may be 40 ft. per sec. or higher. The concentration of catalyst in the reaction zone is generally below 18 lb. per cu. ft. of gas at operating temperature and pressure. The residence time of the gaseous reactants and conversion products in the reaction zone is sufficient to obtain optimum yields of hydrocarbons and/or oxygenated organic compounds. The residence time of the catalyst may vary considerably but in fluid-bed operation is merely a matter of seconds. The catalyst is separated from the effluent, stripped of heavy organic compounds deposited thereon, and recycled without further regeneration. 7 United States patents cited.

JOCHHEIM, H. *See* abs. **2083.**

1768. JOHNSON, C. E. (Standard Oil Co. of Indiana). Extraction of Oxygenated Organic Compounds From Aqueous Solutions Thereof. United States Patent 2,446,231, Aug. 3, 1948; appl. filed Dec. 22, 1945, Serial No. 636,939; 9 claims (*Cl. 260–450*). Chem. Abs., vol. 42, 1948, p. 7903.

Oxygenated organic compounds in diluted aqueous solution such as obtained in the Fischer-Tropsch process, may be recovered by extraction with a disulfide of the type RSSR′, where R and R′ are hydrocarbon groups, and subsequent fractionation of the disulfide solution.

———. *See* abs. **935.**

1769. JOHNSON, E. A. (Standard Oil Co. of Indiana). Hydrocarbon Synthesis With Fluidized Catalyst Regeneration. United States Patent 2,447,505, Aug. 24, 1948; appl. filed Apr. 13, 1944, Serial No. 530,875; 1 claim (*Cl. 260–449.6*). Chem. Abs., vol. 42, 1948, p. 8446.

Catalyst, preferably of the Co type, is continuously transferred from the synthesis zone to a smaller regeneration zone and back to the synthesis zone. In each zone the catalyst is kept in a dense, turbulent phase. The charge gas is an H_2:CO mixture of 2:1 mol. ratio. The regeneration gas is essentially H_2. Its CO content should be low. The gases leaving the regenerator may be recycled. They may also, or alternately, be used for aeration and/or transfer of catalyst in the absence of CO. Thus, partial stripping and regeneration can take place while the catalyst is passing through the cooler. A H_2 deficiency in feed gas may be made up from the regeneration gases. The synthesis and regeneration zones are separated. This is done with baffles and seals when they are in the same chamber. The operation of the seals depends on the relative densities of the fluidized catalyst in different parts of the system. By correlating the effective heights of catalyst column with densities regulated by controlled aeration, directions of catalyst flow may be established and flow rates may be controlled. The fluidized mass of catalyst thus serves as a seal between the synthesis and regeneration zones. 5 United States patents cited.

1770. ——— (Standard Oil Co. of Indiana). Hydrocarbon Synthesis With Fluidized Catalyst Regeneration. United States Patent 2,472,427, June 7, 1949; appl. filed Feb. 27, 1947, Serial No. 731,241; 7 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 8120.

This is in addition to United States Patent 2,447,505 (abs. **1769**). Fluidized bed of catalyst of 2- to 100-micron size is maintained in the synthesis zone and a separate fluidized bed in a much smaller regeneration zone. Catalyst is continuously transferred from the dense, turbulent phase in the synthesis zone to the regenerator and regenerated catalyst from the dense turbulent phase in the regeneration zone back to the reactor. The charge gas is H_2:CO=2:1 mol. ratio. The regeneration gas is essentially H_2. It may contain inert diluents, but the CO content should be low. The treatment with H_2 at a temperature higher than the conversion temperature, removes wax and/or carbonaceous deposits by chemical as well as physical means. The H_2 reacts with the deposits to form hydrocarbons. By correlating the effective heights of catalyst columns with densities, regulated by controlled aeration, directions of catalyst flow may be established and flow rates may be controlled. The fluidized mass of catalyst may serve as seal between the reaction and regeneration zones. 7 United States patents cited.

1771. ——— (Standard Oil Co. of Indiana). Hydrocarbons From Carbon Monoxide and Regeneration of Synthesis Catalyst. British Patent 648,317. Petroleum, vol. 14, 1951, p. 227.

Mixture of CO+H_2 is contacted with an Fe catalyst under fluidized catalyst bed conditions so that a dense turbulent suspended catalyst phase is superposed by a slight dispersed phase. The synthesis products are withdrawn from the latter, and a part of the Fe

catalyst is also withdrawn as a downward moving column directly from the dense phase and introduced into an oxidizing zone through which an oxidizing gas is passed upward at such velocity as to maintain the catalyst in a dense turbulent suspended phase under oxidizing conditions. A gaseous stream is removed from the upper part of the oxidizing zone, and the catalyst is removed separately from the dense phase in this zone as a downward moving column and reduced. It can then be used for further synthesis. Oxidation is effected in the presence of free O_2 at a temperature 700°–2,000° F., and reduction in H_2 within the same temperature range. The Fe particles may be contaminated with S before oxidation.

See United States Patent 2,455,419 (abs. **1772**).

1772. ——— (Standard Oil Co. of Indiana). Hydrocarbons From Carbon Monoxide and Regeneration of Synthesis Catalyst. United States Patent 2,455,419, Dec. 7, 1948. Chem. Abs., vol. 43, 1949, p. 1551.

In the hydrogenation of CO with a fluidized Fe catalyst, the catalyst gradually loses activity owing to accumulation of S compounds. A portion of the catalyst is withdrawn from the hydrogenation zone and passed to a desulfurizing zone in which it flows downward in a fluidized state against a countercurrent stream of air or other oxidizing gas at 1,000°–2,000° F., preferably about 1,500° F. The S is removed as SO_2 and the oxidized catalyst is passed to a reducing zone in which it flows downward in a fluidized state against a countercurrent stream of H_2 or H_2-containing gas and is thus reactivated. The catalyst is cooled and recycled to the synthesis zone or recycled in whole or in part to the oxidizing zone. Gives a flowsheet and construction details of the desulfurizing system.

1773. ——— (Standard Oil Co. of Indiana). [Iron Catalysts for Hydrocarbon Synthesis.] French patent 953,616, Dec. 9, 1949; appl. filed Sept. 30, 1947, in United States Oct. 14, 1944. Chem. Zentralb., 1950, II, p. 367.

Finely divided catalyst, which has a particle size of 10–200 microns, is first activated in an oxidation zone in presence of free O_2 at 371°–1,093° and then reduced with H_2 at the same temperature. As catalyst a finely divided carrier of alumina is used, which has been impregnated with Fe nitrate. Activation of the catalyst is carried out in a column where the solid and finely divided flowing catalyst is in touch with the O_2 or H_2 passing therethrough.

1774. ——— (Standard Oil Co. of Indiana). Process for Producing Hydrogen–Carbon Monoxide Gas Mixtures. United States Patent 2,482,187, Sept. 20, 1949; appl. filed Apr. 3, 1944, Serial No. 529,268; 1 claim (*Cl. 48–196*). Chem. Abs., vol. 44, 1950, p. 823.

Finely divided carbonaceous material, including powdered coal, oil shale, oil sands, etc., is heated by partial combustion with air, the hot, partly carbonized material is withdrawn and mixed with fresh carbonaceous material in another chamber where further heating is secured by blowing with O_2 to maintain temperatures above 1,500° F., and controlled amounts of steam are added to the O_2, thus generating a mixture of CO and H_2 with proportions varying with the amount of steam introduced. The flow rates in both of these chambers is sufficient to keep the material in turbulent motion. CH_4 may be introduced as an auxiliary fuel in either stage. The hot solids from the 2d stage may be mixed with further raw carbonaceous material and introduced into a 3d stage where the heat will be sufficient to carbonize the mixture and drive off hydrocarbons. The coke from this stage is returned to the heating stage.

1775. ——— (Standard Oil Co. of Indiana). Separation of Organic Oxygenated Compounds From Hydrocarbons. United States Patent 2,535,069, Dec. 26, 1950; appl. filed Aug. 12, 1948, Serial No. 43,888; 11 claims (*Cl. 260–450*).

In simple form the process is described by application to a charging stock made up of an organic, oxygenated compound and a hydrocarbon. The mixture is concurrently contacted with an aqueous extractant solution initially containing in excess of 30%, by weight, of the defined class of solubilizer salts, preferably 40–60%. Spaced injection of H_2O to the extraction zone is simultaneously effected so that the aqueous extract contains less than 30% by weight of stabilizer salts, preferably 5–20%. Thus, the hydrocarbon stream leaving the extraction zone is contacted last with concentrated extractant solution so that maximum extraction is effected. The aqueous extract leaving the extraction zone contains a reduced concentration of solubilizer salts so that the % of hydrocarbon contaminant is minimized. 4 United States patents cited.

1776. ——— (Standard Oil Co. of Indiana). Temperature Control of Chemical Reactions With Fluidized Solids. United States Patent 2,393,909, Jan. 29, 1946; appl. filed Apr. 2, 1945, Serial No. 586,236; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 40, 1946, p. 1990.

Temperature of an exothermic reaction of H_2 and CO is controlled and the heat of reaction dissipated in a process comprising the following features: (1) maintaining a mass of finely divided Fe catalyst in a reaction zone, (2) introducing CO and H_2 at a low point in the zone, (3) withdrawing gaseous reaction products from the top of the zone, (4) passing the reacting gases upward through the zone to maintain the catalyst in a dense, turbulent, suspended phase; (5) bringing the catalyst into intimate contact with a solid heat-absorbing material having a greater settling rate than the catalyst, the material being inert under the zone conditions, (6) carrying on the reaction under these conditions and absorbing heat from exothermic reaction by means of the added solids so that the temperature is maintained about 310°–321°, (7) separating the heated solids from the catalyst by the classifying action of the upward flowing gaseous fluids in the reaction zone, (8) removing the solids from a low point in the zone, (9) cooling the solids substantially below the reaction temperature, and (10) returning them to the zone at a high point. A suitable size for the added solid is 10- to 40-mesh. Suitable solids are crushed firebrick, Fe shot, Al pellets, sand, metal oxides, or coke. The diluent solid may also be a S acceptor such as Co, Mo, Cu, or Co molybdate supported on 1 of the solids.

1777. JOHNSON, E. A., AND BECKER, S. B. (Standard Oil Co. of Indiana). Method and Means for Hydrocarbon Synthesis. United States Patent 2,460,508, Feb. 1, 1949; appl. filed July 30, 1946, Serial No. 687,064; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 3175.

One portion of a mixed stream of CO and H_2 gases, ratio 3 : 5 is reacted over a Co synthesis catalyst at 340°–500° F. and 1 atm. pressure, and another portion of this stream is reacted over an Fe synthesis catalyst at 400° F. and 5 atm. Residual gas from the Co catalyst zone is supplied to the Fe catalyst zone. At least a portion of the H_2-rich gas recovered from the Fe catalyst zone is supplied after separation of CO_2 to the Co catalyst zone. Increased outputs in hydrocarbons and other conversion products are obtained by this combined process. A flowsheet is included. 1 foreign and 4 United States patents cited.

1778. JOHNSON, G. W. (I. G. Farbenindustrie A.-G.). Improvements in the Cracking or Pressure Hydro-

genation of Hydrocarbons. British Patent 524,380, Aug. 6, 1940. Chem. Abs., vol. 35, 1941, p. 6777.

Process for the catalytic conversion of hydrocarbons containing more than 15 gm. of H per 100 gm. of C, such as product of a catalytic reduction of CO with H_2, by subjecting them to a cracking treatment or to a hydrogenation treatment under pressure in the presence of an initially highly active catalyst the activity of which has been reduced for example by about 25% by its employment in a cracking of pressure hydrogenation treatment of carbonaceous substances poor in H. Example: a tar oil b. 200°–400° C. is led at 410° C. together with H_2 under a pressure of 200 atm. with a partial pressure of tar oil of 13 atm. over W disulphide rigidly arranged in a reaction vessel for 3 days. The activity of the catalyst is thus reduced by about 25%, which means that to obtain the original result the speed of the vapors and gases led through the vessel must be reduced by about 25%. A fraction of a hydrocarbon mixture b. 200°–325° C. of an oil obtained by the reduction of CO is then led over the same catalyst at the same temperature and at the same pressure. A product consisting to the extent of 70% of benzine is obtained. Only 6% of the initial material is converted into gaseous hydrocarbons.

JOHNSON, H. L. *See* abs. **2347.**

1779. JOHNSON, H. L., AND STUART, A. P. (Sun Oil Co.). Hydrogenation Catalyst Containing Molybdenum Disulfide. United States Patent 2,649,419, Aug. 18, 1953. Chem. Abs., vol. 47, 1953, p. 11,604.

Catalyst having good mechanical strength and high efficiency for efficient use in hydrogenation is formed from Fe oxide, TiO_2, SiO_2, Al_2O_3, and a small amount of volatile matter. It is impregnated with an aqueous solution of $(NH_4)_2MoO_4$ (I). H_2O is expelled by gentle heating and the resulting mass treated with H_2S to convert the (I) to $(NH_4)_2MoS_4$ and the Fe to Fe sulfide. It is then heated to 300° in an atmosphere of H_2 to convert the thiomolybdate to the disulfide. The final composition contains in %: MoS_2 21.0, Fe sulfide (calculated as Fe_2O_3), 10.7; SiO_2, 6.1; TiO_2, 2.4; Al_2O_3, 55.5; and volatile matter, principally H_2O, 4.3.

1780. JOHNSON, P. H. (Phillips Petroleum Co.). Treatment of Synthetic Gasoline. United States Patent 2,501,223, Mar. 21, 1950; appl. filed Nov. 10, 1947, Serial No. 785,146; 7 claims (*Cl. 196–50*).

Raw synthetic gasoline of the Fischer-Tropsch type is preheated and passed over a cracking catalyst, such as bauxite, in a 1st contact zone at 700°–950° F. and 0–200 p. s. i. Undesirable oxygenated compounds are removed, and the odor is improved. Effluent from the 1st zone is passed through a 2d zone containing the same or a different catalyst along with superheated steam, temperature 600°–950° F. pressure 0–200 p. s. i. 20–65 lb. of steam per bbl. gasoline is used in the 2d step. The space velocity in both zones is 0.5–10 liquid vol. charge per vol. catalyst per hr. The size of the 2 zones may be the same or may be varied, depending on the nature of the gasoline treated. Effluent from the 2d zone is fractionated, and the desired product such as a stabilized 700° F. end-point gasoline is separated and recovered. Catalyst can be regenerated with steam and air. Silica alumina and activated montmorillonite are also mentioned as catalysts. Example: 2 runs were made using raw Fischer-Tropsch gasoline b. 110°–385° F., and ASTM unleaded octane No. 62 and a Br No. 67. In each run the charge was passed through a calcined bauxite catalyst at 745° F., 50 p. s. i., and a space velocity 1.4 liquid vol. per vol. catalyst per hr. In the 2d run 63 lb. steam per bbl. gasoline was added. A 3d run was made in which the product of the 1st run was treated in the manner described for the 2d run, except the temperature was 700° F. The following data were obtained:

	Run 1	Run 2	Run 3
ASTM octane rating:			
0 ml. tetraethyl lead	72.2	70.4	76.4
3 ml. tetraethyl lead	81.3	81.6	86.2
Research octane rating:			
0 ml. tetraethyl lead	77.1	73.3	82.0
Bromine number	67	67	85

1 literature and 2 United States patents cited.

JOHNSON, V. C. *See* abs. **2168.**

1781. JOHNSON, W. B. (M. W. Kellogg Co.). Manufacture of Hydrogen. United States Patent 2,656,255, Oct. 20, 1953; appl. filed Feb. 2, 1949, Serial No. 74,213; 13 claims (*Cl. 23–214*).

Claim 1. A process for producing H_2, which comprises combusting C containing material with O_2-containing gas under conditions suitable for the production of a major proportion of CO and a minor proportion of CO_2; passing excess steam upward through an oxidizing zone in the presence of finely divided reduced metalliferous contact material at a velocity effective to suspend the contact material in a pseudo-liquid condition at <1,100° F. but sufficiently high such that H_2 is produced under endothermic conditions at a desired rate by the reaction of steam with the contact material and the contact material is oxidized; passing oxidized contact material from the oxidizing zone to a 1st reduction zone; passing CO, which is prepared from combusting C containing material in excess, upward through said 1st reduction zone at a velocity effective to suspend the oxidized contact material in a pseudo-liquid condition therein at a temperature significantly < the temperature of said oxidizing zone under exothermic conditions such that the metalliferous contact material is reduced by the CO, which is converted to CO_2 and the heat generated therein is sufficient to constitute the principal source of heat for the oxidizing zone; passing a relatively small proportion of contact material from the 1st reduction zone to a 2d reduction zone, wherein the contact material is further reduced by the unconverted CO from the 1st reduction zone at < 700° F. but sufficiently high to obtain the desired rate of reaction; removing an effluent from the said 2d reduction zone comprising CO_2 and substantially free of CO; recycling reduced metalliferous contact material to the said oxidizing zone at a temperature and in an amount sufficient to constitute the principal source of heat thereto; at least a portion of the reduced contact material is recycled from the 1st reduction zone; and recovering H_2 from the oxidizing zone as the product of the process.

1782. ——— (M. W. Kellogg Co.). Synthesis of Organic Compounds. United States Patent 2,579,828, Dec. 25, 1951; appl. filed May 12, 1948, Serial No. 26,595; 4 claims (*Cl. 260–449.6*).

Describes details of a process in which unreacted CO-H_2 mixture from a 1st reaction zone is contacted in a 2d zone with catalyst from the 1st zone previously contacted with a H_2-containing gas for stripping high-boiling organic compounds from it.

See abs. **1767, 2202.**

JOHSWIG, F. *See* abs. **2137.**

1783. JOKLIK, A., AND KECK, R. (Wiener Stadtwerke). [Synthetic Town Gas.] Austrian Patent 174,598, Apr. 10, 1953. Chem. Abs., vol. 47, 1953, p. 5667.

In making synthetic town gas from CH_4-containing hydrocarbons by catalytic oxidation in the gaseous phase, undesired amounts of soot often develop if the O_2 content of the used oxidizing gas is above that of the air. To avoid this, the gasification process is conducted in a closed cycle, town gas being admixed

to the hydrocarbons entering the process. The reaction is conducted in a contact furnace in a single step with dry and cold, optionally cooled, gaseous hydrocarbons as starting materials. Describes a plant for carrying out the process.

JOLLEY, L. J. *See* abs. **202, 203.**

JONES, F. S. B. *See* abs. **278, 2823.**

1784. JONES, J. P., AND AXE, W. N. (Phillips Petroleum Co.). Reaction of Diolefin Polymers With Hydrogen and Carbon Monoxide. United States Patent 2,544,555, Mar. 6, 1951. Chem. Abs., vol. 45, 1951, p. 4967.

Reaction of polymeric hydrocarbons (I), having a greater degree of unsaturation than a monoolefin and a molecular weight of 200–800, with H_2 and CO in the presence of a suitable Fischer-Tropsch catalyst forms a resinous solid O-containing material (II). The reaction is preferably conducted in 2 steps, the formation of a resinous product (III) and the further reaction of (III) with H_2 in the absence of CO either in the presence of the original or a substitute hydrogenating catalyst. The preferred Fischer-Tropsch catalyst is a Co–thoria–kieselguhr mixture (IV) with the respective weight ratio of 100 : 18 : 100. Thus, to a cyclohexane solution of (I), or "claytower polymers", 2 : 1, containing 5% of (IV), an equimolar mixture of H and CO is added at 500 p.s.i. The mixture is agitated and kept at 300° F. for 30 min. before the gases are released. The system is purged of CO, and then H_2 is added at 500 p.s.i. and the mixture maintained at 300° for 30 min. After cooling the chief reaction product is a (II) having properties suitable for use in paints and lacquers.

1785. JONES, M. C. K. (Standard Oil Development Co.). Synthesis Gas. United Staes Patent 2,640,034, May 26, 1953. Chem. Abs., vol. 47, 1953, p. 7198.

Mixtures of H_2 and CO containing more than about 1 mole H_2 per mole CO may be produced from solid carbonaceous materials when heat and reducing gases generated in the manufacture of blue water gas are utilized for the production of makeup H_2 by the reduction of steam. The blue water gas is generated from carbonaceous solids, the necessary heat being obtained by the combustion of carbonaceous solids in a separate heating zone operated to produce substantial amounts of CO, which is used in the reduction of steam to produce makeup H_2. In the steam reduction, the steam is preferably brought into contact with Fe or an Fe alloy, with Mn, W, or the like added to control the activity, to form H_2 and the oxide of the metal. The metal is regenerated using the CO produced in the heating zone of the water-gas generator. By using the fluidized-solids technique in both water-gas and H_2 generators, the process may be operated in a fully continuous manner.

1786. JONES, W. H., LONG, F. M., AND KREBS, R. W. (Standard Oil Development Co.). Method of Regenerating Hydrocarbon Synthesis Catalyst. United States Patent 2,541,654, Feb. 13, 1951; appl. filed June 3, 1947, Serial No. 752,250; 10 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 5392.

In initial stages of the synthesis reaction the catalyst has a relatively high weight of O as compared to C. As the reaction progresses the weight % of C increases. In accordance with the invention, the catalyst is withdrawn from the synthesis zone when the weight % of C is 2–3 times the weight % of O. The catalyst is treated in a relatively O_2-free atmosphere as in a N_2 atmosphere. The C may be reduced by using the O_2 present in the catalyst. The regenerated catalyst, which is also a reduced catalyst, is returned directly to the synthesis zone. The process is particularly applicable when using a synthetic ammonia catalyst, Fe_3O_4 containing 1.5% K_2O and about 3% Al_2O_3. 6 United States patents cited.

1787. ——— (Standard Oil Development Co.). [Regeneration of the Iron Catalysts Used in the Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 962,660, June 6, 1950; appl. filed Mar. 5, 1948, in United States June 3, 1947. Chem. Zentralb., 1950, II, p. 2271.

Regeneration of the fluidized catalyst takes place in an inert N_2 atmosphere at 593°–760°, whereby it is oxidized by the O_2 contained in the catalyst. The catalyst proceeds from the regeneration zone into the reaction zone.

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KAEHLER, H. *See* abs. **3927.**

1788. KAHL, L. (Rütgerswerke A. G.). [Reclaiming Volatile Components From Pitch, Tar, Bitumen, Coal, Resins and Wax.] German Patent 735,469, Apr. 8, 1943; appl. R 101,251 filed Jan. 13, 1938 (*Cl. 10 a–24.02*). Chem. Abs., vol. 38, 1944, p. 2812.

The preheated parent material is injected into a stream of superheated steam or gas. The injected pitch and tar remain in contact with the steam or gas for a fraction of a second only, traveling with it approximately 20 cm. The temperature of the steam or gas is such that the nonvolatile components do not decompose. After leaving the apparatus the mixture is cooled.

KAISER, L. *See* abs. **2045, 2046, 2047.**

KAISER, W. J. *See* abs. **1003.**

1789. KALBACH, J. C. (Hydrocarbon Research, Inc.). Coal Carbonization and Gasification. United States Patent 2,634,198, Apr. 7, 1953. Chem. Abs., vol. 47, 1953, p. 6122.

Coal gas and water gas are produced from coal in a fluidized-bed process in a single vessel. The ground coal is partly carbonized during conveyance by recycle gas in a pipe passing through the fluidized bed to a funnel-shaped chamber within the reactor. The resulting coal gas is thus isolated from the water gas. The partly carbonized material is fed into the main bed at a temperature of 1,300°–1,800° F., where water gas is produced by fluidization with steam and O_2.

1790. ——— (Hydrocarbon Research, Inc.). Conversion of Carbonaceous Materials. Canadian Patent 487,256, Oct. 14, 1952; appl. filed July 21, 1948, Serial No. 577,438; 5 claims.

Coal in a fluidized state is simultaneously hydrogenated and carbonized in the presence of H_2 substantially free from CO at pressure 300–750 p. s. i. g. and 1,000°–1,500° F. The carbonaceous residue is reacted with O_2–containing gas and steam to produce a mixture of CO and H_2. H_2 is separated from the mixture and used to hydrogenate more coal. The CO separated from the mixture of H_2 and CO is mixed with the gaseous product of carbonization to produce a high caloric gas useful as fuel.

1791. ——— (Hydrocarbon Research, Inc.). Fuel Gas. United States Patent 2,609,283, Sept. 2, 1952. Chem. Abs., vol. 47, 1953, p. 849.

High-heating-value fuel gas is produced by simultaneously hydrogenating and carbonizing autogenously a comminuted, solid carbonaceous material containing volatilizable constituents in a dense-phase fluidized bed in the presence of a stream of H_2 at 300–750 p. s. i. g. and about 538°–816°. From the carbonizer a mixture of hydrocarbons and unreacted H is withdrawn, to-

gether with a C-containing residue. The latter is gasified with steam and air to produce CO and H_2. The H_2 is separated from the CO and used in the carbonizer, and the CO is added to the gases from the carbonizer.

1792. ——— (Hydrocarbon Research, Inc.). Fuel Gas. United States Patent 2,639,982, May 26, 1953. Chem. Abs., vol. 47, 1953, p. 7197.

In the hydrogenation of carbonaceous solids at elevated temperature and pressure, a fuel gas of high heating value is produced when (1) the particles of the solids are slurried with a liquid hydrocarbon, which is substantially completely vaporizable under the reaction conditions; (2) the slurry is mixed with a gas rich in H_2 in a reactor; (3) the liquid hydrocarbon is vaporized in the reactor, and a dense fluidized bed of the carbonaceous material is maintained in the reactor by passing the vapors and gas upward through the bed to effect fluidization and hydrogenation; and (4) the hydrogenation products and vaporized hydrocarbon are recovered from the reactor. In the hydrogenation of coal the temperature may range from about 288°–538° and the pressure from about 750–1,000 p. s. i. g. or higher.

See also United States Patent 2,609,283 (abs. **1791**).

1793. ——— (Hydrocarbon Research, Inc.). Fuel Gases of High Heating Value. United States Patent 2,623,816, Dec. 30, 1952. Chem. Abs., vol. 47, 1953, p. 2965.

Coal in fluidized form is carbonized by a current of hot gases from the gasification of the residual coke in a second stage by using O_2 and steam. The mixed gases from the carbonizing chamber are passed through a cyclone to remove fly ash, and then to a converter containing finely divided C. The pressure in the converter is 150–450 p. s. i., and the temperature is 1,000°–1,350° F. Methanation proceeds rapidly in the absence of a catalyst. The C in the converter is maintained in a fluidized state and is supplemented by the C from cracking hydrocarbons in the gas supplied to it. Entrained C is caught by a cyclone collector and returned to the converter. Excess C formed in the converter is returned to the gasification zone. The process is self-sufficient in its heat and energy requirements, even supplying that required for the intial compression of the O_2.

1794. Kalbach, J. C., De Marchi, V. S., and Sullivan, F. W., Jr. (Inland Steel Co.). Method of Reducing Metallic Oxides. United States Patent 2,538,201, Jan. 16, 1951; appl. filed Aug. 17, 1944, Serial No. 549.914; 5 claims (*Cl. 75–26*). Chem. Abs., vol. 45, 1951, p. 2843.

Object of invention is to provide methods and apparatus for establishing and maintaining suitable material transfer, heat exchange, and temperature conditions in metallurgical operations on solid material in a fluidized state, particularly in the reduction of oxides of heavy metals with H_2 and/or CO. 15 United States patents cited.

1795. Kamzolkin, V. P., Kozhenova, K. I., Livshits, V. D., and Sheshin, A. I. [Catalyst for Ammonia Synthesis.] Russian Patent 42,990, May 31, 1935. Chem. Abs., vol. 31, 1937, p. 7202.

Magnetite high in SiO_2 is consecutively ground and magnetically separated; after 1 or 2 separations it is fused with activators. The melt is broken up and subjected to additional separations, whereafter it is fused again without the addition of activators but with the introduction of pure Fe.

Kaneda, S. *See* abs. **604.**

1796. Kapecki, A. F. (Gicaudan Corp.). Process of Preparing Chromium Trioxide Hydrogenating Metal Oxide Catalysts. United States Patent 2,512,653, June 27, 1950; appl. filed Apr. 10, 1945, Serial No. 587,609; 17 claims (*Cl. 252–468*). Chem. Abs., vol. 44, 1950, p. 9087.

Flowable homogeneous mixture is formed consisting of 1–3 mol. CrO_3 and 1–2 mol. of at least 1 acetate of metal selected from Zn, Cu, and Cd, mixing and heating at 95°–300°. The catalysts are used in reduction of long-chain fatty acids or their derivatives to the alcohols corresponding to the fatty acids or fatty acid radicals present in the material reduced. 1 literature ref. and 10 United States patents cited.

Karpen, S., & Bros. *See* abs. **501, 502.**

1797. Karpov, A. Z. [Methanol.] Russian Patent 47,687, July 31, 1936. Chem. Abs., vol. 33, 1939, p. 3398.

MeOH is prepared from oxides of C by hydrogenation in the presence of a catalyst formed from CuO, ZnO, and Cr_2O_3 in the proportions 9 : 15 : 7.

1798. Karwat, E. (Linde Air Products Co.). Converting Hydrocarbon Gas to Carbon Monoxide and Hydrogen. United States Patent 2,170,265, Aug. 22, 1939; appl. filed May 6, 1936, Serial No. 78,294, in Germany May 11, 1935; 9 claims (*Cl. 23–212*). Chem. Abs., vol. 34, 1940, p. 247.

Various details of apparatus and operation suitable for effecting reaction of a CH_4-bearing gas with steam and O_2 in heated coke.

1799. ——— (Gesellschaft für Linde's Eismaschinen A. G.). [Partial Combustion of Methane to Carbon Monoxide and Hydrogen.] German Patent 730,346, Dec. 10, 1942 (*Cl. 12 i–1.01*). Chem. Abs., vol. 38, 1944, p. 472.

1800. ——— (Gesellschaft für Linde's Eismaschinen A. G.). [Separating Gaseous Impurities.] German Patent 707,079, May 8, 1941 (*Cl. 12 i–1.01*). Chem. Abs., vol. 36, 1942, p. 1817.

Describes layout for separating gaseous impurities from gaseous mixtures by freezing.

1801. Kassel, L. S. (Universal Oil Products Co.). Exothermic Gas Reactions. British Patent 692,176, May 27, 1953. Chem. Abs., vol. 47, 1953, p. 8996.

See United States Patent 2,566,337 (abs. **1802**).

1802. ——— (Universal Oil Products Co.). Method of Controlling Exothermic Gas Reactions. United States Patent 2,566,337, Sept. 4, 1951; appl. filed July 26, 1946, Serial No. 686,440; 5 claims (*Cl. 260–449.6*).

Method as described is sepcifically applicable to the synthesis of hydrocarbons from CO and H_2. It comprises passing the gaseous mixture upward through the catalyst bed and controlling the temperature in the bed by passing, countercurrently to the flow of incoming gases, a liquid hydrocarbon fraction consisting essentially of a light, narrow-boiling hydrocarbon fraction and a heavy, substantially nonvolatile hydrocarbon fraction having an initial boiling point substantially higher than the end boiling point of the volatile hydrocarbon fraction. The light hydrocarbons remove the exothermic heat of reaction by vaporization thereof, and the heavy hydrocarbons prevent any temperature gradient throughout the catalyst bed because of decreasing volatility of the light hydrocarbon fraction during its passage downward through the bed and the decreasing volume of reactants as they pass upward therethrough. Formulas are presented for determining the vapor pressures and rates of the components necessary to obtain a satisfactory uniformity of temperature throughout the reaction zone.

Katayama, I. *See* abs. **1879.**

1803. Kaufman, B. I. (M. W. Kellogg Co.). Hydrogenation of Oxygenated Organic Compounds. United States Patent 2,623,893, Dec. 30, 1952; appl. filed

Nov. 9, 1948, Serial No. 59,173; 8 claims (*Cl. 260–450*).

Tail gas from hydrogenation of CO is used for hydrogenation of oxygenated organic compounds. To eliminate CO, the tail gas and steam may be passed over a water-gas shift catalyst such as Ni, Fe–Cr, or Co at 600°–700° F. to form CH_4 or CO_2. After the aldehyde-ketone conversion, the CH_4 and CO_4 may be used by recycling the remaining gases to the gas-making step when CH_4 is formed, or either to the gas-making or synthesis step when CO_2 is formed. 1 literature ref. and 9 U. S. patents cited.

KAUFMAN, H. *See* abs. **1039.**

1804. KAUFMAN, H., AND SIMON, W. (W. E. Currie). [Nonknocking Motor Fuel.] French Patent 854,502, no date. Chem. Zentralb., 1940, II, p. 1817.

See United States Patent 2,228,118 (abs. **1805**).

1805. ——— (W. E. Currie). Production of Nonknocking Motor Fuels. United States Patent 2,228,118, Jan. 7, 1941; appl. filed May 3, 1939, Serial No. 271,506, in Germany May 9, 1938; 10 claims (*Cl. 196–50*). Chem. Abs., vol. 35, 1941, p. 3074.

Oil b. partly above 200° C. and rich in H such as Kogasin, is mixed with an oil of lower H content such as tar middle oil, and the mixture hydrogenated over a catalyst above 400° C and 350 atm. Sulfides of the 6th group metals are preferred as catalysts.

1806. KAUFMANN, H., AND WELZ, H. (I. G. Farbenindustrie A. G.). [Antiknock Gasolines.] German Patent 736,094, Apr. 29, 1943; appl. filed Aug. 5, 1939 (*Cl. 23 b–1.04*). Chem. Zentralb., 1943, II, p. 1168; Chem. Abs., vol. 38, 1944, p. 3816.

Mineral oils, coal, peat, extraction, and hydrogenation products synthesized hydrocarbons are catalytically cracked in the liquid phase with the aid of finely subdivided catalysts, such as oxides or silicates of metals of the 2d, 3d, and 8th groups of the Periodic Table. The rate of flow of the cracking material is kept at 20–40 kg. per l. per hr. The temperature is kept at >460°, preferably at 480°–520°.

1807. ——— (I. G. Farbenindustrie A. G.). [Motor Fuel From Multibranched Alcohols.] German Patent Appl. I 74,066, OZ 13,916, filed Jan. 13, 1943 (*Cl. IV d–12 o*). TOM Reel 15, bag 3,043, item 18, frames 2,419–2,422; TOM Reel 20, item 167, frames 2,682–2,685; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, chap. 101, 1948, p. 82.

Multibranched alcohols, obtained by the catalytic reduction of CO with H_2 under pressure, together with a crude gasoline obtained from the low-temperature distillation or carbonization of hard or brown coal, are passed in presence of H_2 or gases containing it over hydrogenating catalysts under hydrogenating conditions and raised pressure but with the avoidance of cracking. An antiknock motor fuel is obtained by operating under a moderate total pressure, 40–50 atm., and a low partial pressure, 0.5–3 atm., in the presence of catalysts consisting of the sulfides or oxides of metals of groups 6 or 8 in admixture with oxides of metals of groups 2–5. In an example, an almost theoretical yield of a gasoline is obtained with an octane number of 73, or 91 after addition of 0.12% of lead.

1808. KAUZNER, A. [Methanol.] Swiss Patent 150,613, Aug. 16, 1930. Chem. Abs., vol. 26, 1932, p. 4829.

MeOH is prepared synthetically from CO and H_2 under high temperature and pressure, by using catalysts consisting of ZnO and Cr_2O_3, with an addition of Li compound.

KAWAGUCHI CHEMICAL INDUSTRIES CO. *See* abs. **1619.**

1809. KAWAMURA, M., AND OTHERS (Nissin Chemical Industries Co.). [Iron Catalyst for Manufacture of Water Gas.] Japanese Patent 654 (1951), Feb. 16, 1951. Chem. Abs., vol. 46, 1952, p. 11,643.

Waste H_2O from a Cu mine, containing $CuSO_4$, is treated with Fe plates to precipitate Cu; the dissolved Fe is oxidized and precipitated as $Fe(OH)_3$. This is mixed with $K_2Cr_2O_7$, MgO, and dunite; fired at 600°, and molded.

KEARBY, K. K. *See* abs. **192, 193, 194, 1860.**

KECK, R. *See* abs. **1783.**

1810. KEELING, W. O. (Koppers Co.). Manufacture of Gas. United States Patent 2,590,869, Apr. 1, 1952; appl. filed Apr. 21, 1945, Serial No. 589,643; 2 claims (*Cl. 48–196*).

Process for producing synthesis gas from hydrocarbon gas and steam wherein the heat of conversion is supplied by a continuously moving heated body of refractory granules.

KEILIG, F. *See* abs. **3223, 3224.**

1811. KEITH, P. C. (Hydrocarbon Research, Inc.). Catalytic Synthesis of Hydrocarbons. United States Patent 2,506,221, May 2, 1950; appl. filed Feb. 18, 1947, Serial No. 729,217; 6 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 6106.

Synthesis gas is introduced into the lower portion of the reactor and passes upward through a series of successive, independently supported catalyst masses. The effluent from each preceding catalyst mass is mixed with additional synthesis gas in an orifice or constricted passage before uniform redistribution through the next succeeding bed of catalyst. Each zone is separated from the preceding zone not only by a restricted passage, but also by suitable means such as a conical bottom wall concave on its upper surface adapted to distribute the upward flow of gas uniformly throughout the horizontal cross section of the catalyst mass, which it supports. Each zone is provided with individual cooling surfaces immersed in the fluidized powder and provided with an internal coolant. The cooling surface may take any conventional form. 9 United States patents cited.

1812. ——— (Hydrocarbon Research, Inc.). Controlling Catalytic Exothermic Reactions of Gasiform Reactants. United States Patent 2,479,496, Aug. 16, 1949; appl. filed May 18, 1946, Serial No. 670,808; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 8650.

Effluent vapors from the reaction zone are passed concurrently through a 2d or cooling mass of fluidized powder maintained at a temperature below the optimum reaction temperature. In an example a powdered Fe catalyst containing 1–3% K oxide and 2–3% alumina is used with a synthesis gas containing 86% of a mixture of H_2 and CO, 2 : 1 and 14% CO_2. The linear velocity is 1.5 ft. per sec. The reaction mass is held at a temperature of 600° F., with not more than 5° F. variation, and a pressure of 200 p. s. i. The effluent passes directly into a cooling zone containing a smaller mass of powdered catalyst maintained under identical conditions, except that cooling surfaces maintain a catalyst temperature of 400° F. with a fluidized bed only 6 ft. in depth, the effluent gases and entrained particles issue at a temperature of 400° F. and may be passed through separators without material temperature rise. There is no impairment of operation, of catalyst, or of products owing to continuing reaction above the psuedoliquid level of the catalyst bed, even though the effluent gases contain 25% H_2 and 10% CO. The invention is particularly advantageous in the Fischer-Tropsch synthesis. 5 United States patents cited.

1813. ——— (Hydrocarbon Research, Inc.). Fluidizing Process for Gasifying Carbonaceous Solids. United States Patent 2,445,327, July 20, 1948; appl.

filed Aug. 2, 1944, Serial No. 547,722; 3 claims (*Cl. 196–56*).

A reactor that may be used for simultaneous pyrolytic distillation and exothermic gasification of coal, lignite, and oil shale is divided into 2 zones by internal baffling. The 2 zones merge in both the upper and lower regions. In operation the 2 zones are filled with a fluidized solid and are maintained at different fluid-static heads. The solid flows down the zone of greater fluid-static head, through the bottom channel, up the zone of lesser fluid-static head, and through the upper space to the zone of greater head. By "fluid-static head" is meant a pressure condition comparable to a hydrostatic head in a liquid system. Different gases may be introduced into the 2 zones to fluidize and react with the circulating solids. Gases and entrained particles of the treated solids are discharged from the upper space through suitable separators. For illustration the process is applied to carbonization and gasification of coal. 12 United States and 2 foreign patents cited.

1814. ——— (Hydrocarbon Research, Inc.). Hydrocarbon Synthesis. United States Patent 2,558,760, July 3, 1951; appl. filed Aug. 24, 1946, Serial No. 692,874; 7 claims (*Cl. 260–449.6*).

C entrained in the synthesis gas may be wetted and washed out by means of H_2O formed in the C oxide–H_2 synthesis reaction and condensed from the effluents of the reactor. In the process, the synthesis gas, before its passage into the reactor, is passed countercurrently, in scrubbing relationship, through a descending stream of the condensed aqueous solution of oxygenated hydrocarbons formed during the synthesis. 7 United States patents and 1 literature ref. cited.

1815. ——— (Hydrocarbon Research, Inc.). Hydrocarbon Synthesis. United States Patent 2,631,159, Mar. 10, 1953; appl. filed Jan. 31, 1945, Serial No. 575,417; 7 claims (*Cl. 260–449.6*).

Synthesis gas is passed through a number of tubular reaction zones that become one at their upper and lower ends. Catalyst, such as powdered Fe, in fluidized condition fills the reaction zones as well as the merging zones. The tubular zones are surrounded with a coolant such as H_2O, Dowtherm, or Hg. It is important that the tubes have an internal radius of not less than ½ in. and not more than 2 in. The linear velocity should be 0.5–1.5 ft. per sec. In the merging zones the gas velocity may be as low as 0.03 ft. per sec. or lower. The entire reaction mass is maintained at 600° F. 1 literature ref. and 4 United States patents cited.

1816. ——— (Hydrocarbons Research, Inc.). Process for Hydrocarbon Synthesis. United States Patent 2,472,377, June 7, 1949; appl. filed Jan. 31, 1945, Serial No. 575,417; 7 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 7213.

Synthesis gas is passed up through a powdered-Fe catalyst in a number of tubular reaction zones which become 1 at their upper and lower ends. The catalyst fills the merging zones as well as the reactor tubes. The tubes are surrounded by coolant, such as H_2O, Dowtherm, or mercury, and may be elliptical, square, polygonal or circular in shape. The preferred size for the pipes is not less than 1 in. and not more than 2 in. in internal radius. The farthest catalyst particle must be not less than ½ in. and not more than 4 in. away from the closest wall of the tubular zone. The linear velocity of the gases ranges 0.5–1.5 ft. per sec. In the merging zones the velocity may be as low as 0.03 ft. per sec. or even lower. A relatively dense mass of catalyst in the upper zone acts as a stabilizing cap and the mass in the bottom zone as an emergency reservoir to supply catalyst promptly to any reaction tube. A standpipe or equivalent connection between the upper and lower zones likewise helps insure good fluidization. 8 United States patents cited.

1817. ——— (Hydrocarbon Research, Inc.). Process for Stripping Spent Fluid Catalysts. Canadian Patent 476,474, Aug. 28, 1951; appl. filed Aug. 11, 1945, Serial No. 530,206; 11 claims.

Fluid catalysts that have become spent in the conversion zone are revivified during the transfer of the spent catalyst from the conversion zone to the regeneration zone by passing a composite gas stream made up of O_2 of not less than 95% purity and a gaseous supplement thereto, which is predominantly a mixture of C oxides with not less than about 35% by vol. of O_2, upward through a substantially vertical elongate zone and simultaneously moving fluidized spent catalyst downward through the same zone, while maintaining a temperature therein below the deactivation temperature of the catalyst but not below about 800° F.

1818. ——— (Hydrocarbon Research, Inc.). Process for Synthesizing Motor Fuels of High Antiknock Value. United States Patent 2,470,216, May 17, 1949; appl. filed June 21, 1945, Serial No. 600,734; 8 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 5574.

Motor fuels from CO–H_2 reaction are improved by passing the synthetic oil in vapor phase through a mass solid catalyst such as activated alumina or bauxite at temperatures above 700° F., preferably 800°–900° F. The catalyst is regenerated by substantially pure O_2, and the resulting flue gas is essentially CO and CO_2 in ratio 1 : 2 by vol. This gas, which contains all of the C laid down on the catalyst and which normally would represent a loss, is in a form suitable for recycling to the synthesis gas generator. A polymerization step produces an additional gasoline fraction from the normally gaseous hydrocarbons. 1 literature ref. and 9 United States patents cited.

1819. ——— (Hydrocarbon Research, Inc.). Regeneration of Fluid Catalysts. Canadian Patent 476,475, Aug. 28, 1951; appl. filed Oct. 9, 1945, Serial No. 532,597; 6 claims.

Fluid catalysts that have become spent through use are regenerated by contacting with gas containing not less than 95% by vol. of O_2 and circulating the catalyst through the conversion and regeneration zones at such rate that the carbonaceous matter on the catalyst leaving the conversion zone is less than about 0.5 wt. %, and the residual carbonaceous matter on the catalyst leaving the regeneration zone is less than about 0.05 wt. %. The temperature in the regeneration zone is kept below the deactivation temperature of the catalyst but not below about 800° F., so that the carbonaceous matter undergoes combustion.

1820. ——— (Hydrocarbon Research, Inc.). Synthesis Gas. United States Patent 2.642,346, June 16, 1953. Chem. Abs., vol. 47, 1953, p. 8997.

Apparatus for the efficient utilization of the exothermic heat of oxidation in the production of H_2 and CO from CH_4. A granular solid thermophore or catalyst is circulated countercurrent to the gas stream to provide efficient heat transfer from the product gases back to the reaction zone and to preheat the reactants. Preferred operating conditions require the reaction zone maintained at 1,650°–1,850° F. and an O_2 feed of at least 35% and preferably 95% purity.

See also United States Patent 2,526,652 (abs. **769**).

1821. ——— (Hydrocarbon Research, Inc.). Synthesis of Hydrocarbons. United States Patent 2,539,434, Jan. 30, 1951; appl. filed Feb. 25, 1947, Serial No. 730,794; 8 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 4023.

Synthesis gas, immediately after generation, temperature about 1,800° F., is quenched with a suitable

proportion of a largely volatile hydrocarbon product so that its temperature is reduced to any desired level, depending upon the specific hydrocarbon and the relative quantity added. The hydrocarbons used in the quenching may crack under the quenching conditions. Thus the cracking or other endothermic reaction may not only use the heat content of the hot synthesis gas but also may supply products such as olefins to the synthesis reactor. A cracking catalyst may be used. If partial cooling without material chemical change in the hydrocarbon is desired, the temperature is rapidly dropped to below the conversion range. In this case the hydrocarbon is of cyclic character, aromatic or naphthenic. Such a hydrocarbon tends to suppress the formation of gaseous hydrocarbons and promote more valuable liquid hydrocarbons. In an example using appreciable cyclic hydrocarbons as quenching medium the synthesis reaction is promoted in the direction of C_3 and higher hydrocarbons. Of all the CO consumed, 85% produces C_3 and higher hydrocarbons, 10% C_1–C_2 hydrocarbons, and 5% CO_2. 7 United States patents cited.

1822. ——— Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,234,941, Mar. 11, 1941; appl. filed May 18, 1938, Serial No. 208,588; 7 claims (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 4183.

Describes arrangement of apparatus and a process which involves the steps of oxidizing a mixture of CH_4 and CO_2 to produce a CO–H_2 mixture having a ratio 1 : 1, synthesizing the CO mixture in the presence of a hydrogenation catalyst at temperature of approximately 200°, separating the liquid and unreacted gas resulting from the synthesis, oxidizing the CO contained in a portion of the unreacted gas in a 2d oxidizing step, removing CO_2, and recycling another portion of the unreacted gas to be recharged with the CH_4 and CO_2, to the initial oxidizing step. The CO_2 is that which was removed from the 2d oxidizing step.

1823. ——— (M. W. Kellogg Co.). Synthesizing Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,276,274, Mar. 17, 1942; appl. filed Aug. 4, 1937, Serial No. 157,341; 8 claims (*Cl. 260–449*). Chem. Abs., vol. 36, 1942, p. 4693.

Method employing an excess of CO with respect to H_2 involves heating a mixture of CO and H_2 to a synthesizing temperature, bringing the heated mixture into contact with a hydrogenation catalyst in a synthesis zone, separating unreacted gases to obtain a fraction predominating in CO, and admixing at least a part of this fraction with the CO and H_2 being fed to the synthesis zone to maintain the desired excess of CO with respect to H_2 during the synthesis.

———. *See* abs. **2527, 2787, 2788.**

1824. KEITH, P. C., AND RIBLETT, E. W. (Hydrocarbon Research, Inc.). Hydrocarbon Synthesis. United States Patent 2,564,696, Aug. 21, 1951; appl. filed Dec. 3, 1946, Serial No. 713,838; 9 claims (*Cl. 260–449.6*).

In maintaining the activity and selectivity of a fluidized Fe catalyst having a relatively minor alkali content as promoter, the latter is supplemented periodically by injecting a solution of an alkali metal compound, preferably K_2CO_3, directly onto the fluidized catalyst thereby restoring its selectivity and activity for the production of normally liquid hydrocarbons.

1825. KEITH, P. C., WARD, J. T., AND WILSON, D. W. (M. W. Kellogg Co.). Changing Light Hydrocarbon Gases Such as Methane Into Liquid Hydrocarbons. United States Patent 2,243,869, June 3, 1941; appl. filed Jan. 26, 1937, Serial No. 122,340; 2 claims (*Cl. 196–10*). Chem. Abs., vol. 35, 1941, p. 5508.

Describes arrangement of apparatus and a method that involves subjecting a light hydrocarbon gas to a catalytic oxidation reaction at temperatures in excess of 1,000° F. to convert it into a mixture of CO and H_2, synthesizing the mixture of CO and H_2 to liquid hydrocarbons in the presence of a catalyst at temperatures of 375°–425° F., separating liquid hydrocarbons from gases, separating the gases into unreacted CO and H_2 and gaseous hydrocarbons, subjecting part of the gaseous hydrocarbons to a pyrolytic conversion step at temperatures of about 1,000° F., fractionating the pyrolytically converted gases in a fractionating zone together with the synthesized liquid hydrocarbons previously separated, withdrawing a portion of the condensate from the fractionating zone as final product desired, withdrawing the heaviest fraction of the condensate from the fractionating zone and subjecting it to pyrolytic conversion, and fractionating the products of the pyrolytic conversion in the fractionating zone.

KELLNER, H. L. *See* abs. **587.**

1826. KELLOGG, M. W., Co. (International Hydrocarbon Synthesis Co.). [Hydrocarbon Synthesis.] French Patent 866,360, no date. Schmidt, J., Das Kohlenoxyd. Akad. Verlagsgesell., Leipzig, 1950, p. 159.

A liquid medium is introduced at numerous points of the reaction zone.

See British Patent 516,352 (abs. **1208**), French Patent 855,515 (abs. **1217**), and Italian Patent 374,321 (abs. **1591**).

1827. ———. Hydrogenating From Carbon Monoxide. and Hydrogen. British Patent 514,098, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell. Leipzig, 1950, p. 159.

See French Patent 832,038 (abs. **1831**).

1828. ———. Hydrogenating Carbon Oxides. British Patent 624,869, June 17, 1949; appl. filed July 22, 1946. Fuel Abs., vol. 6, 1949, abs. 4119; Chem. Abs., vol. 44, 1950, p. 3700.

Improved procsss is particularly applicable to the large-scale production of hydrocarbons and oxygenated compounds by the hydrogenation of CO. The catalysts that are effective to promote the hydrogenation include mainly the metals of group 8 of the periodic system, particularly Fe, Co, Ni, and Ru.

1829. ———. Hydrogenation of Carbon Monoxide. British Patent 647,489, Dec. 13, 1950. Chem. Abs., vol. 45, 1951, p. 10,546.

Reactor for the hydrogenation of CO consists of a jacketed 2-in. steel pipe 153 in. long with a 0.55-in. inlet pipe at the bottom and a 6-in. pipe conduit at the top, the latter connected to a manifold, which leads to 2 other 6-in. pipe conduits each containing a gas (but not catalyst) permeable filter. Preferably CO and H_2 in a molecular ratio of 1 : 5 to 1 : 10 are passed upward through finely divided Fe at 350°–750° and at a rate greater that 2.2. $ft.^3$ CO per hr. per lb. Fe to maintain the Fe in a pseudo-liquid state. Unconverted gases are partly recycled to the reaction zone together with fresh feed. The 2 filters are used alternately every 15 min. for product withdrawal, the off-stream filter being blown back with feed gas to free it of catalyst. Tables showing results obtained with varying conditions in trial runs and on apparatus diagram are included.

1830. ———. Hydrogenation of Carbon Oxides. British Patent 669,382, 1952. Fuel Abs., 1952, abs. 4971.

Fluidized metallic catalyst comprising Co supported on a bentonite type of support is employed in an improved method for reacting H_2 and a C oxide to produce normally liquid hydrocarbons. Freshly reduced catalyst is maintained in contact with the gaseous mixture at 390°–450° F. A Y-shaped reactor is used.

1831. ———. [Liquid Hydrocarbons.] French Patent 832,038, Sept. 20, 1938. Chem. Abs., vol. 33, 1939, p. 2531.

Light gaseous hydrocarbons are converted into liquid hydrocarbons by subjecting them to the action of O_2 in presence of a catalyst at elevated temperature so as to obtain a gas comprising CO and H_2 and converting this intermediate product into liquid hydrocarbons by synthesis in presence of a catalyst at a temperature of about 200°. The oxidation of the gaseous hydrocarbons may be effected in presence of a Ni catalyst at a temperature of 820°–1,100°.

1832. ———. [Process for Producing Gases Consisting of Carbon Monoxides and Hydrogen.] German Patent Appl. K 155,451, OZ 11,742, filed Aug. 25, 1939 (*Cl. IV b–12 i*). FIAT Reel 162, frames 191–198; PB 68,919.

In a process for converting S-containing mixtures of CH_4 and CO_2 to mixtures of CO and H_2 at high temperatures in presence of a Ni catalyst, the original mixture is first passed over a Co catalyst, which removes virtually all of the S.

See also United States Patent 2,220,849 (abs. **2773**).

1833. ———. [Synthesis Process.] French Patent 924,909, no date. Kainer, p. 206.

Catalyst is suspended in the gas stream and all losses of catalyst are trapped and returned to the process. Excess heat is removed by evaporating low-boiling reaction products, which are injected at many points of the reaction chamber. H_2O may be used instead of hydrocarbons. The catalyst consists of Co, Ni, or Rh on activated bentonite as support.

———. *See* abs. **14, 167, 195, 284, 285, 286, 287, 288, 289, 290, 291, 486, 487, 488, 928, 1058, 1767, 1781, 1782, 1803, 1823, 1825, 1856, 1857, 2013, 2014, 2015, 2065, 2073, 2096, 2187, 2188, 2189, 2190, 2191, 2192, 2193, 2194, 2195, 2196, 2197, 2198, 2199, 2200, 2201, 2202, 2393, 2442, 2447, 2526, 2527, 2733, 2773, 2778, 2783, 2784, 2786, 2787, 2788, 2837, 2838, 2839, 2840, 3439, 3440, 3945, 3987.**

KELTING, M. *See* abs. **505.**

1834. KEMMER, H. [Municipal Gas.] German Patent 617,565, Aug. 21, 1935 (*Cl. 26a–3.02*). Chem. Abs., vol. 30, 1936, p. 843.

Gas, free from CO, is obtained by subjecting coal gas containing CO to successive oxidation by steam and reduction by H_2. The calorific value of the original gas containing CO is raised by oxidizing in the first stage until only 4–5% of CO remains; the H_2 freed in this process is used for the reducing stage. Oxidizing agents such as active C may be employed in the oxidizing stage, and contact agents such Ni, ThO_2, and active C may be used in the reducing stage.

1835. KEMP, L. C. (The Texas Co.). Combination Process for the Hydrogenation of Carbon Monoxide and the Production of Ammonia. United States Patent 2,494,561, Jan. 17, 1950; appl. filed Dec. 29, 1945. Serial No. 637,953; 6 claims (*Cl. 23–198*). Chem. Abs., vol. 44, 1950, p. 3240.

Fe catalyst used for and reduced in activity by the synthesis of ammonia from N_2 and H_2 is subsequently used for converting a CO-H_2 mixture to hydrocarbons. The catalyst is then regenerated to the original activity and reused for the ammonia synthesis.

1836. ——— (Texaco Development Corp.). Higher Boiling Hydrocarbons From Methane. Canadian Patent 421,168, June 27, 1944. Chem. Abs., vol. 38, 1944, p. 5065.

Stream of CH_4 is brought into contact with hot refractory material at temperatures sufficient to decompose the CH_4 into H_2 and C; the H_2 is withdrawn while the C is deposited on the contact material; the CH_4 stream is diverted to another contact chamber; the C is burned on the contact mass in the first chamber to form CO, which is withdrawn; the chambers are alternated in CH_4 decomposition and C burning; and H_2 and CO are continuously combined to form a mixture in the ratio of about 2 : 1 and catalytically converted to liquid hydrocarbon.

1837. ——— (The Texas Co.). Method of Manufacturing Motor Fuel. United States Patent 2,461,064, Feb. 8, 1949; appl. filed Oct. 20, 1945, Serial No. 623,475, 6 claims (*Cl. 260–449.6*). Chem. Abs. vol. 43, 1949, p. 3174.

Hydrogenation of CO is used in conjunction with a fluidized system of catalytic cracking. A portion of the catalyst is continuously regenerated with stripping of the adsorbed hydrocarbons before regeneration. Effluent gases from the Fischer-Tropsch reactor are used in stripping. In cracking the products of the hydrocarbon synthesis are deoxygenated. The olefins so formed then undergo a double-bond shift type of isomerization. The hydrogenation may be in conjunction with hydroforming and the resulting H_2 used to supplement the synthesis gas. 9 United States patents cited.

1838. ——— (The Texas Co.). Method of Manufacturing Motor Fuel. United States Patent 2,461,065, Feb. 8, 1949; appl. filed Oct. 20, 1945, Serial No. 623,476, 6 claims (*Cl. 260–450*). Chem. Abs., vol. 43, 1949, p. 3175.

This patent is similar to United States Patent 2,461,064 (abs. **1837**). 7 United States patents cited.

1839. ——— (The Texas Co.). Motor Fuel. United States Patent 2,286,814, June 16, 1942; appl. filed Oct. 28, 1939, Serial No. 301,739; 10 claims (*Cl. 196–10*). Chem. Abs., vol. 36, 1942, p. 7272.

Describes arrangement of apparatus and a process is employed for the manufacture of high antiknock motor fuel hydrocarbons, which involves catalytically converting a mixture of CO and H_2 to a synthetic hydrocarbon mixture composed mainly of hydrocarbons having 1–10 C atoms/mol., the C_3–C_4 fraction of which consists essentially of aliphatic hydrocarbons composed largely of olefins and relatively free from isobutylene, separating from this synthetic mixture a fraction rich in normal butane and another fraction rich in normal butylenes, subjecting the butane-rich fraction to isomerization so as to form isobutane, separately treating the resulting isobutane with the butylene-rich fraction by contact with an alkylation catalyst maintained under alkylating conditions and in the substantial absence of isobutylene, whereby isobutane is alkylated to produce normally liquid saturated hydrocarbons having a high antiknock value and boiling within the range for motor fuel.

1840. ——— (The Texas Co.). Preparation of Heavy Hydrocarbons of Hydrogen Isotopes. United States Patent 2,577,017, Dec. 4, 1951; appl. filed Nov. 23, 1948, Serial No. 61,592; 9 claims (*Cl. 260–449.6*).

Process refers specifically to the synthesis of deuterocarbons from synthesis gas comprising D_2 and CO to the exclusion of H having an atomic weight of 1. A stream of CO prepared by reacting C with CO_2 at elevated temperature is reacted with the vapor of heavy water under water gas shift reaction conditions to convert the reactants into a mixture of CO_2 and D_2. The CO_2 is separated, and the resulting D_2 and residual CO in the ratio 2:1 are contacted with a synthesis catalyst comprising either Co or Ru under reaction conditions to form the maximum quantities of the desired products. The resulting products withdrawn from contact with the catalyst include the desired fractions of deuterocarbons together with undesired deuterocarbon fractions and the byproduct heavy

water (D_2O). The desired product fractions are recovered by any suitable means of separation, and the residual undesired fractions are reformed in the presence of the byproduct heavy water vapor to form additional synthesis gas consisting of D_2 and CO.

1841. KEULEMANS, A. I. M. (Shell Development Co.). Production of Oxygenated Compounds. United States Patent 2,587,858, Mar. 4, 1952; appl. filed May 1, 1948, Serial No. 24,669; 5 claims (*Cl. 260–604*). Chem. Abs., vol. 46, 1952, p. 5294.

CO and H_2 in a suitable ratio, are reacted with Co in a suitable Co-containing mass in a separate reactor and the Co hydrocarbonyl is continuously fed to the reactor containing an olefin. Thus, at 80° and 150 atm., 45% CO and 55% H_2, preheated, were passed through a mass of Co on pumice at the rate of 2,200 l. per l. of the Co-containing mass per hr., and a C_7–C_8 hydrocarbon fraction containing 89% olefins and 11% paraffins was passed through the same Co on pumice at the rate of 2.2 l. per l. of the Co-containing mass per hr, and the combined gases passed into a separate Oxo reactor consisting of 8% Co on pumice at the rate of 0.5 kg. per l. of catalyst per hr. at 160° and 150 atm. to give 25% by weight of low-boiling hydrocarbons, 64% C_8–H_9 alcohols, and 11% by weight of higher boiling oxygenated products.

———. *See* abs. **3833, 3908.**

1842. KEUNECKE, E. (I. G. Farbenindustrie A. G.). [Oxidation Products of High-Molecular Paraffin Hydrocarbons.] German Patent 626,787, Mar. 10, 1936 (*Cl. 12 o–11*). Chem. Abs., vol. 30, 1936, p. 5588.

Describes apparatus in which the hydrocarbons are subjected in the liquid phase to gases containing O_2 at temperatures <125% in the presence of a Mn-alkali metal catalyst.

1843. ——— (I. G. Farbenindustrie A. G.). [Oxidation Products of High-Molecular Paraffins.] German Patent 721,945, June 30, 1942; appl. I 55,274, filed June 18, 1936 (*Cl. 12 o–11*). Chem. Abs., vol. 37, 1943, p. 5077.

Before oxidation, the entire quantity of the paraffin hydrocarbons or part thereof is mixed with the required quantity of an alkali manganate catalyst, and the mixture is heated for a short time at 100°–200°. The oxidation is then carried out at 80°–120°.

1844. ——— (I. G. Farbenindustrie A. G.). [Oxidation Products of High-Molecular Paraffins.] German Patent 725,485, Aug. 6, 1942 (*Cl. 12 o–11*). Chem. Abs., vol. 37, 1943, p. 5983.

Oxidation is carried out at <135°, using alkali manganates in the form of solutions as accelerators. They are mixed with a part or the entire quantity of the paraffin, and the mixture is heated to an elevated temperature before the oxidation is begun.

See also German Patent 721,945 (abs. **1843**).

———. *See* abs. **3274, 3657.**

1845. KEUNECKE, E., AND KÜRZINGER, A. (I. G. Farbenindustrie A. G.). [Oxidation Products.] German Patent 740,294, Aug. 26, 1943 (*Cl. 12 o–11*). Chem. Abs., vol. 39, 1945, p. 310.

Carboxylic acids, alcohols, and similar substances are obtained by oxidation of hydrocarbon mixtures, which in turn are produced by catalytic reduction of CO with H_2 at >300° C. These mixtures are treated with solvents capable of dissolving constituents having branched chains but not affecting components having straight chains. The mixture is freed, or nearly freed, of branched-chain components, and the residue is oxidized in the usual manner.

1846. KEUNECKE, E., AND NIENBURG, H. (I. G. Farbenindustrie A. G.). [Fatty Acids From Raw Paraffins.] German Patent 744,079, Jan. 8, 1944; appl. I 67,223, OZ 12,204, filed June 20, 1940 (*Cl. 12 o–11*). FIAT Reel 163, frames 2,001–2,004; PB 25,607; FIAT Reel E–29, frames 616–617; PB 70,432; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 31, 1949, p. 1.

Technical crude paraffin obtained in the processing of petroleum or tars or the hydrogenation or pressure extracts of brown coal is purified by first treating it with organic solvents such as the forerunning fatty acids from a previous paraffin oxidation followed by oxidation in the known manner by gases containing molecular O_2.

1847. KEUNECKE, E., KÜRZINGER, A., AND WEISS, B. (I. G. Farbenindustrie A. G.). [Separating Mixtures of Straight-Chain and Branched-Chain High-Molecular Fatty Acids.] German Patent 744,136, Jan. 20, 1944; appl. I 67,281, OZ 12,216, filed June 28, 1940 (*Cl. 12 o–11*). FIAT Reel E 29, frames 763–764; PB 70,432; FIAT Reel 163, frames 2,044–2,048; PB 25,607; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 3, chap. 33, 1949, p. 5.

Gives process for separating mixtures of straight- and branched-chain, high-molecular fatty acids obtained by the catalytic conversion of olefins with CO and H_2 and oxidation of the resulting aldehydes and containing no great amounts of unsaponifiable or unsaponified substances or compounds insoluble in benzine. Fractions of such mixtures, boiling within a narrow temperature range, are treated in the cold with organic solvents, such as methyl formate. The branched-chain fatty acids dissolve, but the straight-chain fatty acids remain unchanged.

1848. KII, T. (Miike Synthetic Oil Co.). [A New Design for Catalyst Tube of Gas Reaction Chamber.] Japanese Patent 287,840. United States Naval Technical Mission to Japan, Index No. X–38(N)–7, Encl. (G), 1946, p. 207.

1849. KIMBERLIN, C. N. (Standard Oil Development Co.). [Fluidized Catalyst.] French Patent 943,408, Mar. 8, 1949; appl. filed Mar. 18, 1947. Chem.-Ztg., vol. 74, No. 9, 1950, p. 120; Chem. Zentralb., 1950, I, p. 1174.

Catalyst consists of 25–40% and 2–7% ThO_2, and if desired up to 1% of Ni on a carrier of kieselguhr or alumina, the whole being held together by a binder of sodium silicate. The Co and Th oxides are precipitated from aqueous solutions, mixed with the carrier and binder, dried, and reduced. The catalyst finds use in the hydrocarbon synthesis from CO and H_2. The catalyst may be formed into a solid bed or used in particle size of 40–80 microns as a fluidized catalyst.

1850. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis Catalyst. United States Patent 2,550,416, Apr. 24, 1951; appl. filed May 21, 1946, Serial No. 671,415, divided and this appl. filed Mar. 20, 1947, Serial No. 736,116; 2 claims (*Cl. 252–441*).

Reduced Fe catalyst adapted to fluid type operation is prepared by bonding Fe oxide with an alkali-metal silicate, heating at 1,100°–1,600° F., further reducing until the Fe oxide has become completely converted to the metallic state, and grinding to an average particle size. A promotional amount of an alkali metal fluoride may also be added. 9 United States patents cited.

1851. ——— (Standard Oil Development Co.). [Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 961,524, May 12, 1950; appl. filed Feb. 20, 1948. Chem. Zentralb., 1951, I, p. 418.

Fe catalyst is used consisting of Fe oxide in combination with Na- or K-silicates, such as, 86.5% Fe_2O_3, 13.5% Na_2O, 3.25% SiO_2. As activating agent Al_2O_3 or alkali fluoride is used. The catalyst is reduced with H_2 at 482°.

1852. KIMBERLIN, C. N., AND SCHEXNAILDER, R. E., JR. (Standard Oil Development Co.). Preparation of Silica Microsphere Supported Iron Group Catalyst. United States Patent 2,488,128, Nov. 15, 1949; appl. filed Dec. 29, 1945, Serial No. 638,419; 4 claims (*Cl. 252–448*). Chem. Abs., vol. 44, 1950, p. 2206.

Active hydrocarbon synthesis catalyst, Co or Fe, is impregnated into silica gel. Hydrosol is suspended in hydrocarbon oil. The suspension is agitated until microspheres are formed. The hydrogel is separated from the oil and washed first with H_2O and then with a monohydric low molecular weight alcohol. The mixture is heated to remove the H_2O and the alcohol. The dried gel is impregnated with a water-soluble salt solution of an Fe group metal and promoter. The impregnated gel is heat treated and reduced. 1 foreign and 7 United States patents cited.

1853. KIMURA, T. (Mitsui Kôzan K. K.) [Synthesis of Methanol.] Japanese Patent 96,341, June 21, 1932. Chem. Abs., vol. 27, 1933, p. 4818.

Trace of H_2O is a mixture of CO and H_2 is eliminated ($< 0.01\%$) by cooling the mixture under pressure of 50,000 atm. or by passing the mixture through active C or silica gel under pressure. The formation of CO_2 and CH_4 is prevented.

1854. KINCAID, J. F., AND STRONG, J. S. (Rohm & Haas Co.). Nickel Carbonyl. United States Patent 2,548,727, Apr. 10, 1951. Chem. Abs., vol. 45, 1951, p. 6357.

$Ni(CO)_4$ is made by treating a fluid aqueous slurry of freshly precipitated $Ni(OH)_2$ (0.1–1.5 moles per l. of slurry) containing a small amount of a complex mixture of S compounds, for example Na_2S or $Na_2S_2O_3$ (4–12 mole %, based on Ni salt), with CO at 60°–200° under a pressure in excess of 1,000 p. s. i. and under alkaline conditions. The $Ni(OH)_2$ is first prepared by mixing in H_2O a water-soluble Ni salt, for example $NiCl_2$ or $NiSO_4$, and an alkali or alkaline earth hydroxide, for example NaOH, KOH, or $Ca(OH)_2$. Over 99% conversion of Ni to $Ni(CO)_4$ is obtained in about 1 hr.

1855. ——— (Rohm & Haas Co.). Nickel Carbonyl. United States Patent 2,548,728, Apr. 10, 1951. Chem. Abs., vol. 45, 1951, p. 6357.

In a process similar to that described in United States Patent 2,548,727 (abs. **1854**) $Ni(OH)_2$ is treated with CO in the presence of 2.5–25 mole % (based on Ni $(OH)_2$) of cyanide ion obtained from Na, K, Ca, Ba, or Sr cyanides.

1856. KING, C. C. (M. W. Kellogg Co.). Separation of Organic Compounds. United States Patent 2,472,837, June 14, 1949; appl. filed Feb. 27, 1947, Serial No. 731,267; 16 claims (*Cl. 260–450*). Chem. Abs., vol. 43, 1949, p. 6643.

Describes process and apparatus for recovering Fischer-Tropsch synthesis products. The normally liquid products are condensed to form an oil product liquid phase and gases containing oxygenated organic compounds and hydrocarbons. The oil products are separated and the gases are subjected to solvent extraction. The extract is fractionated. The fraction containing solvent and oxygenated organic compounds with boiling points above the boiling point of the solvent is separated and the solvent recycled. 1 foreign and 4 United States patents cited.

1857. KING, C. C., AND DICKINSON, N. L. (M. W. Kellogg Co.). Separation of Organic Compounds. United States Patent 2,552,564, May 15, 1951; appl. filed Feb. 27, 1947, Serial No. 731,268; 14 claims (*Cl. 260–450*). Chem. Abs., vol. 45, 1951, p. 9555.

MeOH and H_2O in approximate proportions of 90% MeOH and 10% H_2O is found to be a very satisfactory selective extraction agent when used for the separation of H_2O-insoluble oxygenated compounds obtained from the condensation of reactor gases in the catalytic hydrogenation of C oxides. After the alcoholic solvent treatment, a relatively low-boiling hydrocarbon is introduced into the extraction zone as a wash oil, which causes the formation of a raffinate phase comprising hydrocarbons and an aqueous extract phase comprising oxygenated compounds. The phases are withdrawn and separated. The raffinate phase is further distilled to produce a high- and low-boiling fraction, the latter being utilizable as a wash oil. 8 United States patents cited.

KING, J. A. *See* abs. **966, 967, 2574.**

1858. KIRSHENBAUM, I. (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,509,869, May 30, 1950; appl. filed Oct. 1, 1947, Serial No. 777,374; 3 claims (*Cl. 260–449.6*).

Fluidized Fe catalyst for use in the Fischer-Tropsch synthesis at 550°–750° F. and 150–650 p. s. i. consist of a reduced composite of 80 parts by weight of chromia, 20 parts Fe oxide, and 2 parts K_2CO_3; expressed in wt. % as 60–90 chromia, 5–40 Fe oxide and 0.5–5 alkali metal compound promoter. 8 United States patents cited.

1859. KIRSHENBAUM, I., AND GROVER, R. K. (Standard Oil Development Co.). Hydrocarbon Synthesis Promoter. United States Patent 2,563,607, Aug. 7, 1951; appl. filed Dec. 1, 1948, Serial No. 62,914; 7 claims (*Cl. 260–676*). Chem. Abs., vol. 45, 1951, p. 9847.

Increased yields ranging from 6–22% more of normally liquid hydrocarbons boiling within the gasoline and gas-oil range are obtained by feeding to a reactor adapted to a fluid catalyst operation and containing an Fe-type catalyst, a mixture of C_2H_2 and a synthesis feed-gas mixture of H_2 and CO. The composition of the synthesis gas mixture should be in a ratio of 0.5–2 moles H_2 to 1 mole CO. The amount of C_2H_2 in the total synthesis gas feed varies 4–100 moles H_2+CO per mole C_2H_2. The synthesis gas should be pretreated to remove S compounds and O_2 concentration reduced to 0.01–0.1%. When the linear inlet velocity of C_2H_2 and synthesis gas is 0.3–3.0 ft. per sec. and about 4–80 N $ft.^3$ is supplied to the reactor per lb. of catalyst, the apparent density of the catalyst is 25–75 lb. per $ft.^3$. The total pressure in the reactor is 50–700 p. s. i. g. and the temperature range 400°–750° F. Electron photomicrographs are shown illustrating low cuprene formation and no increase in catalyst disintegration.

1860. KIRSHENBAUM, I., AND KEARBY, K. K. (Standard Oil Development Co.). Hydrocarbon Synthesis Catalyst. United States Patent 2,553,415, May 15, 1951; appl. filed Oct. 1, 1947, Serial No. 777,373; 13 claims (*Cl. 260–449.6*).

Fluidizable Fe catalysts of good stability are obtained by combining Fe in the form of its carbonate with a metal carbonate base, which in itself exhibits a high stability, and then reducing the composite material. A distribution of about 5–40% by weight of $FeCO_3$ and about 60–90% by weight of the carbonate of a Group II metal is preferred. The catalyst may be prepared by precipitating $FeCO_3$ on precipitated metal carbonate support and then reducing the material. Such a catalyst, particularly one comprising $BaCO_3$ and/or $CaCO_3$, is claimed to work well even in the absence of conventional catalyst promoters. 4 United States patents and 1 foreign patent cited.

1861. KITA, G. Catalyst for the Production of Gasoline. British Patent 529,390, Nov. 20, 1940. Chem. Abs., vol. 35, 1941, p. 8259.

Substance constisting mainly of hydroxides and/or carbonates of Fe and Cu is precipitated by an alkali from salts of those elements upon diatomaceous earth. To the substance thus formed a little alkali as well as boric acid or its salts is added. When a mixture of

CO and H_2 is brought into reaction in the presence of this catalyst held at 225°, gasoline is produced.

1862. ———. [Iron Catalyst for Synthesizing Gasoline and Method of Preparing Same.] German Patent Appl. —, filed May 4, 1941; APC SN 391,721.

Method of producing a catalyst comprises the forming of a mixture of Fe compounds (hydroxide and carbonate) with a Cu compound (hydroxide and carbonate) and precipitating the compounds on diatomaceous earth by an alkali and adding an alkali and a compound of boron.

1863. ———. [Iron Catalyst for the Gasoline Synthesis.] Italian Patent 373,833, May 22, 1939, Chem. Zentralb., 1940, II, p. 2986.

Hydroxides or carbonates of Fe and Cu are precipitated from solution on kieselguhr by means of alkali (K_2CO_3) and then converted simultaneously or separately with a small amount of alkali (KOH) and boric acid or its salts. It can previously be activated with Mn or Al_2O_3. The catalyst can be reduced at synthesis temperature (225°–250°) and produces high yields of gasoline of over 120 cc. per $m.^3$ of synthesis gas.

1864. ———. [Method of Preparing an Iron Catalyst in Synthesizing Gasoline.] German Patent Appl. —, filed May 6, 1939, APC SN 272,175.

Method of producing an Fe catalyst comprises forming a nitrate solution containing metals consisting of 100 parts of Fe, 25 of Cu, and 2 of Mn by weight, adding 125 parts by weight of diatomaceous earth and precipitating compounds of said metals on the earth by adding K_2CO_3, washing the precipitate with H_2O and adding thereto 3 parts by weight of KOH, drying the combined precipitate and caustic, adding 20 parts by weight of liquid boric acid to form a resultant product, and drying the product.

1865. ———. [Oil From Carbon Monoxide and Hydrogen by Means of an Improved Catalyst.] French Patent 861,415, Feb. 8, 1941. Chem. Abs., vol. 42, 1948, p. 6091.

Fe and Cu hydroxides are precipitated in kieselguhr and a little H_3BO_3 or borate is added. Mn or Al may also be present.

1866. KITA, G., AND KODAMA, S. (Kyoto Imperial University.). [Manufacture of Hydrocarbon.] Japanese Patent 134,661, Feb. 8, 1940; appl. filed Sept. 13, 1937. U. S. Naval Tech. Mission to Japan, Index No. X–38(N)–7, Encl. (D), 1946, p. 247.

Adiabatic synthesis by 5% reaction and recirculation.

1867. KITA, G., AND MURATA, Y. (Kyoto Imperial University). [Oil Synthesis From Carbon Monoxide and Hydrogen.] Japanese Patent 144,803, Aug. 1, 1941; appl. filed Aug. 20, 1939. U. S. Naval Tech. Mission to Japan, Index No. X–38(N)–7, Encl. (D), 1946, p. 247.

Reduction by high-speed gas flow; saving of reduction time.

1868. KITA, G., KODAMA, S., AND FUJIMURA, K. (Kyoto Imperial University). [Manufacture of Gasoline by Reduction of Carbon Monoxide.] Japanese Patent 98,205, Nov. 11, 1932; appl. filed May 22, 1931. U. S. Naval Tech. Mission to Japan, Index No. X–38(N)–7, Encl. (D), 1946, p. 247.

Normal pressure, Co, Cu, ThO_2, and MgO or U_2O_3 catayist.

1869. KITA, G., KODAMA, S., AND FUJITA, T. (Kyoto Imperial University). [Two-Stage Method of Producing Oil From Water Gas.] Japanese Patent 129,242, Mar. 20, 1939; appl. filed Apr. 14, 1938. U. S. Naval Tech. Mission to Japan, Index No. X–38(N)–7, Encl. (D), 1946, p. 247.

1st stage: Fe catalyst. 2d stage: Co or Ni catalyst.

1870. KITA, G., KODAMA, S., AND MURATA, Y. (Kyoto Imperial University.) [Activation of Oil Synthesis Catalyst.] Japanese Patent 155,493, Mar. 16, 1943; appl. filed Mar. 16, 1941. U. S. Naval Tech. Mission to Japan, Index No. X–38(N)–7, Encl. (D) 1946, p. 248.

Activation of catalyst by preliminary heat treatment.

1871. ——— (Kyoto Imperial University). [Manufacture of Oil.] Japanes Patent 150,548, May 13, 1942; appl. filed Mar. 25, 1940. U. S. Naval Tech. Mission to Japan, Index No. X–38(N)–7, Encl (D), 1946, p. 248.

Recirculation of initial gas containing small excess of H_2.

1872. ——— (Kyoto Imperial University). [Oil Synthesis.] Japanese Patent 154,262, Dec. 16, 1942; appl. filed Apr. 11, 1941. U. S. Naval Tech. Mission to Japan, Index No. X–38(N)–7, Encl. (D), 1946, p. 248.

Activation of Fe catalyst by H_2-rich reduction gas.

1873. KITA, G., MURATA, Y., AND YOSHIOKA, Y. (Kyoto Imperial University). [Two-Stage Method of Producing Oil From Water Gas.] Japanese Patent 147,087, Dec. 10, 1941; appl. filed Mar. 25, 1940. U. S. Naval Tech. Mission to Japan, Index No. X–38(N)–7, Encl. (D), 1946, p. 248.

1st stage: Low reaction temperature. 2d stage: High reaction temperature.

1874. KITA, G., KODAMA, S., FUJITA, T., AND MURATA, Y. (Kyoto Imperial University). [Manufacture of Synthetic Liquid Fuel.] Japanese Patent 142,939, Apr. 12, 1941; appl. filed Aug. 23, 1938. U. S. Naval Tech. Mission to Japan, Index No. X–38(N)–7, Encl. (D), 1946, p. 247.

Low-activity catalyst near inlet of reaction chamber.

1875. KITA, G., KODAMA, S., TSUNEOKA, S., AND MURATA, Y. (Kyoto Imperial University). [Manufacture of Liquid Hydrocarbons.] Japanese Patent 150,952, June 4, 1942; appl. filed Nov. 25, 1940. U. S. Naval Tech. Mission to Japan, Index No. X–38(N)–7, Encl. (D), 1946, p. 248.

Recirculation of H_2 separated from reaction gas.

1876. KITA, G., KOIDE, K., SAWADA, Y., AND MURATA, Y. (Kyoto Imperial University). [Gasoline Synthesis Iron Catalyst.] Japanese Patent 147,086, Dec. 9, 1941; appl. filed Feb. 3, 1939. U. S. Naval Tech. Mission to Japan, Index No. X–38(N)–7, Encl. (D), 1946, p. 248.

Fe catalyst with B compound.

1877. KITA, G., MAKINO, S., MURATA, Y., AND KOIDE, K. (Kyoto Imperial University). [Oil Synthesis by Iron Catalyst From Carbon Monoxide and Hydrogen.] Japanese Patent 147,126, Dec. 11, 1941; appl. filed Aug. 27, 1938. United States Naval Technical Mission to Japan, Index No. X–38(N)–7, Encl. (D), 1946, p. 248.

Fe, Cu, Mn, or Al catalyst.

1878. KITA, G., TSUNEOKA, S., MURATA, Y., AND MAKINO, S. (Kyoto Imperial University). [Oil Synthesis by Iron Catalyst From Carbon Monoxide and Hydrogen.] Japanese Patent 143,373, May 8, 1941; appl. filed Oct. 15, 1937. United States Naval Technical Mission to Japan, Index No. X–38(N)–7, Encl. (D), 1946, p. 247.

Normal pressure, Fe, Cu, kieselguhr, and alkali catalyst. Reduction by reaction gas.

1879. KITA, G., MURATA, Y., TSUNEOKA, S., KATAYAMA, I., AND KOIDE, K. (Kyoto Imperial University).

[Treatment of Gasoline Synthesis.] Japanese Patent 134,662, Feb. 8, 1940; appl. filed Apr. 4, 1938. United States Naval Technical Mission to Japan, Index No. X–38(N)–7, Encl. (D), 1946, p. 247.

Activation of catalysts by slow oxidation.

1880. KIYOHISA. (Miike Synthetic Oil Co.). [Method of Greasemaking From Oxidized Products of Paraffin Hydrocarbons.] Japanese Patent Appl. 13,312, July 12, 1943. U. S. Naval Technical Mission to Japan, Index X–38(N)–7, Encl. (G), 1946, p. 297.

1881. ——— (Miike Synthetic Oil Co.). [Method of Soap Making by Oxidation of Paraffin Hydrocarbons.] Japanese Patent Appl. 14,186. U. S. Naval Technical Mission to Japan, Index X–38(N)–7, Enclosure (G), 1946, p. 297.

KLAMROTH, A. *See* abs. **3760, 3761.**

1882. KLATTE, F., AND SÖLL, J. Methane. United States Patent 1,643,663, Sept. 27, 1927; appl. filed Nov. 30, 1925. Chem. Abs., vol. 21, 1927, p. 3907.

Current of gases containing CO and H_2 is treated with a Ni catalyst at a temperature > 500° and the velocity of flow of the gases is regulated to avoid separation of C and quickly to remove the gases from the hot reaction zone.

KLEIN, H. *See* abs. **2084.**

1883. KLEIN, O. (Ruhrchemie A.-G.). [Compositions for Desulfurizing Gases.] German Patent 664,055, Aug. 19, 1938 (*Cl. 26d–8.04*). Chem. Abs., vol. 33, 1939, p. 838.

Describes apparatus for producing the compounds described in German Patent 659,407 (abs. **2805**).

1884. KLEIN, O., AND MEYER, K. (Braunkohle-Benzin A.-G.). [Reclaiming Cobalt and Thorium From Spent Contact Catalysts.] German Patent 722,553, July 14, 1942; appl. B 186,476, filed Mar. 22, 1939 (*Cl. 12 o–1.03*). FIAT Reel AA–90, frames 1,571–1,572; PB 70,275; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 5, chap. 156, 1949, p. 36; Chem. Abs., vol. 37, 1943, p. 5205.

Catalyst from the hydrogenation of CO is dissolved in H_2SO_4 and filtered. In the filtrate Th is precipitated with K_2SO_4 as the double sulfate. After filtering off the precipitate, the Fe is precipitated as $Fe(OH)_3$ with an alkali carbonate. Finally the Co is precipitated as carbonate. The Co and Fe can be precipitated together by dissolving the precipitate in HNO_3, 1st precipitating the Fe by bringing the pH to about 5.8. The residual Co solution can then be used for making the catalyst for CO hydrogenation.

KLEINE, J. *See* abs. **2664.**

1885. KLEINSCHMIDT, R. V. (E. I. du Pont de Nemours & Co.). Catalytic Exothermic Gaseous Reactions Such as Methanol Synthesis. United States Patent 2,051,774, Aug. 18, 1936. British Chem. Abs., **B**, 1937, p. 991; Chem. Abs., vol. 30, 1936, p. 6765.

Portion of the entering gas such as a CO and H_2 mixture is passed within and in heat exchange relation with, but not in contact with, a catalyst, and this portion of the gas is then combined with another portion of the entering gas, and the gases are subjected to further thermal treatment by heat exchange with, but out of contact with, gases issuing from direct contact with the catalyst, and are then introduced into direct contact with the catalyst. Describes apparatus.

1886. KLEMM, R., AND LINCKH, E. (Standard Catalytic Co.). Catalysts Suitable for Use in Producing Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,292,570, Aug. 11, 1942; appl. filed June 15, 1940, Serial No. 340,768, in Germany Nov. 12, 1938; 4 claims (*Cl. 252–256*). Chem. Abs., vol. 37, 1943, p. 745.

Metal of the Fe group, such as Fe, Co, or Al or the oxide of such a metal, is treated with steam and H_2 at a high temperature (suitably about 800°–1,200°) with use of about 5–50% H_2 in the treating mixture, and the resulting oxidic material is reduced, as by H_2 at 650°. Gives several examples with details.

1887. ——— (I. G. Farbenindustrie A. G.). [Iron Catalyst.] German Patent Appl. I 62,893, filed Nov. 12, 1938 (*Cl. IV b–12 g*). OZ 11,123. Bureau of Mines Transl. T–433, January 1948.

Shaped Fe oxides are mixed with activating substances and treated with H_2-containing steam at high temperature, preferably >600°, and finally reduced (spinel structure).

1888. ——— (I. G. Farbenindustrie A. G.). [Iron Catalyst.] German Patent Appl. I 66,308, OZ 11,964, filed Jan. 19, 1940 (*Cl. IV b–12 g*). FIAT Reel 162, frames 1,055–1,057; PB 69,094; Bureau of Mines Transl. T–433, Jan. 1948; Meyer Transl. PS–C–II, Fischer-Tropsch, vol. 7, chap. 194, 1950, p. 28.

Catalysts consisting mainly of metals of the Fe group, are produced from the metals themselves rather than from the oxides. The metals are mixed with activating substances and then treated and reduced with H_2-containing H_2O vapors at temperatures > 600°. Example: 2,000 gm. of powdered Fe obtained by the decomposition of Fe carbonyl are suspended in a solution of 10 gm. of Ag nitrate in 1.5 l. of H_2O. After the Ag-impregnated Fe is sucked off, washed, and dried 10 gm. of Ti oxide, 20 gm. Ca oxide, and 40 gm. dextrin are added, and the mixture is pressed into pellets and treated for 7 hr. at 800°–850° with H_2O vapor–H_2 mixture obtained by passing steam over red-hot Fe shavings. After reduction with H_2 at 650° this catalyst yields, per $m.^3$ of synthesis gas (1 : 2=CO+H_2) at 100 atm. and 320°, 75 cc. of hydrocarbon oils, and 225 cc. H_2O with 31% of alcohols.

See also German Patent appl. I 62,893 (abs. **1887**).

KLOCKNER-HUMBOLDT-DEUTZ. A. G. *See* abs. **1117.**

KLYACHKO-GURVICH, L. L. *See* abs. **1890.**

1889. KNOBLOCH, W., AND SCHILLER, G. (I. G. Farbenindustrie A. G.) [Catalytic Reduction of Carbon Dioxide to Carbon Monoxide With Hydrogen.] German Patent 730,409, Dec. 10, 1942 (*Cl. 12 i–34*); Chem. Abs., vol. 38, 1944, p. 462.

Alkaline-earth oxides are used as catalysts.

1890. KOBOZEV, N. I., AND KLYACHKO-GURVICH, L. L. [Regenerating the Iron Catalyst for the Synthesis of Ammonia.] Russian Patent 56,324, Jan. 31, 1940. Chem. Abs., vol. 35, 1941, p. 6402.

Spent catalyst is treated with Fe carbonyl at temperatures high enough for the decomposition of carbonyl to metal and CO to form an active layer.

KOCH, H. *See* abs. **671, 709.**

KODAMA, S. *See* abs. **1866, 1868, 1869, 1870, 1871, 1872, 1874, 1875, 3706, 3707.**

1891. KODAMA, S., AND HASHIMOTO, G. (Kyoto Imperial University). [Liquid-Fuel Synthesizing Reaction Chamber.] Japanese Patent 144,921, Aug. 9, 1941; appl. filed Oct. 28, 1939. United States Naval Technical Mission to Japan, Index No. X–38(N)–7, Encl. (D), 1946, p. 247.

Device for insertion of cooling tubes in the reaction chamber.

1892. KODAMA, S., TAHARA, H., AND MURATA, Y. (Kyoto Imperial University). [Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen.] Japanese Patent 156,987, June 10, 1943; appl. filed Oct. 3, 1941. United States Naval Technical Mission to Japan, Index No. X–38(N)–7, Encl. (D), 1946, p. 248.

Middle-pressure Fe catalyst is more alkaline than normal pressure Fe catalyst.

1893. KÖGL, H. (Böhme Fettchemie G. m. b. H.). [Deliming Ashed Hides.] German Patent 713,915, Oct. 23, 1941 (*Cl. 28 a–2*). Chem. Abs., vol. 38, 1944, p. 1904.

Hydroxy fatty acids corresponding to the fatty acids from the first runnings of paraffin oxidation are used for deliming ashed hides.

1894. KOHLE-UND EISENFORSCHUNG G. m. b. H. [Diesel Fuel.] French Patent 877,257, Dec. 2, 1942; appl. filed Nov. 25, 1941. Oel u. Kohle, vol. 39, 1943, Sch. 92.

Refers to improving the quality of tar or tar-oil fuels by adding products from the Fischer-Tropsch process.

1895. ———. [Synthesis of Hydrocarbons.] French Patent 877,792, Dec. 16, 1942; appl. filed Dec. 18, 1941, Chem. Zentralb., 1943, II, p. 1254.

Patent concerns the synthesis of hydrocarbons from CO and H_2 using lean gases such as blast-furnace gas as the raw material. Either before or after compression to the synthesis pressure, the gas is converted by means of steam to the requisite CO : H_2 ratio, the CO_2 washed out and, if necessary, further H_2 added. The synthesis itself is carried out under such conditions that the partial pressure of the reactants are higher than in synthesis at normal pressure and with rich gases. Furthermore, higher synthesis temperatures and greater throughputs are practiced than in synthesis with low inert gas at normal pressure. Under these conditions high yields of hydrocarbons are obtained.

KÖHLER, O. *See* abs. **3923.**

KOIDE, K. *See* abs. **1876, 1877, 1879.**

1896. KOIZUMI, S. (Miike Synthetic Oil Co.). [Thermostat Apparatus in Gas Reaction Chamber Using Catalyst.] Japanese Patent 139,563. United States Naval Technical Mission to Japan, Index No. X–38(N)–7, Encl. (G), 1946, p. 297.

1897. KÖLBEL, H. (Steinkohlen-Bergwerk "Rheinpreussen".). [Diesel Fuel.] German Patent 747,401, no date. Kainer, p. 247.

Kogasin and coal-tar oil are mixed in about equal proportions and treated with 20% of H_2SO_4. The diesel fuel thus made is distinguished by high stability to coking, low combustion residue, high energy efficiency, and extremely low CO in the exhaust.

1898. ———. Diesel Fuels From Coal-Tar Oils. United States Patent 2,209,123, July 23, 1940; appl. filed Sept. 21, 1937, Serial No. 164,985, in Germany Sept. 24, 1936; 8 claims (*Cl. 196–40*). Chem. Abs., vol. 35, 1936, p. 303.

Diesel fuels are prepared from coal tar oils by mixing with a paraffinic oil b. 180°–380°, particularly synthetic Fischer-Tropsch benzine fractions; treating the mixture with H_2SO_4 of approximately 20% concentrated; separating the upper layer of refined oil from an intermediate acid layer and a bottom sediment layer; and washing, drying, and bleaching the refined oil.

1899. ——— (Steinkohlen-Bergwerk "Rheinpreussen"). [Fuel for Fast-Running Diesels.] German Patent 720,830, Apr. 16, 1942 (*Cl. 12 r–1.04*). Chem. Abs., vol. 37, 1943, p. 2546.

Mixture of tar oils, b. 180°–350°, and paraffin hydrocarbon oils is exposed to the action of 0.2–10% of $AlCl_3$, free of H_2O, at room temperature or below. The layer of tar oil-paraffin-hydrocarbon oil is separated and is purified as usual with NaOH, H_2O, and fuller's earth.

1900. ——— (Koppers Co.). Hydrocarbons From Gases Containing Carbon Monoxide and Hydrogen. United States Patent 2,244,710, June 10, 1941; appl. filed Sept. 22, 1938, Serial No. 231,275, in Germany Sept. 23, 1937; 5 claims (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 6094.

Gases are first passed over an Fe catalyst, hydrocarbons produced are removed from the treated gas mixture, and the gas is then further treated in the presence of another 8th group metal such as Co or Ni as a catalyst for the production of additional hydrocarbons, which are also separated.

1901. ——— (Steinkohlen-Bergwerk "Rheinpreussen"). [Lubricating Oil.] German Patent 709,667, July 17, 1941 (*Cl. 12 o–1.01*). Chem. Abs., vol. 37, 1943, p. 3926.

Tar products are condensed with unsaturated or chlorinated paraffin hydrocarbons using $AlCl_3$ or activated Al as catalyst. The tar products are pretreated with the $AlCl_3$ double compounds produced during the condensation reaction.

1902. ——— (Steinkohlen-Bergwerk "Rheinpreussen"). [Motor-Fuel Oil.] German Patent 724,054, Aug. 25, 1942; appl. St 56,117, filed Apr. 23, 1937 (*Cl. 12 r–1.05*). Chem. Abs., vol. 37, 1943, p. 5573.

Mixtures of tar oils or tar fractions, preferably with aliphatic hydrocarbons, b. 160°–360°, are extracted with AcOH at normal temperature. Two layers are formed, the upper of which contains the refined motor fuel. Further refining is performed by washing with H_2O or lye or bleaching with "Tonsil." This process is advantageous for mixing tar oils with hydrocarbons obtained in the Fischer-Tropsch synthesis. The fuels are intended for use in tractors and diesel motors.

1903. ——— (Steinkohlen-Bergwerk "Rheinpreussen"). [Purification of Hydrocarbon Oil Mixtures.] German Patent 730,853, Dec. 24, 1942 (*Cl. 12 r–1.04*). Chem. Abs., vol. 38, 1944, p. 860.

Oil mixtures with a boiling range of 180°–360° and composed predominantly of aliphatic oils with a similar boiling range are treated with gaseous SO_2 at ordinary pressure. Substances precipitated in consequence of this treatment are separated from the purified oil.

1904. KÖLBEL, H., AND ACKERMANN, P. (Steinkohlen-Bergwerk "Rheinpreussen"). [Hydrocarbons From Gaseous Mixtures of Carbon Monoxide, Hydrogen, and Carbon Dioxide.] German Patent 728,217, Nov. 23, 1942; appl. St 57,312, filed Apr. 6, 1938 (*Cl 12 o–1.03*). Chem. Zentralb., 1943, I, p. 1741; Chem. Abs., vol. 37, 1943, p. 6856.

Synthesis is carried out with the aid of Fe catalysts. Before the catalysts attain their maximum effectiveness the feed gas contains no CO_2. After the peak is reached the gas may contain CO_2.

1905. ——— (Steinkohlen-Bergwerk "Rheinpreussen"). [Iron Catalysts.] German Patent 763,307, no date. Kainer, p. 17.

Less than 0.1% of Cu is used as activator. Completely Cu-free Fe catalysts are inactive.

1906. ——— (Steinkohlen-Bergwerk "Rheinpreussen"). [Synthesis Catalyst.] German Patent 752,480, no date; appl. St. 60,776 (*Cl. 12 o–1.03*). Kainer, p. 78. Auszüge deut. Patent-Anmeldungen, vol. 6, p. 361.

Iron catalysts for the hydrogenation of CO are made by precipitating Fe salt solutions with earth alkali carbonates or hydroxides. If desired substitution of these precipitating agents can be made by alkali if the washed-out precipitate is later treated with earth-alkali compounds, particularly barium nitrate solutions.

1907. ——— (Steinkohlen-Bergwerk "Rheinpreussen"). [Synthesis Catalyst.] German Patent 755,822, no date. Kainer, p. 66.

NH_3 can be used with advantage as the precipitant in making catalysts. Wholly Na-free catalysts with long life are obtained, and the consumption of distilled H_2O for washing is greatly reduced.

1908. ———. (Steinkohlen-Bergwerk "Rheinpreussen"). [Synthetic Gasoline.] German Patent 743,569, no date. Kainer, p. 266.

With use of a catalyst containing at least 99.5% Fe, the synthesis is so conducted that mainly unsaturated C_3–C_4 hydrocarbons are produced, and then these are polymerized to high-grade antiknock gasoline.

1909. KÖLBEL, H., AND ENGELHARDT, F. (Steinkohlen-Bergwerk "Rheinpreussen"). [Hydrocarbons.] German Patent 802,876, June 14, 1951; appl. filed Oct. 2, 1948 (*Cl. 12 o*). Chem. Zentralb., 1951, II, p. 3540.

Hydrocarbons are obtained in better yield from CO and H_2 in the gas phase on Fe catalysts under normal or increased pressure by continuously reversing the direction of flow of the synthesis gases over the catalyst each ¼ hr. or more (1–3 hr.). The flow periods are preferably set up at the beginning in short ¼-hr. periods and then extended during the course of the synthesis to several hr.

1910. KÖLBEL, H., AND LANGHEIM, R. (Steinkohlen-Bergwerk "Rheinpreussen"). [Iron Catalyst.] German Patent 766,149, no date. Kainer, p. 18.

Through oxidation of Fe carbonyl with O_2, highly active Fe catalysts can be obtained.

1911. KÖLBEL, H., AND RUSCHENBURG, E. (Steinkohlen-Bergwerk "Rheinpreussen"). [Synthesis Catalysts.] German Patent 765,512, no date. Kainer, pp. 78 and 161.

Sintered dolomite is suitable both as support for Fe catalysts and for precipitating the catalyst from solution. Dolomite is cheaper than kieselguhr and gives catalysts of greater efficiency, since the Ca and Mg therein have activating properties.

1912. KÖLBEL, H., AND ULLMANN, D. (Steinkohlen-Bergwerk "Rheinpreussen"). [Resin and Lacquer Softeners.] German Patent 750,018, no date. Kainer, pp. 269 and 270.

Chlorinated products of synthetic hard paraffin are used as softeners for resins and lacquers and for high-grade lubricants.

KOLLER, K. *See* abs. **763.**

1913. KOLLER, M. [Catalyst Chamber.] Swiss Patent 77,933, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 161.

KOLLING, H. *See* abs. **830, 3752.**

1914. KOLLING, H., ROTTIG, W., AND TRAMM, H. (Ruhrchemie A. G.). [Aromatization and Dehydration of Hydrocarbons.] French Patent 860,007, Aug. 8, 1939. Chem. Zentralb., 1941, II p. 267.

Hydrocarbon oils boiling up to 200° obtained by the synthesis of hydrocarbons from CO and H_2 may be used as the raw material. Synthetic gasoline is made knock-proof by passing over MgO with 30–50% Cr_2O_3.

See German Patent 736,839 (abs. **2833**).

1915. KOL'TSEV, V. V. [Gaseous Mixture for Synthesizing Benzine.] Russian Patent 66,698, July 31, 1946. Chem. Abs., vol. 41, 1947, p. 1832.

Ch_4 is prolized and the C is gasified with the aid of steam. The resulting water gas is combined with the necessary quantity of H_2 obtained in the pyrolysis of CH_4.

KONRAD, W. A. *See* abs. **3823.**

KOOME, J. *See* abs. **1086, 1087.**

1916. KOPPENBERG, H. [Generating Water Gas, Especially Synthesis Gas, From Coal Dust and Steam.] German Patent 727,676, Nov. 9, 1942; appl. K 142,695, filed June 1936 (*Cl. 24 e–1.05*). Chem. Zentralb., 1943, I, p. 1131; Chem. Abs., vol. 37, 1943, p. 6856.

Fresh coal is fed into the generator in 2 batches: 1 is added to circulating gas containing steam when the gas is at its peak, and the 2d is added when the gas is at a lower temperature.

1917. KOPPERS CO., INC. Synthesis Gas. British Patent (Provisional) 18,496, filed 1936.

Synthesis gas is made by a Koppers process, which uses brown-coal briquets.

———. *See* abs. **508, 510, 511, 1810, 1900, 1918, 1919, 1920, 1922, 2059, 2104, 2203, 2204, 2714, 2734, 2735, 2736, 3624.**

1918. KOPPERS, H. (Koppers Co.). Carbon Monoxide and Hydrogen for Synthesizing Hydrocarbons. United States Patent 2,132,533, Oct. 11, 1938; appl. filed Sept. 3, 1936. Chem. Abs., vol. 33, 1939, p. 350.

A method for producing water gas containing CO and H_2 in ratio suitable for catalytical reaction, such as the synthesis of hydrocarbons from bituminous fuel of the character of brown coal, lignite, bituminous coal, and others, comprises flowing through and thereby reacting with a bed of the fuel a heated mixture of steam and water gas, which has been previously heated in a separate heating stage of a cycle to a temperature at which hydrocarbons will decompose and interact with steam; withdrawing part of the gas thus produced from the cycle at a point in the fuel bed where the fuel is substantially free of hydrocarbons; returning the other part of the gases in cycle to the heating stage at a temperature > the dew point of tar and H_2O, after passing through another part of the fuel bed where hydrocarbons are present and flow off with the gas in admixture with it; removing tarry constituents in suspension from the latter gas portion while leaving the vaporlike hydrocarbons therein, after the gas leaves the fuel bed but before it reenters the heating stage; distilling the so-removed tar, and conducting the vapors of distillation from it back into the aforesaid heating stage in contact with the gas in it. Describes apparatus.

1919. ——— (Koppers Co.). Continuous Production of Water Gas. United States Patent 2,148,299, Feb. 21, 1939. Chem. Abs., vol. 33, 1939, p. 4002.

Described apparatus and a method of continuously producing water gas of a predetermined definite composition with respect to its ratio of H_2, CO_2, and CO and free of hydrocarbons, from distillable solid fuels, which comprises maintaining in a bed of continuously descending fuel a water gas reaction zone in which the distillation of the fuel is already completed and a predistillation zone. The hydrocarbon-free water gas is withdrawn from the zone of the fuel bed in which predistillation of the fuel is already completed. A preheated gaseous heat carrier medium of water gas and steam traverse the distillation zone, and the medium is circulated from the distillation zone together with the hydrocarbons through a separate gas heating stage and back to the fuel bed through the water gas reaction zone. Steam is added to the heat carrier medium for the water gas reaction in the fuel bed and for converting the hydrocarbons in the heat carrier medium into CO and H_2 in the heating stage. The improvement comprises cooling the heat-carrier medium, after it issues from the heating stage, but before it enters the water-gas-reaction stage fuel bed down to at least the upper limit of the temperature range critical for producing a gas of predetermined definite composition uniformly with respect to its ratio of $H_2+CO+CO_2$ from the particular fuel being gasified by the heat-carrier medium in the fuel bed.

1920. ——— (Koppers Co.). Hydrocarbon Synthesis From Producer Gas. United States Patent 2,349,438,

May 23, 1944; appl. filed Nov. 25, 1939, Serial No. 306,077, in Germany Dec. 3, 1938; 1 claim (*Cl. 252–373*). Chem. Abs., vol. 39, 1945, p. 1040.

Producer gas, rich in CO_2, is mixed with coke oven gas, natural gas, or residual gas from the synthesis of hydrocarbons or a similar hydrocarbon gas and heated in the presence of steam to 1,100°–1,200°. On account of this heating CO_2 is converted with the hydrocarbons of the coke oven gas, particularly that containing CH_4 into CO and H_2. At the same time the higher molecule C and S compounds present in the producer gas are converted into low S compounds, especially H_2S, which can be removed more easily. The mixture of gases is so calculated as to produce in the final reaction gas CO and H_2 in a ratio of 1:1–2, which is suitable for synthesis of hydrocarbons, such as fuel and lubricating oils.

1921. ——— (Heinrich Koppers G. m. b. H.). [Removing Dust From Gases.] German Patent 677,222, June 21, 1939 (*Cl. 26 d–1.20*). Chem. Abs., vol. 33, 1939, p. 6663.

Tar-free gases containing dust, which tends to form hard cementitious deposits, are washed in a centrifugal washing apparatus fed with H_2O containing an inert solid, such as sandy clay, in suspension. The formation of deposits on the surfaces of the washer is thus restrained. The process may be applied to CO–H_2 mixtures obtained from brown coal or coke.

1922. ——— (Koppers Co.). Water Gas. United States Patent 2,151,121, Mar. 21, 1939; appl. filed June 25, 1936. Chem. Abs., vol. 33, 1939, p. 4771.

Describes process for the production of water gas containing H_2 and CO in the ratio of 2:1 from bituminous fuels by extraneous heating. The fuel is distilled in an upper distillation zone of a fuel bed with hot water gas to recover hydrocarbons from the fuel. The distillate gas is withdrawn in mixture with the water gas from the distillation zone, and the gaseous fluids from the fuel-distillation are treated with steam at high temperature to form H_2 and CO from the hydrocarbons present. The conversion gases are passed through the distilled fuel in a lower contiguous water-gas zone of the fuel bed along with steam, and the distilled fuel and steam are treated at high temperature in the water-gas zone to form water gas in the presence of the conversion gas in it. Part of the water-gas stream is passed from the water-gas zone through the fuel in the upper distillation zone for effecting the fuel distillation mentioned, and the remainder of the water gas is withdrawn from the water-gas zone to a point of use outside the system. The temperatures for the water-gas reaction in the lower water-gas zone and the time interval for reaction of the fuel in it with the conversion gas and steam are regulated by removing such quantity of fuel ungasified from the lower water-gas zone per unit of time that CO and H_2 are produced in the ratio of 2:1. Describes an arrangement of apparatus.

1923. Koppers, H., G. m. b. H. [Continuous Generation of Water Gas Free of Hydrocarbons From Bituminous Fuels.] German Patent 717,247, Jan. 22, 1942 (*Cl, 24 e–1.05*). Chem. Abs., vol. 38, 1944, pp. 2479–2480.

See United States Patent 2,148,299 (abs. **1919**).

1924. ———. [Gas Producer.] German Patent Appl. K 162,061, no date (*Cl. V–24 e*). Auszüge deut. Patent-Anmeldungen, vol. 9, p. 300.

Gas producer for pulverized fuel, which is blown with only a part of the necessary air for gasification into the reaction chamber heated above the fusing point of the ash. The mixture is converted therein with the highly heated remainder of the gasification air and the heated endothermic reactive constituents (H_2O, CO_2) to produce a gas with a very high calorific value.

1925. ———. [Gas Producer.] German Patent Appl. K 162,062, no date (*Cl. V–24 e*). Auszüge deut. Patent-Anmeldungen, vol. 9, p. 301.

Gas producer in which pulverized fuel is blown with a stream of cold O_2 or air rich in O_2 into a reaction zone maintained at higher temperature. The fuel is converted into synthesis gas with highly heated endothermic reacting gases such as steam and CO_2. Addition to German Patent Appl. K 162,061 (abs. **1924**).

1926. ———. [Generating Carbon Monoxide and Hydrogen in a Volume Ratio of 1:2 From Brown-Coal Briquets or Similar Bituminous Fuel.] German Patent 716,078, Dec. 11, 1941; appl. K 138,425 filed June, 1935 (*Cl. 26 a–2*). Chem. Abs., vol. 38, 1944, p. 2192.

See United States Patent 2,151,121 (abs. **1922**).

1927. ———. [Hydrocarbons From Sulfurous Gases Containing Carbon Monoxide and Hydrogen.] German Patent Appl. K 149,907, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 251.

Fe catalysts are started 1st with a synthesis gas free from S compounds such as that which has already passed over a catalyst of group 8 of the periodic system. Thereafter operation is continued with S-containing gas after full efficiency is attained relative to the yield of liquid hydrocarbons.

1928. ———. [Synthesis Gas.] German Patent Appl. K 152,169, no date (*Cl. IV b–12 i*).

Production of H_2 and CO through conversion of gases containing hydrocarbons, such as coke-oven, cracking, and natural gases, by means of steam and/or CO_2. The gas–steam–CO_2 mixture is heated in a towerlike heat accumulator in such a way that the temperature difference between the gas mixture and the heat-accumulator charge does not exceed 300°.

1929. ———. [Synthesis Gas.] German Patent Appl. K 162,172, no date (*Cl. V–24 e*). Auszüge deut. Patent-Anmeldungen, vol. 9, p. 301.

Pulverized fuels are gasified with O_2 in a reaction zone maintained at a high temperature, the blast mixture being led in through a burner nozzle. Addition to German Patent Appl. K 162,062 (abs. **1925**).

1930. ———. [Synthesis Gas.] German Patent Appl. K 163,111, no date (*Cl. V–24 e*). Auszüge deut. Patent-Anmeldungen, vol. 9, p. 301.

In producing synthesis gas of definite composition, the fuel before being blown into the reaction chamber is mixed with O_2, steam of 1,000°–1,200° temperature is passed into the reaction zone, and the temperature of the chamber is maintained at all points above the decomposition temperature of the high-molecular tarry substances and S compounds.

1931. ———. [Synthesis Gas.] German Patent Appl. K 163,511, no date (*Cl. V–24 e*). Auszüge deut. Patent-Anmeldungen, vol. 9, p. 302.

Pulverized fuel in a fluidized state is gasified with O_2 and steam while being heated with purge gas in such a way that the powdered fuel is passed into the reaction zone along with O_2 before it has made contact with the purge gas-steam mixture, and is there contacted with the highly preheated mixture of endothermic reacting gasification agents such as steam and CO_2. The use of a highly heated recycle gas stream decreases the O_2 consumption and through the creation of turbulent conditions increases the conversion.

1932. ———. [Synthesis Gas.] German Patent Appl. K 163,512, no date (*Cl. V–24 e*). Auszüge Deutscher Patent-Anmeldungen, vol. 9, p. 302.

In gasifying pulverized coal in the fluidized state in the presence of O_2, the blast pipes for the fuel-O_2 mixture, extending through the walls of the gasifier, and the final mixing chamber are cooled with a cooling liquid flowing in a cooling jacket. By such means and exothermic reaction between O_2 and C outside the gas producer is prevented. Addition to German Patent Appl. K 162,062 (abs. **1925**).

1933. ———. [Synthesis Gas.] German Patent Appl. K 165,274, no date (*Cl. V–24 c*). Auszüge deut. Patent-Anmeldungen, vol. 9, p. 304.

In producing synthesis gas from powdered fuels and hydrocarbon gases, the latter are passed into the reaction chamber along with the endothermic reacting gasification agents. The reaction chamber is thus maintained at a higher temperature. Addition to German Patent Appl. K 162,062 (abs. **1925**).

1934. ———. (H. Koppers Industrielle Maatschappij N. V.). [Synthesis Gas.] Italian Patent 346,263, July 2, 1936.

See British Patent 466,737 (abs. **1936**) and French Patent 810,012 (abs. **1939**).

1935. ———. [Synthetic Hydrocarbons From Water Gas.] German Patent Appl. K 148,007, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 251.

Hydrocarbons are produced from gases containing CO and H_2, such as coke water gas, by passing them over an Fe catalyst. The unconverted residual gas is mixed with a gas containing CO and H_2 in the proportion of 1:2 and thereafter passed over a Co or Ni catalyst.

1936. ——— (H. Koppers Industrielle Maatschappij N. V.). Water-Gas Plant. British Patent 466,737, June 3, 1937. Chem. Abs., vol. 31, 1937, p. 8893.

In producing a mixture of H_2 and CO, preferably in the ratio 2:1, suitable for the Fischer-Tropsch synthesis, by passing a mixture of coal distillation gas and steam through the hot bed of a water gas generator, the mixture of gases is preheated in a regenerator, previously heated to a high temperature by the "blow" gases from the generator, before entering the generator, so as to insure a substantial conversion of the hydrocarbons in the coal gas before contact with the hot fuel bed.

———. *See* abs. **1921, 2060, 2061, 3751.**

1937. KOPPERS, H., INDUSTRIELLE MAATSCHAPPIJ N. V. [Converting Carbon Monoxide and Hydrogen Into Hydrocarbons.] French Patent 843,874, July 11, 1939. Chem. Abs., vol. 34, 1940, p. 7091.

Method of producing oily hydrocarbons from a mixture of CO and H_2 under normal, higher, or reduced pressure consists in passing a gas containing CO and H_2 in a proportion other than 1:2 over an Fe catalyst, eliminating the oily hydrocarbons, mixing the gas with CO and H_2 in such a proportion that the ratio CO:H_2 in the mixture is 1:2, and passing the mixture over Ni or Co catalyst.

1938. ———. [Gas Containing Carbon Monoxide and Hydrogen.] Belgian Patent 416,369, Dec. 1, 1936; appl. filed July 3, 1936. Chem. Bentralb., 1937, II, p. 4145.

Mixture of steam and coke-oven gas is heated to such a temperature that the hydrocarbons and the steam are decomposed.

1939. ———. [Hydrogen-Carbon Monoxide Mixtures.] French Patent 810,012, Mar. 13, 1937. Chem. Abs., vol. 31, 1937, p. 6853.

Describes a system for producing H_2–CO mixtures, suitable for the synthesis of hydrocarbons by treating coke in a discontinuously operated water gas generator with a preheated mixture of steam and coke-oven gas.

1940. ———. Manufacture of Hydrocarbons From Carbon Monoxide and Hydrogen. British Patent Appl. 27,807, Sept. 23, 1938.

Process for the manufacture of hydrocarbons from gases containing CO and H_2, such as coke water gas at normal, higher, and lower pressure, by means of catalysts of the Fe group comprising the flow of the synthesis gas 1st of all over an Fe catalyst, then the removal of the hydrocarbons produced from the gas treated, further treating the gas being led over the Fe catalyst in the presence of a Co or Ni catalyst for the production of additional hydrocarbons, and finally separating from the gas the hydrocarbons formed.

1941. ———. [Production of Synthesis Gas.] Italian Patent 379,825, Oct. 18, 1939. Chem. Zentralb., 1942, II, 973.

Describes apparatus for conserving heat in endothermic gas reactions such as the conversion of hydrocarbons with steam with formation of CO and H_2.

1942. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 843,847, July 11, 1939; appl. filed Sept. 23, 1938. Chem. Zentralb., 1940, I, p. 2424.

Gases, such as water gas, containing CO and H_2 in proportion of 1 : 1 to 1 : 1.25 are first converted over Fe catalyst (Fe+Cu) at 225°–250° to olefin-rich hydrocarbons according to $2\ CO+H_2=CO_2+(CH_2)_x$. The residual gas rich in H_2, after separation of the liquid hydrocarbons and CO_2 and correction of the gas composition to CO : H_2=1 : 2, is used for the production of more liquid hydrocarbons at 185°–200° over a Co or Ni catalyst according to $CO+2\ H_2=H_2O+(CH_2)_x$. The Fe catalyst is put into operation with a S-free gas; after reaching its highest efficiency (after about 5 days) the Fe catalyst has become insensitive to S and can then be further operated with a S-containing gas.

1943. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Italian Patent 366,213, Sept. 23, 1938. Chem. Zentralb., 1940, I, p. 2424.

See French Patent 843,847 (abs. **1942**).

———. *See* abs. **1934, 1936.**

KOTZEBUE, M. H. *See* abs. **200.**

KOTZSCHMAR, A. *See* abs. **3260.**

1944. KOTZSCHMAR, A., SCHEUERMANN, A., AND MEISENHEIMER, K. (I. G. Farbenindustrie A. G.). [Process for Producting Solid Hydrocarbons by Reacting Carbon Monoxide With Hydrogen at Ordinary Temperature.] German Patent Appl. I 63,879, Feb. 20, 1939 (*Cl. 12 o–1.03*). FIAT Reel K 30, frames 7,617–7,619; PB 73,587.

This is an addition to German Patent Appl. I 63,778 (abs. **1490**). The method of reacting CO with H_2 in the presence of Co catalysts is further developed. The process works in the presence of catalysts that contain Co and possibly Fe and/or Ni at a pressure well above 2 atm. The catalysts are produced by very gradual precipitation to reduce Co compounds from Co salt solutions while maintaining a precipitation time of > 3 hr.

KOZACIK, A. P. *See* abs. **2762.**

KOZHENOVA, K. I. *See* abs. **1795.**

KRATZER, M. B. *See* abs. **1112.**

1945. KRAUCH, C., AND PIER, M. (I. G. Farbenindustrie A. G.). [Preparation of Valuable Organic Compounds.] German Patent 671,606, Feb. 10, 1939; appl. B 121,376, filed Aug. 21, 1925 (*Cl. 12 o–1.03*). FIAT Reel AA–90, frames 1,512–1,514; PB 70,275; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 6, chap. 167, 1949, p. 10; Chem. Abs., vol. 33, 1939, p. 6338.

Coal tars, mineral oils, and resins are treated with a mixture of H_2 and CO; for example, water gas, under

high temperature and pressure in the presence of MeOH-forming catalysts (except alkali or alkaline earth compounds) alone or used with Mo, W, or Cr, to give organic products. Thus, vaporized tar from brown coal is treated with a mixture containing CO 10% and H_2 90% at 200 atm. and 450° in the presence of a ZnO catalyst to give a mixture of MeOH and C_6H_6. Another example mentions steel containing Cu or Al as the catalyst.

1946. KRAUCH, C., HOCHSCHWENDER, K., AND SCHUNCK, W. (I. G. Farbenindustrie A. G.). [Oily Products.] German Patent 553,785, May 23, 1923. Chem. Abs., vol. 26, 1932, p. 5713.

Oily products consisting chiefly of oxygenated organic substances such as higher alcohols and aldehydes, together with MeOH, are obtained by leading a mixture of H_2 and oxides of C, in which the ratio of H_2 to oxide is at least 2 : 1, over a contact mass at high temperature and pressure. The contact mass contains no Fe, Ni or Cr, or only very small quantities of these. Examples mention catalysts of ZnO in fused $K_2Cr_2O_7$ and CuO with PbO.

1947. ——— (I. G. Farbenindustrie A. G.). Oxygenated Organic Compounds From Carbon Oxides and Hydrogen. United States Patent 1,889,251, Nov. 29, 1932; appl. filed May 22, 1924, Serial No. 715,191. Chem. Abs., vol. 27, 1933, p. 1359.

Gaseous mixture such as may be formed mainly of CO and H_2 is passed, at elevated temperature and pressure, over a catalyst such as one prepared from ZnO and $K_3Cr_2O_7$ by reduction with H_2 capable of inducing formation of MeOH, at a velocity so much < that required for substantially pure MeOH production that substantially all the MeOH formed is converted into higher oxygenated compounds such as higher alcohols and aldehydes.

See also German Patent 559,892 (abs. **1377**).

1948. KRCZIL, F. [Siliceous Material.] Czechoslovak Patent 60,124, no date. Kanier, p. 34.

See German Patents 581,123 (abs. **1952**) and 596,093 (abs. **1951**), French Patent 748,584 (abs. **1949**), and Spanish Patent 129,625 (abs. **1950**).

1949. ———. [Siliceous Materials.] French Patent 748,584, July 6, 1933. Chem. Abs., vol. 27, 1933, p. 5491.

Siliceous materials, such as kieselguhr, infusorial earth, kaolin, and clay, are purified or regenerated by calcination in the presence of hot gases, which keep the material in a whirl or suspended through the operation. The gases may be inert or chemically active to produce purification.

1950. ———. [Siliceous Material.] Spanish Patent 129,625, no date. Kainer, p. 34.

See German Patents 581,123 (abs. **1952**) and 596,093 (abs. **1951**), French Patent 748,584 (abs. **1949**), and Czechoslovak Patent 60,124 (abs. **1948**).

1951. ———. [Treatment of Kieselguhr and Like Siliceous Materials.] German Patent 596,093, Apr. 26, 1934 (*Cl. 12i–38.02*). Chem. Abs., vol. 28, 1934, p. 4548.

The process of German Patent 581,123 (abs. **1952**) is modified by replacing the heating or inert gases wholly or in part by gases or vapors having a chemical action on the siliceous material or on the impurities associated with it. Thus, gas mixtures containing O_2, CO_2, Cl, HCl, or SO_2 may be used. Indicates various methods of procedure.

1952. ———. [Treatment of Siliceous Materials.] German Patent 581,123, July 21, 1933. Chem. Abs., vol. 27, 1933, p. 5161.

In preparing natural siliceous materials such as kieselguhr for use as adsorbents, or in regenerating such materials after use as adsorbents, the materials are calcined in apparatus to which heating or inert gases are supplied in such a manner that the materials are continuously or intermittently loosened or whirled or carried in suspension by the gases. The materials may be preliminarily ground and pretreated by known methods.

KREBS & Co. A.-G. *See* abs. **2012.**

1953. KREBS, R. W. (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,614,114, Oct. 14, 1952. Chem. Abs., vol. 47, 1953, p. 1374.

Hydrocarbons and oxygenated hydrocarbons are synthesized from CO and H_2 in the presence of a fluidized, powdered Fe catalyst contained in a reactor with a portion of the fluidized catalyst maintained in a reducing atmosphere with respect to Fe. The ratio of the reducing to the oxidizing zones may vary, but should not exceed 20% of the total catalyst volume, and a 10% ratio is preferred. When Fe of low O content is charged to the reactor after a day's continuous operation, the Fe will contain 20–22%, by weight, combined O. This process permits the O content to be reduced to 10–15%, for example, so that the catalyst will be maintained in a high state of activity during an increased life period.

1954. ——— (Standard Oil Development Co.). [Hydrocarbon Synthesis With Fluidized Catalysts.] Swedish Patent 127,678, Mar. 21, 1950; appl. filed Nov. 5, 1946. Chem. Zentralb., 1951, I, p. 1826.

Catalyst should have the following particle sizes: Below 25% O–20μ, 30–85% 20–80μ, and below 45% above 80μ. The gas velocity in the catalyst should be 6–300 or better 6–45 cm. per sec. Co and Fe catalysts with usual promoters are used.

1955. ——— (Standard Oil Development Co.). Method for Regeneration of a Hydrocarbon Synthesis Catalyst. United States Patent 2,506,302, May 2, 1950; appl. filed June 30, 1947, Serial No. 758,207; 21 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 6605.

Content of carbonized synthesis catalyst is reduced or completely removed by contact with a metal oxide reducible by C at a temperature below the fusion temperature of the catalyst. A temperature is maintained conducive to removing the C in the form of C oxides and simultaneously reducing the metal oxide. Oxides of Fe, Ni, Mn, Ti, V, Co, Cr, Mo, and Cu are suitable. Preferably the catalyst itself in the unreduced state is used. The amounts of metal oxide required varies. When using Fe_2O_3 with an Fe catalyst to reduce the C content from 35% by weight to 5% by weight, the Fe_2O_3 required will be 2 lb. per lb. catalyst to be decarbonized. This corresponds to an O excess of 22%. The catalyst should contain a limited amount of O, 5–20% by weight of the catalytically active metal component. When Fe_2O_3 is used decarbonizing temperatures 1,200°–1,400° are suitable for Fe catalyst. 4 United States patents cited.

1956. ——— (Standard Oil Development Co.). Method of Sintering a Catalyst. United States Patent 2,510,823, June 6, 1950; appl. filed June 30, 1947, Serial No. 758,206; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 8094.

Fe fines, which cannot be maintained in the reaction zone under fluid conditions because of their small particle size, are sintered 1,300°–2,000° F. to form agglomerates large enough for the fluidizing range 20–200 microns. The coarser particles are separated by gaseous classification and returned to the reaction zone without grinding. The sintering is done in a reducing atmosphere so that the Fe or other metal remains in an unoxidized state. 1.5 ton catalyst fines (below 20 microns) per hr. are sintered at 1,700° F. in a

vessel 20 ft. in sintering section diameter and 3 ft. in quenching- or collecting-zone diameter. The gas velocities are 0.2 ft. per sec. and 1 ft. per sec. in the sintering and quenching zones respectively. The fines are agitated to induce agglomeration. 3 United States patents cited.

1957. ——— (Standard Oil Development Co.). Slurry Handling. United States Patent 2,518,337, Aug. 8; 1950; appl. filed Apr. 26, 1946, Serial No. 665,073; 2 claims (*Cl. 260–449*).

Catalyst that has been used in hydrocarbon synthesis is dewaxed by solvent treatment. The usual practice is to return the catalyst to the reaction zone in a slurry with a concentration of ½-lb. catalyst per gal. solvent. According to this invention the concentration is raised to 5–10 lb. catalyst per gal. solvent. This flowable, but not pumpable, slurry is treated with hydrocarbon gases to form a froth, which is returned to the reaction zone. The amount of solvent oil returned to the system per unit volume of catalyst is reduced 20%. 2 literature refs. and 2 foreign and 8 United States patents cited.

1958. ——— (Standard Oil Development Co.). Two-Stage Reduction Process for Producing Metal Catalyst. United States Patent 2,481,226, Sept. 6, 1949; appl. filed Oct. 17, 1945, Serial No. 622,930; 4 claims (*Cl. 75–26*). Chem. Abs., vol. 44, 1950, p. 824.

Fe oxide and Co oxide are reduced in a 2-stage operation. Impure H_2 is used in the 1st stage and highly purified H_2 in the 2d stage. Considerable expense is saved by this method for the production of hydrogenation catalysts. Details of the reducing process are claimed. 5 United States patents cited.

———. *See* abs. **885, 1786, 1787, 3360, 3851.**

1959. KREBS, R. W. AND LEWIS, W. K. (Standard Oil Development Co.). Method and Apparatus for Carrying Out Exothermic Catalytic Reactions. United States Patent 2,627,522, Feb. 3, 1953; appl. filed Oct. 29, 1948, Serial No. 57,366; 7 claims (*Cl. 260–449.6*). Chem. Abs., vol. 47, 1953, p. 4146.

The exothermic fluid-type reaction zone is subdivided into at least 2 sections, arranged in series with respect to the flow of reactants. The gaseous reactants are first passed at a relatively high velocity upward through a reaction zone containing heat-exchange surfaces immersed in the catalyst. Then the gases are passed at a relatively low velocity conducive to formation of a dense fluidized catalyst phase through a 2d reaction zone that is free of heat exchange surfaces. Catalyst cooled below the reaction temperature in the 1st section flows with the high velocity gases continuously into the 2d section to absorb the heat of reaction. The catalyst from the 2d section is continuously returned to the 1st section for cooling. The rate of catalyst circulation is controlled so that optimum reaction temperatures are maintained in the 2d section. 10 United States patents cited.

1960. KREJCI, J. C. (Phillips Petroleum Co.). Synthesis-Gas Manufacture. United States Patent 2,605,174, July 29, 1952; appl. filed Jan. 4, 1949, Serial No. 69,114; 10 claims (*Cl. 48–196*).

Process relates to the production of synthesis gas by the partial combustion of a preheated mixture of CH_4 or natural gas and O_2 in a specially designed tangential flame furnace.

KREMP, F. *See* abs. **155, 156.**

KROENIG, W. *See* abs. **2665.**

1961. KROEPELIN, H. (Braunkohle-Benzin A.-G.). [Procedure for Emptying Granular Masses From Reaction Tubes.] German Patent 711,422, Aug. 28, 1941 (*Cl. 12g–1.01*). Chem. Abs., vol. 37, 1943, p. 3981.

Process is particularly applicable to emptying of contact furnaces used for the synthesis of hydrocarbons from CO and H_2 by the Fischer-Tropsch process.

1962. KRUPP, F., A.-G. [Benzine Synthesis From Carbon Monoxide and Hydrogen Under Pressure.] German Patent 766,024, no date; appl. K 150,067 (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 251.

Describes structure of the tubes holding the catalyst.

1963. ———. [Catalyst Chamber.] French Patent 841,008, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 162.

1964. ———[Catalyst Chamber With Heat Exchange.] German Patent 685,372, no date. Schmidt, J., Das Kohlenoxyd. Akad. Verlagsgesell., Leipzig, 1950, p. 161.

1965. ———. [Heat-Exchanger Construction.] German Patent Appl. K 163,252, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 256. Addition to German Patent 741,280 (abs. **66**).

1966. ———. [Raising the Viscosity of Motor Benzol and Benzine.] German Patent Appl. K 165,060, no date (*Cl. IV d–23 c*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 808.

Synthetic fatty acids from the benzine synthesis (b. 180°–350°) are mixed with a synthetic spindle oil (b. 200°–350°) from the benzine synthesis consisting of unbranched aliphatic hydrocarbons, warming to about 150°–180° while stirring, and then allowing to cool.

———. *See* abs. **66, 164, 905, 2097, 2525.**

1967. KRUPP, F., GUSSTAHLFABRIK. [Paraffin-Water Emulsions.] German Patent Appl. K 162,979, no date (*Cl. IV c–22 g*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 619.

Stable paraffin–H_2O emulsions are made by saponifying the fatty acid mixtures b.>about 230° from the Fischer-Tropsch synthesis process. Also by partial saponification of the fatty acids with 5–10 C atoms in the molecule.

1968. KRUPP TREIBSTOFFWERK G. m. b. H. [Converter.] German Patent Appl. K 147,143, filed July 5, 1937 (*Cl. IV b–12 g*). PB Report 412, May 15, 1945.

Reactor for the Fischer-Tropsch process in which the cross section of the catalyst bed decreases from inlet to outlet according to the contraction in volume of the reacting gases.

1969. ———. [Multistage Synthesis.] German Patent Appl. K 148,919, filed Dec. 20, 1937 (*Cl. IV b–12 g*). PB Report 412, May 15, 1945.

Carrying out Fischer-Tropsch synthesis, or other reactions with large heat effects, in a plurality of stages and introducing between stages enough cold charge gas to hold the desired temperature in the subsequent stage.

1970. ———. [Process and Apparatus for Extracting Paraffin Deposits From Catalyst Converters.] German Patent Appl. K 160,334, filed Mar. 1, 1941 (*Cl. IV d–12 o*). TOM Reel 177, frames 1,769–1,785; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 62, 1948, p. 158.

Method and equipment are described with diagrams for extracting Fischer-Tropsch converters of their paraffin deposits. The method involves the use of sprays of the solvent through a specially constructed pipe extending from the outside into the top of the converter and provided with nozzles for distributing the solvent uniformly. The process and apparatus as described can also be converted to other uses, such as the extraction of S from gas purification masses and

of resins and other substances absorbed on active C, silica gel, and the like.

1971. ———. [Process for Obtaining Gasoline Rich in Olefins by Cracking Hydrocarbon Oils.] German Patent Appl. K 163,068, Dec. 8, 1941 (*Cl. IV d–23 b*). TOM Reel 177, frames 1,659–1,660; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 44, 1948, p. 107.

Olefin-rich gasoline is obtained by cracking hydrocarbon oils at high temperatures in the presence of the residual gases that arise in the course of cracking, hydrogenation, or synthesis.

1972. ———. [Process for Producing an Iron Catalyst for Gasoline Synthesis.] German Patent Appl. K 154,575, PA 411,292, filed May 26, 1939 (*Cl. IV d–12* o). FIAT Reel B–196, frames 236–240; PB 83,253.

In producing an Fe catalyst for the synthesis of gasoline from CO and H_2, a substance consisting essentially of Fe and Cu hydroxides or their carbonates or mixtures of these hydroxides and carbonates is precipitated from solutions of the salts of these metals by alkali and deposited on diatomaceous earths and then mixed with a small amount of alkali and boric acid or 1 or 2 of their salts. The alkali and boric acid are added simultaneously or separately. Previous to the addition of boric acid or its salts, activity promoters such as pyrolusite (MnO_2), alumina or the like may be added. It is said that this catalyst greatly improves the yield of gasoline from about 50 ml. to >120 ml. per $m.^3$ of synthesis gas. A further advantage consists in the H_2 reduction of the catalyst at the reaction temperature instead of a higher one.

———. *See* abs. **929.**

KUBICO, M. *See* abs. **872.**

KÜHNEL, P. *See* abs. **373.**

1973. KÜMMEL, P. [Protection of Rubber Articles.] Belgian Patent 450,170, May 1943. Chem. Abs., vol. 41, 1947, p. 6762.

Rubber is protected against aging by means of contact paraffins, preferably rich in isoparaffins obtained in the synthesis of benzine or of paraffin by the Fischer-Tropsch process and preferably having a m. p. of 60°–66°.

1974. ———. [Synthetic Paraffin.] French Patent 893,371. Kainer, no date, p. 249.

Fractions of synthetic paraffin melting >100° and rich in isoparaffins are used in making candles.

1975. ———. [Synthetic Paraffin.] French Patent 893,372. Kainer, no date, p. 249.

Synthetic paraffin containing isoparaffins and melting at 60°–66° is used as an antiager for rubber.

See Belgian Patent 450,170 (abs. **1973**).

KUNZE, H. *See* abs. **3887.**

KUPPINGER, O. *See* abs. **2666.**

1976. KUROI, C. [Production of Carbon Monoxide–Hydrogen Mixtures.] Japanese Patent 102,118, Sept. 22, 1933; appl. filed Nov. 11, 1931. Chem. Zentralb., 1934, I, p. 2072.

Hydrocarbon gases with an excess of H_2 are passed at elevated temperature and, if desired, decreased pressure into a reaction space containing the oxides of Co, Ni, or Fe and, if desired, oxides of Al, Cu, Cr, and V.

KÜRZINGER, A. *See* abs. **1845, 1847.**

KYOTO IMPERIAL UNIVERSITY. *See* abs. **758, 1866, 1867, 1868, 1869, 1870, 1871, 1872, 1873, 1874, 1875, 1876, 1877, 1878, 1879, 1891, 1892, 3706, 3707.**

1977. KYOWA CHEMICAL ENTERPRISES Co. [Aliphatic Saturated Alcohols With More Than Two Carbon Atoms From Hydrogen and Carbon Dioxide.] Japanese Patent 154,318, Dec. 21, 1942. Chem. Abs., vol. 44, 1950, p. 1525.

CO_2 and H_2 can be condensed at high temperatures under high pressures to aliphatic saturated alcohols according to $nCO_2+6nH=CnH_{2n+1}OH+(2n-1)H_2O$ in the presence of MnO [Mn–$(OH)_2$ or $MnCO_3$] mixed with Fe oxide (hydroxide or carbonate) and a Cd, Cr, Al, Cu, or alkali metal oxide, singly or in combination. For example, over 300 cc. of a dried granular mixture of $Mn(OH)_2$, $Fe(OH)_3$, Cd $(OH)_2$, and CuOH (5 : 1 : 2 : 5 mol.), after heating at 400° in a stream of H_2, was passed H_2 mixed with CO_2, 24.7% at 397°–400°/150–160 atm. and space velocity 1,500 to give a liquid, which, after dehydrating by distillation was fractionated into EtOH, PrOH, BuOH, and MeOH, yields 20%, 18%, 8%, and a small amount respectively.

1978. ———. [Preparation of Aliphatic Saturated Alcohols From Carbon Dioxide and Hydrogen.] Japanese Patent 162,927, Mar. 15, 1944. Chem. Abs., vol. 41, 1947, p. 5142.

Mixture of 1 part each of Mn, Cu, and Zn hydroxides, 0.2 part Fe_2O_3, and 0.125 part KOH (the oxides or carbonates of each may be used, Cr may be substituted for Cu, and another alkali metal for K) is dried into bean-sized lumps with the addition of kieselguhr and then dehydrated at 400° and reduced in H_2 gas just before use. The CO_2–H_2 mixture, CO_2 25.5%, is heated in the presence of this mixed catalyst at 400° per 150 atm. The resulting liquid, after distilling off the H_2O, refining with CaO and KOH, and desiccating, is fractionated into 39.5% EtOH, 33.5% PrOH, 8.3% iso-BuOH, and 18.7% MeOH. The total alcohol yield is 53 cc. from 3.45 l. of gas mixture.

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1979. LAATSCH, W. [Production of Synthesis Gas.] German Patent 723,215, July 30, 1942; appl. L 99,223, filed October 11, 1939. Chem. Zentralb., 1942, II, p. 1990.

In the catalytic conversion of CH_4-containing gases with steam and CO_2 at about 925°, a part of the synthesis gas is passed over an Fe oxide catalyst with steam at about 500°, the CO_2 separated from the H_2 and together with fresh steam added to the CH_4-containing initial gas, the H_2 being used to heat the catalyst and the steam.

1980. LACHINOV, S. S. [Catalyst for Ammonia Synthesis.] Russian Patent 38,135, Aug. 31, 1934. Chem. Abs., vol. 30, 1936, p. 1955.

Fe is heated in a stream of O_2 with the addition of activators such as Al_2O_3 or KNO_3, and after oxidation is complete the product is maintained for some time at the melting point.

1981. ———. [Catalysts for Synthesis of Ammonia.] Russian Patent 52,802, Mar. 31, 1938. Chem. Abs., vol. 34, 1940, p. 5608.

Mixture of Fe with activators is oxidized in O_2 under pressure and then reduced.

See also Russian patent 52,409 (abs. **1982**).

1982. ———. [Iron Catalyst for Ammonia Synthesis.] Russian Patent 52,409, Jan. 31, 1938. Chem. Abs., vol. 34, 1940, p. 3890.

Fe or its oxides or both are fused in an oxidizing atmosphere with activators, and the temperature is increased to the melting point of the activators.

1983. LACHINOV, S. S., AND TELEGIN, V. G. [Iron Catalyst for Ammonia Synthesis.] Russian Patent 52,384, Dec. 31, 1937. Chem. Abs., vol. 34, 1940, p. 3032.

Reducing gases are passed through a mass of oxide at a volume velocity not <4,000, with stepwise increase of temperature 375°–500°.

1984. LACOMBLE, A. E. (Shell Development Co.). Method for Conducting Chemical Reactions in Fluid Media. Canadian Patent 464,217, Apr. 4, 1950; appl. filed Oct. 8, 1946.

Hydrogenation of oxides of C is effected by passing a gaseous mixture of H_2 and CO under reaction conditions of temperature and pressure through a narrow space between 2 concentric, relatively smooth surfaces composed of Fischer-Tropsch synthesis catalyst. The inner surface is rotated in such a manner and the reaction zone is of such cross section and length that the desired throughput and space velocity are maintained with nonturbulent, eddylike flow. A substantially uniform temperature is maintained throughout the reaction zone by removing the exothermic heat through the walls. One of the walls may be transparent to light of a catalyzing wavelength.

LAGELBAUER, E. *See* abs. **2378.**

1985. LAIDLER, K., AND WISNIEWSKI, J. (Bamag, Ltd.). Gasification by Fluidization Process. British Patent 647,706, Dec. 20, 1950.

Lignite, brown coal, reactive coke, etc., are contacted under fluidized conditions with steam and air at pressures of 10–20 atm. to produce a gas containing H_2 and C oxides with or without N_2 and/or CH_4.

LAINAU, C. A. *See* abs. **1003, 1048.**

LAING, B. *See* abs. **2529, 2530.**

1986. LAMB, S. A. (Imperial Chemical Industries Ltd.). Production of Aldehydes From Olefins. British Patent 667,093, Jan. 31, 1949. British Abs., 1952, B II, p. 584; Chem. Abs., vol. 47, 1953, p. 5426.

Aldehydes may be obtained in improved yields from a mixture of olefins containing C_2H_4 by decreasing the C_2H_4 content in the mixture to < 5% by distillation before carbonylation and treating the resulting mixture with CO and H_2 (1 : 3) at 100°–180° and 200–300 atm. in the liquid phase and in presence of a catalyst, which is a Co salt of an organic carboxylic acid (Co naphthenate or acetate) dissolved in the liquid. Thus, 2 : 2 : 4–trimethylpent–3–ene freed from C_2H_4 by distillation and containing Co naphthenate (0.1% Co) is fed at 100 cc per hr, together with H_2–CO (3 : 1) mixture at 200 l. peh hr. into a Cu-lined converter of 1-l. capacity at 145° and 250 atm. A product is obtained containing 10 wt. % of CO group, corresponding to nonyl aldehyde (50%).

1987. LANCE, D., AND ELWORTHY, E. G. Formaldehyde, Formic Acid, and Methanol From Methane. British Patent 352,687, Mar. 24, 1905. Chem. Abs., vol. 1, 1907, p. 380.

Process of manufacturing formaldehyde, formic acid, MeOH, and other derivatives, consisting in oxidizing CH_4 with hydrogen peroxide in the presence of ferrous sulfate, $CH_4+H_2O_2=CH_3OH+H_2O$, or also by persulfuric acid obtained by subjecting a sulfuric acid of 1.35–1.50 to an electric current of 500 amp. to the square decimeter. There is formed persulfuric acid, $H_2S_2O_8$, which takes up H_2O and gives monosulfuric acid, H_2SO_5, and sulfuric acid. CH_4 can be oxidized by ozone or by monopersulfuric acid, with the addition of permanganates to obtain formic acid, which is distilled at 340°–350° with lime to obtain MeOH, which, oxidized, finally gives formaldehyde.

1988. ———. Methyl Alcohol From Methane. British Patent 7,297, Mar. 26, 1906. Chem. Abs., vol. 1, 1907, p. 1193.

Process of manufacturing MeOH from CH_4, consisting in carrying on the oxidation in the presence of hydrogen peroxide alone, or with either monopersulfuric acid or ferrous sulfate or in the presence of monopersulfuric acid alone.

1989. LANDGRAF, A., AND ROELEN, O. [Oxygen-Containing Derivatives of Aliphatic Hydrocarbons.] Norwegian Patent 64,956 no date.

See United States patent 2,415,102 (abs. **1991**).

1990. ———. [Oxygen-Containing Derivatives of Aliphatic Hydrocarbons.] Swedish Patent 102,819; no date.

See United States Patent 2,415,102 (abs. **1991**).

1991. ———. Oxygen-Containing Derivatives of Aliphatic Hydrocarbons. United States Patent 2,415,-102, Feb. 4, 1947. Chem. Abs., vol. 41, 1947, p. 3116.

Mixtures of C_{10}–C_{19} alkenes are separated into C_{10}–C_{12}, b. 165°–220°, C_{13}–C_{14}, b. 220°–255°, C_{15}–C_{16}, b. 255°–295°, and C_{17}–C_{19} b. 295°–330°, fractions, and each fraction is converted, catalytically, with CO and H_2, to the aldehyde. These aldehydes, or the alcohols or acids derived from them, are readily separable by distillation into pure compounds iso-AmOH, b. 130°, and *sec*-AmOH, b. 113°, were obtained from isobutylene. 1–Butene gave AmOH, b. 138°.

LANE, S. C. *See* abs. **3364.**

LANGHEIM, R. *See* abs. **1910.**

LANGHEINRICH, H. *See* abs. **1037, 1038.**

1992. LANNING, W. C. (Phillips Petroleum Co.). Hydrocarbon Synthesis Process. United States Patent 2,573,795, Nov. 6, 1951; appl. filed Aug. 16, 1948, Serial No. 44,447; 8 claims (*Cl. 260–449.6*).

Describes a method for synthesizing hydrocarbons and oxygenated organic compounds by passing a $CO:H_2$ mixture in the ratio of 1 : 1 to 1 : 3 through a fluidized bed of catalyst at suitable reaction conditions and for simultaneously effecting regeneration of the catalyst. The reactor consists of a single, vertical, elongated chamber in which 2 zones of differing temperature conditions are maintained, the lower comprising at least ½ of the catalyst bed wherein the temperature is from 290°–340° and suitable for the synthesis reaction, and the upper having a temperature of 300°–500° suitable for the regeneration. The temperature in the upper or regenerating zone is maintained at a suitable level by introducing fresh synthesis gas or additional H_2-rich gas such as tail gas from the process. The agitation and turbulence of the fluidized bed causes a constant interchange of catalyst particles between the 2 zones, whereby the synthesis reaction and the regeneration of the catalyst are effected simultaneously.

1993. ——— (Phillips Petroleum Co.). Prevention of Solid Deposits in Fischer-Tropsch Plant Lines. United States Patent 2,572,633, Oct. 23, 1951; appl. filed Sept. 10, 1948, Serial No. 48,718; 8 claims, (*Cl. 260–449.6*). Chem. Abs., vol. 46, 1952, p. 711.

In the hydrogenation of CO to produce hydrocarbons and oxygenated products in the presence of a fluidized catalyst, condensation and accumulation of solid materials in the lines down stream from the synthesis and the catalyst regeneration zones are prevented by injecting into the effluent 10–50 mol. % of a selected hydrocarbon or product fraction b. 200°–400°, which is partially vaporized upon coming in contact with the hot effluent gases. The effluent gas containing the vaporized portion is then cooled enough to condense the latter, and the waxlike material dispersed in the

effluent gas is carried down with the condensing material and removed from the system.

1994. LAPESSÉ, G. V. E. [Hydrogenation Catalyst.] French Patent 977,108, Mar. 28, 1951. Chem. Abs., vol. 47, 1953, p. 3496.

An Al tape, 12 mm. wide and 0.4 mm. thick, is passed at the rate of 1 m. per sec. before a sandblast jet and then before an oxyacetylene spray pistol, which is adjusted to give an oxidizing flame and is fed with a 90 : 10 mixture of Ni oxide and Ce oxide. When both sides of the foil have been coated, small rolls of the coated Al are reduced in H_2. The coating may be a metal which is oxidized after the spraying or the metal from the pistol may be oxidized during the spraying. The Al support may be replaced by active C, cement, porcelain, Fe, Co, Ni, and Zn.

1995. ———. [Hydrogenation Catalyst.] French Patent 977,109, Mar. 28, 1951. Chem. Abs., vol. 47, 1953, p. 3496.

Describes an apparatus in which the catalyst mentioned in French Patent 977,108 (abs. **1994**) is used for a hydrogenating process.

LAPPE, F. *See* abs. **782, 2689.**

1996. LAPPE, F., PIER, M., RUMPF, W., AND STERN, G. (I. G. Farbenindustrie A.-G.). [Oxygenated Organic Compounds From Carbon Monoxide and Hydrogen.] German Patent 580,695, July 14, 1933. Chem. Abs., vol. 28, 1934, p. 171.

Parts of the apparatus that come into contact with CO are made of or lined with steel containing a substantial proportion of Mn. Addition to German Patents 559,892 (abs. **1377**) and 490,248 (abs. **2679**).

1997. LARSON, A. T. (E. I. du Pont de Nemours & Co.). Aliphatic Esters. United States Patent 2,135,450, Nov. 1, 1938; appl. filed Dec. 13, 1935, Serial No. 54,324; 20 claims (*Cl. 260–496*). Chem. Abs., vol. 33, 1939, p. 992.

For the production of an ester such as MeOAc or Et propionate, an aliphatic ether such as Me_2O or Et_2O is condensed with CO in the presence of a halide of an amphoteric element such as BF_3 or of elements which on hydrolysis form weak bases to give an ester under elevated pressure, an aliphatic ether being added to the reaction mixture and the ester formed is distilled from the resulting solution.

1998. ——— (E. I. du Pont de Nemours & Co.). Amine Synthesis. United States Patent 2,497,310, Feb. 14, 1950. Chem. Abs., vol. 44, 1950, p. 4489.

Organic amines are prepared by treating an unsaturated compound containing a nonbenzenoid double bond with CO, H_2, and NH_3 or a substituted amine having at least 1 H attached to the amino N. At 160°–260° with 100–2,000 atm., Co, Ni, Ru, Fe, and Cu compounds, particularly carbonyls, are satisfactory catalysts. Et_2O (75 ml.), 17 gm. NH_3, 20 gm. fused Co catalyst, and 28 gm. C_2H_4 were heated 1.5 hr. at 170°–262° under 470–755 atm. of gas ($4H_2$: CO); distillation gave a mixture of propylamines. C_2H_4 (14 gm.), 17 gm. NH_3, 64 ml. cyclohexane, and 10 gm. reduced CuO catalyst heated in a Ag-lined pressure vessel 1 hr. at 246°–250° under 560–850 atm. gas (CO : $2H_2$) gave on distillation 13.1 gm. Pr_2NH, b. 108°–125°, and a mixture of $EtCONH_2$ and 2-ethyl-3,5-dimethylpyridine.

1999. ———. Ammonia Synthesis. United States Patent 1,667,322, Apr. 24, 1928. Chem. Abs., vol. 22, 1928, p. 2035.

Catalyst is prepared by forming particles from an intimate mixture of Fe oxide, K_2O, and MgO and treating the particles with a H_2-containing gas at 300°–700°.

2000. ———. Ammonia Synthesis. United States Patent 1,667,323, Apr. 24, 1928. Chem. Abs., vol. 22, 1928, p. 2035.

Fe oxide and the oxides of Mg and Na are used in a process similar to that described in United States Patent 1,667,322 (abs. **1999**).

2001. ——— (E. I. du Pont de Nemours & Co.). Carboxylic Acids. United States Patent 2,448,375, Aug. 31, 1948. Chem. Abs., vol. 43, 1949, p. 670.

Aliphatic carboxylic acids, such as $EtCO_2H$, are prepared by the reaction of steam, CO, and an olefinic hydrocarbon at 500–1,500 atm. in the presence of a catalyst, such as NiCO or CoCO and active C, at 200°–400°.

2002. ——— (E. I du Pont de Nemours & Co.). Catatlyst for Methanol Production. United States Patent 1,844,857, Feb. 9, 1932; appl. filed May 14, 1925. Chem. Abs., vol. 26, 1932, p. 1946.

Catalyst for effecting reactions between H_2 and CO is formed by melting together an oxide of a metal, such as Ti, Cr, Mn, Zn or Mo, and a readily reducible oxide of a good heat-conducting metal, such as Cu oxide, to produce a uniform mixture of the oxides, followed by cooling, granulating, and reducing the granulated material with H_2 at an elevated temperature to form a catalytic oxide intimately associated with a good heat-conducting metal.

2003. ——— (E. I. du Pont de Nemours & Co.). Catalysts for Producing Methanol. United States Patent 1,939,708, December 19, 1933; appl. filed June 28, 1927. Chem. Abs., vol. 28, 1934, p. 1364.

Catalyst for gaseous phase reactions, such as the production of MeOH from CO and H_2, comprises the reaction product of a fused mixture of Cu oxide, Mn oxide, and an oxide of Mg, Al, or Si.

See also United States Patent 1,908,484 (abs. **2004**).

2004. ——— (E. I. du Pont de Nemours & Co.). Catalysts Suitable for Methanol Synthesis. United States Patent 1,908,484, May 9, 1933; appl. filed Apr. 27, 1931. Chem. Abs., vol. 27, 1933, p. 3724.

In preparing a catalyst, a solution of a sexivalent Cr compound, such as chromic acid, is mixed with a soluble hydroxide, such as NH_4OH, and the salt of a heavy metal, the hydroxide of which is oxidizable by the sexivalent Cr, such as $FeSO_4$.

See also United States Patents 1,844,129 (abs. **2008**) and 1,844,857 (abs. **2002**).

2005. ——— (Lazote, Inc.). Methanol. Canadian Patent 307,671, Jan. 13, 1931. Chem. Abs., vol. 25, 1931, p. 972.

MeOH is manufactured by passing a gaseous mixture containing CO and H_2, at a pressure of 400–1,000 atm. and a temperature of 250°–500°, over a heated catalyst consisting of the reduction product of a fused mixture of Cu oxide and an oxide of one of the elements of the group Mn, W, Zn, Cd, and Mo.

2006. ——— (E. I. du Pont de Nemours & Co.). Methanol Synthesis. United States Patent 2,061,470, Nov. 17, 1936. Chem. Abs., vol. 31, 1937, p. 710.

Gaseous mixture containing H_2 and an oxide of C is subjected at an elevated temperature and pressure (suitably 250°–400° and 900 atm.) to the action of a catalyst comprising the reduction product of a fused mixture containing 1–5% of an oxide of Cr, V, Zr, Al, Mg, Ti, Th, Si, or Ce and about 95–97% of Cu oxide and Mn oxide (the Cu oxide being excess).

2007. ——— (E. I. du Pont de Nemours & Co.). Organic Acids From Ketones. United States Patent 2,273,785, Feb. 17, 1942; appl. filed Aug. 12, 1939, Serial No. 289,830; 14 claims (*Cl. 260–540*). Chem. Abs., vol. 36, 1942, p. 3810.

Aliphatic ketone, such as methyl ethyl ketone for the production of methyl-sec-butylacetic acid, and H_2O are heated in the liquid phase with CO at a temperature < 350° (suitably 150°–165°) and under a pressure at least of 10 atm. (suitably 700 atm.) in the presence of a liquid catalyst comprising BF_3 and H_2O.

2008. ——— (E. I. du Pont de Nemours & Co.). Synthesis of Methanol. United States Patent 1,844,129, Feb. 9, 1932; appl. filed Apr. 14, 1927, Serial No. 183,905. Chem. Abs., vol. 26, 1932, p. 1946.

Gaseous mixture containing CO and H_2 is passed over a heated catalyst consisting of the reduction product of a fused mixture of Cu oxide and an oxide of one of the elements Mn, W, Zn, Cd, and Mo.

2009. ——— (E. I. du Pont de Nemours & Co.). Synthesis of Organic Acids From Olefinic Hydrocarbons, Water, and Carbon Monoxide. United States Patent 2,079,216, May 4, 1937; appl. filed Mar. 25, 1933, Serial No. 662,854; 4 claims (*Cl. 260–116*). Chem. Abs., vol. 31, 1937, p. 4345.

For the production of an aliphatic monocarboxylic acid such as propionic acid, an olefin such as C_2H_4 is reacted with H_2O and CO (suitably at a temperature of about 325° and under a pressure of about 700 atm.) in the substantial absence of O_2 in a vessel, the inner surfaces of which are lined with a metal containing at least 95% Cu.

2010. Larson, A. T., and Vail, W. E. (E. I. du Pont de Nemours & Co.). Aliphatic Carboxylic Acids. United States Patent 1,924,765, Aug. 29, 1933; appl. filed Nov. 25, 1931, Serial No. 577,392; 10 claims (*Cl. 260–116*). Chem. Abs., vol. 27, 1933, p. 5340.

Production of aliphatic carboxylic acids such as propionic acid from steam, CO, and an olefinic hydrocarbon such as C_2H_4 is effected in the presence of active C and an NH_4 halide such as NH_4Cl.

2011. Latta, J. E. (Stanolind Oil & Gas Co.). Method of Forming Highly Active Catalytic Surfaces. United States Patent 2,548,801, Apr. 10, 1951; appl. filed Aug. 9, 1949, Serial No. 109,423; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 5910.

Mixture of raw hydrocarbon synthesis catalyst and oil or wax as binding agent are used as a catalytic coating for the synthesis reactor. The mixture is deposited on the walls of the reactor and then is subjected to reducing action to obtain a substantially pure metal catalyst, after which the synthesis process can be carried on in the reactor. The oil or wax formed during the synthesis acts as a continuously generated binder to hold the catalyst as a film on sides of the reactor. 6 United States patents cited.

———. *See* abs. **3861.**

2012. Laubi, O. (Krebs & Co. A. G.). Carbon Monoxide-Hydrogen Mixture From Hydrocarbons. Swiss Patent 267,907, July 1, 1950. Chem. Abs., vol. 45, 1951, p. 2182.

Hydrocarbons heated to high temperatures decompose almost entirely into saturated and unsaturated lower hydrocarbons of the aliphatic series and then into C and H_2 if the temperature is high enough. Such C formation may be avoided by adding O_2 or H_2O vapor. It is advantageous to supply the O_2 by means of a metal oxide, such as Fe_2O_3, and then to recirculate the reaction products over this oxide after at least partial removal of CO_2 and H_2O. This process may also be used for the simultaneous reduction of metallic oxides to the metal. The reaction products consist essentially of H_2 and CO.

Laudenklos, H. *See* abs. **3224, 3953, 3954, 3955, 3956.**

Lauer, G. G. *See* abs. **195.**

2013. Lauer, G. G., and Passino, H. J. (M. W. Kellogg Co.). Separation of Organic Compounds. United States Patent 2,516,127, July 25, 1950; appl. filed Apr. 20, 1948, Serial No. 22,108; 28 claims, (*Cl. 260–450*). Chem. Abs., vol. 45, 1951, p. 1156.

To effect precipitation of the alkaline earth salts of the acids so that phase separation as described in United States Patent 2,516,126 (abs. **2015**) can take place, certain low-boiling solvents are added to the mixtures of H_2O-insoluble nonacid oxygenated organic C_{4+} compounds. The addition of the solvent gives a phase separation, the upper phase containing oxygenated compounds substantially free of acids and acid salts, dissolved in the solvent, and the lower phase containing all of the acids present in the original mixture in the form of their corresponding alkaline earth salts and the remaining oxygenated compounds. The solvent is a H_2O-insoluble organic C_5–C_{12} compound, such as a hydrocarbon or a mixture of saturated and unsaturated hydrocarbons, or an O_2-containing organic compound, such as an ether or a ketone. 5 United States patents cited.

2014. Lauer, G. G., and Pratt, R. S. (M. W. Kellogg Co.). Separation of Iron From Hydrocarbons. United States Patent 2,540,129, Feb. 6, 1951; appl. filed Oct. 31, 1947, Serial No. 783,450; 4 claims, (*Cl. 196–44*). Chem. Abs., vol. 46, 1952, p. 2272.

Fe is separated from mixtures, containing it, a hydrocarbon, and a carbonyl, produced in the catalytic hydrogenation of C oxides by treating the mixture with an aqueous solution containing about 1–40 wt. % $NaHSO_3$ to produce a ferruginous sulfite without reacting with the carbonyl and separating the sulfite solution from the mixture. Example: 2 l. of a mixture comprising C_4 and higher hydrocarbons and H_2O-insoluble oxygenated organic compounds in minor amounts was found to contain 0.152 wt. % Fe as Fe_2O_3. The mixture was agitated for 5 min. with 400 ml. of a 5% by wt. aqueous solution of Na_2SO_3. After settling, the lower aqueous phase containing $Fe_2(SO_4)_3$ was withdrawn, and the upper oil phase was again treated with 20% of its volume of the same solution. After a total of 5 washes the oil was found to contain 0.002% Fe as Fe_2O_3.

2015. Lauer, G. G., Passino, H. J., and Segesser, J. R. (M. W. Kellogg Co.). Separation of Organic Compounds. United States Patent 2,516,126, July 25, 1950; appl. filed Mar. 2, 1948, Serial No. 12,524; 17 claims, (*Cl. 260–450*). Chem. Abs., vol. 45, 1951, p. 1155.

In Fischer-Tropsch synthesis there is obtained a hydrocarbon-rich phase containing oxygenated organic acid and nonacid compounds having at least 4 C atoms/mol. The acids are separated as their corresponding alkali salts by using at least 1 compound such as oxide, hydroxide, or carbonate of the alkaline earth metals, Co, Ba, Mg, in amount sufficient to convert all of the acids to a solution of their corresponding alkaline earth salts. In phase separation, the upper phase contains the nonacid oxygenated compounds and hydrocarbons and the lower phase the alkaline earth salts and the remaining nonacid oxygenated compounds and hydrocarbons. The lower phase is treated with enough alkali, such as NaOH or KOH, to convert the alkaline earth salts to their corresponding alkali salts and to form the hydroxide of the alkaline earth metal. The hydroxide is then separated by filtering or centrifuging. The lower phase is also treated with an aqueous solution of a H_2O-soluble alcohol in amount sufficient to absorb all of the alkali salts of organic acids present. Nonacid oxygenated compounds are extracted with a H_2O-soluble organic compound such as a C_5–C_{12} hydrocarbon. The 3 treating agents may be mixed or used in successive steps in any desired order. The treated lower phase material is phase

subjecting an oxalate to thermal decomposition in an oxidizing atmosphere.

2024. ——— (E. I. du Pont de Nemours & Co.). Catalyst for Hydrogenation Reactions. United States Patent 1,746,782, Feb. 11, 1930; appl. filed June 12, 1926, Serial No. 115,692. Chem. Abs., vol. 24, 1930, p. 1649.

In the process of United States Patent 1,746,781 (abs. **2023**) a chromite catalyst is used, prepared by calcining at a red heat a sexivalent Cr salt containing a hydrogenating metal, for example, Zn chromate.

2025. ——— (E. I. du Pont de Nemours & Co.). Catalyst for Hydrogenation Reactions. United States Patent 1,746,783, Feb. 11, 1930; appl. filed Nov. 3, 1928, Serial No. 317,119. Chem. Abs., vol. 24, 1930, p. 1649.

In producing MeOH from CO and H_2, catalysts are employed comprising a chromite prepared by igniting an exothermic double salt containing sexivalent Cr and a hydrogenating metal, for example, a double chromate of NH_4 and Zn.

2026. ——— (Canadian Industries, Ltd.). Catalyst for Organic Reactions. Canadian Patent 315,876, Oct. 6, 1931. Chem. Abs., vol. 26, 1932, p. 1296.

Catalyst is prepared by heating a double chromate of a nitrogen base and Mn to its spontaneous decomposition temperature. The product may be used for synthesis of MeOH.

2027. ———. Catalysts for Methanol Synthesis. British Patent 272,555, June 12, 1926. Chem. Abs., vol. 22, 1928, p. 1782.

Catalysts are prepared by (*a*) igniting a metallic chromate or dichromate at 600°–1,000°; or, (*b*) prolonged heating to redness of mixtures of metallic oxides or salts such as chlorides with alkali chromates or dichromates; or, (*c*) igniting at redness a double chromate or dichromate of a metal with NH_3 or an organic base, such as aniline and pyridine. The product is preferably washed with a weak acid, such as diluted HOAc, to remove compounds other than chromites, and the porous material is then dried. It may be used in MeOH synthesis or for producing other oxygenated organic compounds for producing H_2 from CO and steam or for dehydrogenation processes, such as production of aldehyde from alcohol. For producing MeOH, the chromites of Zn, Cu, Cd, Mg, Mn, Ag, and Fe or their mixtures are suitable. Several examples given.

2028. ——— (E. I. du Pont de Nemours & Co.). Catalysts Suitable for Use in Hydrogenation Reactions. United States Patent 2,066,153, Dec. 29, 1936. Chem. Abs., vol. 31, 1937, p. 1172.

Catalyst is prepared by precipitating from an aqueous medium with a chromate of a N base, such as $(NH_4)_2CrO_4$, a mixture of metal chromates, such as those of Zn, Cu, and Cd, at least one of which is a chromate of a hydrogenating metal, the oxide of which, when exposed for several hr. in the pure state to the action of H_2 at 400°, will remain substantially in the oxide form, and another of which is a chromate of a metal, the oxide of which, when likewise treated with H_2, will be reduced substantially to the metal, and the mixture of metal chromates is converted into one containing the corresponding metal chromates. Various details and examples given.

2029. ———. Catalytic Production of Oxygenated Carbon Compounds. British Patent 301,806, June 12, 1926. Chem. Abs., vol. 23, 1929, p. 4306.

Catalysts for use in reactions such as that of CO with H_2 or steam or in dehydrogenation of compounds such at EtOH are prepared by heating to decomposition a double chromate of a nitrogenous base such as NH_4 or pyridine and 1 of the metals Zn, Cu, Cd, Mg, Mn, Ag, and Fe. The catalysts may be rendered more active by leaching with a "weak" acid such as 5–10% HOAc. Examples are given of the production of MeOH and higher alcohols from CO and H_2. Preparation of basic $ZnNH_4$ chromate, $MnNH_4$ chromate, and Zn bichromate tetrapyridine described.

2030. ——— (E. I. du Pont de Nemours & Co.). Catalytic Reactions Such as the Production of Ethyl Acetate From Ethyl Alcohol. United States Patent 1,964,001, June 26, 1934. Chem. Abs., vol. 28, 1934, p. 5076.

Reaction such as the production of EtOAc from EtOH is effected with a catalyst containing a plurality of hydrogenating metal chromites such as those of Zn, Cu, and Cd. Various examples given.

2031. ——— (E. I. du Pont de Nemours & Co.). Catalytic Reactions Such as the Production of Oxygenated Organic Compounds From Hydrogen and Carbon Oxides. United States Patent 1,984,884, Dec. 18, 1934; appl. filed June 6, 1928, Serial No. 283,447 (*Cl. 260–156*). Chem. Abs., vol. 29, 1935, p. 1099.

As a catalytic material in effecting reactions such as production of MeOH, material comprising difficultly reducible basic and acidic oxides, a material amount of which are in loose chemical combination, are employed, such as oxides of Zn and Cr, with the acidic oxide or oxides predominating in the catalyst.

2032. ——— (E. I. du Pont de Nemours & Co.). Methanol Synthesis. United States Patent 1,829,046, Oct. 27, 1931; appl. filed Dec. 21, 1929, Serial No. 415832. Chem. Abs., vol. 26, 1932, p. 737.

Reaction mixture comprising CO and H_2 is passed at a temperature of about 350°–475° and under a pressure of about 280 atm. or higher over a catalyst prepared by heating a double chromate of an N base, such as NH_4 and Mn, to its spontaneous decomposition temperature. General reference is made to the use of a similar catalyst in various reactions.

———. *See* abs. **205.**

2033. LAZIER, W. A., AND ZEISBERG, F. C. (E. I. du Pont de Nemours & Co.). Catalysts for Hydrogenation, Dehydrogenation, or Synthesis of Organic Compounds. British Patent 313,093, June 6, 1928. Chem. Abs., vol. 24, 1930, p. 860.

In various processes such as MeOH synthesis or conversion of iso-Pr alcohol into acetone, mixtures of basic and acidic oxides (with the latter in excess) are used, prepared either by admixture or by igniting compounds, such as basic $ZnNH_4$ chromate, with or without small additions of alkali metal compounds, such as sulfates, phosphates, chromates, hydroxides, carbonates, metallates, or organic salts.

2034. LAZOTE, INC. [Purifying Hydrogen; Ammonia Synthesis; Hydrogenation of Oils.] French Patent 623,068, Sept. 22, 1926. Chem. Zentralb., 1927, II, p. 2570.

See British Patent 258,887 (abs. **3944**).

———. *See* abs. **2005, 3745, 3944.**

LEE, H. *See* abs. **2432.**

2035. LEFFER, F. W. (Universal Oil Products Co.). Apparatus for Effecting Fluidized Contact Between Solid Particles and Fluid Mediums. United States Patent 2,584,391, Feb. 5, 1952; appl. filed Mar. 29, 1947, Serial No. 738,130; 5 claims (*Cl. 23–288*).

Apparatus is described for nonmechanically contacting fluid media with finely divided solid particles in exothermic reactions, such as the Fischer-Tropsch synthesis, or for the catalytic hydrogenation of olefinic compounds with regeneration of the catalysts.

2036. ——— (Universal Oil Products Co.). Diesel Engine Fuel. United States Patent 2,281,362, Apr. 28,

1942; appl. filed Jan. 13, 1939, Serial No. 250,772; 8 claims (*Cl. 196–48*). Chem. Abs., vol. 36, 1942, p. 5636.

Arrangement of apparatus and a process are described for treating a synthetic hydrocarbon oil resulting from the interaction of CO and H_2 to produce a diesel fuel of unusually high cetane number.

2037. LEFORT, T. E. Catalyzer for Methanol Synthesis. Canadian Patent 276,300, Dec. 13, 1927. Chem. Abs., vol. 22, 1928, p. 1980.

Catalyzer consists of a finely ground mixture of Zn and Bi_2O_3 in the proportion of 3 mol. Zn : 1 mol. Bi_2O_3.

LEITHE, W. *See* abs. **2085.**

2038. LEPRESTRE, R. (Applied Chemicals, Inc.). Liquid Hydrocarbons From Natural Gas and Superheated Steam. United States Patent 2,258,511, Oct. 7, 1941; appl. filed May 13, 1939, Serial No. 273,533; 3 claims (*Cl. 260–449*). Chem. Abs., vol. 36, 1942, p. 642.

Describes apparatus and a process that involves simultaneously injecting natural gas and superheated steam under a pressure in excess of a minimum of 5,000 p. s. i. into a chamber heated to approximately 1,000°–1,100° F. and then subjecting the heated mixture to a catalyst of Fe oxide and passing the product to a condenser.

LEVY, W. J. *See* abs. **2823.**

2039. LEWIS, W. K. (Standard Oil Development Co.). Gas Rich in Carbon Monoxide. United States Patent 2,631,934, Mar. 17, 1953. Chem. Abs., vol. 47, 1953, p. 6637.

Gas rich in CO is prepared in a 2-stage process from solid carbonaceous material. In the 1st zone, fluidized carbonaceous material is brought into contact at 1,500°–2,000° F. with feed gas rich in CO_2, steam, and O_2 to reduce CO_2 and steam completely and obtain product gas high in CO. The carbonaceous material is withdrawn and charged to a 2d zone where, at 1,500°–2,500° F. for combustion of C but low enough to prevent sintering of ash, steam and O_2 are brought into contact with the fluidized mass to prepare feed gas for the 1st zone.

2040. ——— (Standard Oil Development Co.). Production of Fuel Gases. United States Patent 2,623,817, Dec. 30, 1952; appl. filed Apr. 3, 1946, Serial No. 659,409; 14 claims (*Cl. 48–203*). Chem. Abs., vol. 47, 1953, p. 2964.

Cool water gas is obtained from carbonaceous material in a 2-stage process—a reduction stage and an oxidation stage. The raw material of 10- to 50-mesh size is mixed with an inert heat carrier, such as 10- to 100-mesh sand, and fed to the reduction stage. The material then passes from the reduction stage to the oxidation or C cleanup stage where all the air required for the production of the ultimate gas is supplied. Off gas from the oxidation stage is fed to the reduction stage. The heat carrier allows use of preheated air in the oxidation zone without any loss in capacity. The heated carrier is then conveyed to the reduction zone where it supplies heat for the endothermic reactions. 1 literature ref., 1 foreign patent and 9 United States patents cited.

2041. ——— (Standard Oil Development Co.). Production of Gas Mixture Containing Carbon Monoxide and Hydrogen. United States Patent 2,607,670, Aug. 19, 1952; appl. filed Aug. 15, 1947, Serial No. 768,892; 3 claims (*Cl. 48–196*).

Synthesis gas is produced by contacting hydrocarbon gases with a fluidized metal oxide catalyst capable of oxidizing hydrocarbons to CO and H_2 at temperatures below the sintering temperature of the metal oxide but high enough to cause conversion of a major part of the hydrocarbons. The product gas from this step containing unconverted hydrocarbons is contacted in a 2d step with O_2 at a temperature high enough to complete the oxidation of the hydrocarbons to CO and H_2. A satisfactory temperature for the 1st step is 1,400°–1,600 F. and for the 2d, 2,100°–2,300° F. About 8–12% by vol. of O_2 of 95% purity is usually sufficient. As catalyst of the reaction TiO_2 promoted with a composite of a major proportion of Fe_2O_3 and minor proportions of NiO and Cr_2O_3, is of particular advantage. Gas velocities of about 1–2 ft. per sec. have been found suitable for proper fluidization and residence time.

2042. ——— (Standard Oil Development Co.). Temperature Control Means. United States Patent 2,474,583, June 28, 1949; appl. filed Jan. 19, 1946, Serial No. 642,397; 6 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 6478.

Describes method for abstracting heat from a system comprising a lower dense phase and an upper dilute phase suspension of powdered catalyst in a gas. In one modification the catalyst to be cooled is passed through a drum, either vertical or horizontal, in such a way as to maintain a dense bed of catalyst in the drum. At the top part of the drum above the dense bed are boiler tubes in which steam is generated. A liquid product of proper boiling range is injected into the drum. The liquid, on falling on the dense bed, is immediately vaporized by the hot catalyst, which is thereby cooled. The vapors rise to the top part of the drum where they are condensed on the boiler tubes and the cycle continued indefinitely. In a calculation of the necessary heat transfer surface to abstract the heat from the reaction zone for a hydrocarbon synthesis plant producing 10,000 bbl. liquid hydrocarbons per day, the figure of 26,700 sq. ft. for this method is compared to 228,000 sq. ft. for boiler tubes disposed within the dense phase. 1 foreign patent and 9 United States patents cited.

———. *See* abs. **1959.**

2043. LEWIS, W. K., AND GILLILAND, E. R. (Standard Oil Development Co.). Control Method in Reactions Between Hydrocarbons and Metal Oxides. United States Patent 2,603,608, July 15, 1952; appl. filed Nov. 29, 1950, Serial No. 198,144; 12 claims (*Cl. 252–373*). Chem. Abs., vol. 46, 1952, p. 9829.

Present method for controlling a CH_4 re-forming operation wherein it is desired to produce a suitable hydrocarbon synthesis gas. The metal oxide used as catalyst of the conversion is CuO on silica gel at a temperature 2,000°–2,400° F. Control of the reformer gas composition is closely related to the CO_2 content of the gas stream.

2044. LEWIS, W. K., AND MAIN, T. C. (Standard Oil Development Co.). [Synthetic Hydrocarbons.] French Patent 955,836, Jan. 19, 1950; appl. filed Nov. 19, 1947; in United States, Nov. 22, 1946. Chem. Zentralb., 1950, II, p. 339.

Hydrocarbons and oxygenated derivatives are produced from CO and H_2 by use of a fluidized catalyst of powdered Fe at temperature and pressure, respectively, of 274°–343° and 17.5–49.2 atm. To maintain the heat capacity in the catalyst bed, there is added to the fine catalyst material about 60% of a somewhat larger particle size Fe powder of 80–200μ. The total amount of fine catalyst material of 0–20μ should not exceed 20%.

LEY, H. *See* abs. **2822.**

2045. LICHTENBERGER, T., AND KAISER, L. [Carbon Monoxide and Hydrogen.] French Patent 812,376, May 8, 1937. Chem. Abs., vol. 32, 1938, p. 1,059.

Gas produced in a shaft gas generator and steam pass downwardly through the fuel and then through a fused salt bath so that the CO_2 is completely reduced to CO

Ethylene. United States Patent 2,135,459, Nov. 1, 1938; appl. filed July 7, 1936, Serial No. 89,457; 11 claims (*Cl. 260–533*). Chem. Abs., vol. 33, 1939, p. 996.

Process for the preparation of aliphatic carboxylic acids such as propionic acid from a hydrating agent such as H_2O, CO and an olefin such as C_2H_4 is carried out in the presence of an added condensing agent containing BF_3 and not more than 5-mol. proportions of H_2O (suitably 1–3 mols.). Gives several examples with details.

2070. ——— (E. I. du Pont de Nemours & Co.). Synthesis of Organic Acids Higher Than Acetic Acid. United States Patent 2,162,459, June 13, 1939. Chem. Abs., vol. 33, 1939, p. 7820.

Process for the preparation of acids, such as propionic acid and their esters, involves treating CO in the presence of a volatile catalyst containing B and F atoms, such as BF_3, with a saturated aliphatic monohydric alcohol, such as EtOH, containing at least 2 C atoms or compounds which give such alcohols upon hydrolysis.

2071. LOHRISCH, W. (J. Pintsch Kom.-Ges.). [Process for the Production of Synthesis Gas.] German Patent 744,224, July 21, 1944; appl. P 84,975, filed Oct. 7, 1942 (*Cl. 26 a–18.01*). TOM Reel 67, item 75, frames 1,120–1,121; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 6, chap. 174, 1949, p. 31.

3 CH_4 with 1 CO_2 and 2 H_2O are passed through a heat exchanger to the converter, which is heated to reaction temperature by combustion of another CH_4, and there converted into synthesis gas with proportions of 4 CO : 8 H_2. The latter passes through the heat exchanger to storage and gives up its heat to the incoming raw gas mixture. The hot gases from the combustion of the CH_4, after heating the converter, are used to produce the steam for the process and then are scrubbed for the CO_2. The steam and the CO_2 thus produced are combined with the raw CH_4 to begin another cycle.

LONDON TESTING LABORATORY, LTD. *See* abs. **3625, 3633.**

LONG, F. M. *See* abs. **1786, 1787.**

LONGLEY, R. I., JR. *See* abs. **622.**

2072. LORENZ, L. (Badische Anilin- u. Soda-Fabrik). [Purification and Separation of the Alcohols Belonging to the Isobutyl Series and Obtained by the Hydrogenation of Carbon Monoxide.] German Patent 801,988, Jan. 29, 1951; appl. filed Oct. 2, 1948 (*Cl. 12 o–5.02*). Chem. Zentralb., 1951, II, p. 1060; Chem. Abs., vol. 45, 1951, p. 5175.

Hydrogenation products of CO or their fractions containing alcohols are converted into vinyl ethers, these are fractionally distilled and the pure fractions saponified. The main fraction of a technical isobutyl alcohol boiling within 1° (HO number 26.5, ketone number 2.4) is vinylated with C_2H_2 after addition of 2% Na. The vinyl mixture yields on fractional distillation 90% of a fraction (I) (b. 82°–83°) and a residue, which on further distillation yields in addition to higher boiling residues a fraction (II) (b. 92°–93°). (I), saponified by warming with H_2O with addition of 0.5% H_2SO_4. The distillation yields pure iso-BuOH, b. 107°, HO number 26.8–27, ketone number 0, output about 90%. Similarly, (II) gives pure sec-AmOH, b. 113°, HO number 22.6–22.7, ketone number 0.

LORENZ, W. *See* abs. **2107, 3232.**

2073. LOUGHRAN, R. T. (M. W. Kellogg Co.). Treatment of Hydrocarbon Waxes. United States Patent 2,651,655, Sept. 8, 1953; appl. filed June 29, 1949, Serial No. 101,961; 9 claims (*Cl. 260–450*).

Claim 1. A method for refining a liquid waxy product produced by condensing the product of hydrogenation of oxides of C in the presence of a hydrogenation catalyst at a temperature of 300°–700° F. and at a pressure between atmospheric pressure and 500 p. s. i., said waxy product containing color-imparting metallo-organic compounds and color-imparting unsaturated hydrocarbons, which comprises: Dissolving said waxy product in a solvent; contacting the resulting solution at elevated temperature with a solid adsorbent to separate from said solution said color-imparting metallo-organic compounds; withdrawing the solution from contact with said adsorbent; and further decolorizing the thus partially decolorized waxy product by subjecting said product to hydrogenation in the presence of a hydrogenation catalyst at a temperature of 150°–400° F. and at a pressure of 75–1,500 p. s. i. g. for a residence time at least of 30 min. to convert unsaturated color-imparting hydrocarbons to their corresponding paraffins.

2074. LOWES, A. P., AND IMPERIAL CHEMICAL INDUSTRIES, LTD. Oily Condensation Products. British Patent 493,715, Oct. 12, 1938. Chem. Abs., vol. 33, 1939, p. 2623.

Oily condensation products are obtained by treating with a hydroxide or an anhydrous sulfate or phosphate of Fe, Cr, or Al at $> 200°$ the crude reaction products obtained by the condensation of chlorinated aliphatic hydrocarbons of high molecular weight with aromatic hydrocarbons by the aid of $AlCl_3$ or Al and separating the oily constituents, for example, by decantation or filtration. In an example, chlorinated paraffin containing 22% Cl 650 is treated with C_6H_6 1,050 in the presence of $AlCl_3$ 50 parts and the whole heated to 75° for 3 hr.; the reaction mass separates into 2 layers the lower of which is heated with 40 parts of anhydrated $FeSO_4$ for 30 min. at 300°; the C_6H_6 distills off and the $AlCl_3$ and $FeSO_4$ form a granular, solid mass, which is removed by filtration after cooling, a red-green fluorescent oil of viscosity 200 centistokes at 100° F. being obtained.

2075. LOWES, A. P., WHITE, D. E., AND IMPERIAL CHEMICAL INDUSTRIES, LTD. Lubricating Oils. British Patent 483,316, Apr. 19, 1938. Chem. Abs., vol. 32, 1938, p. 7258.

In the manufacture of lubricating oils by the condensation of chlorinated aliphatic hydrocarbons of high molecular weight with C_6H_6 or its homologs, the chlorinated hydrocarbon is 1st mixed with the aromatic hydrocarbon in the absence of a condensing agent, the mixture is cooled to cause the separation of solids, which are removed, and the residual liquid is then subjected to condensation in the presence of a condensing agent, if desired, with the addition of a further quantity of the aromatic hydrocarbon. Among examples, a mixture of chlorinated paraffin containing 22% Cl with C_6H_6 is cooled to —5°, the solids that separate are filtered off, more C_6H_6 is added, and the mixture heated with $AlCl_3$.

2076. ———. Lubricating Oils. British Patent 485,165, May 11, 1938. Chem. Abs., vol. 32, 1938, p. 7716.

In manufacturing condensation products by condensing a chlorinated aliphatic hydrocarbon of high molecular weight with an aromatic hydrocarbon, for example, C_6H_6, PhMe, by the aid of $AlCl_3$, the upper layer is separated after the condensation and treated at ordinary or slightly elevated temperature (30°–40°) with a solid alkaline-reacting material or with an aqueous solution of NH or of an alkaline NH salt to prevent the formation of an intractable oil emulsion when the excess of C_6H_6 or PhMe is steam distilled off. Chlorinated paraffin wax is preferred as the aliphatic constituent.

LÜBEN, R. *See* abs. **756, 757, 3240.**

LUDEMAN, C. G. *See* abs. **2757.**

LUENING, W. D. *See* abs. **3364.**

2077. LÜHRS, A. (J. Schlickum & Co.). [Saponified Pastes.] German Patent 744,713, Nov. 25, 1943 (*Cl. 22 g–6.02*). Chem. Abs., vol. 39, 1945, p. 3179.

Oxidation products of synthetic paraffins or ceresin are taken together with at least 50% of unsaponifiable substances, such as natural or synthetic paraffins or ceresin. The mixture is saponified with an excess of alkali in the presence of a neutral alkali salt, for example, NaCl.

LUKE, O. V. *See* abs. **2349.**

LURGI GESELLSCHAFT FÜR WÄRMTECHNIK. *See* abs. **2835.**

2078. LUSBY, O. W. Catalysts for Production of Oxygenated Organic Compounds. United States Patent 1,900,829, Mar. 7, 1933; appl. filed June 4, 1927. Chem. Abs., vol. 27, 1933, p. 2961.

Heat resisting catalyst suitable for use in promoting reactions, such as MeOH production from H_2 and C oxides, consists of an intimate mixture of ZnO and a larger proportion of an oxide of Cr.

2079. LUSH, E. J. Formaldehyde; Methane. British Patent 180,016, Feb. 12, 1921. Chem. Abs., vol. 16, 1922, p. 3315.

A gaseous mixture of CO and H_2, such as suction or water gas, is forced under pressure through a catalytic mass consisting of a hydrogen-activating catalyst, such as Ni or Co, and a hydrated metal oxide, such as Al_2O_3 or rare earths, the activity of the mass being maintained either by the introduction of steam into the gaseous mixture or by periodic treatment with steam. HCHO is removed from the product by scrubbing with H_2O; the residual gas, which contains CH_4 and H_2, is of value as illuminating gas.

2080. LUTHER, M. (I. G. Farbenindustrie A. G.). [Oxidation Products of Paraffin Wax.] German Patent 535,068, Aug. 4, 1929. Chem. Abs., vol. 26, 1932, p. 1434.

Oxidation products of solid aliphatic hydrocarbons are separated from unaltered hydrocarbon by centrifuging at a temperature at which the hydrocarbon remains solid. Separated mixtures of oxidation products may be fractionated by centrifuging at a temperature $<$ the melting point of the mixture. Examples are given.

See also German Patent 518,389 (abs. **2082**).

2081. ——— (I. G. Farbenindustrie A. G.). [Preparation of Fat Acids and Alkali Salts From Alkali Soaps and Mineral Acids.] German Patent 707,227, May 15, 1941 (*Cl. 23d–4*). Chem. Abs., vol. 37, 1943, p. 2952.

Mivture of alkali soap and concentrated aqueous solutions of alkali salts of mineral acids is treated with a concentrated mineral acid, preferably the same as in the mixture, dissolved preferably in an alkali solution, preferably the same as in the mixture. The fatty acid and the alkali salt are separated without evaporating the aqueous solution. The mother liquor is used for dissolving further quantities of alkali soap.

———. *See* abs. **494, 742, 2374, 3924, 3925.**

2082. LUTHER, M., AND FRANZEN, H. (I. G. Farbenindustrie A. G.). [Oxidation Products of Paraffin Wax.] German Patent 518,389, Aug. 6, 1927. Chem. Abs., vol. 25, 1931, p. 2558.

Separation of the oxidation products from unaltered hydrocarbon as described in German Patent 467,930 (abs. **2727**) is assisted by pressing the mass. The mixture of oxidation products and unaltered hydrocarbons may first be saponified, and the unsaponifiable portion of the oxidation products then separated from hydrocarbon by warming and pressing.

2083. LUTHER, M., AND JOCHHEIM, M. (I. G. Farbenindustrie A. G.). Separation of Components of Oily Mixtures Produced by the Catalytic Hydrogenation of Carbon Oxides. United States Patent 1,704,751, Mar. 12, 1929; appl. filed Feb. 3, 1927. Chem. Abs., vol. 23, 1929, p. 1907.

Alcohols may be readily isolated from the mixtures by converting them into aldehydes by dehydrogenation, separating the aldehydes by distillation or combination with bisulfite, and thereafter reconverting them into alcohols, or the alcohols may be oxidized to acids and separation of the acids effected. Alternatively, the material may be treated with partly or wholly dehydrated hydrate-forming salts, such as $MgCl_2$, $Ca(NO_3)_2$, or $CaCl_2$, whereby, on cooling, preferably with addition of a precipating agent, such as benzine, molecular compounds separate, which are subsequently decomposed by addition of H_2O. Products are thus obtained which are of lighter color, lower boiling point, and more agreeable odor than the original material. Inorganic acids may be used for recovery of ketones in the oily mixtures under treatment, suitably by washing on the countercurrent plan. Gives several examples, with details of procedure.

2084. LUTHER, M., AND KLEIN, H. (I. G. Farbenindustrie A. G.). [Oxidation Products of Paraffin Hydrocarbons.] German Patent 539,572, Mar. 16, 1928. Chem. Abs., vol. 26, 1932, p. 2197.

Oxidation products of paraffin hydrocarbons and waxes are improved by subjecting them to O_2 or O_2-containing gas mixtures at temperatures $<$ those of the original oxidation process. Gives example.

See German Patent 535,068 (abs. **2080**).

2085. LUTHER, M., AND LEITHE, W. (I. G. Farbenindustrie A. G.). [Soap.] German Patent 708,125, June 5, 1941 (*Cl. 23 d–4*). Chem. Abs., vol. 37, 1943, p. 2953.

Soap is made from fat acids obtained by oxidizing paraffinic hydrocarbons. The fat acids are saponified and the soap solution treated with a salt solution of *p*H 5.5–7.5.

2086. LUTHER, M., AND PIEROH, K. (I. G. Farbenindustrie A. G.). [Working Up the Reaction Products of Hydrogen With Oxides of Carbon.] German Patent 551,167, Nov. 5, 1926. Chem. Abs., vol. 26, 1932, p. 4342.

To isolate the alcohols from a fraction b.$>$100° of the products obtained by the catalytic reaction of H_2 with oxides of C, the fraction is dehydrogenated so as to convert the alcohols into the corresponding aldehydes, which are readily separated from the other compounds present, for example, by distillation or by means of bisulfite. The aldehydes can then be reduced to the alcohols or oxidized to acids. The dehydrogenation may be effected by passing the fraction at 460° over lithopone or ZnO deposited on pumice. Gives examples.

2087. LUTHER, M., AND SÖNKSEN, H. (I. G. Farbenindustrie A. G.). [Oxygenated Organic Compounds.] German Patent 548,188, Mar. 2, 1926. Chem. Abs., vol. 26, 1932, p. 3513.

Crude mixture of oxygenated organic compounds b.$>$150°, obtained by the catalytic hydrogenation of CO, is treated with a partly or completely dehydrated salt capable of forming a hydrate, for example, anhydrous $MgCl_2$ or $CaCl_2$. Solid molecular compounds of the salt with the oxygenated organic compounds are precipitated, and by separating and decomposing the molecular compounds, for example, by treatment with H_2O, mixtures of oxygenated organic compounds are obtained, which are of better color and smell than the crude mixture and can be used as lacquer solvents or for the manufacture of softening agents. The pre-

is made in the process for recovering, in a substantially pure state, a number of chemicals, including alcohols, aldehydes, ketones, and organic acids, as well as the hydrocarbons produced. The method involves the substantially separate processing of the alcohols and acids wherein the loss of alcohols and acids due to esterification is largely avoided.

2107. MANN, A., AND LORENZ, W. (Braunkohle-Benzin A. G.). [Catalytic Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] German Patent 710,128, Sept. 4, 1941; appl. B 181,294, filed Dec. 29, 1937 (*Cl. 12 o–1.03*). Chem. Abs., vol. 37, 1943, p. 3589.

Reaction is catalyzed by reduced metals of the Fe group, especially Co. The metal is reduced, then passivated by prolonged treatment with CO_2 at room temperature, followed by careful oxidation with air at room temperature, so that the temperature rise is at the most 3°–7°.

2108. MANNES, L. (Henkel & Cie, G. m. b. H.). [Paraffin Mixtures.] German Patent 712,693, Oct. 23, 1941; appl. H 155,634, filed Apr. 29, 1938 (*Cl. 23 b–1.04*). Chem. Abs., vol. 37, 1943, p. 4552.

High-molecular paraffins, particularly those obtained in hydrogenating CO, are cracked at 350°–420°, and the fraction b. at 320°–450° is hydrogenated.

2109. MANNES, L., AND SEIFERT, W. (Henkel & Cie, G. m. b. H.). [Cleaning Agent.] German Patent 735,569, Apr. 15, 1943 (*Cl. 22 g–14*). Chem. Abs., vol. 38, 1944, p. 3057.

As cleaning agent is used, an emulsion of alkaline alkali salts and unsaponifiable components are obtained as byproducts of paraffin oxidation.

2110. MANNESMANNRÖHREN-WERKE. [Catalyst Chamber.] Netherlands Patent 49,151, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 162.

See British Patent 464,242 (abs. **2111**), and French Patent 807,703 (abs. **2113**).

———. *See* abs. **10, 1763, 3241.**

2111. MANNESMANNRÖHREN-WERKE AND RUHRCHEMIE A. G. Apparatus for the Production of Synthetic Hydrocarbons From Oxides of Carbon and Hydrogen With the Use of Solid Contact Masses. British Patent 464,242, Apr. 14, 1937. Chem. Abs., vol. 31, 1937, p. 6518.

Apparatus comprises a cooling device that includes at least 5 rows of cooling tubes superposed 1 row on the other at a small distance apart and having at least 5 tubes in each row, together with flat plates arranged perpendicular to the tubes and positioned at a few mm., for example, 7 mm., from each other, the tubes extending through each of the plates, and the plates and portions of the tubes extending therethrough being enclosed in a jacket. Cooling liquid is circulated through the tubes. The solid contact masses are arranged between the plates.

2112. ———. [Catalyst Furnace.] Austrian Patent 158,769, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 162.

Heat exchange features are emphasized.

See British Patent 464,242 (abs. **2111**) and French Patent 807,703 (abs. **2113**).

2113. ———. [Contact Apparatus for the Production of Hydrocarbons From Carbon Oxides and Hydrogen.] French Patent 807,703, Jan. 20, 1937. Chem. Abs., vol. 31, 1937, p. 5809.

Describes cooling means.

2114. ———. [Hydrogenation of Carbon Monoxide.] German Patent 763,553, no date; appl. M 139,149 (*Cl. 12 o–1.03*).

CO is hydrogenated in heat exchangers of tubular boilers with vertical tubes containing the catalyst.

MANSYŪ KAGAKUKŌGYŌ K. K. *See* abs. **1091, 1092.**

2115. MANTELL, R. M. (Allied Chemical & Dye Corp.). Preparation of Internally Oxidized Catalysts. United States Patent 2,517,223, Aug. 1, 1950; appl. filed Aug. 23, 1948, Serial No. 45,790; 8 claims (*Cl. 75–22*). Chem. Abs., vol. 44, 1950, p. 9592.

Metal for the catalyst is mixed with a solid substance, which will decompose at a temperature < the sintering point of the catalyst metal, liberating a fluid oxidizing substance. The mixture is compressed into the desired form and heated in air or O_2-containing gas to decompose the solid substance and oxidize the metal, 300°–400° C. Firm, highly porous metal oxide bodies are produced. Cu, Fe, Ni, Co, Cr, Mo, Zn, Ag, or mixtures or alloys may be used. Nitrates, permanganates, and dichromates may be used as oxidant in amount 1–25% of the weight of the metal. 1 literature ref. and 5 United States patents cited.

MARECEK, E. *See* abs. **3258, 3259.**

MARINESCO, N. *See* abs. **2183.**

2116. MARISIC, M. M. (Socony-Vacuum Oil Co.). Production of Gases Containing Hydrogen and Carbon Monoxide. United States Patent 2,430,432, Nov. 4, 1947; appl. filed Apr. 19, 1944, Serial No. 531,816; 5 claims (*Cl. 23–212*). Chem. Abs., vol. 42, 1948, p. 1411.

Impregnation of porous glass with hydrogenation metals, such as Ni, Co, etc., results in catalysts that are better hydrogenation catalysts than the corresponding impregnated silica gels. They are also more rugged and can withstand higher temperatures for longer periods of time. Materials such as Li_2O, MgO, Al_2O_3, ZrO_2, SnO_2, MoO_3, V_2O_5, etc. have been found to be effective promoters. 5 United States patent references cited.

2117. MÄRKISCHE SEIFEN-INDUSTRIE. [Alcohol Sulfonates.] German Patent 722,591, July 23, 1942; appl. M 134,700, filed June 5, 1936 (*Cl. 12 o–23.02*). Chem. Abs., vol. 37, 1943, p. 5081.

As parent materials are used, the alcohol-containing oxidation products obtained as byproduct in the hydrogenation of C oxides by the Fischer-Tropsch process. These oxidation products or the alcohols separated from them are sulfonated. The compounds formed show desirable emulsifying and cleansing characteristics.

2118. ———. [Base for Aqueous Emulsified Cleaning Agent.] German Patent 725,113, July 30, 1942 (*Cl. 22 g–14*). Chem. Abs., vol. 37, 1943, p. 6061.

Products of direct saponification of oxidized paraffinic hydrocarbons are used.

2119. ———. [Carboxylic Acids.] German Patent Appl. M 133,836, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 266.

Production of mixtures of aliphatic carboxylic acids by hydrogenation of C oxides and oxidation of the resulting hydrocarbons with b. p. 250°–450°.

2120. ———. [Carboxylic Acids.] German Patent Appl. M 139,097, no date (*Cl. 12 o–11*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 269.

Mixtures of high-molecular aliphatic carboxylic acids are obtained by oxidation of the hydrogenation products of CO by air or by gases evolving O_2.

2121. ———. [Fat Acids.] German Patent 736,471, May 13, 1943 (*Cl. 12 o–11*). Chem. Abs., vol. 38, 1944, p. 2970.

High-molecular aliphatic hydrocarbons are mixed with up to 50% by weight of corresponding high-molecular decomposition products of aliphatic hydro-

carbons, and the mixture is oxidized. The exact amount of the decomposition products is determined by their nature and depends essentially on their content of unsaturated components.

2122. ———. [Fatty Acids.] German Patent 732,719, Feb. 11, 1943 (*Cl. 12 o–11*). Chem. Abs., vol. 38, 1944, p. 751.

Fatty acids are obtained by oxidizing fractions, b. 250°–420°, of the products derived from the hydrogenation of CO. The mixture is divided into fractions with b. p. intervals of 40°–60° and individually oxidized at increasing temperatures of 100°–120°.

See also German Patent 729,962 (abs. **2126**).

2123. ———. [Fatty Acids by Oxidation of Synthetic Paraffin.] Austrian Patent 160,381, no date. Kainer, p. 278.

2124. ———. [Fatty Acids From Hydrocarbons.] German Patent 763,022, no date; appl. M 135,302 (*Cl. 12 o–11*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 267.

Obtaining fatty acids from hydrocarbons by oxidation with molecular O_2 and catalysts, of which the one consists of non-gas-forming compounds, evolving O_2 (superoxides, peracids, or their salts), and the other chemical compounds already used for the corresponding oxidations.

2125. ———. [High-Molecular Fatty Acids.] German Patent 714,775, Nov. 13, 1941; appl. M 137,422 filed Mar. 10, 1937 (*Cl. 12 o–11*). Chem. Abs., vol. 38, 1944, p. 1753.

Hydrogenation products of CO are used as parent compounds. The oxidation is carried out with molecular O_2 and with the aid of accelerators in 2 steps: (1) The temperature is kept at 115°; (2) at 100°. Compounds yielding O_2—for example, $KMnO_4$ or similar compounds—are used.

2126. ———. [High-Molecular Fatty Acids.] German Patent 729,962, Dec. 3, 1942 (*Cl. 12 o–11*). Chem. Abs., vol. 38, 1944, p. 379.

Alcohol mixtures b. 180°–350°, with individual differences of 30°–80°, are oxidized with air or other gas containing molecular O_2 at 80°–135°, depending on the boiling point of the alcohols.

2127. ———. [Oxidation of Hydrocarbons.] German Patent Appl. M 135,840, no date (*Cl. 12 o–11*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 267.

To reduce the amount of compounds insoluble in petroleum ether, small amounts, about 0.05–0.5%, of peroxides or other compounds evolving O_2 are added to the catalysts.

2128. ———. [Oxidation of Hydrocarbons.] German Patent Appl. M 137,625, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 268.

Oxidation of hydrocarbons, obtained by the hydrogenation of CO with m. p. $<50°$, with gases containing O_2.

2129. ———. [Process for Separating Unsaponifiable Components From Saponifiable Oxygenated Hydrocarbons.] German Patent Appl. M 138,824, July 31, 1937 (*Cl. IV a–23 e*). FIAT Reel K–20, frames 472–474; PB 70,211.

Separation of the unsaponifiable portions of the saponified products of hydrocarbon oxidation is carried out as follows: The soap, freed from the major part of the unsaponifiable substances by heating under pressure and then expanding, is subjected to a further distillation in a finely divided solid form on a conveyor belt or worm.

2130. ———. [Recovery of Alcohols.] German Patent Appl. M 153,302, no date (*Cl. 12 o–5*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 277.

Primary aliphatic alcohols are recovered from the products of CO hydrogenation through separation by means of a 5-fold excess of $CaCl_2$.

2131. ———. [Soap From Hydrocarbons.] German Patent 704,428, Feb. 27, 1941 (*Cl. 23 e–1*). Chem. Abs., vol. 36, 1942, p. 2174.

To separate the unsaponified portion from soap obtained from oxidation products of hydrocarbons, the whole is heated under pressure; then the unsaponified fraction is allowed to vaporize into an evacuated vessel kept at an elevated temperature. The soap is dropped onto a heated conveyor where the last traces of the unsaponified fraction vaporizes.

2132. ———. [Soap From Hydrocarbons.] German Patent 706,951, May 8, 1941 (*Cl. 23d–4*). Chem. Abs., vol. 36, 1942, p. 2174.

An improvement in the process wherein the 2 successive evaporations are conducted in 2 separate vessels. The preheated mixture is sprayed into the 1st vessel. Here, the volatile components volatilize and the soap falls into a 2d vessel, whence it is picked up on a heated conveyor on which the remaining unsaponified constituents are removed. Addition to German Patent 704,428 (abs. **2131**).

2133. ———. [Sulfuric Acid Esters From Fatty Alcohol Mixtures.] German Patent Appl. M 136,992, no date (*Cl. 12 o–23.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 268.

Sulfuric acid esters are obtained by sulfonating fatty alcohol mixtures containing 10–18 C atoms, which were produced by reduction of such carboxylic acid mixtures as arise through the oxidation of the hydrocarbons occurring in the hydrogenation of CO.

2134. MARSCHNER, R. F. (Standard Oil Co. of Indiana). Recovery of Oxygenated Compounds and Hydrocarbons From Mixtures. United States Patent Reissue 23,433, Nov. 27, 1951; appl. filed Dec. 27, 1950, Serial No. 202,831; 7 claims (*Cl. 260–450*). Original United States Patent 2,533,675, Dec. 12, 1950; appl. filed Oct. 30, 1945, Serial No. 625,519; 4 claims (*Cl. 260–450*).

The product of the hydrogenation of CO is cooled to effect substantial condensation of normally liquid components to form a gas phase, an oil-product liquid phase, and a H_2O product liquid phase. The phases are separated, and the oil-product liquid phase is extracted, with an aqueous liquor including dissolved organic oxygenated compounds to produce a raffinate comprising hydrocarbons and an aqueous extract comprising additional H_2O-soluble oxygenated organic compounds. The H_2O and oxygenated organic compounds contained in the aqueous extract are combined with the H_2O product liquid phase to produce a mixture comprising organic acids and nonacidic organic compounds. The acids are separated from the nonacidic components of the mixture.

See also United States Patent 2,533,675 (abs. **2135**).

2135. ——— (Standard Oil Co. of Indiana). Recovery of Oxygenated Compounds and Hydrocarbons From Mixtures. United States Patent 2,533,675, Dec. 12, 1950; appl. filed Oct. 30, 1945, Serial No. 625,519; 4 claims (*Cl. 260–450*). Chem. Abs., vol. 45, 1951, p. 2182.

Gaseous product from the hydrogenation of CO is cooled, and the normally liquid hydrocarbons are removed by condensation. The mixture separates to a gas phase, a 1st liquid hydrocarbon phase and a 1st aqueous phase, all containing organic oxygenated compounds. The 1st aqueous phase is fractionated. The overhead fraction consists predominantly of low-boiling organic oxygenated compounds substantially free from organic acids. The bottom aqueous fraction

following constants: Hydroxyl No. 186, carbonyl No. 72, saponification No. 18, and acid No. 2.2; after hydrogenation, 273, 34, 12, and 1.0, respectively.

2157. MATHY, E. V. (Phillips Petroleum Co.). Production of Hydrocarbons. United States Patent 2,471,228, May 24, 1949; appl. filed Sept. 3, 1946, Serial No. 694,543; 3 claims (*Cl. 196–52*).

Mixture of gas oil and steam are passed through an elongated catalyst zone in contact with a bauxite cracking catalyst impregnated with about 5% by weight of Ni oxide synthesis catalyst. The temperature is 950°–1,000° F. and the flow rate 1 liquid vol. gas oil per volume of catalyst per hr. A mixture of H_2 and CO in 3 : 1 vol. ratio is passed into the catalyst zone at a number of points along its length, 50,000 cu. ft. per hr. Hydrocarbons heavier than CH_4 are formed. Cracked hydrocarbons and synthesized hydrocarbons including gasoline are recovered. 6 United States patents cited.

2158. MATTOX, W. J. (Standard Oil Development Co.). [Catalytic Reduction of Carbon Monoxide With Iron Catalyst in the Fluidized State.] French Patent 978,243, Apr. 11, 1951; appl. filed Dec. 27, 1948. Chem. Zentralb., 1952, I, pp. 3273.

Catalyst particles are substantially larger than are those generally used in the synthesis of hydrocarbons and <20% of them are 0–20μ. In the synthesis a part of the Fe is transformed into Fe carbide and finer particles are simultaneously formed, which must be removed periodically for the fluidization to proceed. Before using the catalyst the greatest part of the Fe oxide is reduced to metallic Fe. In an example, the pretreatment of a hydrocarbon-synthesis catalyst, similar to an NH_3-synthesis catalyst, takes place under reducing conditions with a CO-containing gas.

2159. ——— (Standard Oil Development Co.). [Fluidized Catalysts for the Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 963,758, July 20, 1950; appl. filed Mar. 23, 1948; in United States, June 12, 1947. Chem. Zentralb., 1950, II, p. 2271.

Catalysts consist of the known metals of the Fe group in inert carrier materials. The finest catalyst particles of a size <20μ occurring in the usual production of catalysts and in use in the process are separated from the catalyst materials and converted into a coarse-grained product through special treatment by pressing and agglomeration. If desired, the essentially carbonaceous product is first subjected to an oxidizing heat treatment and thereafter to reduction.

2160. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,623,058, Dec. 23, 1952. Chem. Abs., vol. 47, 1953, p. 2966.

Normally liquid hydrocarbons and oxygenated compounds are synthesized by: Bringing a gas mixture containing CO and H_2 into contact with a bed of fluidized catalyst containing an Fe-group metal under temperature and pressure conditions suitable for formation of a vaporous carbonyl compound of the metal; withdrawing spent solids from the bottom of the bed and the mixture of metal carbonyl vapors and residual gas from above the bed; and bringing the gaseous mixture into contact with a 2d turbulent bed, this time of a substantially inactive carrier material of fluidizable size and with a high disintegration resistance, at conditions of temperature and pressure conducive to decomposition of the carbonyl compound into CO and the metal with deposition of the metal on the carrier. The carrier is withdrawn from the bottom of the 2d bed, cooled, and is then mixed with a stream of the feed vapors to the 2d catalyst zone. With an Fe catalyst, suitable conditions in the 1st reactor are about 343°–399° and 200–400 p. s. i. The carrier may be mainly SiO_2 impregnated with a small amount of promoter. Usual conditions in the 2d reactor are 121°–399° and 0–600 p. s. i.

2161. ——— (Standard Oil Development Co.). Preconditioning Hydrocarbon Synthesis Catalyst and Removing Fines Therefrom. United States Patent 2,601,121, June 17, 1952; appl. filed Apr. 29, 1948, Serial No. 24,067; 6 claims (*Cl. 252–443*).

Fe catalyst in powdered form is preconditioned to adapt it for fluidization in the synthesis of hydrocarbons. A fluidized bed of the catalyst is treated with a CO–H_2 mixture containing 1–5 mol. of H_2 per mol. of CO at 500°–900° F. A substantial proportion of the Fe is converted to its carbide. Fines formed in this treatment are eliminated.

2162. ——— (Standard Oil Development Co.). Process of Regenerating a Fluidized Fischer-Tropsch Catalyst. United States Patent 2,515,245, July 18, 1950; appl. filed June 11, 1947, Serial No. 754,027; 3 claims (*Cl. 252–417*). Chem. Abs., vol. 44, 1950, p. 8625.

Oxidizing treatment is carried out in at least 2 stages. In the 1st step controlled oxidation of the active metal component of the carbonized catalyst takes place without appreciable combustion of C. In the 2d step, combustion of C on the catalyst takes place to the desired degree without appreciable further oxidation of the active metal component. Steam and/or CO_2 may be used as oxidizing gas in the 1st stage and O_2, air, or air diluted with O_2 or steam is suitable for the 2d stage. Using CO_2 in the 1st stage, the partial pressure ratio of CO : CO_2 should be slightly lower than .54, temperature 550° F. With steam, the partial pressure should be slightly lower than 27, temperature 550°; at temperature 600°–800° F. the CO : CO_2 partial pressure ratio may be 0.01–0.6 and the partial pressure ratios of H_2 : H_2O=0.5–27. The conditions for the 2d stage are more severe to remove the C from the preoxidized catalyst. Enough O_2 is kept available to remove the desired amount of C. C will burn in preference to further oxidation of the metal component. Temperature for 2d stage is 700°–1,400° F. and may be high enough to cause sintering. The decarburized catalyst may be returned to the reaction or, if desired, reduced before it is used again. The 1st mild oxidation stage permits recovery of a major proportion of heavy hydrocarbons and waxes adsorbed on the catalyst in addition to the fixed C deposits. Highly phrophoric metal components of the carbonized catalyst are reoxidized in the 1st stage under conditions that do not result in sintering, thus conditioning the catalyst against undesired changes in the 2d stage. Depending on whether CO_2 or steam is used in the 1st stage, the off gases are rich in CO or H_2 and may be added to the synthesis feed gas. Return of the unreduced, mildly oxidized catalyst directly to the synthesis stage may improve the yield of oxygenated compounds. The 2d stage gives a convenient means for economical sintering of synthesis catalyst such as pyrite ashes or other iron catalysts at high carbon concentration. Operating advantages include decreased O_2 requirements, considerable latitude in operating pressures, and lower oxidation temperatures. 16 United States patents cited.

———. *See* abs. **3826.**

2163. MAX, N. (N. V. de Bataafsche Petroleum Maatschappij). [Production of Aldehydes and Alcohols.] Swedish Patent 130,809, Feb. 13, 1951; appl. filed Apr. 9, 1949. Chem. Zentralb., 1952, I, p. 2256.

Crude products obtained by Oxo synthesis from CO, H_2, and olefins over Co catalyst are first freed from volatile Co compounds entrained thereby and then steam distilled to recover the aldehydes and, if desired, finally reduced to alcohols. Recovery of the Co compounds takes place by treating with H_2 at about 150° and 40–50 atm.

2164. ——— (Shell Development Co.). Recovery of Aldehydes. United States Patent 2,514,961, July 11, 1950. Chem. Abs., vol. 44, 1950, p. 9473.

Aldehydes containing 6–10 C atoms, obtained from the reaction of olefins with CO and H_2 in the presence of a Co-containing catalyst, are recovered in poor yield when distilled directly. If they are pretreated 80°–160° at 25–60 atm. in the absence of CO and in an atmosphere of H_2, 87–97% is recovered by steam distillation without the formation of condensation products. The steam distillate is dried with Na_2SO_4 and distilled at reduced pressure, giving an aldehyde of 96–98% purity and a recovery of 80–93%. The aldehydes are virtually free of Co.

2165. MAXTED, E. B. Revivification of Catalysts. British Patent 644,239, Oct. 4, 1950; appl. filed July 10, 1948. Chem. Abs., vol. 45, 1951, p. 2608.

Hydrogenation catalysts consisting of/or containing metallic Ni, Co, Cu, or Fe, which have become poisoned during use, are revivified by treatment with a peracid of Mo, W, Cr, V, P, or salt thereof and washing and drying.

2166. MAY, W. G., AND SWEETSER, S. B. (Standard Oil Development Co.). Hydrocarbon Synthesis With Two-Stage Coke Gasification. United States Patent 2,620,348, Dec. 2, 1952. Chem. Abs., vol. 47, 1953, p. 2462.

To eliminate recycling, a 2-stage synthesis unit is operated in conjunction with a 2-stage coke-gasification unit. In the 1st gasification unit, steam and O_2 are used to produce a product gas with H_2:CO ratio of 1.0–1.5. This gas is fed to the 1st synthesis unit, where liquid hydrocarbons and a tail gas of high H_2:CO ratio are produced with the aid of an Fe catalyst. Coke from the 1st gasification stage passes to a 2d stage, where it is gasified with CO_2, O_2, and steam to produce a gas with a H_2:CO ratio of 0.5–0.8. This gas is mixed with the tail gas from the 2d stage to give a gas with a H_2:CO ratio of 0.8–1.2, which is utilized in a 2d synthesis stage.

2167. MAYER, I. (Standard Oil Development Co.). Hydrocarbon Synthesis With Catalyst Reconditioning. United States Patent 2,562,806, July 31, 1951; appl. filed Apr. 23, 1948, Serial No. 22,794; 7 claims (*Cl. 260–449.6*).

In the process of synthesizing hydrocarbons by reacting CO+H_2 in the presence of a fluidized Fe catalyst in a reaction zone, the activity of the catalyst is maintained at a high level, and its tendency to disintegrate is repressed, by treating it in a catalyst conditioning zone with the tail gases from the synthesis reaction zone for enough time to convert a substantial portion of the Fe to Fe carbide. The gas is passed through the conditioning zone at a rate of about 100 cu. ft. per hr. per lb. of catalyst to suppress the formation of CO_2 and Fe oxide. Carbiding of the catalyst is carried out at pressures 60–600 p. s. i. g. Diagrams.

See abs. **2149, 2150, 2151.**

2168. MAYER, I., AND JOHNSON, V. C. (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,642,448, June 16, 1953. Chem. Abs., vol. 47, 1953, p. 8996.

Improvements in the Fischer-Tropsch synthesis of hydrocarbons with high yields of desired products are obtained by charging a mixture of CO and H_2 to a reaction zone containing a fluidized bed of powdered Fe catalyst having an average particle size of 30–50 μ. The average particle size can be maintained by appropriate changes in operating variables, catalyst replacement rate, and particle size of catalyst added.

2169. MAYER, I., AND OGORZALY, H. J. (Standard Oil Development Co.). Production of Liquid and Gaseous Fuels by Synthesis From Coal. United States Patent 2,543,795, Mar. 6, 1951; appl. filed Oct. 1, 1949, Serial No. 119,142; 7 claims (*Cl. 48–202*). Chem. Abs., vol. 45, 1951, p. 4912.

In a continuous process for producing a fuel gas of high-heating value, due to the presence of increased quantities of CH_4, a subdivided carbonaceous material and a subdivided catalyst are charged into an initial zone where the carbonaceous solid and catalyst form a turbulent, well-mixed fluidized mass, which is then contacted with CO and H_2 under carbonization and CH_4-synthesis conditions for a sufficient time to cause substantial conversion to CH_4. Then those carbonaceous solids, which have been carbonized, and the catalyst are withdrawn from the synthesis zone and subjected to a separation process. The temperature of the separated catalyst is next adjusted to help maintain the proper temperature in the synthesis zone, to which it is returned while the carbonized carbonaceous material is treated so as to obtain a mixture of CO and H_2 synthesis gas, which is then also charged into the synthesis zone from which the fuel gas is finally recovered.

2170. MAYHEW, R. L. (Hydrocarbon Research, Inc.). Heat Exchanger for Synthesis-Gas Generator. United States Patent 2,594,329, Apr. 29, 1952; appl. filed Apr. 30, 1947, Serial No. 745,052; 3 claims (*Cl. 48–196*). Chem. Abs., vol. 46, 1952, p. 7744.

Gas-cooler and steam-generator arrangement in the synthesis-gas generator is claimed.

2171. ——— (Hydrocarbon Research, Inc.). Heat Exchanger for Synthesis-Gas Generator. United States Patent 2,594,330, Apr. 29, 1952; appl. filed May 6, 1947, Serial No. 746,346; 2 claims (*Cl. 48–196*). Chem. Abs., vol. 46, 1952, p. 7744.

See United States Patent 2,594,329 (abs. **2170**).

2172. MAYLAND, B. J. (Phillips Petroleum Co.). Carbon Monoxide and Hydrogen Synthesis Gas. United States Patent 2,618,543, Nov. 18, 1952. Chem. Abs., vol. 47, 1953, p. 2963.

Efficiency of a hydrocarbon partial-oxidation synthesis-gas-manufacturing process for production of CO and H_2 is greatly increased by recovering elemental C formed in the reaction as an aqueous slurry and recycling this slurry to quench the gases from above 1,200° F. (preferably 1,500°–1,800° F.) to about 800°–900° F., at which temperature no further C formation will take place. Steam is then condensed from the gas, and the elemental C is recovered as an aqueous slurry, which is again recycled for partial gasification in the quenching stage. Efficiency of the process for manufacture of H_2 and CO from natural gas is thus raised from about 80% of theoretical to 83.5%. In United States Patent 2,618,611 (abs. **2179**), a synthesis gas of high H_2:CO ratio is made by first partly oxidizing a hydrocarbon gas, cooling the products to <1,500° F., and treating the gaseous mixture with a reduced Fe or Ni water-gas shift catalyst at 800°–1,500° F. in the presence of 0.01–0.25 mole of O_2 per mole of CO. Contrary to Rideal (Jour. Chem. Soc., vol. 115, 1919, pp. 993–1006), who stated that at 400° C. H_2 is burned more rapidly than CO, the ratio H_2:CO may actually be increased instead of decreased. In an example, a synthesis gas made from pure CH_4 by partial combustion with O_2 had the following compound: H_2 60.99, CO 32.1, CO_2 1.06, and H_2O 5.85 mole %. The H_2:CO ratio of this gas was 1.9. After 0.03 mole O_2 was added and mixture allowed to come to equilibrium over a reduced-Fe shift catalyst at 1,200° F., the gas had a composition of H_2 59.99, CO 27.1, CO_2 6.06, and H_2O 6.85 mole %, and the H_2:CO ratio was 2.21. If natural gas with small percentages of heavier hydrocarbons is used, the H_2:CO ratio is 1.6:1.7 for the 1st step. This gas can also be improved by addition of O_2 and the shift reaction.

In an aldehyde-ketone mixture obtained in the catalytic hydrogenation of oxides of C, the aldehydes can be selectively hydrogenated to alcohols, without substantial hydrogenation of the ketones, by subjecting the mixture to hydrogenation at 75°–575° F. and 15–2,000 p. s. i. absolute in the presence of a hydrogenation catalyst such as a mixture of Cu oxide and Cr oxide in a ratio of about 1 : 2. 1 literature ref. and 6 United States patents cited.

2190. ——— (M. W. Kellogg Co.). Separation of Organic Compounds. United States Patent 2,596,160, May 13, 1952; appl. filed Jan. 30, 1948, Serial No. 5,333; 20 claims (*Cl. 260–450*). Chem. Abs., vol. 46, 1952, p. 8354.

Mixture of products formed by the hydrogenation of CO over an alkalized Fe catalyst is freed of hydrocarbons and H_2O by solvent extraction and the residual O-containing compounds (alcohols 51%, aldehydes 6%, ketones 3%, esters 5%, and acids 35%) are hydrogenated over a Cu catalyst at 260° and 3,500 p. s. i. to a mixture of alcohols. Thus the aqueous phase of the original reaction product is extracted with a solvent, such as Et_2O, and the organic (hydrocarbon-rich) phase with aqueous MeOH. The resulting essentially H_2O- and hydrocarbon-free extracts are then combined and hydrogenated; the desired hydrogenation may be accomplished under milder conditions if the mixture of O-containing compounds is subjected to conventional conditions serving to esterify the carboxylic acid components.

2191. ——— (M. W. Kellogg Co.). Separation of Organic Compounds. United States Patent 2,632,765, Mar. 24, 1953; appl. filed Feb. 27, 1947, Serial No. 731,269; 8 claims (*Cl. 260–450*).

Gives process and apparatus for separation of oxygenated organic compounds present in the reactor gas obtained in the catalytic hydrogenation of oxides of C. The oil phase and the aqueous are separated. The oil phase is extracted with an aqueous solution of a light alcohol to obtain a raffinate containing hydrocarbons and an extract containing oxygenated organic compounds. The extract is contacted with a hydrocarbon wash oil and distilled to obtain a low-boiling solvent fraction and a high-boiling oxygenated organic compound fraction. The oxygenated organic compounds are separated from the high-boiling fraction and combined with the aqueous phase. The mixture is distilled to separate the nonacid oxygenated compounds from the organic acids. 1 literature ref., 1 foreign patent, and 13 United States patents cited.

2192. ——— (M. W. Kellogg Co.). Synthesis of Organic Compounds. United States Patent 2,539,847, Jan. 30, 1951; appl. filed June 25, 1947, Serial No. 756,949; 4 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 5391.

CO is hydrogenated to produce oxygenated organic compounds by using a Co (1 part) catalyst promoted with thoria (0.05–0.5 part) supported on bentonite type clay (0.5–3 parts). 75% by weight of the catalyst is smaller than 150 μ, and at least 25% is smaller than 40 μ. The catalyst is in a pseudoliquid state. The reaction pressure is 200–300 p. s. i. and the temperature 350°–450° F. The preferred space velocity is 500–800 vol. total feed gas per hr. per vol. catalyst. The CO_2 concentration of gaseous feed mixture is $<2\%$. The liquid hydrocarbon fraction containing the oxygenated organic compounds C_6–C_7 alcohols is recycled to the reaction zone to increase the yield. A yield of oil 97–126 cc. and a yield of H_2O 99–171 cc. per m^3 fresh feed gas have been obtained. 1 literature ref. and 7 United States patents cited.

2193. ——— (M. W. Kellogg Co.). Synthesis of Organic Compounds. United States Patent 2,542,422, Feb. 20, 1951; appl. filed Oct. 31, 1947, Serial No. 783,382, in Great Britain July 25, 1947; 19 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 5391.

In a continuous process for the hydrogenation of CO in the presence of a freshly reduced, finely divided, fluidized Fe catalyst, the latter is pretreated by contacting with synthesis gas whose H_2 : CO mol. ratio is between about 1 : 1 and 1 : 4 at a pressure between 15 and 85 p. s. i. and at a temperature of above 450° F. The gas is passed through the freshly reduced catalyst at a sufficient velocity to maintain the catalyst in a fluidized condition, while the pressure is gradually raised to above 100 p. s. i. g. during contact with at least about 200 standard $ft.^3$ of synthesis gas per lb. of Fe calculated as the elementary material. During the initial contact the pressure does not exceed 100 p. s. i. g., and the temperature is established at about 600° F. Somewhat higher figures are used when the catalyst contains an alkali as a promoter. 2 United States patents and 1 literature ref. cited.

———. *See* abs. **287, 288, 291, 2839, 2840.**

2194. McGRATH, H. G., AND BURTON, W. P. (M. W. Kellogg Co.). [Processing the Reaction Products of Carbon Monoxide Hydrogenation for the Separation of Oxygenated Compounds.] French Patent 978,270, Apr. 11, 1951; appl. filed Dec. 28, 1948. Chem. Zentralb., 1952, I, p. 3733.

The cooled mixture is separated into a gaseous, noncondensed product, an oily, and an aqueous condensate. The oily condensate is washed with H_2O, a part of the oxygenated compounds being absorbed. The aqueous and the oily condensates are distilled with the separation of a proportional high-boiling fraction. This fraction is utilized for washing the noncondensed gaseous product, thereby obtaining an aqueous solution of oxygenated products, which is worked up. The oily condensate after being washed with H_2O is extracted with aqueous alcohol, whereby the greater part of the oxygenated organic compounds is adsorbed. These extracted oxygenated compounds, which contain aldehydes and ketones, are hydrogenated thereby being partly converted into the corresponding alcohols.

2195. ——— (M. W. Kellogg Co.). Separation of Reaction Products of Hydrogenation of Oxides of Carbon. British Patent 670,336, 1952. Fuel Abs., 1952, abs. 4972.

Oxygenated organic compounds in high yield and free from hydrocarbons are separated by a series of processes, including condensation and solvent extraction.

2196. McGRATH, H. G., AND HILL, L. R. (M. W. Kellogg Co.). Hydrogenation of Carbon Oxides. United States Patent 2,640,844, June 2, 1953. Chem. Abs., vol. 47, 1953, p. 8771.

See British Patent 656,560 (abs. **2202**).

2197. McGRATH, H. G., AND RUBIN, L. C. (M. W. Kellogg Co.). Preparation of Reduced Magnetite Synthesis Catalyst. United States Patent 2,543,327, Feb. 27, 1951; appl. filed Mar. 18, 1947, Serial No. 735,536; 9 claims (*Cl. 252–472*). Chem. Abs., vol. 45, 1951, p. 4024.

A catalyst for production of organic compounds by CO hydrogenation is prepared by fusing magnetite at about 2,000° F. The actual temperature will vary depending on the ingredients accompanying the magnetite. Al, silica, or Ti oxide tend to lower the fusion temperature of magnetite. After fusion and solidification, the mass is crushed and ground and reduced in H_2 at 900°–1,600° F. at atmospheric pressure. The reduction may be carried out at 600°–800° F. at superatmospheric pressure. The reduction is continued until 90–95% of the magnetite is reduced, indicated by cessation of H_2O formation. Promoters that may be added to the magnetite ore are metals, Si and their oxides, nitrates, sufates, chlorides, carbo-

nates, hydroxides, and organic compounds. Calcining may have much the same effect as fusion since it causes dispersion of the promoters on the surface of the naturally occurring magnetite. Gives 9 examples of use of this type of catalyst. 1 foreign and 10 United States patents cited.

2198. ——— (M. W. Kellogg Co.). Synthesis of Organic Compounds. United States Patent 2,580,-116, Dec. 25, 1951; appl. filed Dec. 27, 1948, Serial No. 67,391; 12 claims (*Cl. 260–449.6*).

Presents details of a Fischer-Tropsch synthesis process, which is carried out in the presence of a finely divided, alkali-containing, reduced Fe catalyst containing not more than a minor proportion by weight of material having a particle size greater than 250μ. The feed mixture of H_2–CO–CO_2 is passed upward through the catalyst at enough velocity to suspend it in the gases in a dense, fluidized condition.

2199. McGrath, H. G., Passino, H. J., and Rubin, L. C. (M. W. Kellogg Co.). Separation of Organic Compounds. United States Patent 2,470,782; appl. filed May 24, 1949, Serial No. 709,871; 15 claims (*Cl. 260–450*). Chem. Abs., vol. 43, 1949, p. 7213.

Describes apparatus and process for separating oxygenated compounds from Fischer-Tropsch product by solvent extraction. An aqueous or anhydrous glycol is used as solvent. 1 foreign patent and 7 United States patent cited.

2200. ——— (M. W. Kellogg Co.). Separation of Organic Compounds. United States Patent 2,571,-151, Oct. 16, 1951; appl. filed Nov. 14, 1946, Serial No. 709,872; 18 claims (*Cl. 260–450*). Chem. Abs., vol. 46, 1952, p. 711.

Organic acids and alcohols contained in an oil product liquid phase obtained from the condensation of the reaction product produced in the catalytic hydrogenation of CO are recovered by fractionating the oil product into a fraction b. $<$ 200° F., 1 $>$ 430° F., and an intermediate one comprising hydrocarbons, organic acids, and alcohols. This last-named fraction is extracted with a solvent comprising a light alcohol, such as MeOH, EtOH, PrOH, or ethylene glycol, to produce an extract phase comprising organic acids and alcohols and a raffinate phase comprising hydrocarbons and then separating the 2 phases thus produced. Descriptive flowsheets included.

2201. ———(M. W. Kellogg Co.). Separation of Oxygenated Organic Compounds From the Products of the Hydrogenation of Carbon Monoxide. United States Patent 2,635,111, Apr. 14, 1953. Chem. Abs., vol. 47, 1953, p. 7762.

Reaction products of the hydrogenation of CO are condensed to yield an aqueous phase and an oil phase. The aqueous phase is distilled to yield 2 fractions, 1 rich in organic acids, the other in alcohols and aldehydes. The latter fraction is contacted with an alkali, then the salts and excess alkali are removed and the remainder of the fraction is extracted with a low-boiling hydrocarbon, for example, pentane, to remove any hydrocarbons present. The pentane is separated from the O compounds by azeotropic distillation.

See also United States Patents 2,571,151 (abs. **2200**) and 2,568,717 (abs. **288**).

2202. McGrath, H. G., Hill, L. R., Jewell, J. W., and Johnson, W. B. (M. W. Kellogg Co.). Hydrogenation of Carbon Oxides. British Patent 656,560, Aug. 29, 1951. Fuel Abs., 1951, abs. 4,057; Chem. Abs., vol. 47, 1953, p. 2193.

Gaseous mixture comprising H_2 and CO or CO_2 is contacted at a velocity of at least 5 ft. per sec. with a powdered hydrogenating catalyst of such size that the catalyst is moved in the direction of flow of the gaseous mixture in a relatively dilute condition. All of the catalyst particles are continuously moved in the direction of flow of the gases through the reaction zone by entrainment in contrast to being held in suspension in a pseudo-liquid dense phase of solids.

2203. McGurl, G. V. (Koppers Co., Inc.). Changing the Composition of a Combustible Gas by Diffusion. United States Patent 2,497,898, Feb. 21, 1950. Chem. Abs., vol. 44, 1950, p. 4230.

When gas appliances are supplied with a mixed gas such as coke oven and water gas, the specific gravity should be maintained as constant as possible. Mixed gases containing a high % of coke-oven gas have too low a specific gravity for satisfactory use in place of the usual mixed gas, owing to the high H_2 content. This can be reduced by diffusion through porous tubes with a gas such as producer gas for the sweep gas. The tubes are made from a Cu screen coated with corrosion-resistant Ni and have 6,400 openings per sq. in. 7 tubes were used, 1.25 in. internal diameter and 24 in. effective length. In 1 example the feed rate of coke-oven gas was 643 ft.^{3} per hr., this increased on passage through the apparatus to 708 ft.^{3}, 520 ft.^{3} per hr. of producer gas was used, this decreased to 455 ft.^{3} The H_2 content of the coke oven gas decreased from 55.6–40.1%, and the specific gravity increased from 0.37–0.538. The H_2 content of the producer gas increased from 10.8 to 29.5, and the specific gravity was reduced from 0.87 to 0.697. By varying the rate of flow of the 2 gases, the relative H_2 contents of the 2 gases can be varied widely as H_2 diffuses much more rapidly than the other gas constituents. The producer gas can thus be converted into a satisfactory gas for Fischer-Tropsch synthesis.

2204. ——— (Koppers Co., Inc.). Changing the Composition of Coke-Oven Gas. British Patent 632,231, Apr. 21, 1947; British Abs., B, I, 1950, p. 610.

Streams of coke-oven gas (I) and a sweep gas (II) of high specific gravity (producer gas), heated above their dew points, are passed concurrent or countercurrent along opposite sides of a porous boundary (with pore size 1–100 times greater than the mean free path of the (I) molecules), maintaining a suitably higher pressure on the (II) side to secure a free flow from (II) to (I) and a counterdiffusion from (I) to (II), whereby the higher diffusion velocity of the light constituents (H_2) will cause a net increase in the H_2 content of (II). The specific gravity of (I) is increased by 42–50% and that of (II) decreased by 12–20%. Examples show that the molecular ratio CO : H_2 of producer gas may be widely varied permitting the production of synthesis gas.

2205. McKay, J. F., Jr., and Jasion, L. Z. (Standard Oil Development Co.). Selective Crabgrass Herbicidal Compositions Containing Oxo Bottoms. United States Patent 2,575,282, Nov. 13, 1951. Chem. Abs., vol. 46, 1952, p. 1702.

An improved composition comprises a H_2SO_4-treated kerosine, sp. gr. 0.775–0.825, b. 400°–505° F., and 0.1–10% by weight (based on total composition) of a mixture of oxygenated organic compounds produced as a still-bottoms product remaining after removing the major portion of low-boiling alcoholic components by distillation in the 2-stage process for producing oxo alcohols. Gives a typical component of oxo alcoholic bottoms and formulations.

See United States Patent 2,327,066 (abs. **2803**).

2206. McKeever, C. H. (Rohm & Haas Co.). Cobalt Carbonyl. United States Patent 2,476,263, July 12, 1949. Chem. Abs., vol. 43, 1949, p. 9397.

Stable solutions of Co carbonyl are prepared by causing a suspension of a Co compound to react in a neutral organic liquid with CO at above 140° and at superatmospheric pressure. Yields of 80% minimum

2226. ———. [Catalyst for the Carbon Monoxide Hydrogenation.] French Patent 871,536, Apr. 29, 1942; appl. filed Apr. 16, 1941, in Germany, Nov. 8, 1938. Chem. Zentralb., 1942, II, p. 1656.

Fe catalysts are used which were obtained from ferrites or alkali ferrites by chemical conversion or by hydrolysis. The best raw material is that from the decomposition of bauxite. The finished catalyst should contain 30–40% of alkali carbonate or 5–30% of alkali silicate calculated on the Fe. Oxides of other metals as Cu, Cr, Al can be present. The catalyst is reduced at 250°–400° and finally subjected to a mild reoxidation with steam at 200°–400°. The catalyst gives yields of liquid and solid hydrocarbons of 105–135 gm. per $m.^3$ of synthesis gas. The hydrocarbons consist of 30% paraffin, 25% high-boiling oils, and 37% gasoline.

2227. ———. [Catalyst Furnace.] French Patent 871,230, Apr. 13, 1942; appl. filed Apr. 1, 1941. Chem. Zentralb., 1942, II, p. 1086.

Gives construction details.

2228. ———. [Catalyst Furnace.] German Patent Appl. M 151,275, PA 467,032, filed June 27, 1941 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 298–302; PB 83,253.

In operating a catalyst furnace in which exothermic reactions at temp. 220°–400° are carried out and in which the catalyst is kept at a constant temperature by means of closely lying elements cooled by boiling liquids, naphthalene or its hydrogenation products is used as the cooling medium, especially with Fe catalysts operating under pressures of 3–30 atm. The naphthalene should be free from phenols, cresols, coumarone, indene, or the like, but may contain organic cyclic compounds of S such as thionaphthene.

2229. ———. [Catalyst Furnace for Carbon Monoxide Hydrogenation.] German Patent 765,687, no date; appl. M 143,170 (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 270.

Catalyst rests in lamellarlike inserts with the cooling tubes passing through. The inserts are so arranged in a pressure vessel that their walls are not stressed by the gas pressure. The cooling tubes are connected with their ends within the pressure vessels to a common collecting tube.

2230. ———. [Catalyst Regeneration.] Indian Patent 24,733, no date. Schmidt, J., Das Kohlenoxyd. Akad. Verlagsgesell., Leipzig, 1950, p. 156.

Paraffin is removed by extraction with N- or O-containing solvents (acetone, esters, anilin, nitrobenzene, triethanolamine).

2231. ———. [Catalysts for Carbon Monoxide Hydrogenation.] German Patent Appl. M 146,710, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 272.

CO is hydrogenated to polymembered hydrocarbons in the presence of Fe catalysts at 5–25 atm. pressure and 200°–300°. The catalyst is made by precipitation from metal salt solution on to a support such as kieselguhr, reducing with H_2 or other gases at 200°–400°, followed by mild oxidation by steam. The catalyst contains ferrous oxide. Activators such as difficultly reducible metal oxides (Al_2O_3), Cu, and alkali compounds can be added.

2232. ———. [Catalysts for Carbon Monoxide Hydrogenation.] German Patent Appl. M 146,804, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 272.

CO is hydrogenated in catalyst furnaces having close-lying cooling elements. Fe catalysts are used which have been reduced at 300°–400° only until 50–90% of the Fe is transposed into metal.

2233. ———. [Catalysts for Carbon Monoxide Hydrogenation.] German Patent Appl. M 147,496, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 272.

Catalysts for the hydrogenation of CO, especially for obtaining liquid and solid hydrocarbons, are made by precipitation and contain Fe and Fe compounds and water glass, especially potash water glass, and other additions. Addition to German Patent Appl. M 145,617 (abs. **894**).

2234. ———. [Catalysts for Carbon Monoxide Hydrogenation.] German Patent Appl. M 149,446, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 274.

Hydrocarbons are obtained by the hydrogenation of CO, the catalyst consisting of naturally occurring Fe hydroxide or that obtained by hydrolysis together with alkali.

2235. ———. [Catalytic Hydrogenation of Carbon Monoxide.] German Patent 759,843, Nov. 8, 1938 (*Cl. IV d–12 o*). FIAT Reel R–8, frames 7,422–7,438; PB 73,522.

Process for the catalytic conversion of CO and H_2 in the proportion of 1:2–2:1 into hydrocarbons at normal or increased pressure and temperatures at 150°–300° characterized by the feature that to 1 catalyst vessel, furnished with catalysts that consume CO and H_2 in the ratio of 1:2, another catalyst vessel is joined, which is also provided with catalysts that consume more than 1 vol. of CO to 2 vol. of H_2. The result is that a considerably greater gas conversion is attained than would be possible with the same amount of raw gas but with only a single catalyst unit. One vessel contains an Fe catalyst, the other a Co catalyst, and the temperature, pressure, and gas-throughput conditions in both vessels are maintained independently of each other corresponding to the conditions desired in the current stage of operation. The gas conversion in the 1st vessel is extended somewhat farther than is required for the last vessel and the regulation of the most favorable end-gas composition is undertaken beyond the 1st vessel by means of the raw gas withdrawn before the 1st stage. All or a part of the reaction products inclusive of CO_2 are removed between the catalyst vessels. The olefin hydrocarbons, C_2–C_4 and above, are left in the reaction end-gas of the 1st vessel for the purpose of further conversion in the 2d vessel to higher liquid or solid hydrocarbons.

2236. ———. [Catalytic Hydrogenation of Carbon Monoxide.] German Patent 763,855, no date; appl. M 140,588 (*Cl. 12 o–1.03*).

Catalytic hydrogenation of CO with Co or Fe catalysts under excess pressure. To increase the olefin content of the reaction product, the partial pressure of the H_2 in the CO–H_2 gas mixture is measured at 0.1–0.2 times the applied superatmospheric pressure.

2237. ———. [Catalytic Hydrogenation of Carbon Monoxide.] German Patent 764,590, no date; appl. M 139,142 (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 269.

CO is catalytically hydrogenated in a catalyst furnace provided with a cooling system in the presence of a Co catalyst at 5 atm. pressure. The number of normal l. of throughput per hr. and gm. of Co metal in the catalyst is kept <0.2 times the operating pressure and a temperature of 170°.

2238. ———. [Conversion of Carbon Monoxide.] German Patent Appl. M 156,865, no date (*Cl. IV b–26 a*). Auszüge deut. Patent-Anmeldungen, vol. 15, p. 334.

In the catalytic conversion of CO and H_2 to liquid and solid hydrocarbons, steam in amounts of 20–150 gm. per $m.^3$ of initial gas is added to the synthesis gas before and during the hydrogenation.

2239. ———. [Detoxification of Gas.] German Patent Appl. M 142,791, no date (*Cl. IV b–26 d*). Auszüge deut. Patent-Anmeldungen, vol. 15, p. 369.

Catalysts that have been used for the hydrogenation of CO to liquid and solid hydrocarbons and oxygenated compounds are used for the detoxification of coke oven, water, and illuminating gases or of city gas produced by pressure gasification with O_2.

2240. ———. [Equipment for Performing Catalytic Gas Reactions Under Pressure.] German Patent Appl. M 152,364, Nov. 10, 1941 (*Cl. IV d–12 o*). FIAT Reel R–6, frames 4,868–4,875; PB 73,554.

Equipment is described whereby several catalyst furnaces are housed in 1 vertical or horizontal pressure cylinder in such a way that the individual catalyst furnaces can be removed therefrom and neither the catalyst nor the cooling agent touches the walls of the pressure vessel. Includes diagrams. Addition to German Patent 765,687 (abs. **2229**).

2241. ———. Exothermic Catalytic Gas Reactions. British Patent 683,516, Nov. 26, 1952. Chem. Abs., vol. 47, 1953, p. 5100.

In the production of hydrocarbons by the catalytic hydrogenation of CO, the cooling medium used for the contact reactor boiled at 190°–250° and was a mixture of saturated hydrocarbons with a high proportion of C_{11}, C_{12}, C_{13}, and a smaller proportion of C_{14} hydrocarbons. The catalyst was a normal mixture of Co 100, ThO_2 5, MgO 8, and kieselguhr 200 parts. The synthesis gas was a pressure gasification gas, which had been produced under a pressure of 20 atm. from brown coal and was composed of CO, 1.2%; C_nH_m, 0.1%; CO, 23.3%; H_2, 54.6%; CH_4, 18.6%; and N_2, 2.3%. The operation was carried out in 1 stage with recycling of the synthesis gas by using 1 vol. fresh gas to 2 vol. recycled gas. The temperature at the top of the reactor was 190° and 210° at the bottom. The gas load on the catalyst was 300 $m.^3$ per $m.^3$ of catalyst per hr. The reactor was operated at a gas pressure of 20 atm. The yield was gasoline, 60%; diesel oil, 25%; crude paraffin, 12%; and hard wax, 3%. The product gas consisted of CO_2, 7.2%; C_nH_m, 0.5%; CO, 1.0%; H_2, 0.8%; CH_4, 82.3%; and N_2, 8.2% and was freed from liquid and solid products, but still contained C_3 and C_4 hydrocarbons. The gas had a heating value of about 840 B. t. u. per cu. ft. and was suitable as pipeline gas for long-distance transmission or for use as a chemical raw material.

2242. ———. Gas Producers; Gaseous Mixtures. British Patent 431,030, June 28, 1935. Chem. Abs., vol. 30, 1936, p. 273.

In a process as described in British Patent 364,407 (abs. **2283**) for obtaining a combustible gas rich in H_2 and CH_4 and in which solid fuel is gasified under high pressure with O_2, or air admixed with O_2, and steam, air and steam are used and the CO and part of the N_2 are removed from the resulting gas in a separate plant. The air is compressed to 20–30 atm., but pressures up to 200 atm. may be used, the higher the pressure the lower the N_2 content of the gas, and steam is mixed with the air (1:6), the mixture being superheated to about 500°. CO_2 and H_2S are removed by washing with H_2O under pressure and by treatment with NaOH and the CO and part of the N_2 are removed by cooling, CH_4 and other gaseous hydrocarbons together with H_2 and N_2 being left. The residual CO and N_2 may be used for superheating the gasifying medium. The CO may be converted into CH_4 or H_2 catalytically before its separation from the mixed gases. The separated CO may be converted into CH_4 and, or, H_2, which is mixed with the gas before or after it is treated in the separating plant.

2243. ———. Gases Rich in Hydrogen. British Patent 504,529, Apr. 26, 1939; appl. filed July 26, 1938. Chem. Abs., vol. 33, 1939, p. 7997.

In the production of gas mixtures containing CO and H_2 in the volume ratio of about 1 : 2 for synthesis purposes by the gasification of fuels under several atm. pressure by means of O_2-steam mixtures, the proportion of O_2 used being about 0.1–0.2 $m.^3$ per $m.^3$ of gas produced (calculated at normal temperature and pressure), CO_2 is added to the gasification medium in amounts of 0.5–3 times the vol. of O_2 employed. In an example, coke is gasified under 10 atm. pressure with a gas mixture comprising about 0.13 $m.^3$ O_2, 0.65 kg. steam and 0.2 $m.^3$ CO_2 to produce a gas mixture in which the CO and H_2 are 21 and 42%, respectively. CO_2 is washed from the gas mixture under pressure, and a part is returned to the producer for addition to the gasification medium. Inferior tars or oils or gaseous hydrocarbons may be added to the gasification medium and are cracked in the product.

2244. ———. [Gasification of Solid Fuels.] French Patent 843,515, July 5, 1939. Chem. Abs., vol. 34, 1940, p. 6799.

Method of producing a gas free from CH_4 and in which the volume ratio of CO to H_2 is equal to 1 : 2 consists in distilling the solid fuels under high pressure, 5–50 atm., using a gasification agent composed of O_2 and water vapor to which a quantity of CO_2 has been added.

2245. ———. Hydrocarbon Synthesis. British Patent 672,259, 1952. Fuel Abs., 1952, abs. 519.

Catalytic hydrogenation of CO with catalysts, which contain Fe, alkali metal compounds (preferably O-containing K compounds), and difficultly reducible nonvolatile reactive acid anhydrides. The ratio of metal compound to anhydride (calculated in terms of alkali metal oxide) by weight is 1 : 2.5–1 : 7.

2246. ———. [Hydrocarbon Synthesis.] Indian Patent 25,276, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 175.

See United States Patent 2,244,196 (abs. **1007**).

2247. ———. [Hydrocarbon Synthesis.] Italian Patent 362,725, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 176.

See British Patent 507,366 (abs. **1028**).

2248. ———. [Hydrocarbon Synthesis.] Italian Patent 390,888, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 162.

See French Patent 871,230 (abs. **2227**).

2249. ———. [Hydrocarbon Synthesis.] Netherlands Patent 54,877, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 176.

2250. ———. [Hydrocarbon Synthesis.] Swedish Patent 103,374, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 176.

2251. ———. [Hydrocarbon Synthesis.] Swiss Patent 211,487, no date. Schmidt, J., Das Kohlenoxyd, Verlagsgesell., Leipzig, 1950, p. 175.

See United States Patents 2,224,048 and 2,244,196 (abs. **1021** and **1007**).

2252. ———. [Hydrocarbon Synthesis From Carbon Dioxide and Hydrogen.] Belgian Patent 424,929, May 9, 1938; appl. filed Nov. 30, 1937.

See French Patent 832,967 (abs. **2265**).

2253. ———. Hydrocarbons. British Patent 510,350, July 31, 1939; appl. filed Nov. 29, 1937. Chem. Abs., vol. 34, 1940, p. 5274.

Hydrocarbons containing mainly paraffin that is solid at room temperature are produced by the catalytic conversion of gases containing CO and H_2 by disposing the catalysts in a contact furnace between cooling elements narrowly spaced apart and adapted to remove substantially all the heat generated in the

Production of valuable hydrocarbon mixtures is effected in stages by the catalytic hydrogenation of CO. During the initial stage, the new gas added contains more H_2 than CO. After the 1st stage, gases rich in H_2 are fed. Before the final phase, H_2 is to be supplied in such a way that the synthesis gas is composed of, at most, 1.8 vol. parts of H_2 per vol. part of CO.

2277. ———. [Process for Separating Free Fatty Acids From Animal, Plant or Synthetic Oils or Fats.] German Patent Appl. M 152,335, filed Nov. 4, 1941 (*Cl. IV a–23 a*). FIAT Reel R–6, frames 4,853–4,859; PB 73,554.

Process consists of saponifying the free fatty acids with alkalies, drying the fatty-acid soaps in the oil-soap flakes mixture under vacuum, and recovering the soap by means of some adsorbing agent.

2278. ———. [Process for the Catalytic Conversion of Gas Mixtures Containing Carbon Monoxide and Hydrogen.] German Patent Appl. M 153,760, Mar. 28, 1942 (*Cl. IV d–12 o*). FIAT Reel R–6, frames 5,124–5,136; PB 73,554.

Similar to German Patent 759,843 (abs. **2235**).

2279. ———. [Process for the Catalytic Conversion of Gas Mixtures Containing Carbon Monoxide and Hydrogen.] German Patent 754,821, Dec. 18, 1936; appl. M 136,644 (*Cl. 12 o–1.03*). FIAT Reel R–8, frames 7,186–7,191; PB 73,522.

In catalytically transforming CO and H_2 into hydrocarbons consisting mainly of paraffins and olefins at temperatures below those requisite for CH_4 formation, undesired side reactions are limited by 1st passing the gas mixture through a catalyst of low effectiveness and then through one of higher activity. It may be accomplished by gradually increasing the catalyst strength step by step in the direction of the gas flow, by using 2 or more reactors with ascending catalyst activity, or by grading the catalyst activity in each individual step or group of steps in such a way that per unit volume of catalyst equal amounts by weight of the reacting gases are converted. By such means the yield of the lighter and medium hydrocarbons is increased, and the total yield improved by the addition of 1 or more reaction steps in which a catalyst with higher or highest activity promotes a high degree of synthesis. A suitable catalyst for the 1st step is one with content of active metal greatly diluted by means of the carrier substance such as pumice alumina or the like, 50–55 gm. of metal per l. of bulk volume increasing to 80 gm. or more in the last step.

2280. ———. [Process for the Catalytic Conversion of Gas Mixtures Containing Carbon Monoxide and Hydrogen Into Hydrocarbons.] German Patent Appl. M 136,969, PA 53,099, filed Jan. 23, 1937 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 315–320; PB 83,253.

In the process for the catalytic synthesis of hydrocarbons from CO and H_2, the operations are carried out under conditions (relative to the composition and arrangement of the catalyst, the gas composition and its velocity, the reaction temperature, and the cooling) that in the synthesis at atmospheric pressure would lead to the production of more gasoline than oil or to the greater formation of lower C_1–C_4) hydrocarbons, and in connection with which pressure of 1.5 atm. or more, preferably 10–100 atm., is used. Catalysts are used that under favorable conditions of synthesis under atmospheric pressure give a yield $<$ 100 gm. of liquid products per N m.^{3} of synthesis gas, reckoned as $CO+2H_2$. The catalyst efficiency in the synthesis under pressure is maintained at virtually the same level by increasing the temperature or the pressure with increasing operating time or by reducing the gas throughput or by a combination of all these means. Example: 100 gm, of $Co(NO_3)_2$ containing traces of NiFeCu, and As are dissolved with 20 gm. of $Th(NO_3)_4$ in H_2O and 150 gm. kieselguhr added. Under strong stirring the metal is then precipitated using a solution of potash. The precipitate is suction filtered, washed with hot H_2O, and reduced at 350° with H_2. This catalyst, still containing traces of Fe, Cu, and As, yields by the synthesis from $CO : H_2 = 1 : 2$ and at the maximum temp. of 230° and atmospheric pressure 8 gm. oil and 40 gm. gasoline per N m.^{3} synthesis gas. By adding diluent gases such as N_2, CH_4, or H_2O vapor, the formation of oil and gasoline recedes, and soon oil formation entirely ceases. If the same catalyst and gas, a pressure of 10 atm., and a temp. of 200°–220° are used, 50 gm. of gasoline and 70 gm. of oil are produced per N m.^{3} of synthesis gas. By adding diluent gases as above, oil formation recedes with increasing gas addition. The total yield of oil and gasoline, however, remains about the same with a suitable gas throughput such as 2 m.^{3} of gas per hr. per kg. of Co. The modification in the process, which has as its object the increase in the gasoline yield through the use of diluent gases, has the advantage of extending greatly the life of the catalyst.

2281. ———. [Process for the Catalytic Hydrogenation of Gases Containing Carbon Monoxide.] German Patent 754,367, July 17, 1937; appl. M 138,698 (*Cl. 12 o–1.03*). FIAT Reel R–8, frames 7,153–7,158. PB 73,522.

In catalytically hydrogenating gases containing C oxides at increased temperature and pressure, 1 or more of the reactors operating with recycling of the reaction gases are connected with 1 or more that operate without recycling. The gases remain for a longer time in the reactors operating without recycling than in those with recycling. Also in the final step of the operation, a more efficient catalyst mass is used and both the temperature and the pressure are maintained at a higher level than in the preceding steps. Likewise in those reactors operating with recycling, the gas mixture contains more than 1 vol. of $CO : 2$ of H_2, and the composition of the exit gases before or at their entrance into the reactors not using recycling is corrected with reference to the H_2 content. By such means, a residue gas is obtained in which the constituents applicable to the synthesis are virtually exhausted. The method also has a special advantage for MeOH or higher alcohol synthesis in that the longer contact time makes possible a near approach to equilibrium conditions.

2282. ———. [Process for the Fine Purification of Gas.] German Patent Appl. M 154,098, Apr. 30, 1942 (*Cl. IV h–26 d*). FIAT Reel R–6, frames 5,196–5,202; PB 73,554.

In the fine purification of synthesis gas under pressure, the gas throughput is kept at 360–2,500 N m.^{3} per m.^{3} of purifying mass per hr. with the temperature at the lower rate 190°–200° and at the higher rate 230°. Example: To the normal purifying mass usually used for the removal of organic S from synthesis gas is added 30% of Na_2CO_3. The gas before its entrance into the purifying box is heated to the reaction temperature. The box is kept under 20 atm. pressure. The gas throughput is 2,500 N m.^{3} per hr. at 230°. The desulfurization is satisfactory, the S content being reduced to 0.2 gm. per 100 N m.^{3} or less. The composition of the gas in its passage through the box is scarcely changed. Higher hydrocarbons are not formed.

2283. ———. Producer Gas. British Patent 364,407, Mar. 10, 1930. Chem. Abs., vol. 27, 1933, p. 2020.

A combustible gas rich in H_2 and CH_4 is obtained by gasifying fuels under elevated pressure, such as 10–30 atm. with O_2 and an excess of steam, for example, 5–10 vol. to 1 of O_2. The fuel may be inferior brown coal. Describes apparatus.

2284. ———. [Production of Hydrocarbons.] British Patent 670,299, 1952. Fuel Abs., 1952, abs. 518.

Synthesis gas containing CO and H_2 is passed through a succession of layers of catalyst. The temperature of the gas leaving 1 layer of catalyst is reduced by cooling by an amount approximately equal to or only slightly less than the increase in temperature produced in the layer of catalyst before the gas traverses the next layer.

2285. ———. [Production of Hydrocarbons.] German Patent Appl. M 143,385, PA 913, 619, filed Nov. 18, 1938 (*Cl. 12 o–1.03*). FIAT Reel B–196, frames 214–235; PB 83,253.

Describes process for converting CO and H_2 into hydrocarbons at temperatures below that at which CH_4 is formed, wherein higher pressure, preferably 7–15 atm., is used and the synthesis gas is diluted, up to 20–50%, by inert gases or by the tail gas from the process itself. The catalyst consists of Co : ThO_2 : kieselguhr, the amount of Co being <33% by weight of the finished catalyst, preferably 0.5–40 gm. of active metal per l. of catalyst, and that of the activator 18% of the active metal. Example: With a catalyst consisting of Co 15% : ThO_2 2% : kieselguhr 83%, a temp. of 198°–225°, a pressure of 10 atm., and a gas flow of 100 *N* l. of 90% synthesis gas per l. of catalyst per hr., a yield of 140 gm. of liquid products per *N* $m.^3$ of inert-free synthesis gas was obtained in a 2-stage, 2 reactors in series, operation. The product consisted of 15% paraffin, 30% oil, and 55% gasoline. The catalyst life was 5 mo.

2286. ———. [Production of Hydrocarbons.] German Patent 754,368, Nov. 14, 1938 (*Cl. IV d–12o. FIAT* Reel R–8, frames 7,159–7,170; PB 73,522.

In a process for increasing the production of paraffin by synthesis from CO and H_2 at atmospheric or higher pressures and at temperatures below those necessary for CH_4 formation, the collection of paraffin on or within the catalyst is kept <100% of the weight of the paraffin-free catalyst, preferably even <20%, by the continuous trickling of a solvent over the catalyst. The specified solvent is that obtained by cooling the exit gases from the reactor and collecting the condensate. Certain definite means can be used to increase the paraffin yield: The use of thicker catalyst layers, more than 10 mm.; a longer contact period of the gases within the catalyst, preferably more than 3 min.; the use of highly concentrated catalysts, for example with >40% active metal; a ration of CO : H_2>1 : 2 in the synthesis gas; and the use of gas mixtures, which contain >90% of CO+H_2.

2287. ———. [Production of Hydrocarbons.] German Patent 756,242, Feb. 21, 1938 (*Cl. 12 o–1.03*). FIAT Reel R–8, frames 7,270–7,280; PB 73,522; Chem.-Ztg., vol. 69, No. 1, 1945, p. 17.

In catalytically converting CO and H_2 in proportion of 1.1 : 2 and more to hydrocarbons, principally of olefinic and paraffinic nature, a temperature, below that necessary for CH_4 formation and at atmospheric pressure, is contrasted to the reaction temperature, which, at 0.7 atm. H_2-partial pressure, is necessary for a 60% conversion of the reactants. An increase in the temperature, together with a reduction of the H_2-partial pressure in the catalyst mass, is feasible so that the increase in temperature may amount to at least 3° and at most 10° for each 0.1 atm. reduction in the H_2-partial pressure of 0.7 atm. Example: A catalyst containing 33% Co, 6% ThO_2, and 61% kieselguhr is placed in an Fe tube 1 cm. inside diameter to a depth of 3 m. The tube is surrounded by a pressure H_2O jacket in which the H_2O can be kept at a constant temperature. Through the catalyst tube, which contains 60 gm. of catalyst corresponding to 20 gm. Co, is passed 23 *N* l. per hr. of synthesis gas (58% H_2, 29% CO, 13% inerts) corresponding to a throughput of 1 l. ideal gas per gm. Co per hr. The temperature is maintained at 180°. The catalyst converts 0.6 l. CO+H_2 per gm. Co per hr. with formation of 120 gm. liquid products per *N* $m.^3$ of converted CO+2 H_2. The composition of the liquid product obtained is as follows:

Gasoline up to 200°	55% by weight
Oil 200°–300°	35% by weight
Paraffin >300°	10% by weight

The olefin content of the gasoline is 30%, of the oil 15%. The life of catalyst is about 2 months.

2288. ———. [Production of Hydrocarbons and Illuminating Gas.] French Patent 956,192, Jan. 25, 1950; appl. filed Apr. 11, 1944. Chem Zentralb., 1951, I, p. 954.

Gas obtained by the gasification of solid fuels under pressure is freed from condensable hydrocarbons, compounds of hydrocarbons, CO_2, S compounds, and resin formers and then used in the presence of Fe catalysts to hydrogenate CO. The H_2-rich gas contains preferably >2 vol. H_2 : 1 CO and >10% CO. The finished gas should contain >2% and <10%, preferably 4–8% of CO. The throughput of gas amounts to >100$m.^3$ preferably >200$m.^3$ per $m.^3$ catalyst per hr., without the recycle gas used. The catalysts are obtained by hydrolysis or precipitation of the Fe compounds and may contain carrier substance as well as promoters. The synthesis may take place in 2 or more steps with removal, between the steps, of the reaction products liquid at the reaction temperature; the later steps operate at higher gas throughput and/or temperature than the preceding ones. The converters are provided with closely lying cooling elements and layers of solid catalyst. The temperature is 250°–350° and the pressure 10–25 atm. Gasoline, oils, paraffin, and organic oxygenated compounds are formed and continuously removed from the residual gas.

2289. ———. [Products of Carbon Monoxide Hydrogenation.] German Patent Appl. M 159,172, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 281.

Gases of high calorific value together with liquid hydrocarbons are obtained from gases containing CO and H_2 by catalytic hydrogenation with Co or Ni catalysts at elevated pressure.

2290. ———. [Purifying Synthesis Gas.] German Patent Appl. M 151,366, no date (*Cl. IV b–26 d*).

To remove organic S compounds from synthesis gas, mixtures of alkali compounds and finely divided metals, for example, Zn dust, are used.

2291. ———. [Purifying Synthesis Gas.] German Patent Appl. M 152,550, no date (*Cl. IV b–26 d*).

Organic S compounds are removed from gases with exhausted catalysts from the benzine synthesis as the fine purifying mass, if desired after addition of alkali.

2292. ———. [Recovering Hydrocarbons.] French Patent 851,182, Jan. 4, 1940. Chem. Abs., vol. 36, 1942, p. 2119.

Method of separating condensable hydrocarbons from a gaseous hydrocarbon mixture comprises effecting the reexpulsion of the volatile constituents of the enriched washing oil using hot gases containing condensable hydrocarbons. The hot gases are caused to pass in countercurrent to the trickling washing agent. The thus purified washing agent is used again for washing gases rich in volatile constituents. Describes an apparatus.

2293. ———. [Reduction of Iron Catalysts.] German Patent Appl. M 158,462, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 280.

Hydrocarbons prepared by hydrogenation of CO contain appreciable amounts of alcohols, aldehydes, ketones, carboxylic acids, and phenols. Alcohols are separated by extraction with an aqueous solution of bisulfite adducts of aldehydes and ketones. Carboxylic acids are separated by extraction with an aqueous solution of an alkali metal carbonate and phenols by extraction with aqueous caustic alkali. The bisulfite solution, which should contain 7%–20% adducts of both aldehydes and ketones, is, in practice, the bisulfite solution used to extract aldehydes and ketones from the hydrocarbons before, or simultaneously with, extraction of the alcohols. Describes the method in detail with the help of flow diagrams.

2315. MICHAEL, W. (I. G. Farbenindustrie A. G.). [Catalysts for Producing Valuable Hydrocarbons From Carbon Monoxide and Hydrogen.] German Patent Appl. I 67,082, OZ 12,169, filed May 28, 1940 (*Cl. IV d–12 o*). FIAT Reel 163, frames 1,841–1,844; PB 25,607; Bureau of Mines Transl. T–433, Jan. 1948; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 6, chap. 163, 1949, p. 1.

In converting CO to liquid, solid, and gaseous hydrocarbons, catalysts are used that are made by thermal treatment of Fe compounds in presence of reducing gases at temperatures >500° but < the melting points of the metal compounds used until sintering occurs. Example: Precipitated $Fe(OH)_2$, to which 5% Al hydroxide is added, is heated in H_2 to 850°. Over the catalyst, thus produced, is passed at 12 atm. pressure and 220°–320° a mixture of CO and H_2 in proportion of 1 : 2. There is formed, in good yield, a mixture of gaseous, liquid, and solid hydrocarbons containing a small amount of oxygenated compounds. The use of this catalyst is said to avoid the disadvantages of excessive gas formation, destruction of catalysts through carbonyl formation, and deposition of C connected with catalysts reduced at 400°. Appears to correspond to United States Patent 2,183,145 (abs. **2329**).

2316. ——— (I. G. Farbenindustrie A. G.). [Conversion of Carbon Monoxide With Hydrogen.] German Patent Appl. I 70,663, OZ 13,042, filed Oct. 14, 1941 (*Cl. IV d–12 o*). FIAT Reel 170, frames 9,365–9,369; PB 64,235; Bureau of Mines Transl. T 433, Jan. 1948; Meyer Transl. PC–S–II, Fischer-Tropsch vol. 6, chap. 173, 1949, p. 29.

In converting CO with H_2 into multibranched hydrocarbons besides liquid and solid oxygenated organic compounds in presence of Fe catalysts, a catalyst is used that is made by burning Fe carbonyl and reducing the resulting oxide with H_2 at 450°. The synthesis process is carried out in the liquid phase with finely divided catalyst suspended in oil at 250° and 20 atm. pressure, the synthesis gas ($CO : H_2 = 5 : 4$) being admitted to the pressure vessel through a ceramic foam plate in the form of fine bubbles. A product is obtained in high yield consisting of 36% gasoline, 34% middle oil, and 30% paraffin with 60–70% of olefins.

2317. ——— (W. E. Currie). Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,254,806, Sept. 2, 1941; appl. filed Aug. 19, 1938, Serial No. 225,727, in Germany Aug. 26, 1937; 2 claims (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 8259.

Hydrocarbons such as those of benzine boiling-point range are produced with use, as a catalyst, of sintered Fe to which an alkali metal compound, which in aqueous solution has a neutral or acid reaction, such as KCl, has been added.

2318. ——— (I. G. Farbenindustrie A. G.). [Iron Catalyst.] German Patent Appl. —, OZ 9,261, filed Feb. 25, 1936. Bureau of Mines Transl. T–433, January 1948.

Difficultly reducible oxides are added before sintering. Appears to correspond to German Patent 729,290 (abs. **2334**).

2319. ——— (I. G. Farbenindustrie A. G.). [Iron Catalyst.] German Patent Appl. —, OZ 9,919, filed Apr. 14, 1937. Bureau of Mines Transl. T–433, January 1948.

Fe catalyst sintered at different temperature stages. Appears to correspond to United States Patent 2,254,748 (abs. **2332**).

2320. ——— (I. G. Farbenindustrie A. G.). [Iron Catalyst.] German Patent Appl. —, OZ 9,960, filed May 5, 1937. Bureau of Mines Transl. T 433, January 1948.

Sintered catalyst from Fe carbonyl. Appears to correspond to United States Patent 2,183,146 (abs. **2330**).

2321. ——— (I. G. Farbeninduserie A. G.). [Iron Catalyst.] German Patent Appl. —, OZ 11,217, filed Dec. 22, 1938. Bureau of Mines Transl. T–433, January 1948.

Compact Fe is oxidized, then reduced.

2322. ——— (I. G. Farbenindustrie A. G.). [Liquid-Phase Process.] German Patent Appl. —, OZ 10,189, filed Aug. 26, 1937. Bureau of Mines Transl. T–433, January 1948.

Synthesis with sintered Fe in the liquid phase. Appears to correspond to United States Patents 2,220,261 and 2,254,806 (abs. **2331** and **2317**).

2323. ——— (I. G. Farbenindustrie A. G.). [Liquid-Phase Process.] German Patent Appl. I 68,979, OZ 12,591, filed Feb. 22, 1941 (*Cl. IV d–12 o*). FIAT Reel 168, frames 7,243–7,250; PB 68,510; Bureau of Mines Transl. T–433, January 1948; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 6, chap. 179, 1949, p. 45.

Synthesis is carried out in the liquid medium with a suspended catalyst stirred by a vertical stirrer with large vanes arranged on a vertical shaft at right angles to the motion. The stirring is rapid enough to cause the liquid level to drop on the shaft or its elongation to the lower or middle part of the liquid layer at rest and intersect the surfaces of the stirrer.

2324. ——— (I. G. Farbenindustrie A. G.). [Process for Converting Carbon Monoxide With Hydrogen.] German Patent Appl. I 70,917, OZ 13,105, filed Nov. 20, 1941 (*Cl. IV d–12 o*). FIAT Reel 166, frames 5,333–5,335; PB 68,808; Bureau of Mines Transl. T–433, January 1948.

In an improvement of the process for the catalytic conversion of CO with H_2 to hydrocarbons with >1 C atom in the molecule in presence of Fe catalysts in accordance with German Patent 756,609 (abs. **1580**), Fe oxide produced by treating porous Fe, such as a used Fe catalyst at 750° with air is ground to powder, moistened with a borax solution containing 0.5 wt. % of borax calculated on the Fe, formed into pellets, and then reduced at 600° with H_2 and finally treated for 6 hr. at 850° in a H_2 atm. until sintering takes place. By passing $CO + H_2 = 4 : 5$ at 320° and 20 atm. over this catalyst, in accordance with the recycle process described in German Patent Appl. I 61,591, a conversion of 82% of the gas into hydrocarbons, mainly of gasoline boiling range, is obtained.

2325. ——— (I. G. Farbenindustrie A. G.). [Process for Converting Carbon Monoxide With Hydrogen.] German Patent Appl. I 70,918, OZ 13,106, filed Nov. 20, 1941 (*Cl. IV d–12 o*). FIAT Reel 166, frames 5,366–5,338; PB 68,809; Bureau of Mines Transl. T–433, January 1948.

Fe oxidizes with air to which about 50% of steam has been added. Addition to German Patent 756,609 (abs. **1580**) and German Patent Appl. I 70,917 (abs. **2324**).

———. *See* abs. **2676, 2677.**

2326. MICHAEL, W., AND BÜTTNER, A. (I. G. Farbenindustrie A. G.). [Antiknock Gasoline.] German Patent 738,709, July 22, 1943; appl. filed June 4, 1940 (*Cl. 23 b–1.04*). Chem. Abs., vol. 38, 1944, p. 4790.

The temperature at which the vapors are passed over the catalyst is 400°–450°, and preferably 440°. Addition to German Patent 735,276 (abs. **2328**).

2327. ——— (Alien Property Custodian). Catalyst for Synthesizing Hydrocarbons. United States Patent 2,365,094, Dec. 12, 1944; appl. filed Aug. 9, 1940, Serial No. 351,958, in Germany Dec. 22, 1938; 7 claims (*Cl. 260–449.6*). Chem. Abs., vol. 39, 1945, p. 3642.

Compact Fe bodies are treated with an oxidizing gas at such a high temperature and such a time that the Fe becomes completely oxidized without melting. The oxide formed is reduced to metal by treating it with a reducing gas. During both the oxidation and reduction the Fe bodies do not change their shape. This catalyst is used for synthesizing hydrocarbons of $>$ 1 C atom from CO and H_2.

2328. ——— (I. G. Farbenindustrie A. G.). [High-Antiknock Gasoline.] German Patent 735,276, Apr. 8, 1943 (*Cl. 23 b–1.04*). Chem. Abs., vol. 38, 1944, p. 2810.

Gasoline is synthesized from CO and H_2 with the aid of Fe-containing catalysts. This gasoline is passed in vapor state at 300°–400° over earths such as Al_2O_3, MgO, ZnO, or $AlPO_4$.

2329. MICHAEL, W., AND JAECKH, W. (I. G. Farbenindustrie A. G.). Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,183,145, Dec. 12, 1939; appl. filed Nov. 1, 1937, Serial No. 172,238, in Germany, Nov. 30, 1935; 6 claims (*Cl. 260–449*). Chem. Abs., vol. 34, 1940, p. 2573.

Conversion is effected, suitably at a temperature of about 280°–360° under 12 atm. pressure, with use of a catalyst prepared by a thermal treatment of an Fe compound such as precipitated Fe hydroxide at a temperature $>$ 600° and in the presence of a reducing gas such as H_2 but $<$ the melting point of the Fe compound or that of the Fe produced in the treatment, the temperature employed being high enough to effect at least partial sintering of the product.

2330. ——— (I. G. Farbenindustrie A. G.). Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,183,146, Dec. 12, 1939; appl. filed May 4, 1938, Serial No. 205,983, in Germany May 5, 1937; 5 claims (*Cl. 260–449*). Chem. Abs., vol. 34, 1940, p. 2573.

Relates to a process (United States Patent 2,183,145, abs. **2329**) in which the catalyst used is prepared by heating a carbonyl compound such as that of Fe to a temperature $>$ 500° to effect decomposition and partial sintering.

2331. ———(W. E. Currie). Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,220,261, Nov. 5, 1940; appl. filed Aug. 19, 1938, Serial No. 225,726, in Germany Aug. 26, 1937; 1 claim (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 1604.

In the production of hydrocarbons containing $>$ 1 C atom in the mol., reaction of CO and H_2 is effected in the presence, as catalyst, of sintered Fe, which is surrounded by a hydrocarbon oil (suitably at 330° under 40 atm. pressure).

2332. ——— (W. E. Currie). Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,254,748, Sept. 2, 1941; appl. filed Apr. 9, 1938, Serial No. 201,128, in Germany Apr. 14, 1937; 3 claims (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 8259.

Process for the conversion of CO and H_2 into hydrocarbons containing 1 C atom in the mol. comprises bringing the CO and H_2 into contact at a reacting temperature 150°–450° with a catalyst prepared by reducing a compound of a metal of the Fe group, reducible to the metal at a temperature $<$500°, by treatment at an elevated temperature $<$500° with a reducing gas and then treating the reduced substance in the absence of an oxidizing gas at such a high temperature $>$500° but $<$ the melting point of the reduced substance and for such a time that at least partial sintering of the reduced substance takes place.

2333. ——— (W. E. Currie). Hydrogenating Carbon Monoxide. United States Patent 2,211,022, Aug. 13, 1940; appl. filed Feb. 19, 1937, Serial No. 126,664, in Germany Feb. 25, 1936; 6 claims (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 604.

Process for the thermal conversion of CO with H_2 into liquid and solid hydrocarbons and gaseous hydrocarbons containing $>$1 C atom per mol. involves heating the CO and H_2 with a catalyst prepared by precipitating from a solution of an Fe group metal compound such difficultly soluble or insoluble compound of the metal, such as Fe hydroxide, as is easily reducible to the metal by heating in the presence of H_2, adding to the precipitated compound such compound of another metal such as Al hydroxide as by heating yields an oxide not reducible to metal by H_2 below 900°, and subsequently heating the resulting mixture in the presence of a gas having a reducing action to a temperature $>$500° for a time sufficient to effect sintering.

2334. ——— (I. G. Farbenindustrie A. G.). [Process for the Reaction of Carbon Monoxide and Hydrogen.] German Patent 729,290, Dec. 15, 1942; appl. I 54,417, filed Feb. 26, 1936 (*Cl. 12 o–1.03*). FIAT Reel AA–90, frames 1,575–1,577; PB 70,275; Meyer Transl. PC-S-II, Fischer-Tropsch, vol. 5, chap. 155, 1949, p. 33; Chem. Abs., vol. 38, 1944, p. 470.

To obtain products that contain chiefly gaseous, liquid and/or solid hydrocarbons from the reaction of CO and H_2, special catalysts are used. These catalysts consist of precipitated Fe compounds readily reducible with H_2, such as ferric hydroxide, carbonate, basic acetate, and oxalate, mixed with a compound of Al, Be, Mn, Zn, Th, Ce, and Zr, which in heating forms the oxide and is only difficultly reduced with H_2. A 3d easily reducible metal compound may be added also. Subsequently this mixture is dried and reduced with H_2 at 800°–850° C.

See also French Patent 814,636 (abs. **1274**).

2335. MICHAEL, W., AND PLAUTH, E. (Standard Catalytic Co.). Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,279,052, Apr. 7, 1942; appl. filed June 6, 1939, Serial No. 277,630, in Germany June 7, 1938; 15 claims (*Cl. 260–449*). Chem. Abs., vol. 36, 1942, p. 5337.

Describes arrangement of apparatus, and a process is employed for the synthesis of hydrocarbons with $>$1 C atom in the mol. and contingently minor amounts of from liquid to solid O-containing derivatives such as alcohols, which involves returning to the reaction space gases that have already been subjected to the reaction, the volume of the gases returned per unit of time being at least 20 times that of the fresh gas introduced in the same unit of time.

hydrocarbons as well as oxygenated organic compounds, a mixture of Fe_3O_4 with 1–15 wt. % of an alkali metal such as K_2CO_3 is heated in the presence of a free O_2-containing gas at 750°–1,400° F. to convert the major portion of the Fe_3O_4 to crystalline γ–Fe_2O_3, the purpose of the alkali metal being to stabilize the γ–Fe_2O_3 to prevent its conversion into the less desirable α–Fe_2O_3 form. The mixture of γ–Fe_2O_3 crystals and the stabilizing agent is then subjected to a reducing gas such as H_2 at 750°–1,400° F. for a time from 10 min. to 24 hr. before its use as catalyst. In actual practice it is preferred to contact the synthesis gas in the ratio of H_2 : CO=2 : 1 to 1 : 1 at feed rates of 1–1,500 vol. per vol. catalyst per hr. at 450°–675° F. and 10–600 p. s. i. g. Examples.

2345. ——— (Standard Oil Development Co.). Preparation of a Fischer-Tropsch Catalyst. United States Patent 2,567,297, Sept. 11, 1951; appl. filed July 5, 1949, Serial No. 103,108; 4 claims (*Cl. 252–474*).

A Fischer-Tropsch catalyst is prepared by mixing γ–Fe_2O_3 monohydrate with 1–15 wt. % of a stabilizing agent selected from the oxides, hydroxides, and carbonates of the alkali metals, heating the mixture to 750°–1,400° F. in the presence of a free O_2-containing gas for 10 min. to 24 hr. to obtain a mixture of crystalline γ–Fe_2O_3 and stabilizing agent, and subsequently contacting the mixture with a reducing gas at 750°–1,400° F. for 10 min. to 24 hr.

2346. ——— (Standard Oil Development Co.). Synthesis of Hydrocarbons With a Reduced Gamma Iron Oxide Catalyst. United States Patent 2,567,295, Sept. 11, 1951; appl. filed Jan. 3, 1949, Serial No. 69,068; 15 claims (*Cl. 260–449.6*).

CO–H_2 mixture is passed at 450°–675° F. and a pressure of 10–600 p. s. i. over a catalyst prepared by reducing at 750°–1,400° F. a mixture of Fe_2O_3 in the form of γ–oxide crystals and 1–15 wt. % based on the oxide of an alkali metal stabilizing agent. Hydrocarbons and oxygenated compounds produced.

2347. Mills, I. V., and Johnson, H. L. (Sun Oil Co.). Hydrogenation Catalyst. United States Patent 2,635,081, Apr. 14, 1953. Chem. Abs., vol. 47, 1953, p. 6642.

A catalyst especially suitable for the hydrogenation of hydrocarbon oils consists essentially of a spent cracking catalyst containing deposited thereon 10–25% MoS_2; the cracking catalyst was previously used in the cracking of hydrocarbon oils until its cracking activity had been reduced to at least 30% of its initial activity. The MoS_2 is advantageously deposited thereon by impregnating the spent catalyst with an aqueous solution of $(NH_4)_2MoO_4$, treating the impregnated catalyst with H_2S, and heating the composition at about 300° in an atmosphere of H_2. The catalysts are especially suitable for the hydrogenation of the aromatic constituents of petroleum fractions.

Mills, S. E. *See* abs. **772.**

Mineral Pigments Corp. *See* abs. **2136.**

2348. Minotte, M. E. H. (Compagnie de Béthune). Nitrogen, Hydrogen and Carbon Monoxide from Residual Coke-Oven Gases. United States Patent 1,875,253, Aug. 30, 1932; appl. filed June 21, 1929. Chem. Abs., vol. 26, 1932, p. 6079.

Gases are mixed with a suitable proportion of air and subjected to incomplete combustion in a gas generator filled with highly heated refractory material under conditions to prevent the formation of N oxides and the CO_2 content of the gas mixture is maintained at about 4% or 5% by regulating the relative volumes of air and coke-oven gases; the resulting gaseous mixture is purified from residual hydrocarbons by catalytic action, the CO_2 is absorbed in NH_3 solution, and the resulting gas containing CO and N_2 may be used for MeOH and NH_3 synthesis.

2349. Mitchell, R. L., and Luke, O. V. (Celanese Corp. of America). Oxidation Control. United States Patent 2,653,962, Sept. 29, 1953; appl. filed July 28, 1951, Serial No. 239,178; 16 claims (*Cl. 260–452*).

Claim 1. In the production of oxygenated organic compounds from aliphatic hydrocarbons by a process that includes passing an O-containing gas through a liquid reaction mixture containing an aliphatic hydrocarbon, the steps that comprise allowing a part of said reaction mixture, including unreacted hydrocarbon, H_2O of reaction, and other oxidation products, to distill over, condensing the overhead distillate, allowing the condensate to separate into a hydrocarbon phase and an aqueous phase and, while said separated phases are contiguous, subjecting at least 1 of said phases to extraction to remove oxygenated organic compounds therefrom.

Mitsubishi Chemical Industries Co. *See* abs. **3705.**

Mitsui Kôzan K. K. *See* abs. **1620, 1853.**

Mittasch, A. *See* abs. **783.**

2350. Mittasch, A., and Pier, M. Methanol. United States Patent 1,569,775, Jan. 12, 1926; appl. filed Sept. 4, 1924. Chem. Abs., vol. 20, 1926, p. 768.

Reaction of CO and H_2 to produce CH_3OH is effected under pressures >50 atm. (in 1 example 220 atm.) and at temperatures of 250°–600° in the presence of catalysts such as an equimolecular association of oxides of Cr and Mn in granular form. Fe is excluded from the catalyst, the walls of the apparatus in contact with the reacting mixture, and from the reacting materials themselves. Among the catalysts that may be used are oxides of V, U, Al, or other oxides which are nonreducible under the conditions of working, or metals such as Cu, Ag, Pb, or Zn in conjunction with a metal oxide or a metal salt acting as a promoter, especially those derived from metals of the 4th to 7th groups of the periodic system. Alloys of Cr, Mn, Cu, and Zn are referred to as suitable.

See abs. **94** and **2366.**

2351. ——— (I. G. Farbenindustrie A. G.). [Methanol and Its Homologs.] German Patent 565,309, Sept. 22, 1923. Chem. Abs., vol. 27, 1933, p. 1012.

Catalytic reaction under pressure of H_2 with oxides of C is effected in the complete absence of Fe, that is, the apparatus is lined with material free from Fe, a contact mass free from Fe is used, for example, a mixture of Cr_2O_3 and MnO, and the gases are freed from Fe, if necessary. MeOH and its homologs are obtained to the substantial exclusion of other products.

See also German Patent 544,665 (abs. **2364**).

2352. ——— (I. G. Farbenindustrie A. G.). [Methyl Alcohol.] German Patent 622,595, Dec. 2, 1935 (*Cl. 12 o–5.01*). Chem. Abs., vol. 30, 1936, p. 3444.

Method of German Patent 544,665 (abs. **2364**) for obtaining MeOH or other organic compounds containing O by the catalytic hydrogenation of oxides of C at temperatures about 450° and at about 200-atm. pressure, is modified by employing the contact masses of German Patents 565,880 (abs. **3765**) and 600,677 (abs. **3288**), the temperature required being < 450°.

See also German Patent 608,361 (abs. **3287**).

2353. ——— (I. G. Farbenindustrie A. G.). [Oxygenated Organic Compounds From Oxides of Carbon.] German Patent 628,427, Apr. 4, 1936 (*Cl. 12 o–5.01*). Chem. Abs., vol. 30, 1936, p. 4510.

As catalysts in the reaction of oxides of C with H_2 and/or hydrocarbons at a raised temperature and pressure, use is made of mixtures containing com-

pounds of K, Rb, or Cs and readily reducible metal oxides or their compounds or reduction products. Oxides or compounds of Cu, Ag, Au, Sn, Pb, Sb, Bi, Cd, Tl and the metals of the Pt group may be used, but the presence of Fe, Ni, or Co should be avoided. The products are mainly MeOH and other lower alcohols. Gives examples.

See German Patent 612,229 (abs. **1379**).

2354. ——— (I. G. Farbenindustrie A. G.). [Oxygenated Organic Compounds From Oxides of Carbon.] German Patent 636,682, Oct. 15, 1936 (*Cl. 12 o–5.01*). Chem. Abs., vol. 31, 1937, p. 2228.

As catalysts in the reaction of oxides of C with an excess of H_2 and/or hydrocarbons at a raised temperature and pressure, use is made of mixtures containing compounds of K, Rb, or Cs and metals or metalloids that form difficultly reducible oxides. Al, B, Cr, Mn, Mo, Si, Ti, Nb, Ta, V, W, and Zr or their alloys, including their carbides, hydrides, and nitrides, are suitable. The proportion of the compound of K, Rb, or Cs should be of the order of 5%. The products are mainly MeOH and other lower alcohols. Gives an example. Addition to German Patent 628,427 (abs. **2353**).

See also German Patent 637,446 (abs. **2355**).

2355. ——— (I. G. Farbenindustrie A. G.). Oxygenated Organic Compounds From Oxides of Carbon. German Patent 637,446, Oct. 28, 1936; appl. filed Mar. 27, 1923 (*Cl. 12 o–5.01*). Chem. Abs., vol. 31, 1937, p. 700.

As catalysts for the hydrogenation of oxides of C at a raised temperature and pressure, use is made of V, Cb, and Ta or their alloys, including their hydrides, nitrides, and carbides. Mixtures containing these metals and alloys may also be used.

2356. ——— (Badische Anilin- u. Soda-Fabrik). Production of Methanol and the Higher Homologs.] French Patent 585,169, Feb. 23, 1925, appl. filed Sept. 2, 1924. Chem. Zentralb., 1926, I, p. 2241.

See United States Patent 1,569,775 (abs. **2350**), and British Patent 240,955 (abs. **94**).

2357. Mittasch, A., and Schneider, C. (Badische Anilin- u. Soda-Fabrik). [Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 468,427, Feb. 13, 1914. Jour. Soc. Chem. Ind., B, 1914, p. 984.

See German Patent 293,787 (abs. **2360**) and United States Patent 1,201,850 (abs. **2358**).

2358. ——— (Badische Anilin- u. Soda-Fabrik.). Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 1,201,850, Oct. 17, 1916; appl. filed Feb. 11, 1914, Serial No. 818,054. Chem. Abs., vol. 10, 1916, p. 3143.

Catalytic mass formed of asbestos, oxide of Co or Os, and NaOH is treated under 100 atm. pressure and at a temperature of 300°–400° with a mixture of H_2 1 and CO 2 parts or more. Some C is deposited and CH_4, higher hydrocarbons, and their oxidation products, aldehydes, are formed and are recovered by condensing under pressure. A catalytic mass, formed by heating an inert carrier with $Zn(NO_3)_2$ and K_2CO_3, when treated under 120 atm. pressure at a temperature of 360°–420° with a mixture containing CO, 62%; H_2 28%; CO_2, 4%; CH_4, 2%; and N_2, 4% effects the production chiefly of higher hydrocarbons and their derivatives with but slight deposition of C. Catalytic materials for effecting similar reactions may be formed of Ce, Cr, Co, Mn, Mo, Os, Pd, Ti, Zn, or their oxides in various mixtures with carriers and alkali metal hydroxides. About two-thirds of the compounds formed are of the saturated series and the rest olefinic.

2359. ———. (Badische Anilin- u. Soda-Fabrik). [Process for Producing Hydrocarbons and Their Derivatives.] German Patent 295,203, Nov. 8, 1916; appl. filed June 23, 1915 (*Cl. 12 o–1*). Chem. Zentralb., 1916, II, p. 1095.

The processes of German Patents 293,787 and 295,202 (abs. **2360** and **111**) are improved by the use of catalysts containing the carbide of metals such as Fe, Mo, W, and the like.

2360. ———. (Badische Anilin- u. Soda-Fabrik). [Production of Hydrocarbons and Their Derivatives.] German Patent 293,787, Aug. 23, 1916; appl. filed Mar. 8, 1913 (*Cl. 12 o–1*). Chem. Zentralb., 1916, II, p. 530.

Liquid or light hydrocarbons, as well as the oxygenated derivatives, can be obtained by treating the C oxides with H_2 in the presence of catalysts under raised pressure of several atmospheres. Depending upon the nature of the catalyst and the operating conditions, various products can be obtained, such as hydrocarbons of saturated or unsaturated nature, alcohols, aldehydes, ketones, and acids. To produce large amounts of liquid products it is preferred to use gas mixtures in which the H_2 content is less. Various elements and compounds can be used as catalysts: Cr, Co, Mn, Mo, Os, Ti, Zn, or their oxides and other compounds.

See also abs. **80**, **2357**, and **2358**.

2361. Mittasch, A., Balz, O., and Traeger, K. (Badische Anilin- u. Soda-Fabrik). [Methane From Carbon Monoxide and Hydrogen.] German Patent 366,791, Jan. 11, 1923; appl. filed Feb. 12, 1921. Chem. Zentralb., 1923, II, p. 740.

A mixture of 3.4–3.6 vol. parts H_2 and 1 vol. CO is passed at about 240° over a catalyst consisting of reduced Ni activated with Al_2O_3 and deposited on alumina. A gas mixture is obtained consisting of 84% CH_4, 15% H_2, 1% CO, which can be further treated if desired.

2362. Mittasch, A., Pier, M., and Müller, C. (Badische Anilin- u. Soda-Fabrik). [Methanol.] Norwegian Patent 41,140, Mar. 30, 1925; appl. filed Sept. 12, 1923. Chem. Zentralb., 1928, I, p. 407.

See British Patent 229,714 (abs. **91**), Canadian Patent 251,483 (abs. **2667**), and French Patent 571,354 (abs. **2670**).

2363. ——— (I. G. Farbenindustrie A. G.). Methanol Synthesis. United States Patent 1,791,568, Feb. 10, 1931; appl. filed Sept. 15, 1923. Chem. Abs., vol. 25, 1931, p. 1844.

In synthesis of MeOH from H_2 and C oxides in the presence of a catalyst such as potash-lime or potash-alumina more than 2 vol. of H_2 for each vol. of CO and more than 3 vol. of H_2 for each vol. of CO_2 are employed. Gives several examples.

See also Swiss Patent 107,200 (abs. **2669**) and United States Patent 1,788,170 (abs. **2674**).

2364. ——— (I. G. Farbenindustrie A. G.). [Methyl Alcohol.] German Patent 544,665, Feb. 23, 1923. Chem. Abs., vol. 26, 1932, p. 3521.

MeOH and other organic compounds containing O are prepared by the catalytic hydrogenation of CO at temperatures of at least 450° and under pressures of about 200 atm. A greater volume of H_2 than CO is present and the action is carried out in the presence of catalyzers consisting of metal oxides, which are not reduced to the metal under the conditions of the reaction. The catalyzers consist of oxides of the alkali, alkaline earth, or earth metals and contain no Fe, Ni, or Co. In an example, a mixture of 75 parts of H_2 and 25 parts of CO are subjected to a pressure of 500–1,000 atm. at 550° over a contact mass prepared

from Al_2O_3 and KOH. The product is a light-brown liquid boiling under 100° and consisting principally of MeOH and other alcohols. Gives other examples.

See also United States Patent 1,823,468 (abs. **2646**).

2365. MITTASCH, A., PIER, M., AND WINKLER, K. (Badische Anilin- u. Soda-Fabrik.) [Methanol.] Danish Patent 33,495, July 28, 1924; appl. filed Sept. 24, 1923.

See United States Patent 1,558,559 (abs. **2366**).

2366. ——— (Badische Anilin- u. Soda-Fabrik). Methanol. United States Patent 1,558,559, Oct. 27, 1925; appl. filed Sept. 6, 1923. Chem. Zentralb., 1926, I, p. 2147; Chem. Abs., vol. 20, 1926, p. 209.

Mixture of C oxides with at least about an equal volume of H_2 at a temperature of 200°–600° and under a pressure of 50 atm. or higher is passed over a catalyst containing an intimate mixture of at least 2 oxides (nonreducible to metals under the conditions of the process) of metals belonging to different periodic groups such as Zn and Cr, Zn and U, Zn and V, Zn and W, Mg and Mo, or Ce and Mn. The more basic oxide is used in larger proportion and Fe and Ni should be absent.

2367. ——— (I. G. Farbenindustrie A. G.). [Organic Compounds.] German Patent 660,619, May 31, 1938 (*Cl. 12 o–27*). Chem. Abs., vol. 32, 1938, p. 6664.

Method for producing liquid hydrocarbons by the action of H_2 on olefins at high temperature and pressure in the presence of oxygenated metal compounds as catalysts, is modified by replacing the H_2 by a mixture of H_2 and CO_2. Thus a mixture of C_2H_4, CO_2, and H_2 is passed over active SiO_2 at 500 and 150 atm. to give a product containing higher alcohols and ketones. Addition to German Patent 539,990 (abs. **2372**).

2368. ——— (Badische Anilin- u. Soda-Fabrik). [Performing Organic Catalysis Particularly Hydrogenation.] German Patent 415,686, June 27, 1925; appl. filed July 24, 1923. Chem. Zentralb., 1925, II, p. 1802.

Hydrogenation of CO or CO_2 with H_2 under pressure to MeOH or higher molecular O-containing compounds takes place readily and with good results in the presence of mixtures of metal oxides from groups 2–7. Example: A gas mixture free from Fe carbonyl and consisting of 30 parts CO; 64, H_2; 4, N_2; 1, CH_4; and 1, CO_2 is passed at 200 atm. pressure and 400° over a catalyst consisting of 90 parts ZnO and 10 Cr_2O_3. The reaction gases, on cooling under pressure, yield good amounts of almost pure MeOH.

2369. ——— (Badische Anilin- u. Soda-Fabrik). [Production of Methanol.] French Patent 571,356, May 16, 1924; appl. filed Oct. 1, 1923. Chem. Zentralb., 1926, I, p. 2147.

See United States Patent 1,558,559 (abs. **2366**).

2370. MITTASCH, A., WINKLER, K., AND PIER, M. (Badische Anilin- u. Soda-Fabrik). Oxygenated Organic Compounds. Canadian Patent 251,484, July 7, 1925; appl. filed Nov. 7, 1923. Chem. Abs., vol. 19, 1925, p. 3272.

Methanol is produced by passing a mixture of C oxides and H_2 at elevated temperature and pressure over a catalyst containing oxides of Zn and Cr, with an excess of ZnO. The product is separated from the gases by cooling.

See also United States Patent 1,558,559 (abs. **2366**).

2371. ——— (Badische Anilin- u. Soda-Fabrik). [Preparation of Organic Compounds by Means of Catalytic Gas Reactions.] German Patent 441,433, Sept. 27, 1923. British Chem. Abs., B, 1927, p. 924.

As catalysts, especially for reduction of C oxides, are used in addition to oxide of Zn or Cd difficultly reducible O compounds of at least 2 metals of the higher groups of the periodic system. Such mixed catalysts are very resistant to catalyst poisons, and when used in the reduction of C oxides yield alcohols almost exclusively. A mixture of 70% H_2 and 30% CO at 200 atm. passed at 400°–420° over a catalyst containing Zn oxide (1–2 mol.) and Cr trioxide (1 mol.) gives nearly pure methyl alcohol. Addition of alkali hydroxides to the catalyst leads to formation of higher alcohols. Other combinations of catalysts are oxides of Zn, Cr, and U or V; Cd, Cr, and W; Zn, Mn, and V; Zn, V, and U; Zn, Cd, Cr, and U. The metals Cu, Ag, Pb, or Th or their oxides may be added, but Fe compounds are to be avoided. Ethylene is reduced quantitatively to ethane when led with H_2 at 380°–400° over a mixture of Zn oxide (3 mol.), Cr oxide (2 mol.), and U oxide (1 mol.). Describes the preparation of higher alcohols from alcohol, CO, H_2, and N_2.

2372. MITTASCH, A., WINKLER, K., AND URBAN, W. (I. G. Farbenindustrie A. G.). [Liquid Hydrocarbons.] German Patent 539,990, Mar. 1, 1924. Chem. Abs., vol. 26, 1932, p. 2197.

Unsaturated hydrocarbons are hydrogenated to form liquid saturated hydrocarbons in a single stage by treatment with H_2 under pressure in the presence of a metal-oxide catalyzer, which is not reduced to the metal under the conditions of the reaction. Such catalyzers are $ZnO \cdot Cr_2O_3$, $ZnO \cdot MnO$, $KOH \cdot ZnO \cdot Cr_2O_3$.

See also German Patent 538,012 (abs. **116**).

2373. MITTASCH, A., MÜLLER, C., SCHLECHT, L., AND SCHUBARDT, W. (I. G. Farbenindustrie A. G.). Synthesizing Hydrocarbons From Carbon Oxides and Hydrogen. United States Patent 1,698,602, Jan. 8, 1929. Chem. Abs., vol. 23, 1929, p. 1135.

Gaseous mixture comprising oxides of C and somewhat less H_2 than is theoretically necessary for the conversion of the oxides of C into CH_4 is subjected to the action of a metal catalyst such as Fe, which is prepared from the corresponding metal carbonyl.

2374. MITTASCH, A., PIER, M., WIETZEL, R., AND LUTHER, M. (I. G. Farbenindustrie A. G.). [Oxygenated Organic Compounds.] German Patent 625,757, Feb. 14, 1936 (*Cl. 12 o–5.01*). Chem. Abs., vol. 30, 1936, p. 5588.

High molecular organic compounds containing O and insoluble in H_2O are obtained by passing a mixture of H_2 or hydrocarbons and oxides of C over a contact agent containing alkalies and hydrogenating or dehydrogenating constituents in suitable proportions at high temperatures and pressure. In the example, the contact agent contains 1 part of K_2CO_3, 1 part of V_2O_3 and 1 part of CuO. H_2 and C are passed over at 480° under pressure to give a yield containing 40% MeOH, 25% iso-BuOH, 20% H_2O, and the rest higher alcohols and esters.

See also German Patent 544,665 (abs. **2364**) and 628,427 (abs. **2353**).

2375. MITTELDEUTSCHE STAHLWERKE A. G. [Converter for the Fischer-Tropsch Process.] German Patent Appl. M 149,748, R 159, filed Jan. 23, 1941 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 303–309; PB 83,253.

This patent application has to do with a pressure converter for the Fischer-Tropsch process having stationary lamellae bundles inserted into a diagonally divided pressure vessel in which all feed and outlet pipes for H_2O, steam, and gas are arranged compactly in the immovable cover of the pressure vessel, while the vessel is movable. The cover piece may also be built out so that it becomes the middle piece to which 2 or more vessels with lamellae bundles are connected. The middle piece may be provided with 1 or more separating walls so that chambers having the same or

different pressure zones are formed. Arrangements are provided for moving the bundles for repair or cleaning.

2376. ——— [Heat-Exchange Apparatus, Particularly for Contact Furnaces for the Synthesis of Hydrocarbons.] German Patent 659,133, Apr. 26, 1938 (*Cl. 17 f–5.23*). Chem. Abs., vol. 32, 1938, p. 5266.

2377. Moak, O. W., and Spicer, W. E. (Standard Oil Development Co.). Water-Gas Shift Catalyst Preparation and Water-Gas Shift Process. United States Patent 2,631,086, Mar. 10, 1953; appl. filed Oct. 27, 1949, Serial No. 123,995; 11 claims (*Cl. 23–212*).

Gives a process for preparing a catalyst consisting of Fe oxides (93%) and Cr oxides (7%) but superior in activity and durability to the conventionally prepared catalyst. Cr trioxide is used in place of Cr nitrate. Since the amount of H_2O required to dissolve the necessary amount of CrO_3 is smaller than the amount needed to dissolve the $Cr(NO_3)_3$ and since the amount of H_2O is adjusted exactly to the amount required for extrusion, the wetting and drying steps are eliminated. Solubility of $Cr(NO_3)_3$ in H_2O is substantially < than that of chromic acid in terms of total amount of Cr that may be dissolved. Decomposition of the nitrates and disposal of the N oxides are eliminated. After extrusion and pelleting, the particles are activated at 1,000°–1,300° F. 5 United States patents cited.

Moegenburg, H. *See* abs. **3928.**

Moehl, R. W. *See* abs. **3884.**

2378. Mohr, J., and Lagelbauer, E. Treating Waste Materials Such as Garbage and Trash. United States Patent 2,238,367, Apr. 15, 1941; appl. filed Mar. 18, 1938, Serial No. 196,626; 6 claims (*Cl. 202–15*). Chem. Abs., vol. 35, 1941, p. 4942.

Treatment of municipal and industrial wastes containing C-bearing material for producing various products of value involves carbonizing the material by heating in the presence of air or O_2 in an amount insufficient to effect complete combustion. Volatile and nonvolatile products of carbonization including CO are formed and simultaneously hydrogenated under conditions tending to cause reactions to take place between them by subjecting the products to the action of H_2 and the influence of heat and pressure in the presence of a hydrogenation catalyst.

2379. Mohr, O. (I. G. Farbenindustrie A. G.). [Purifying Synthetic Organic Products of Carbon Monoxide.] German Patent 508,953, Aug. 5, 1924. Chem. Abs., vol. 25, 1931, p. 709.

Synthetic organic products of CO and H_2 such as CH_3OH and isobutyl alcohol, are purified by treating them with an oxidizing agent such as $KMnO_4$, H_2O_2, HClO, HBrO, and free alkali. Gives examples.

See also French Patent 650,543 (abs. **1517**).

Monsanto Chemical Co. *See* abs. **622.**

2380. "Montecatini" Società Générale per L'industria mineraria e chimica. [Catalyst for Methanol Synthesis.] German Patent Appl. M 161,685, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 281.

Catalysts for the synthesis of MeOH are made by mixing chromic acid with Mn hydrate, drying, and pressing into pills.

2381. ———. [Catalysts for Synthesis of Methanol and Higher Alcohols From Carbon Monoxide and Hydrogen.] French Patent 957,315, Feb. 2, 1950; appl. filed Dec. 16, 1947. Chem. Zentralb., 1951, I, p. 117.

Catalyst consists of CrO mixed with $Mn(OH)_2$. 2,300 kg. Mn $(NO_3)2{\cdot}6\ H_2O$ are dissolved in a like amount of H_2O. With exclusion of air and in presence of a nonoxidizing inert gas such as N_2 or CO_2, 3,220 kg. of a boiling solution of KOH (30° B.) are introduced and stirred for ½ hr. The mixture is filtered and the $Mn(OH)_2$ washed with water with exclusion of air.

2382. ———. [Combined 2-Stage Production of Methanol and Higher Alcohols and Hydrocarbons by the Fischer-Tropsch Process.] French Patent 957,372, Feb. 17, 1950; appl. filed Dec. 17, 1947. Chem. Zentralb., 1951, I, p. 1406.

Residual gases obtained in the 1st stage of alcohol synthesis and containing substantial amounts of N_2 and CH_4, are used, with synthesis gas, in the 2d stage of the process for the synthesis of hydrocarbons.

2383. ———. [Continuous Preparation and Conversion of Water Gas Into Synthesis Gas.] Italian Patent 439,334, Sept. 16, 1948. Chem. Abs., vol. 45, 1951, p. 848.

Formation of water gas, by passing O_2 and steam and/or CO_2 through a water-gas generator, is regulated so that the temperature of the water gas and steam issuing is at 400°–500°. The gas then passes through a S-resistant catalyst to convert the water gas into synthesis gas.

2384. ———. Heat Exchangers for Gaseous Exothermic Catalytic Reactions. British Patent 671,573, May 7, 1952. Chem. Abs., vol. 46, 1952, p. 9287.

Gaseous exothermic reactions over a catalyst at high temperature and under pressure are controlled by removing the heat of reaction by circulating H_2O through tubes situated in the interior of the catalyst chamber. The heat is removed by evaporation of the H_2O at a number of zones spaced between successively deeper catalyst layers in the direction of gas flow. The quantities of H_2O evaporated in each zone are independently controlled to produce steam at high pressure, which is condensed with H_2O to form steam at low pressure and the condensate is recirculated.

2385. ———. [Purification of Synthetic Alcohols.] French Patent 957,415, Feb. 17, 1950; appl. filed Dec. 18, 1947, in Italy June 17, 1944. Chem. Zentralb., 1950, II, p. 1875.

Synthetic alcohols from CO and H_2, which contain as byproducts aldehydes, ketones, and free fatty acids, are purified by catalytic hydrogenation in presence of Ni, Co, or Cu or mixtures thereof, likewise with small amounts of other metals such as Zn, Cr, Fe, or Ag and a carrier substance such as silica gel or active C. The byproducts are converted by the hydrogenation into alcohols. The hydrogenation products are diluted with H_2O to facilitate the fractionation of the alcohols.

———. *See* abs. **644, 842.**

2386. "Montecatini" Società Genérale per l'industria mineraria ed agricola. [Catalyst for Preparation of Methanol and Higher Alcohols From Carbon Monoxide and Hydrogen.] Italian Patent 352,746, June 10, 1937. Chem. Zentralb., 1938, I, p. 3387.

An alloy of metals, Cu–Al, Ag–Al, Cu–Si, Ag–Si, is treated with a reagent, NaOH, which dissolves 1 or more of the constituents and leaves the rest as a skeleton. This skeleton can be used by itself or mixed with other materials, which effect alcohol formation such as ZnO or CrO_3.

2387. Montgomery, C. W. (Gulf Research & Development Co.). Low-Pressure Hydrogenation Process. United States Patent 2,561,530, July 24, 1951; appl. filed Nov. 19, 1948, Serial No. 61,037; 9 claims (*Cl. 196–30*). Chem. Abs., vol. 46, 1952, p. 3748.

In the process of hydrogenating or desulfurizing hydrocarbon vapors with H_2 in presence of a catalyst comprising at least 2% of an Fe group metal on a porous solid carrier, such as silica gel, decrepitation of the catalyst is avoided by employing instead a catalyst having less than about 0.8 of a statistical mono-

layer of the Fe group metal substantially evenly distributed on the pore surface of the carrier and determined in accordance with the formula:

$$n=2.09\times10^{20}\frac{w}{100-w}\frac{r^2}{MS}$$

where n is the number of statistical layers on the support, w the wt. % Fe group metal on the reduced catalyst, r the radius of the Fe group metal atom in cm., M the atomic weight of Fe group metal, S surface area of the support in $m.^2$ per gm. The process has also a special value in connection with the Fischer-Tropsch process.

———. *See* abs. **807.**

2388. MONTGOMERY, C. W., AND BROWN, C. S. (Gulf Research & Development Co.). Catalytic Desulfurization of Hydrocarbons. United States Patent 2,640,009, May 26, 1953. Chem. Abs., vol. 47, 1953, p. 7771.

Treatment of a hydrogenating catalyst combined with a solid refractory cracking catalyst with wet steam improves the desulfurization of hydrocarbon vapors brought into contact with it in the presence of H_2. This treatment also reduces the amount of gas and C formed during the process. In the examples, a West Texas crude oil was treated by using Ni oxide on SiO_2–Al_2O_3 as the cracking catalyst.

2389. MONTGOMERY, C. W., AND GILBERT, W. I. (Gulf Research & Development Co.). Process for Deoxygenating and Isomerizing a Fischer-Tropsch Stock. United States Patent 2,589,273, Mar. 18, 1952; appl. filed Sept. 17, 1948, Serial No. 49,845; 11 claims (*Cl. 260–450*).

Synthetic motor fuel containing olefins and oxygenated compounds is simultaneously deoxygenated and isomerized while being passed at 300°–600° over a catalyst comprising Al_2O_3 impregnated with anhydrous HCl.

2390. MONTGOMERY, C. W., AND HORNE, W. A. (Gulf Research & Development Co.). Hydrocarbon Synthesis. United States Patent 2,602,810, July 8, 1952. Chem. Abs., vol. 46, 1952, p. 9286.

Hydrocarbons of gasoline grade are produced by the reaction of H_2 and CO in the presence of an Fe catalyst (I) consisting of 50–100% reduced Fe_2O_3. Reactor feed gas at an initial temperature of 430°–475° F. and at 25–600 p. s. i. containing H_2 and CO in a 15–30 : 1 mole ratio and consisting of recycle gas (II) and fresh feed (III) in an 8–15 : 1 vol. ratio, the (III) containing H_2 and CO in a 2.8–4 : 1 mole ratio, is conducted over a fixed bed of (I) having a maximum temperature of 600°–630° F. and a temperature gradient of 125°–165° F. to give a 98% conversion of CO; oxygenated compounds and hydrocarbons containing >3 C atoms are condensed to give (II). A typical distribution in the hydrocarbon product is gas 4.8, gasoline (b. to 400° F.) 69.9%, b. 400°–700° F. 18.7%, and b. >700° F. 6.6% by weight.

2391. ——— (Gulf Research & Development Co.). Hydrocarbon Synthesis. United States Patent 2,638,477, May 12, 1953. Chem. Abs., vol. 47, 1953, p. 8999.

Fracturing of the synthesis catalyst is prevented by removing C by oxidation prior to the point at which fracturing begins. In a fixed-bed recycle operation wherein the volume ratio of recycle gas to fresh synthesis gas is within the range of 5 : 1 to 50 : 1, the maximum allowable pressure drop increase across the catalyst bed before burning off C from the catalyst is $p=40A/B$, where A=volume of fresh synthesis gas per hr. and B=volume of recycle gas per hr.

2392. ——— (Gulf Research & Development Co.). Synthesis of Hydrocarbons. United States Patent 2,602,811, July 8, 1952; appl. filed Dec. 28, 1949, Serial No. 135,442; 8 claims (*Cl. 260–449.6*). Chem. Abs., vol. 46, 1952, p. 9287.

Hydrocarbons are synthesized from CO and H_2 in a series of fixed catalyst beds containing Fe synthesis catalyst. The reaction mixture comprises H_2 and CO but contains initially only 2% CO, 80% H_2, and diluents consisting essentially of N_2 and CO_2. The ratio of H_2 : CO in the reaction mixture is at least 40 : 1. Makeup gas comprising CO is added between each of the beds and is adjusted to obtain a reaction gas mixture fed to the last of the beds of no more than a 4% CO content and a minimum ratio of H_2 : CO=15 : 1. The reaction mixture is passed across the 1st catalyst bed at a rate to produce a temperature gradient of 125°–165° F. The reaction mixture fed to the 1st bed is preheated, and those fed to the subsequent beds are cooled to a reaction initiation temperature of 430°–525° F. In general it is preferred to operate so that the maximum temperature at the exit side of the bed is about 610°–630° F. Operating under these conditions, a temperature gradient of 100°–200° F. (preferably 125°–165° F.) is maintained in each of the beds, The hot products of reaction are cooled to condense at least the normally liquid hydrocarbons and other compounds boiling above the hydrocarbons. Preferably the condensation is carried out so as to condense most of the C_4 and heavier hydrocarbons and oxygenated compounds formed in the reaction.

2393. MONTGOMERY, W. B., AND RAPASKY, F. (M. W. Kellogg Co.). Catalyst Chamber. United States Patent 2,504,215, Apr. 18, 1950; appl. filed Jan. 5, 1944, Serial No. 517.140; 5 claims (*Cl. 23–288*). Chem. Abs., vol. 44, 1950, p. 5577.

Describes apparatus for catalytic hydrocarbon conversion in which the vapors are passed through tubes containing powdered catalyst. Fresh catalyst is constantly being supplied and spent catalyst is constantly being removed. 1 foreign patent and 12 United States patents cited.

2394. MOORE, F. J. (The Texas Co.). Method of Effecting Catalytic Reactions. United States Patent 2,440,109, Apr. 20, 1948; appl. filed Feb. 6, 1945, Serial No. 576,472; 6 claims (*Cl. 260–449.6*). Chem. Abs., vol. 42, 1948, p. 4732.

In the catalytic hydrogenation of CO, the catalyst in finely divided form is suspended in a suitable carrier liquid to form a column of slurry in the reaction zone, the slurry being moved by injection of a mixture of the reacting CO–H_2 in proper proportions for the reaction, the mixture of slurry, unreacted gas, and the products of the reaction being discharged from the upper part of the reaction zone and recycled after removal of the reaction products. The reaction zone is surrounded by a cooling liquid to remove the exothermic heat and maintain the proper conversion temperature. The reaction may be carried out under pressure. 1 United States patent application and 8 United States patents cited.

2395. MORAN, J. N. (Phillips Petroleum Co.). Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen by Means of a Fluidized Fixed Bed. United States Patent 2,612,512, Sept. 30, 1952; appl. filed Sept. 16, 1947, Serial No. 774,385; 3 claims (*Cl. 260–499*). Chem. Abs., vol. 47, 1953, p. 1359.

Describes improved type of reactor whereby fluidization of the catalyst is facilitated, removal of the exothermic heat of reaction is promoted, and linear space velocities through the reactor are maintained. Suitable reaction conditions when using a reactor of the type described are a temperature 300°–320° C., a pressure of about 10–20 atm. and a space velocity 1,500–5,000 vol. of synthesis gas per vol. of catalyst per hr.

See abs. **753, 754.**

2396. MORBECK, R. C. (Standard Oil Development Co.). Method of Production of an Iron Catalyst for Hydrocarbon Synthesis. United States Patent 2,580,039, Dec. 25, 1951; appl. filed Sept. 16, 1948, Serial No. 49,641; 4 claims (*Cl. 260–449.6*).

A Fischer-Tropsch catalyst for use at a temperature of 675°–750° F. is formed from a dense turbulent mass of finely divided, reduced, fresh, red Fe oxide particles of fluidizable size sintered in an atmosphere of H_2 at 1,550–1,650° F. and promoted with a minor amount of an alkali carbonate. Sintering is effected subsequent to the reduction and after addition of the promoter. The catalyst has very low C formation tendencies.

2397. MORGAN, G. T., AND TAYLOR, R. [Aldehydes and Alcohols.] French Patent 669,643, Feb. 14, 1929. Chem. Abs., vol. 24, 1930, p. 1866.

Aliphatic aldehydes and primary alcohols are prepared by the catalytic condensation of CO and H_2, in which the catalyst contains Co besides ZnO and Cr_2O_3 or ZnO and MnO_2 or the 3 oxides, the Co being in a form reducible at the beginning of the operation or during the condensation. Gives examples.

2398. ———. Catalytic Production of Aldehydes and Alcohols From Carbon Monoxide and Hydrogen. British Patent 313,061, Feb. 28, 1928. Chem. Abs., vol. 24, 1930, p. 861.

Catalyst is used containing Co (suitably in the form of its chromate or nitrate as prepared) together with Zn and Cr oxides or Zn and Mn oxides (or a mixture of all these oxides). Cu also may be present or may constitute the lining of the reaction chamber. High temperatures and pressures used.

2399. MORGAN, G. T., AND TONGUE, H. High-Pressure Reaction Apparatus for Ammonia or Methanol Synthesis. British Patent 325,678, Feb. 6, 1929. Chem. Age, 1930, p. 400; Chem. Abs., vol. 24, 1930, p. 4124.

Reaction vessels are provided with heating devices, such as externally accessible and removable tubes containing electric heaters extending into the apparatus from 1 end. Describes various structural details.

MORGAN, J. P. *See* abs. **3255.**

2400. MORII, K., AND TANABE, T. (Nitto Chemical Industries Co.). [Catalyst for the Synthesis of Ammonia.] Japanese Patent 9 (1951), Jan. 9, 1952. Chem. Abs., vol. 47, 1953, p. 278.

Al_2O_3 or $Al(OH)_3$, MgO, K_2O, and CaO are used as catalyst promoters for Fe_3O_4, which is derived from Fe grains by firing the molded product.

MORLEY, R. J. *See* abs. **38.**

2401. MORRELL, C. E. (Standard Oil Development Co.). Oxygenated Organic Compounds for Use in Internal-Combustion-Engine Fuels. United States Patent 2,626,209, Jan. 20, 1953. Chem. Abs., vol. 47, 1953, p. 7771.

By a vapor-phase catalytic process an aqueous mixture of oxygenated organic compounds (I), such as is produced in the Fischer-Tropsch process, is converted to ketones (II) suitable for incorporation into fuel mixtures for internal-combustion engines. (I) are compounds containing up to 10 C atoms and are catalytically converted to ketones containing 3–13 C atoms. Reaction conditions are adjusted for complete conversion of acid and aldehyde constituents of (I) to prevent their inclusion in fuels with subsequent corrosion and instability effects. Thus, 1 mole of vaporized (I) is mixed with 3–20 moles of steam and brought into contact at 360°–600° for 0.1–10 min. at atmospheric pressure with a fixed or fluidized bed of catalyst consisting of mixed Fe–Mn–Zn oxides. The condensed aqueous phase of the product is extracted with a hydrocarbon solvent suitable for later use as a motor fuel, and the extract is dried. The solvent may be a cracked gasoline, a polymer gasoline, a virgin naphtha stock, or a synthesis oil fraction. It should be free of unstable, corrosive, and highly H_2O-soluble compounds and should have an initial boiling range of 50°–130° to obtain maximum H_2O entrainment during drying of the extraction mixture.

See also United States Patent 2,569,384 (abs. **2403**).

2402. ——— (Standard Oil Development Co.). Separation of Close-Boiling Oxygenated Compounds From Their Liquid Mixtures. United States Patent 2,591,714, Apr. 8, 1952. Chem. Abs., vol. 46, 1952, p. 11,226.

Relative volatilities of alcohols, with respect to nonalcoholic organic compounds, are altered; and the relative volatilities of nonalcoholic organic compounds are also altered by using hydrocarbon solvents in the extractive distillation. A refined white oil, b. 396°–522° F., is used. The volatilities are lowered in the following descending order: Alcohols (highest), ketones, aldehydes, esters, ethers, and hydrocarbons (least). Thus separation is affected of a mixture containing anhydrous EtOH, iso-PrOH, MeCOEt, PrCHO, and EtOAc.

See also United States Patents 2,569,384 (abs. **2403**) and 2,591,713 (abs. **2409**).

———. *See* abs. **315, 814.**

2403. MORRELL, C. E., AND MCATEER, J. H. (Standard Oil Development Co.). Recovery of Oxygenated Compounds From Hydrocarbon Oils. United States Patent 2,569,384, Sept 25, 1951; appl. filed Dec. 19, 1947; 11 claims (*Cl. 260–450*). Chem. Abs., vol. 46, 1952, p. 1745.

Aliphatic, neutral, oxygenated compounds, comprising alcohols, aldehydes, ketones, esters, and acetals, are separated from a mixture of neutral and acidic oxygenated hydrocarbons by selective liquid-liquid extraction with a solvent comprising 2–10 wt. % of aqueous AcOH at a temperature between the freezing point of the solvent and 125°. The neutral, oxygenated compounds are separated from the extract phase. If other high homologs of AcOH are present in the AcOH, they should be restricted to no more than 35 wt. % of the AcOH. The acid-H_2O bottoms obtained by fractional distillation of the H_2O layer separated from the products of hydrocarbon synthesis by the Fischer-Tropsch synthesis may be used for this purpose. A typical analysis of the bottoms is: H_2O, 95.50; carboxylc acids, 4.47; and other organic oxygenated compounds, 0.03 wt. %. The 4.47% acids is approximately AcOH, 75; propionic acid, 20; and butyric and higher acids, 5 wt. %. The other organic compounds are not harmful.

2404. ——— (Standard Oil Development Co.). Recovery of Oxygenated Compounds From Hydrocarbon Oils. United States Patent 2,569,385, Sept 25, 1951; appl. filed Feb. 12, 1948, Serial No. 7,966; 10 claims (*Cl. 260–450*).

Aliphatic, low-molecular, oxygenated compounds containing 1–6 C atoms per molecule are recovered from a mixture of these with hydrocarbons obtained by the catalytic hydrogenation of CO, by selectively extracting them by means of a dilute aqueous solution of a water-soluble aliphatic carboxylic acid, such as acetic acid in the proportion of 2–5 wt. %, at a temperature 125°–375° (preferably 175°–250°). 2 phases are thus formed: An extract phase comprising the oxygenated compounds, and a raffinate phase containing the hydrocarbons. The 2 phases are separated by any known means such as fractional or extractive distillation or solvent extraction. An alternative process involves the use as solvent of the aqueous acid bottoms containing 2–10 wt. % of acid recovered from the H_2O layer of a hydrocarbon synthesis reaction product.

2405. MORRELL, C. E., AND ROBEY, R. F. (Standard Oil Development Co.). Distillation of Aldehydes and Ketones. United States Patent 2,576,030, Nov. 20, 1951. Chem. Abs., vol. 46, 1952, p. 6141.

In the distillation of aldehydes and ketones, which boil below EtOH and do not form azeotropes with H_2O from aqueous alcoholic solution, the formation of acetals and ketals is prevented by adding at the top of the distillation zone small amounts of H_2O (not more than 50 vol. % of the internal liquid reflux) preferably containing a small amount of an acid. The method is particularly applicable to the Fischer synthesis and to the products of hydrocarbon oxidation.

2406. MORRELL, C. E., BIRIBAUER, F. A., AND CARLSON, C. S. (Standard Oil Development Co.). Distillation of Oxo Alcohols. United States Patent 2,589,018, Mar. 11, 1952; appl. filed Dec. 31, 1948, Serial No. 68,472; 6 claims (*Cl. 202–40*).

Describes an improved continuous distillation process for the purification of crude synthetic alcohols containing high-boiling impurities and obtained by the Oxo process. The method consists essentially of at least 2 stages in a closely related sequence of operation. It is especially applicable to alcohols of the C_8 and C_9 classes.

2407. MORRELL, C. E., CARLSON, C. S., AND SMITH, P. V. (Standard Oil Development Co.). Distillation of Oxygenated Organic Compounds. United States Patent 2,551,625, May 8, 1951; appl. filed Dec. 30, 1947, Serial No. 794,589; 9 claims (*Cl. 202–39.5*). Chem. Abs., vol. 46, 1952, p. 521.

Describes method for separating widely boiling mixtures of oxygenated organic compounds by the controlled use of H_2O or solvents of high H_2O content as a reflux medium in continuous fractional distillation. The process is made possible by finding that when such a complex mixture is distilled in the presence of a sufficiently large volume % of aqueous reflux, the volatilities of the oxygenated compounds are altered to such an extent that separation becomes possible in presence of excess H_2O. Chemical reactions that occur in the absence of H_2O are also substantially prevented. Examples and flowsheet.

2408. ——— (Standard Oil Development Co.). Distillation of Oxygenated Organic Compounds. United States Patent 2,588,272, Mar. 4, 1952; appl. filed Dec. 1, 1950, Serial No. 198,522; 8 claims (*Cl. 202–39.5*).

Mixture of wide-boiling oxygenated organic compounds can be separated from the total H_2O layer obtained in the Fischer-Tropsch synthesis process by distillation as follows: A H_2O layer containing 84.6 mol. % alcohols, 11.2 mol. % carbonyls (ketones and aldehydes), 0.2 mol. % esters, and 4.0% acids on a H_2O-free basis is distilled in a 1-inch i. d. perforated plate column, having 30 plates above and 30 below the feed point, at a feed rate of 485 cc. per hr., H_2O being introduced as reflux at the top of the column at a rate of 945 cc. per hr. so that the top plate contains 98 mol % H_2O. The feed is introduced at 91° and the H_2O at 94°. The overhead temperature is kept at 84° and the reflux ratio at 15:1. A total of 6.2% of organic material based on the feed and consisting of ketones, aldehydes, esters, and a small amount of alcohols is removed overhead. A bottoms fraction consisting of an aqueous solution of alcohols and acids is withdrawn and passed to a 2d distillation zone similar to the 1st at a rate of 1,310 cc. per hr. and at 91°. The reflux ratio of the 2d tower is 5:1. Alcohols are removed overhead at 79°. A solution of acids in H_2O is removed from the bottom and returned to the top of the 1st column as reflux. The mol % of components in the feed appearing in the overhead of the extractive distillation column is: Alcohols 1.98, carbonlys 17.9, esters 91.0, and acids 0.0. The process is made possible by the discovery that when a mixture of oxygenated compounds, such as those described, are fractionally distilled in the presence of a large enough volume % of aqueous reflux, the volatilities of the oxygenated compounds are altered to such an extent that separations, which were impossible by ordinary fractionation, become possible in the presence of excess H_2O, and chemical reactions that occur in the absence of H_2O are substantially prevented.

2409. ——— (Standard Oil Development Co.). Extractive Distillation of Alcohol-Containing Mixtures. United States Patent 2,591,713, Apr. 8, 1952. Chem. Abs., vol. 46, 1952, p. 11,226.

Hydrocarbon oil is used as the extractive-distillation solvent to separate alkanols containing 1–4 C atoms from higher-mol. oxygenated organic compounds consisting of alkanols and neutral oxygenated nonalcoholic organic compounds having no more than 5 C atoms. The separation is carried out in a distillation tower in which the ascending alkanol vapors are countercurrent to the condensate from the said vapors dissolved in a liquid solvent consisting of 25–100 vol. % higher boiling alkanol, which has at least 5 C atoms per mol. and 0–75 vol. % hydrocarbon.

2410. ——— (Standard Oil Development Co.). Separation of Normal Alcohols From Branched-Chain Alcohols. United States Patent 2,551,626, May 8, 1951; appl. filed June 24, 1948, Serial No. 34,897; 8 claims (*Cl. 202–39.5*). Chem. Abs., vol. 46, 1952, p. 521.

Crude mixtures, such as those obtained from the Fischer-Tropsch synthesis, are given a preliminary treatment to remove undesirable nonalcoholic compounds and the alcohols then subjected to extractive distillation to obtain an overhead fraction containing branched primary, secondary, and tertiary alcohols and a bottom fraction containing normal primary alcohols. The normal primary alcohols are then separated by straight distillation. When a mixture of oxygenated compounds is fractionally distilled in presence of a liquid reflux containing a large vol. % of H_2O, the volatilities of the oxygenated compounds are altered enough so that separation can be made. When the primary alcohols are separated from undesirable branched-chain alcohols, the boiling point of many primary alcohols are too close to permit separation. However, when EtOH is the major component and other alcohols are present in small amounts relative to EtOH, substantially complete separation of the primary alcohols can be obtained if the amount of H_2O in the reflux is maintained between 86–91 mol. %.

2411. MORTENSON, C. W. (E. I. du Pont de Nemours & Co.). Reaction Products of Acrylonitrile With Macromolecular Ketones. United States Patent 2,396,963, Mar. 19, 1946. Chem. Abs., vol. 40, 1946, p. 3937.

Polymer (I) having recurring units containing CH_2 groups adjacent to carbonyl groups is treated with acrylonitrile (II) in the presence of an alkaline condensing agent to introduce β-cyanoethyl groups (III) on the C adjacent to the carbonyl group. An ethylene–CO copolymer useful as (I) is prepared by placing 0.5 part of diethyl peroxide and 100 parts of dioxane (IV) in a Ag-lined pressure vessel, evacuating, pressuring to 600–700 atm. with a gaseous mixture of 30% CO and 70% C_2H_4 by weight, and heating to 130° for 18 hr. The polymeric product (V) is steam distilled to remove (IV), filtered, and dried; yield, 90 gm. of white, waxlike solid, m.p. 130°, 43% CO based on C–H analysis. A mixture of 10 parts of (II) and 2 parts of 40% aqueous trimethylbenzylammonium hydroxide (VI) is added during 1 hr. to 5 parts of (V) dissolved in 20 parts of (IV). Cooling is necessary to control the exothermic reaction, and the temperature is held at 35°–40°. The reaction solution when poured onto

H_2O precipitates a light yellow solid which is soluble in acetone and pyridine and contains 1.71 (III) per carbonyl based on C, 67.9%; H, 6.62%; and N, 15.3%. A mixture of 12 parts of (VI) and 50 parts (II) are added over 1.5 hr. to a solution of 20 parts of (V) dissolved in 100 parts (IV). The reaction temperature is held at 30°–35° by external cooling, and the product, isolated as above, contains 10.96% N or 0.81 (III) per carbonyl. Ten parts of a similar reaction product containing 0.4 (III) per carbonyl is refluxed with 120 parts of 16% aqueous NaOH. The insoluble material slowly dissolves with evolution of NH_3 and on acidification of the solution a polycarboxylic acid containing C, 55.4%; H, 63%; and N, 1.29% is precipitated. A propylene–ethylene–CO copolymer is prepared by a method such as is used for preparation of (V), and in a similar reaction with (II) forms a product containing N 7.62% or 0.6 (III) per carbonyl; it is slowly soluble in concentrated NaOH with evolution of NH_3. A mixture of 30 parts of (II) and 7 parts of (VI) is added over 1 hr., with cooling, to a solution of 7 parts of polymethyl vinyl ketone in 100 parts of (IV). The product, isolated as before, contains N 12.4% or 1.25 (III) per carbonyl. The products are said to be useful as insecticides or in thermosetting compositions. The polyacids obtained on hydrolysis are said to be useful as tanning or dispersing agents.

2412. Morway, A. J., and Smith, P. V. (Standard Oil Development Co.). Oxo-Bottoms Base Lubricating Grease. United States Patent 2,653,132, Sept. 22, 1953; appl. filed Dec. 17, 1949, Serial No. 133,664; 14 claims (*Cl. 252–42*).

Claim 1. A new and improved grease composition, which comprises a synthetic oil thickened to a grease consistency with about 5.0–20.0% by wt. of the lithium soap of a high molecular weight substantially saturated fatty acid, said synthetic oil being the residue of distillation at a temperature of about 210° C. of the mixture of products obtained by subjecting a monoolefin to the action of CO and H_2 in the presence of a Co catalyst at a temperature of 300°–350° F. and under a pressure of about 3,000 p. s. i., which has been hydrogenated to a predominately primary alcohol mixture containing 1 more C atom than the mono-olefin.

2413. Mosesman, M. A. (Standard Oil Development Co.). Alpha Iron Oxide-Alkali Metal Ferrate Catalyst and Process of Preparation. United States Patent 2,470,785, May 24, 1949; appl. filed June 28, 1948, Serial No. 35,741 (*Cl. 252–474*). Chem. Abs., vol. 43, 1949, p. 6338.

Process is similar to that described in United States Patent 2,455,696 (abs. **2420**). The catalyst comprises a major portion of α–Fe_2O_3 and an alkali metal ferrate promoter.

2414. ——— (Standard Oil Development Co.). Alpha Iron Oxide-Alkali Metal Pyroantimoniate Catalyst and Process of Preparation. United States Patent 2,465,313, Mar. 22, 1949; appl. filed Dec. 20, 1946, Serial No. 717, 584; 11 claims (*Cl. 252–474*). Chem. Abs., vol. 43, 1949, p. 4448.

Gives method for preparing a catalyst adapted for use in Fischer-Tropsch synthesis. Fe oxide, α, γ, or ferro-ferric is mixed with an alkali metal pyroantimoniate preferably K pyroantimoniate. The mixture is heated to a high temperature in the presence of an oxidizing atmosphere until the mass is oxidized. Then the oxidized mass is contacted with a reducing atmosphere at superatmospheric temperature to obtain an active metallic mass. The pyroantimoniate accounts for 0.2–20% and the Fe oxide for 80–99.8% of the catalyst mass.

2415. ——— (Standard Oil Development Co.). [Catalysts for the Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 957,262, Feb. 15, 1950; appl. filed Dec. 15, 1947, in United States Dec. 20, 1946. Chem. Zentralb., 1951, I, p. 1551.

Mixture of Fe oxide and an alakli-metal pyroantimoniate is heated at about 537° in an oxidizing atmosphere and then at 260°–371° in a reducing atmosphere. The initial mixture consists of 95% Fe_3O_4 and 5% K-pyroantimoniate. In general, the pyroantimoniate accounts for 0.2%–20% and the Fe_3O_4 to 80%–99.8% of the catalyst mass.

See also United States Patents 2,465,313 and 2,465,314 (abs. **2414** and **2419**)

2416. ——— (Standard Oil Development Co.). Ferro–Ferric Oxide–Alkali Metal Ferrate Catalyst and its Method of Preparation. United States Patent 2,470,786, May 24, 1949; appl. filed July 29, 1948, Serial No. 41,413; 10 claims (*Cl. 252–474*). Chem. Abs., vol. 43, 1949, p. 6338.

Process similar to that described in United States Patent 2,455,696 (abs. **2420**). The catalyst comprises a major portion of ferro–ferric oxide and an alkali metal ferrate.

2417. ——— (Standard Oil Development Co.). Ferro-Ferric Oxide–Alkali-Metal Pyroantimoniate Catalyst and Process of Preparation. United States Patent 2,465,315, Mar. 22, 1949; appl. filed June 23, 1948, Serial No. 34,844; 11 claims (*Cl. 252–474*). Chem. Abs., vol. 43, 1949, p. 4448.

Preparation of this catalyst appears to correspond to that given in United States Patent 2,465,313 (abs. **2414**).

2418. ——— (Standard Oil Development Co.). Gamma Iron Oxide–Alkali Metal Ferrate and Process of Preparation. United States Patent 2,470,784, May 24, 1949; appl. filed June 23, 1948, Serial No. 34,843; 10 claims (*Cl. 252–474*). Chem. Abs., vol. 43, 1949, p. 6338.

Describes the preparation of a catalyst comprising a major portion of γ–Fe_2O_3 and an alkali metal ferrate as a promoter. Powdered Fe_2O_3 is mixed with 0.2–20.0 wt. % of K_2FeO_4 in the presence of a small amount of alcohol, dried at 230° F., pilled, heated at 1,000° F. in the presence of air for 4 hr., and then reduced at 700°–1,600° F. for 24 hr. The catalyst is adapted for use in the Fischer-Tropsch synthesis.

See also United States Patent 2,455,696 (abs. **2420**).

2419. ——— (Standard Oil Development Co.). Gamma Iron Oxide–Alkali-Metal Pyroantimoniate Catalyst and Process of Preparation. United States Patent 2,465,314, Mar. 22, 1949; appl. filed June 9, 1948, Serial No. 32,052; 11 claims (*Cl. 252–474*). Chem. Abs., vol. 43, 1949, p. 4448.

Preparation of this catalyst appears to correspond to that given in United States Patent 2,465,313 (abs. **2414**).

2420. ——— (Standard Oil Development Co.). Iron Oxide–Alkali Metal Ferrate Catalyst and Its Method of Preparation. United States Patent 2,455,696, Dec. 7, 1948; appl. filed Dec. 20, 1946, Serial No. 717,582; 10 claims (*Cl. 252–231.5*). Chem. Abs., vol. 43, 1949, p. 1950.

Catalyst especially adapted for the Fischer-Tropsch synthesis is prepared from an admixture of Fe oxide and alkali-metal ferrate such as K ferrate in an amount 0.2–20% by weight of Fe oxide. The mixture is heated to 1,000° F. for about 4 hr. in presence of an oxidizing atmosphere then to 700°–1,600° F. for about 24 hr. in a reducing atmosphere. Example: To an aqueous solution containing 340 parts by weight of $Fe(NO_3)_3 \cdot 9H_2O$ is added 90 parts by weight of NH_4OH. $Fe(OH)_3$ is filtered dry and then slurried

with 100 parts by weight of distilled H_2O. To the slurry is added 50 parts by weight of solid KOH, and while the suspension is held at<140° F., 50 parts of liquid Br and solid KOH are added with continual stirring. Excess KOH is added. After cooling, the K ferrate is decanted and dried under partial vacuum. It is washed free from alkaline contaminants and redried. 5 parts by weight of the K ferrate are added to 100 parts of ferro-ferric oxide. The mixture is ball-milled for 4 hr., dried, and pilled. The improved catalyst may be used for periods up to 1,000 hr. The amount of oxygenated material in the hydrocarbons produced is kept low.

2421. ——— (Standard Oil Development Co.). Iron Oxide–Alkali Metal Pyroantimoniate Catalysts and Process of Preparation. United States Patent 2,454,398, Nov. 23, 1948; appl. filed Dec. 20, 1946, Serial No. 717,584; 10 claims (*Cl. 252–231.5*). Chem. Abs., vol. 43, 1949, p. 1950.

Gives method for preparation of a Fischer-Tropsch synthesis catalyst. A mixture of 80–99.8% by weight of Fe oxide and 0.2–20% by weight of an alkali metal pyroantimoniate is heated at a super-atmospheric temperature of about 1,000° F. in presence of free O_2-containing atmosphere. The mixture is reduced at superatmospheric temperature 500°–900° F.

2422. ——— (Standard Oil Development Co.). Method for Preparing a Fischer-Tropsch Catalyst. United States Patent 2,503,963, Apr. 11, 1950; appl. filed Aug. 15, 1949, Serial No. 110,472; 4 claims (*Cl. 252–474*). Chem. Abs., vol. 44, 1950, p. 5568.

Approximately 2 parts of finely divided Fe is mixed with 3 parts of alkali metal nitrate such as K, Na, or Li nitrate. The mixture is ignited and a reaction product is formed. A dense white cloud of K is formed and removed from the reaction zone. The product is sufficiently cooled for handling and removed from the Fe plate. It is heated in free O_2-containing atmosphere at 1,000° F. for 4 hr. After calcining it is ground to a fine powder and pilled to ⅛-in. pills. The pills are reduced in H_2 for 24 hr. at 700° F. and atmospheric pressure. The H_2 is fed at 100 vol. per volume catalyst per hr. 1 foreign patent and 1 United States patent cited.

2423. ——— (Standard Oil Development Co.). Method for Synthesizing Hydrocarbons and Oxygenated Compounds. United States Patent 2,537,688, Jan. 9, 1951; appl. filed Dec. 20, 1946, Serial No. 717,587; 15 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 4430.

H_2 : CO=2 : 1–1 : 1 mixture is contacted with a catalyst obtained by reducing a mixture of Fe oxide and alkali metal ferrate at superatmospheric temperatures. The feed rates are 100–1,500 vol. feed per vol. catalyst per hr. The temperature is 450°–675° F. and the pressure 100–500 p. s. i. In preparing the catalyst, Fe oxide in the form of ferro–ferric oxide or α or γ Fe oxide may be mixed with 0.2–20% K ferrate, based on the Fe oxide, using a small amount of alcohol for the mixing. The paste is dried and then heated in a free O_2-containing atmosphere to 1,000° F. The mass is reduced in H_2 at 700°–1,600° F. A mixture of iron filings and K nitrate may be ignited on an Fe surface to supply the K ferrate. 2 literature refs. and 5 United States patents cited.

2424. ——— (Standard Oil Development Co.). Preparation of an Iron–Alkali Metal Ferrate Catalyst. United States Patent 2,503,964, Apr. 11, 1950; appl. filed Dec. 20, 1946, Serial No. 717,583; 4 claims (*Cl. 252–474*). Chem. Abs., vol. 44, 1950, p. 5568.

Gives method of preparation similar to that described in United States Patent 2,503,963 (abs. **2422**). The additional step is that the ignited mixture is added to Fe oxide in amount 0.2–20% by weight of Fe oxide before calcining. A variation includes 3 mixtures: 1 part Fe and 2 parts alkali metal nitrate, 1 part Fe and 1 part metal nitrate, and reaction products from the 1st and 2d mixtures with Fe oxide. No references cited.

2425. ——— (Standard Oil Development Co.). Synthesis of Hydrocarbons and Oxygenated Compounds. United States Patent 2,438,449, Mar. 23, 1948; appl. filed Dec. 20, 1946, Serial No. 717,586; 11 claims (*Cl. 260–449.6*). Chem. Abs., vol. 42, 1948, p. 3933.

CO and H_2 are brought in contact with a catalyst obtained by reducing at superatmospheric temperature Fe oxide either in the form of α, γ, or ferro–ferric oxide in admixture with an alkali metal pyroantimoniate such as potassium pyroantimoniate. The pyroantimoniate makes up 0.2–20% of the catalyst mass and the Fe oxide 80–99.8%. The temperature range for the reaction is 450°–675° F. and the pressure 100–500 p. s. i. The H_2–CO ratio range is 2 : 1–1 : 1 and the feed rate 100–1,500 vol. of feed per vol. of catalyst per hr. The catalyst may be fixed-bed or fluidized. Appreciable amounts of alcohols, carbonyls, and organic acids were obtained. 1 United States patent and 3 foreign patents cited.

———. *See* abs. **3273.**

MOUNTAIN COPPER CO., LTD. *See* abs. **2099.**

2426. MUELLER, E. [Catalysts.] Italian Patent 370,762, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 153.

CO+H_2 converted at 300°, 2–50 atm., over Fe, Ni, Co+metalloid compounds (halogens, HCl, ClO_2, SO_2, NO_2, PCl_3, P_2O_5, nitrides).

See Italian Patent 371,292 (abs. **2427**).

2427. ———. [Catalysts.] Italian Patent 371,292, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 153.

See Italian Patent 370,762 (abs. **2426**).

MÜLLER, C. *See* abs. **2362, 2363, 2364, 2373, 2667.**

2428. MÜLLER, C., FRANKENBURGER, W., AND GRASSNER, F. (I. G. Farbenindustrie A. G.). [Process for Purifying Liquid Organic Substances.] German Patent 452,066, Nov. 5, 1927; appl. filed Aug. 31, 1924. Chem. Zentralb., 1928, I, p. 2303.

Synthetic MeOH from the catalytic hydrogenation of CO under pressure containing metallic impurities such as metal carbonyls $Fe(CO)_4$ is purified therefrom by means of short-wave light rays in the presence of O_2-containing gases. Mercury vapor lamp is a good source of light.

2429. ——— (I. G. Farbenindustrie A. G.). Removing Metal Carbonyl From Organic Liquids. United States Patent 1,679,256, July 31, 1928; appl. filed Aug. 17, 1925. Chem. Abs., vol. 22, 1928, p. 3669.

Synthetic MeOH or other liquids containing < 10% of metal carbonyl such as Fe carbonyl are exposed to the action of ultraviolet rays, which also act on aldehydes or ketones present. Ozone also may be used.

2430. MÜLLER, C., SCHLECHT, L., AND SCHUBARDT, W. (I. G. Farbenindustrie A. G.). [Catalytic Production of Hydrocarbons.] German Patent 505,319, Aug. 16, 1930; appl. I 28,147, filed May 23, 1926 (*Cl. 12 o–1*). FIAT Reel AA 88, frames 3,984–3,985; Chem. Abs., vol. 24, 1930, p. 5764.

See British Patent 271,452 (abs. **1184**).

2431. ——— (I. G. Farbenindustrie A. G.). [Hydrocarbons.] German Patent 487,379, May 11, 1926. Chem. Abs., vol. 24, 1930, p. 2139.

Hydrocarbons, mainly liquid, are produced by the thermal decomposition of metal carbonyls in the presence of a sufficient amount of H_2 or of gases containing

H_2, for example, water gas, or steam. A catalyst, for example, NH_3, may be present also. Gives examples.

See also British Patent 270,705 (abs. **1325**).

2432. MÜLLER, R., AND LEE, H. (Chemische Fabrik von Heyden A. G.). Thorium Oxide of High Reactivity. United States Patent 2,202,637, May 28, 1937. Chem. Abs., vol. 34, 1940, p. 6779.

For the obtainment of a highly reactive Th oxide suitable for use as a catalyst, a complex salt containing Th oxalate, together with Na_2CO_3 or NH_4 carbonate or oxalate, is heated to about 285°–450° until a sample taken from the heated mass becomes soluble in boiling concentrated HNO_3 in the minimum time.

See French Patent 828,334 (abs. **359**).

2433. MÜLLER-CUNRADI, M. (I. G. Farbenindustrie A. G.). Purification of Methanol Derived From Carbon Monoxide and Hydrogen. German Patent 430,-623, Jan. 15, 1924. British Chem. Abs., 1926, B, p. 901.

The substances are treated in the hot liquid or gaseous condition by distillation with oxalic acid. Crystalline or anhydrous oxalic acid (2% or less) is added to the liquid before distillation, or the vapor of the liquid is passed over a layer of oxalic acid or of material impregnated with oxalic acid. Acid oxalates may also be used in place of oxalic acid.

———. *See* abs. **2268, 2269, 2670, 2685, 2686, 2687, 2688.**

2434. MÜLLER-LUCANUS, H., AND WEINGAERTNER, E. A. (Braunkohle-Benzin A. G.). [Separation of Condensable Components From Hot-Oil Vapor-Gas Mixtures.] German Patent 733,841, Mar. 4, 1943; appl. filed June 26, 1938 (*Cl. 23 b–1.03*). Chem. Zentralb., 1943, II, p. 96; Chem. Abs., vol. 38, 1944, p. 1096.

This method applies to cases such as the reaction products of synthesizing hydrocarbons from CO and H_2. These hot vapor–gas mixtures tend to form a fog when a cold liquid nonmiscible with the condensate; for example H_2O, is injected into them. Thus, before injecting the cooling liquid to the oil vapor gas mixture a larger volume of oil vapor is added, which is taken from the condensate of fractions thereof. The amount of the oil vapor added is such that the entire mixture does not reach its dew point.

2435. MUNDAY, J. C. (Standard Oil Development Co.). Catalytic Conversion of Hydrocarbons. United States Patent 2,420,558, May 13, 1947; appl. filed July 20, 1944, Serial No. 545,813; 2 claims (*Cl. 196–52*).

Gives fluid catalyst process in which high catalyst concentrations, high circulation rates, and short contact times are provided. 15 patent refs. cited.

2436. ——— (Standard Oil Development Co.). [Synthesis Vessel and Process.] French Patent 922,493, no date. Kainer, p. 204.

Reduction of CO by H_2 takes place in a vertical cylindrical furnace in which a layer of pulverized Fe or Co catalyst is kept in suspension and whirled about by a stream of synthesis gas entering through a perforated plate from below.

MUNGEN, R. *See* abs. **1112.**

MURATA, Y. *See* abs. **1867, 1870, 1871, 1872, 1873, 1874, 1875, 1876, 1877, 1878, 1879, 1892.**

2437. MURPHREE, E. V. (Standard Oil Development Co.). Process for Thermal Cracking of Viscous Hydrocarbon Oils and Simultaneous Recovery of Synthesis Gas. Canadian Patent 469,242, Nov. 7, 1950; appl. filed Apr. 12, 1946. Chem. Zentralb., 1951, I, p. 1825.

Finely divided inert material such as coke, suspended in a viscous hydrocarbon oil, is continuously circulated through 3 separate zones such as the cracking, combustion, and water-gas zones. The viscous oil is decomposed by thermal cracking into volatile hydrocarbons and coke. The coke is deposited on the highly heated, solid, inert material and progresses with it into the combustion chamber where the material is partly consumed and thereby heated. From the combustion chamber it goes directly into the water-gas chamber where it comes into contact with water vapor and forms CO and H_2, which is used for hydrocarbon synthesis. Diagram shown.

2438. MURPHREE, E. V., AND PECK, E. B. (Standard Oil Development Co.). Hydrocarbons From Oxides of Carbon and Hydrogen. United States Patent 2,256,622, Sept. 23, 1941; appl. filed May 29, 1940, Serial No. 337,774; 9 claims (*Cl. 260–449*). Chem. Abs., vol. 36, 1942, p. 250.

Describes apparatus and a process for the manufacture of hydrocarbons containing >1 C atom in the mol. from oxides of C and H_2 in which the reaction temperature is controlled by passing a synthesis gas mixture comprising oxides of C and H_2 under synthesizing conditions through a plurality of alternate catalyst reacting and cooling zones, passing a suitable cooling liquid through the cooling zones, and bringing the gases into contact with the cooling liquid to maintain its temperature within a predetermined temperature range.

2439. MURPHREE, E. V., TYSON, C. W., CAMPBELL, D. L., AND MARTIN, H. Z. (Standard Catalytic Co.). System for Carrying Out Catalytic Reactions Between Carbon Monoxide and Hydrogen. United States Patent 2,360,787, Oct. 17, 1944; appl. filed Dec. 27, 1940, Serial No. 371,922; 8 claims (*Cl 260–449.6*). Chem. Abs., vol. 39, 1945 p. 3900.

This system is designed for using a powdered catalyst suspended in the reacting mixture and provides for regenerating at least part of the catalyst. The feeding of the catalysts to the reaction zone requires no moving parts in the described assembly.

2440. MURPHY, C. R. (Warren Petroleum Corp.). Process for the Production and Purification of Oxygenated Hydrocarbons. United States Patent 2,579,847, Dec. 25, 1951; appl. filed Dec. 23, 1948, Serial No. 67,002; 9 claims (*Cl. 260–451*).

Acid-free, oxygenated hydrocarbon compounds are produced by separating the high-boiling constituents of the reaction mixture, including color bodies and the major portion of the acids formed in the reaction, by cooling the gaseous reaction product to < the dewpoint of the acids and color bodies, separating these, and then passing the low-boiling constituents to an accumulating zone where separation of the nonvolatile oxygenated compounds from the volatile portion of the mixture takes place.

2441. MURRAY, W. J. (Stanolind Oil & Gas Co.). Revivification of Adsorbents. United States Patent 2,529,624, Nov. 14, 1950; appl. filed Oct. 13, 1948, Serial No. 54,314; 4 claims (*Cl. 260–450*).

Organic oxygenated compounds are removed from a hydrocarbon solution by adsorption. If desired the bulk of the oxygenated compounds can be removed with a solvent. The adsorbed compounds can then be eluted from the solid adsorbent by a more polar material, which may be an organic oxygenated compound. Some eluant remains upon the adsorbent, and this is displaced by contact with a hydrocarbon vapor at a temperature high enough to vaporize the eluant. The gases are recovered, and the eluant and hydrocarbon are separated. 1 literature ref. and 1 United States patent cited.

2442. MYDDLETON, W. W. (M. W. Kellogg Co.). Dewaxing Catalysts Used for Hydrocarbon Synthesis. United States Patent 2,259,961, Oct. 21, 1941; appl.

filed Aug. 26, 1937, Serial No. 161,105, in Great Britain May 21, 1937; 6 claims (*Cl. 260–449*). Chem. Abs., vol. 36, 1942, p. 882.

In the synthesis of hydrocarbons from a mixture consisting principally of CO and H_2, in the presence of a granular catalyst, such as one formed of Ni and oxides of Mn and Al on kieselguhr, a mode of operation is employed that involves interrupting the reaction at predetermined intervals, removing the relatively nonvolatile material during such interruption by passing over the catalyst a solvent for such material while the catalyst is substantially at the reaction temperature, such solvent being at a temperature > the reaction temperature and continuing the reaction.

2443. ———. Hydrocarbon Oils. British Patent 509,325, July 14, 1939; appl. filed Jan. 22, 1938. Chem. Abs., vol. 34, 1940, p. 4545.

In production of hydrocarbon oils from gaseous mixtures of CO and H_2 by catalytic synthesis, a catalyst to which an alkali-metal carbonate has been added is used, and S, which acts as a poison affecting the olefin hydrogenating power of the catalyst while leaving substantially unchanged its power to form oil from the gaseous mixture, is introduced with the gaseous mixture into the reaction chamber. The catalyst preferably comprises Co and may be impregnated before use with K_2CO_3. Blue water gas containing appreciable quantities of S may be passed at not over 5 atm. pressure through, or in contact with, a catalyst having a Co base, the temperature of the synthesis reaction being maintained at 180°–210°.

2444. ——— (Synthetic Oils, Ltd.). [Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 859,686. Kainer, no date, p. 246.

See British Patent 519,722 (abs. **2455**).

2445. ———. Nickel Catalysts. British Patent 397,295, Aug. 24, 1933. Chem. Abs., vol. 28, 1934, p. 1153.

Catalysts are prepared by mixing Ni oxide with a Si ester, decomposing the ester, and heating the mixture in a reducing atmosphere. In an example NiO, prepared from $NiCO_3$, is mixed with a PhMe solution of Et orthosilicate and NH_4OH is added. The coagulated product is broken into granules, dried, and reduced in H_2. The catalyst may be used for the hydrogenation of cottonseed oil.

2446. ——— (Synthetic Oils, Ltd.). [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 858,789, no date. Chem. Zentralb., 1941, II, p. 3291.

See British Patent 517,794 (abs. **2449**).

2447. ——— (M. W. Kellogg Co.). Temperature Control in Effecting Exothermic Catalytic Reactions Such as Hydrocarbon Production From Hydrogen and Carbon Monoxide. United States Patent 2,255,126, Sept. 9, 1941; appl. filed Aug. 26, 1937, Serial No. 161,106, in Great Britain May 21, 1937; 6 claims (*Cl. 260–449*). Chem. Abs., vol. 36, 1942, pp. 250–251.

In effecting exothermic reactions between gases such as H_2 and CO, overheating of the catalyst is prevented by initially passing the gases over the catalyst at a flow rate substantially < the desired full flow rate and subsequently increasing the rate of flow inversely as a function of temperature to the desired full rate.

2448. ——— (Synthetic Oils, Ltd.). Treating Catalysts. Belgian Patent 435,849. Chem. Zentralb. Part 1, 1941, p. 2618.

See British Patent 517,794, (abs. **2449**).

2449. ——— (Synthetic Oils, Ltd.). Treating Catalysts. British Patent 517,794, Feb. 8, 1940; appl. filed Aug. 6, 1938. Chem. Zentralb., 1941, I, p. 2618; Chem. Abs., vol. 35, 1941, p. 7701.

Catalysts to be used in the synthesis of hydrocarbon oils are protected from atmospheric oxidation by immersing them in a liquid composed of organic compounds containing hydroxyl and/or carbonyl groups.

2450. Myddleton, W. W., and Synthetic Oils, Ltd. [Gasoline, Oils, Resins, and Other Hydrocarbons.] French Patent 830,560, Aug. 3, 1938. Chem. Abs., vol. 33, 1939, p. 1487.

See British Patent 491,778 (abs. **2451**).

2451. ———. Hydrocarbons. British Patent 491,778, Sept. 8, 1938. Chem. Abs., vol. 33, 1939, 1133.

Antiknock motor fuel and higher boiling hydrocarbons for use as solvents, kerosine, diesel oil, and lubricants are produced by passing a mixture of CO and H_2 in a ratio between 1:2 and 1:1 by vol. over a Co or Ni catalyst at about 200° and not over 3 atm. pressure, separating the product b. < 150° from the higher boiling product, catalytically hydrogenating the latter > 120° at atm. or increased pressure, and fractionating the resultant product to separate fractions for use as solvents, oils, and lubricants. The initial synthesis may be effected in a plurality of stages with removal of products between stages. A suitable catalyst contains Ni, oxides of Mn and Al, and kieselguhr. The initial gas may contain, for example, CO_2, N_2, and H_2O vapor. The higher boiling products may be vaporized and passed with H_2 over a catalyst containing Ni, Mn, Al, and SiO_2 obtained as described in British Patent 397,295 (abs. **2445**).

2452. ——— (Formerly Robinson Bindley Processes, Ltd.). Hydrocarbons. British Patent 495,575, Dec. 15, 1938; appl. filed May 21, 1937. Chem. Abs., vol. 33, 1939, p. 2902.

In synthesizing hydrocarbons the reaction gas is 1st passed over the catalyst at below the full rate, and the flow is subsequently increased gradually or stepwise to the full rate. An increased output can thus be obtained without overheating of the catalyst, and the dimensions thereof may be greater than usual, for example, a layer 6 ft. deep and 1 in. in diameter, in which case the flow may be 6 l. per hr. for the 1st 10 min., increasing stepwise to 900 l. per hr. after 2.5 hr.

2453. ———. [Motor Fuel.] French Patent 858,790, Dec. 3, 1940; appl. filed Aug. 5, 1939, in England Aug. 6, 1938. Chem. Zentralb., 1941, I, p. 2761.

Knockproof fuel is obtained when acetone vapor mixed with H_2 or H_2-containing gas is passed over Co or Th oxide at a temperature 180°–210° and high pressure. By addition of CO synthetic hydrocarbons also can be produced. The products obtained may be used as such or especially as additions to synthetic benzine.

Se also Belgian Patent 435,850 (abs. **2454**).

2454. ———. [Production of Fuel.] Belgian Patent 435,850, Apr. 11, 1940; appl. filed Aug. 5, 1939, in Great Britain Aug. 6, 1938. Chem. Zentralb., 1941, I, p. 2489.

Mixture of acetone vapor and H_2 is passed at 180°–210° over a catalyst of ThO_2 and Co_2O_3.

See also French Patent 858,790 (abs. **2453**).

2455. ———. Synthesizing Hydrocarbon Oils From Carbon Monoxide and Hydrogen. British Patent 519,722, Apr. 4, 1940; appl. filed Aug. 31, 1938. Chem. Abs., vol. 36, 1942, p. 251.

Gaseous mixture containing CO and H_2 in a ratio of 1:1–1:1.5 by volume is subjected to a catalytic synthesizing reaction in the conventional working conditions. The product of the reaction (a fraction of which boils predominantly 180°–330°) is segregated and treated in the presence of a hydrogenating catalyst with further H_2 in conditions similar to those used in the first synthesizing reaction.

2456. Myddleton, W. W., Aicher, A. A., and Synthetic Oils, Ltd. Methods of Producing Hydrocarbon Oils From Gaseous Mixtures of Hydrogen and Carbon Monoxide. British Patent 573,982, Dec. 17, 1945; appl. filed Jan. 14, 1941. British Coal Utilisation Research Assoc., Monthly Bull., vol. 10, 1946, Abs. 1153; Chem. Abs., vol. 43, 1949, p. 4835.

Operating conditions are adjusted to give only 50–80% of the theoretical yield, thereby prolonging the life of the catalyst, reducing the amount of cooling surface required, and obtaining a substantially constant yield of hydrocarbon oils over a longer reaction period.

2457. ———. Reactivation of Catalysts. British Patent 575,829, Mar. 7, 1946; appl. filed Oct. 11, 1943. British Abs. 1946, I, 197B; Chem. Abs., vol. 41, 1947, p. 6693.

Catalyst used in the manufacture of hydrocarbon oils from H_2 and CO is regenerated at 7- to 10-day intervals in a stream of H_2 containing entrained hydrocarbon oils from the process.

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2458. N. V. de Bataafsche Petroleum Maatschappij. Active Metal Catalysts. Improved Hydrosilicate Process. British Patent Appl. 15,040, 1948. Gas World, vol. 61, 1949, p. 222.

Catalysts of long life containing particularly active metals can be obtained by converting the metals, wholly or partly, into hydrosilicates followed by reduction. A wide range of carrier materials and of metals may be used. Fe, Co, Ni, and other metals of the 8th group are employed. The active metal may be precipitated from its dissolved salts by means of a soluble silicate, in the presence of a carrier, and converted into the hydrosilicate. For the production of Co catalysts, reduction should be done at moderate temperature, 300°–400°, if an active catalyst is to be formed, and only part of the active metal should be converted into hydrosilicate. The catalyst may also be obtained from SiO_2 by precipitating thereon all the active metal in the form of a basic compound followed by steam treatment.

2459. ———. [Catalyst for General Use.] Netherlands Patent 53,471, Nov. 16, 1942. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 153; Chem. Abs., vol. 41, 1947, p. 3592.

Tabashir, being a microporous very pure SiO_2 found in bamboo stalks, is used as such or combined with Ni, Co, ThO_2, ZrO, Cr_2O_3, Mo_2O_3, W_2O_3, NiS, $AlCl_3$, $SbCl_3$, or $FeCl_3$ for catalytic dehydrations; for example, isopropyl ether from isopropyl alcohol, esterifications and hydrolysis, condensations, such as alcohol and NH_3 or amines.

2460. ———. [Catalytic Production of Carbon Monoxide and Hydrogen From Hydrocarbons or From Methane and Steam.] French Patent 967,234, Oct. 27, 1950; appl. filed June 4, 1948. Chem. Zentralb., 1951, I, p. 1406.

Ni or MgO is used as catalyst. A gas stream, which keeps the catalyst in suspension, is passed therethrough so that the conversion takes place in the fluid state. The reaction temperature is 300°–750°. A part of the catalyst removed from the reaction chamber continuously is recycled into the regeneration chamber. Regeneration takes place by treatment with steam.

2461. ———. Control of Temperature. British Patent 657,526, Sept. 19, 1951. Jour. Inst. Petrol., vol. 38, 1952, p. 98A; Chem. Abs., vol. 46, 1952, p. 10,191.

Temperature in an oxo process using a stationary hydroformylation catalyst is controlled by recycling cooled liquid reaction product containing dissolved catalyst to the reaction zone.

2462. ———. Decomposing Carbon Monoxide-Containing Cobalt Compounds in Products Obtained in the Oxo Reaction. British Patent 672,421, May 21, 1952. Chem. Abs., vol. 47, 1953, p. 2767.

An olefinic starting material, mixed with a finely divided Co-containing catalyst, is passed with H_2 and CO into a high-pressure reactor maintained at 130°–180°; the product issuing from this reaction space is cooled before releasing the pressure, which causes the solution of volatile Co compounds in the liquid. The liquid is then passed to a tank at 1–10 atm. at 95°–105°, and a flushing gas is passed through the liquid 1 hr. or more to remove the liberated CO completely. The liquid may be preheated and then hydrogenated to convert the aldehydes into alcohols.

2463. ———. Decomposition of Metal Compounds Dissolved in Oxygen-Containing Organic Products. British Patent 667,824, Mar. 14, 1950. British Abs., 1952, B II, p. 584; Chem. Abs., vol. 47, 1953, p. 2197.

Metal compounds (for example, carbonyls used as catalysts) present in O-containing products obtained by interaction of CO with organic compounds in presence of carbonyls are decomposed to recoverable metal by heating at 150°–220° and 10–80 atm. with H_2 containing 0.1–50% of CO. Thus, the product obtained by formylation of an alkene fraction of 6–8 C in presence of a suspended Co catalyst on kieselguhr and containing about 0.25% of dissolved Co is passed at 200° and 25 atm. with a mixture of CO and H_2 (41.1% : 54%) through a pumice-filled tube, to give an aldehyde effluent free from Co.

2464. ———. Hydrocarbon Complexes With Thiourea. British Patent 650,571, Feb. 28, 1951. Chem. Abs., vol. 45, 1951, p. 8037.

Thiourea has been found to form crystalline complexes with isoparaffins, naphthenes, isoolefins, and cycloolefins either in the pure state or in admixture with other materials. Since the crystalline complexes are insoluble in hydrocarbons, their formation provides a means of separating, concentrating, and purifying specific hydrocarbons from impurities or diluting materials. Although the exact nature of the complexes is not known, they appear to be molecular in character since both the hydrocarbon and the thiourea are readily recoverable in substantially pure form. A list of isoparaffins, naphthenes, isoolefins, and cycloolefins, which form complexes with thiourea, is presented.

See also French Patent 964,693 (abs. **655**).

2465. ———. Hydrocarbons and Oxygen Derivatives. British Patent 640,311, July 19, 1950; appl. filed Jan. 15, 1948. Chem. Abs., vol. 44, 1950, p. 9658.

Hydrocarbons are produced by treating CO with H_2 at elevated temperatures and in the presence of a catalyst that contains less than 2% alkali silicate and a metal of the Fe group. In preparing the catalyst the metal of the Fe group is partly precipitated using a dissolved silicate so that it is partly in the form of a silicate and partly in the form of a readily reducible basic compound. Preferably 5–30% of the metal of the Fe group is present as the silicate. Kieselguhr may be used as the catalyst support if it has been sintered. It then no longer gives rise to the formation of silicates. A proper control of the quantity of silicate results in the formation of less paraffin wax and also of paraffin wax having a lower molecular weight. O derivatives of hydrocarbons may be prepared by passing olefins together with CO and H_2 over a catalyst of the type described.

2466. ———. Hydrogenation, Dehydrogenation, Desulfurization, Hydroforming, and Reforming Catalysts. British Patent 668,592, Mar. 19, 1952. Chem. Abs., vol. 47, 1953, p. 235.

10% aqueous solution of $Ni(NO_3)_2$ was added to 15% solution of $(NH_4)_2WO_4$ in 50% aqueous $NH_2CH_2CH_2OH$. No precipitate was formed so that the solution could be used to impregnate an inert carrier, such as SiO_2 gel or Al_2O_3 to prepare a catalyst. Corresponding results were obtained by using $Co(NO_3)_2$ instead of $Ni(NO_3)_2$ as well as when the $(NH_4)_2WO_4$ solution was replaced by $(NH_4)_2MoO_4$ solution. The use of $NH_2CH_2CH_2OH$ avoids formation of a precipitate, which interferes with impregnation of the carrier material.

2467. ———. Molded Catalysts. British Patents 641,332, appl. filed Apr. 6, 1948; and 641,333, filed July 7, 1948, in Netherlands July 10, 1947. Petroleum (London), vol. 14, 1951, p. 25.

Molded catalysts containing active metals and carrier and having great mechanical strength and high catalytic activity are prepared by wholly or partly converting the active metal (Fe group, Cu, Mn) into a hydrosilicate by precipitation from solution of its salt with an agent consisting wholly or partly of soluble silicate, mixing the powdered product with a powdered carrier (Al or Mg oxide), compressing the mixture to shaped pieces and reducing these with H_2 to obtain the metal, at least partly, in the active form. A claim is made for the method, catalyst, and its use in CO–H_2 synthesis.

2468. ———. Nickel Catalysts for Obtaining Hydrogen and Carbon Dioxide From Hydrocarbons and Steam. British Patent 314,944, July 5, 1928. Chem. Abs., vol. 24, 1930, p. 1476.

Finely divided Ni suitable for use as a catalyst for preparing H_2 and CO_2 from mixtures of CH_4 or other hydrocarbons and steam is obtained by precipitating Ni hydroxide from a Ni salt, as by the action of NaOH on Ni nitrate, under conditions such that the whole of the Ni is precipitated. The Ni hydroxide is separated by filtration, washed, dried and reduced with H_2 at 350°. A carrier may be present during the precipitation.

2469. ———. [Oxo Derivatives and Alcohols From Olefins.] Netherlands Patent 63,799, July 15, 1949. Chem. Abs., vol. 44, 1950, p. 1127.

Synthesis of Oxo derivatives from olefins, H_2, and CO, and of alcohols by subsequent hydrogenation, for example, United States Patent 1,741,308 (abs. **1757**) is improved by recycling a mixture of the residual gases from both stages, after it is brought to the necessary CO content with fresh gas. Describes new apparatus, consisting of a pressure vessel for the Oxo synthesis within a concentric pressure vessel for the hydrogenation reaction, or just the reverse, both vessels being heated separately at different temperatures under the same pressure of 100–200 atm.

2470. ———. Oxygenated Compounds. British Patent 651,144, Mar. 14, 1951, in Netherlands May 2, 1947. Petroleum, vol. 14, 1951, p. 200; Chem. Abs., vol. 45, 1951, p. 9037.

Oxygenated compounds comprising aldehydes and alcohols are prepared from hydrocarbons with <12 C atoms and containing at least 1 olefinic double bond by treatment with $CO+H_2$ in the presence of a suspended hydroformylation catalyst transported to the reaction zone in the form of a suspension consisting at least partly of an oil more viscous than any olefinic hydrocarbon with <12 C atoms. The suspension is prepared from the high-boiling substances obtained in the process itself with boiling point > that of the desired products. The viscous suspension contains 10–50 wt. % of catalyst.

2471. ———. [Oxygenated Compounds From Olefins.] French Patent 963,290, July 4, 1950; appl. filed Mar. 15, 1948. Chem. Zentralb., 1951, I, p. 3418.

Olefins are treated with CO and H in the presence of a catalyst in the form of Co deposited on pumice. About 8% Co is present. Conversion of the olefins to aldehydes takes place at 200 atm. and 140°–180°. The catalyst is regenerated by oxidation and final reduction. Oxidation takes place with air at 400°–900°.

2472. ———. Oxygenated Hydrocarbon Products. British Patent 675,719, July 16, 1952. Chem. Abs., vol. 47, 1953, p. 4895.

Describes mechanical arrangement of the Oxo process for catalytically oxygenating olefinic hydrocarbons to alcohols and aldehydes with CO, H_2, and Co catalysts.

2473. ———. Oxygenated Organic Compounds. British Patent 644,665, Oct. 18, 1950; appl. filed in Netherlands, May 2, 1947. Petroleum (London), vol. 14, 1951, p. 25; Chem. Abs., vol. 45, 1951, p. 4738.

In converting olefinic hydrocarbons into O-containing derivatives by the Oxo reaction, it has been found that the CO–H_2 gas mixture may be passed through a zone containing metallic Co to form aldehydes. The volatile Co compounds, for example, hydrocarbonyl, may be fed in the gas phase, thus dispensing with pumps; or the Co may be placed on a carrier such as pumice, kieselguhr, etc. Only a portion of the gas mixture may be passed through the Co-containing zone and the temperature in any case is 80°–120° with partial pressures of at least 30 atm.

2474. ———. Oxygen-Containing Organic Compounds. British Patent 646,744; appl. filed Nov. 29, 1950, in Netherlands, May 2, 1947. Petroleum (London), vol. 14, 1951, p. 81; Chem. Abs., vol. 45, 1951, p. 7137.

In the production of such compounds as aldehydes and alcohols by the treatment of suitable hydrocarbons with a CO–H_2 mixture in the presence of a hydroformylation catalyst, the novel feature claimed is the preheating of the 3 reacting materials. A hydroformylation catalyst is defined as one that assists in the addition of a H—C=O group and H atom to an olefinic double bond of which at least 1 must be present in the hydrocarbon used. The preheating temperature is 80°–130°, and it is not necessary for the reactants to be mixed during the whole preheating period. A suspended Co-containing catalyst may be used and may be incorporated before or during preheating as a liquid or gaseous compound.

2475. ———. Oxygen-Containing Organic Compounds. British Patent 662,528, Dec. 5, 1951. Chem. Abs., vol. 46, 1952, p. 4560.

Modification of the hydrocarbon-conversion process described in British Patent 644,665 (abs. **2473**) uses a pressure in the preliminary oven that is appreciably lower than the pressure to be used in the Oxo reaction and which does not exceed 75 atm.

2476. ———. [Preparation of Alcohols and Aldehydes From Olefins.] Netherlands Patent 64,137, Sept. 15, 1949. Chem. Abs., vol. 44, 1950, p. 1526.

In the preparation of oxygenated derivatives from olefins, CO, and H_2, the gases containing CO and H_2 are first led through a preheater with carrying material containing Co under such conditions that volatile Co addition products are formed. The gaseous mixture together with the olefins, is then introduced into the reactor, also filled with pumice containing Co. Losses of Co in the reactor are thus compensated by the volatile Co compounds introduced. Alternatively the gas containing CO and H_2 and the olefins are led together through the preheater. For example, a high-pressure tower is filled with pumice containing 30%

Co and water gas 2,200 l. per hr. per l. catalyst and C_7–C_8 olefins 2.2 l. were introduced at 80° and 150 atm. The gases took up 1% by weight of Co and were led to the reactor.

2477. ———. [Preparing Higher Aliphatic Alcohols by the Oxo Process.] Netherlands Patent 67,010. Dec. 15, 1950. Chem. Abs., vol. 45, 1951, p. 5711.

Process of preparing aliphatic alcohols and other oxygenated compounds from olefins, CO, and H_2 at about 150° and 200 atm. in 2 stages, catalytic addition followed by hydrogenation, is improved by recycling a part of the gas from the last stage to the 1st stage at such a rate that the reaction gas contains CO and H_2 in a ratio 1 : 1. Preferably 3 stages are used in which H_2 free from CO is introduced into the 3d stage and recycled there; part of the recycling gas is led to the 2d stage in which H_2 with some CO is recycled, and a part of this gas is introduced into the 1st stage, together with CO, so that here a gas mixture containing $CO : H_2 = 1 : 1$ is recycled. The gases in the last stage being free from CO, there is no danger of poisoning the catalyst, nor is it necessary to transform the CO catalytically to CH_4.

2478. ———. [Process for Extracting Hydrocarbon Mixtures.] French Patent 952,262, Nov. 14, 1949; appl. filed Aug. 22, 1947. Chem. Zentralb., 1950, II, p. 2269.

AsF_3, which is fluid at normal temperatures, is used admixed with only a small quantity of hydrocarbon oils as the selective extraction agent. 2 layers are formed. The process is suitable for treating mineral oils and their fractions, hydrocarbon mixtures obtained by hydrogenation, polymerization, or by the Fischer-Tropsch synthesis, and products from coal or lignite processing. Instead of pure AsF_3, mixtures of it with $SbCl_3$ can be used; $SnCl_4$, $TiCl_4$ and/or solvents that have a selective action, such as propane, benzine, CS_2, may be present. Mineral oils, which contain asphalts and/or ash-forming constituents, are treated with several % of AsF_3 (also, halogenides of P, As, Sb, or Bi) whereby these impurities precipitate. For example, a mixture of 37 vol. xylol and 63 of cetane is stirred with 44 of AsF_3 for 1 min. at 20°. The upper layer consists of 10.8% by weight of AsF_3, 23.2 of xylol, and 66 of cetane; the lower layer of 88.2% by weight of AsF_3, 11.4 of xylol, and 0.4 of cetane.

2479. ———. Process for the Catalytic Production of Carbon Monoxide and Hydrogen From Hydrocarbons and Steam. British Patent 637,776, May 24, 1950; appl. filed June 2, 1948, in Netherlands, June 6, 1947; 5 claims.

Fluidized catalyst, 10–200 microns, is used in a stationary or substantially stationary bed. Heat is supplied from without. A portion of the catalyst may be continuously withdrawn and recycled after it is heated to the desired temperature. The gases that have heated the catalyst, may be passed around the walls of the reactor to lower radiation loss. Not only CH_4, but also higher paraffin hydrocarbons may be used.

2480. ———. Production of Alcohols From Olefinic Hydrocarbons. French Patent 966,139, Oct. 2, 1950, appl. filed May 10, 1948. Chem. Zentralb., 1951, I, p. 1663.

Olefins are treated with CO and H_2 and the aldehydes thus formed are catalytically hydrogenated to the corresponding primary alcohols or are treated with $NaHSO_3$. The mixture of alcohols is converted with phthalic anhydride into the monoester, which is then isolated and purified. The purified ester is obtained, and this yields the pure alcohols by saponification.

2481. ———. Production of Aldehydes and Alcohols. British Patent 655,024; appl. filed Dec. 17, 1948. Ind. Chemist, vol. 27, 1951, pp. 373–374.

When treating olefins with H_2 and CO at high temperatures and pressures to form aldehydes and then alcohols by hydrogenation, the Co catalyst under the reaction conditions of stage 1 is partly brought into a vaporous state and partly into the form of soluble compounds. It must be precipitated on to the carrier before the product of stage 1 is distilled or hydrogenated. This product of stage 1 must 1st be cooled to enable gases to be separated from the liquid products, and then heated to decompose the dissolved Co compounds; serious difficulties occur in this heating because Co deposits are formed on the walls of the preheater and soon render it inoperative. This difficulty can be avoided by contacting the liquid product containing soluble Co compounds with a nonoxidizing gas, particularly one containing H_2, and in presence of solid carrier material for at least 30 min. at 30°–50° and under a pressure of <10 atm. The product is then treated with a gas containing H_2 at 150°–200° and under 20–25 atm. until the Co is virtually removed. In stage 1 unstable Co compounds are decomposed, Co being precipitated on to the large surface of the carrier rather than on to the small surface of the walls of the reactor. Preheating can then be continued without danger of further deposition. Step 2 for removing Co should also be effected in presence of a solid carrier. Diagram.

2482. ———. [Production of Hydrocarbons and Oxygenated Derivatives Thereof.] French Patent 959,863, Apr. 5, 1950; appl. filed Jan. 17, 1948. Chem. Zentralb., 1951, I, p. 520.

Alcohols and aldehydes are made from CO and H_2 in the presence of olefins or paraffins, for example CH_4. There is used as catalyst a silicate of a metal of Group VIII of the periodic system, such as Ni or Cu on a carrier of kieselguhr, Al_2O_3, carborundum, Mg silicate, Mg carbonate, or $BaSO_4$. According to examples CH_4 is mainly formed.

2483. ———. Production of Molded Catalyst. British Patent Appl. 18,201 and 18,294, 1948. Chem. Age, vol. 60, 1949, p. 364.

Molded catalysts containing active metals and diluent, with great mechanical strength and catalytic activity, may be produced by converting active metal wholly or partly into hydrosilicate, mixing this in pulverized state with a powdered diluent, compressing, and reducing this mixture. Catalytically active metals are Fe, Ni, and Co as well as Cu and Mn. They may be compressed in various forms and are applicable to a wide range of catalytic reactions, especially in the synthesis of hydrocarbons. They are very suitable for use in the liquid phase. Describes the method of preparation beginning with initial solutions: (a) Co, Th, and Mg as nitrates; (b) anhydrous Na_2CO_3 in H_2O; (c) Na silicate. The resulting suspension is vigorously stirred; mixed with alumina, which had previously been heated to 600° for 2 hr. and cooled; rapidly filtered, washed, dried, powdered, and pelletted; and reduced in H_2 at 430° for 1 hr. The catalyst finally consisted of 100 Co : 650 active Al_2O_3 : 8 MgO : 5 ThO_2 : 28 SiO_2. Patent application 18,294 is similar to the above, but is limited chiefly to metals that are wholly or partly converted into hydrosilicates with β-alumina as carrier.

2484. ———. [Production of Oxygenated Compounds of Hydrocarbons, Especially Alcohols.] French Patent 956,067, Jan. 24, 1950, appl. filed Nov. 28, 1947. Chem. Zentralb., 1950, II, p. 701.

Olefins are treated with $CO + H_2$ under pressure in 2 stages. In the 1st step Oxo compounds, particularly aldehydes, are formed. These are converted in a 2d step, by H_2 free from CO in the presence of a Co catalyst, to the corresponding alcohols. Both process steps are carried out in a high-pressure vessel with separate

reaction chambers. The operating temperature in both steps is about the same. The Oxo reaction is carried out preferably at 100°–200° and the hydrogenation step at 150°–250°. The pressure is the same in both cases at about 100–300 atm.

2485. ———. [Production of Oxygenated Organic Compounds.] French Patents 965,313 and 965,314, Sept. 8, 1950, appl. filed Apr. 26, 1948. Chem. Zentralb., 1951, I, p. 1070.

Aldehydes and alcohols are produced from olefinic compounds with at least 1 double bond by treatment with a gas containing CO and H_2 in presence of a metal such as Co at 80°–120° under a pressure of at least 30 atm. Water gas (CO 45% and H_2 55%) is contacted in a high-pressure converter with a Co catalyst on pumice at 200 atm. and 110°. Finally the gas mixture is treated in the converter with an octene fraction at 140°–180° and 200 atm. The conversion product is hydrogenated over a Ni-kieselguhr catalyst at 150° whereby nonyl alcohol is formed. Octane and some higher boiling fractions also occur. The catalyst for reacting the water gas with the olefin compounds is preferably used in the form of a suspension in a high-boiling viscous oil; for example, a 50% suspension of Co on pumice in the oil is fed by a pump and then mixed with the olefinic raw material and the water gas in the reaction chamber.

2486. ———. [Production of Oxygenated Organic Compounds.] French Patent 965,316, Sept. 8, 1950; appl. filed Apr. 26, 1948. Chem. Zentralb., 1951, I, p. 1070.

Olefins are treated with CO and H_2 in presence of a finely divided metallic Co, which forms the Co–hydrocarbonyl at temperatures not over 130°. An olefinic hydrocarbon fraction with 5–8 C atoms is treated with water gas (CO 40.7% and H_2 54%) in presence of the catalyst at 107°. Conversion of 87% of the olefins into oxygenated compounds is reported.

2487. ———. Production of Oxygen-Containing Hydrocarbon Derivatives. British Patent 643,503, Nov. 3, 1947. British Abs., 1951, B, II, p. 287.

Describes preparation of O_2-containing hydrocarbons by interaction of alkenes with CO and H_2 at >1 atm. in presence of an oxo synthesis catalyst. In a 1st stage with countercurrent flow oxo components (aldehydes) are formed and converted into alcohols by hydrogenation, the H_2 or H_2-containing gas remaining being mixed with the excess of gas containing CO and H_2 from the previous stage. This gas is then adjusted to the correct composition and reused in the oxo reaction. After the oxo stage, the products are passed upwards while passing through H_2 for removal of dissolved and combined CO whereafter the liquid products flowing downwards are treated with H_2 and hydrogenated. The synthesis may be carried out in a plurality of stages in separate reaction zones in series by adding H_2 free from CO to a last stage and recycling the same therethrough, recycling H_2 containing a minor proportion of CO in an intermediate stage, adding CO to the 1st synthesis stage and recycling a CO–H_2 mixture therethrough, withdrawing a portion of recycle gas from the last synthesis stage and adding it to the recycle gas in an intermediate stage, and withdrawing a portion of recycle gas from an intermediate stage and adding to the recycle gas in a 1st synthesis stage. The amount of gas transferred is adjusted to maintain the ratio of H_2: CO in the recycle gas in the 1st synthesis stage not less than 1:1. Diagrams.

2488. ———. Purification of Synthetic Alcohols by Hydrogenation With an Improved Nickel Catalyst. British Patent 659,981, Oct. 31, 1951. Chem. Abs., vol. 46, 1952, p. 10,190.

C_9 alcohol (I) containing 4.7% aldehyde was passed at a rate of 0.5 kg. per l. catalyst per hr. over a catalyst containing Ni, 40%; SiO_2, 11.2%; and Al_2O_3, 48.8%. The temperature was 150° and the pressure 150 atm. After hydrogenation the aldehyde content of (I) decreased to 0.04%. Describes preparation of the catalyst in detail.

2489. ———. Purified Oxo-Alcohols and Esters. British Patent 643,610, Sept. 20, 1950; appl. filed Apr. 9, 1948, in Netherlands May 9, 1947. Chem. Abs., vol. 45, 1951, p. 5711.

Alcohols having at least 4 C atoms are prepared by the Oxo process. To improve the color of esters produced therefrom, these alcohols are purified by distillation and hydrogenation. Alcohols are converted into esters by any known method, and these may be further refined by treatment with $KMnO_4$ in acetone. Products are suitable for use as plasticizers.

2490. ———. [Selective Hydrogenation of Diolefins to Mono-olefins.] Netherlands Patent 68,159, July 15, 1951. Chem. Abs., vol. 47, 1953, p. 2194.

Mixture (I) containing diolefins (II) and mono-ölefins is hydrogenated by passing it over a Ni sulfide (III) catalyst with H_2 in excess under a pressure of 1–10 atm. at 150°–350° and a liquid space velocity of 0.6–10 per hr. A mol. ratio H_2 to (II) of 10–12 to 1 is preferred. It is advantageous to carry on the hydrogenation in 1 stage until the (II) content of (I) is <1–5% by vol. The remaining (II) may be removed by polymerization or by extraction. By adding S or H_2S to the reaction mixture the catalyst is kept active. For example, a C_5 fraction containing 57% (II), 42.7% olefins, and 0.6% acetylenes was subjected to selective diene hydrogenation with (III) on activated alumina as a catalyst; 3.1 atm. pressure, mol. ratio H_2 to (II) ±10–12:1, space velocity 0.8–0.9, and average temp. 216°. The hydrogenated product contained 0.7% (II) and 98% mono-olefins. It was a suitable alkylation feed stock.

2491. ———. Separation of Hydrocarbons From Oxygenated Derivatives. British Patent 661,916, Mar. 17, 1949. British Abs., B, II, 1952, p. 221; Chem. Abs., vol. 47, 1953, p. 2193.

A mixture of organic compounds containing hydrocarbons and substantially H_2O-insoluble oxygenated compounds derived from hydrocarbons is extracted with 2 solvents flowing countercurrent to each other, 1 solvent consisting of liquid SO_2 and the other of paraffinic hydrocarbons boiling outside the boiling range of the mixture. The paraffinic hydrocarbons are pure hydrocarbons substantially free from aromatic hydrocarbons; for example, medicinal paraffin oil. The extraction is performed at <—10°.

2492. ———. Separation of Oxygen-Containing Compounds Derived From Hydrocarbons. British Patent 664,205, June 30, 1949. British Abs., B, II, 1952, p. 315; Chem. Abs., vol. 46, 1952, p. 10,190.

A mixture of H_2O-insoluble O-containing compounds is separated into a fraction containing compounds with a more pronounced polar character and a fraction with a less pronounced polar character by subjecting it to the action of 2 solvents flowing countercurrent to each other. One solvent consists of substances that contain 2 or more polar groups or of 1 polar group and a highly polarizable remainder; hydroxy compounds are the preferred polar solvent, such as diethylene glycol. The other solvent consists of paraffinic hydrocarbons with a boiling range outside that of the mixture to be separated, such as liquid paraffin. Good results are obtained using mixtures b. 110°–250°, the initial and final b. p. of the mixture being not more than 40° apart.

2493. ———. [Shaped Catalysts.] Netherlands Patent 66,312, Aug. 15, 1950. Chem. Abs., vol. 44, 1950, p. 10966.

In manufacturing supported catalysts containing metals of Group VIII of the periodic system, Cu and/or Mn, the metals are entirely or partly precipitated as reducible hydrosilicates, which are mixed in dry powdered form with the dry powdered carrier material. The mixture is pressed to form pellets and reduced. Contrary to the catalysts obtained by mixing the components in wet form, the carrier material is added before or after precipitation of the hydrosilicates. These catalysts as a rule have a low activity or are difficultly reducible if supports are used giving high mechanical strength. The new catalysts are very active also in case of using such supports, and are suitable for synthesis of hydrocarbons from CO- and H_2-containing gases, especially if employed in a fixed bed, with circulation of the evaporating oil with a high ratio of recirculating gas or in the fluid phase. The catalysts may be shaped into pellets, tablets, cylinders, Raschig rings, or the like.

2494. ———. [Shaped Catalysts.] Netherlands Patent 66,313, Aug. 15, 1950. Chem. Abs., vol. 44, 1950, p. 10967.

Though supported catalysts containing metals of Group VII of the periodic system, Cu and/or Mn, obtained by precipitating the metals entirely or partly as reducible hydrosilicates, mixing the carrier material with the other components in wet form before or after precipitation of the hydrosilicates, and then drying, pressing, and reducing the mixture, as a rule have a much lower activity if supports are used giving high mechanical strength than in using supports giving a lower mechanical strength. Catalysts with high activity are obtained in using β–Al_2O_3. In comparing pressed catalysts comprising activated Al_2O_3, α–Al_2O_3, and β–Al_2O_3, all of them containing 190 gm. Co per l., which are able to withstand pressures up to 5, 2, and 9 kg., respectively, used for hydrocarbon synthesis, the activity of the catalyst with activated Al_2O_3 was much lower than that of the α–Al_2O_3-supported catalyst, but the activity of the catalyst with β–Al_2O_3 about equaled that of the latter.

———. *See* abs. **649, 653, 654, 655, 1087, 1098, 1099, 2163, 2212, 3301, 3795, 3797, 3800, 3908.**

N. V. INTERNATIONALE HYDROGENEERINGSOCTROOIEN MAATSCHAPPIJ.

See International Hydrogenation Patents Co., Ltd.

N. V. INTERNATIONALE KOOLWATERSTOFFEN SYNTHESE MAATSCHAPPIJ.

See International Hydrocarbon Synthesis Co.

2495. N. V. INTERNATIONALE MAATSCHAPPIJ VOOR HYEREERINGS-TECHNIEK EN CHEMIE (International Hydrogenation Engineering & Chemical Co.). Destructive Hydrogenation. British Patent 501,318, Feb. 24, 1939. Chem. Abs., vol. 33, 1939, p. 6039.

In the production of antiknock motor fuels by the hydrogenation of liquid hydrocarbons in the vapor phase at >380° and >40 atm. in presence of stationarily arranged catalysts, the hydrogenating gas employed comprises a mixture of H_2 and gaseous hydrocarbons containing more than 1 C atom in the mol., the volume of the gaseous hydrocarbons exceeding that of the H_2. Thus, middle oil, b. 180°–325°, obtained in the synthesis of benzine from CO and H_2 is mixed with 40% by weight of butane and heated with H_2 under 300 atm. pressure up to 530°, the H_2 partial pressure being 70 atm., so that about 2.5 l. butane are present per l. of H_2. The mixture is then passed over a catalyst comprising oxides of Mo, Zn, and Mg. 42% of the middle oil and 24% of the butane are converted into benzine having an octane no. of 69.5.

2496. NAHIN, P. G., AND HUFFMAN, H. C. (Union Oil Co. of California). Supported Catalyst and Preparation Therefor. United States Patent 2,510,189, June 6, 1950; appl. filed Feb. 16, 1948, Serial No. 8,750; 9 claims (*Cl. 252–455*). Chem. Abs., vol. 44, 1950, p. 8102.

Gives preparation for a catalyst in which combined oxides of Co and Mo are impregnated on alumina. The Co and Mo salts are dissolved in an aqueous NH_3 solution having an NH_3 concentration 5–15 molar in which the molar ratio of NH_3 to Co is at least 2 times the ionic charge of Co. The impregnated carrier is dried and calcined. 4 United States patents cited.

2497. NAMIKAWA, T. [Water Gas.] Japanese Patent 98,957, Jan. 9, 1933. Chem. Abs., vol. 27, 1933, p. 5944.

Reaction tube containing Ni catalyst is put in the center of a water gas generator. A gas containing hydrocarbons is decomposed with steam in the reaction tube, and the gases formed are passed through the hot coke around the reaction tube, producing water gas. The gas, for example, contains 25–34% CO and 57–59% H_2.

2498. NARAGON, E. A. (The Texas Co.). Upgrading Olefinic Stocks. United States Patent 2,562,989, Aug. 7, 1951; appl. filed Sept. 15, 1948, Serial No. 49,463; 1 claim (*Cl. 196–50*).

Olefinic stocks boiling within the gasoline range for use as motor fuel are improved by subjecting them to a combined isomerization and hydrogenation in the presence of added H_2 at a temperature 600°–775° F. and over a catalyst consisting essentially of 81% activated Al_2O_3 impregnated with 5% Mo oxide, 10% B oxide, and 4% silica. Describes preparation of the catalyst. Gives example using hexylene as the olefin material. The liquid products obtained by the operation were substantially paraffinic in character and approximated 93% by weight of the hexylene feed. The products contained quantities of such high-octane hydrocarbons as 2-methylpentane, 3-methylpentane, and 2, 3-dimethylbutane.

———. *See* abs. **2342.**

2499. NARAGON, E. A., MILLENDORF, A. J., AND VERGILIO, J. H. (The Texas Co.). Regeneration of a Cobalt Oxo Synthesis Catalyst. United States Patent 2,542,558, Feb. 20, 1951; appl. filed Jan. 29, 1949, Serial No. 73,532; 12 claims (*Cl. 252–416*). Chem. Abs., vol. 45, 1951, p. 3966.

Co catalysts are regenerated by contacting them with steam at a temperature 600°–1,000° F. for a period of at least 4 hr. and then further reducing them by contact with H_2 at a temperature of approximately 450°–750° F. for a period of at least 12 hr. 4 United States patents cited.

2500. NARAGON, E. A., VERGILIO, J. H., AND MILLENDORF, A. J. (The Texas Co.). Regenerating Cobalt Catalysts by Oxidation. United States Patent 2,626,246, Jan. 20, 1953; appl. filed Jan. 29, 1949, Serial No. 73,533; 7 claims (*Cl. 252–416*).

Co catalysts that have been used in conversion of CO, H_2, and olefins to carbonylic products can be regenerated by contact with an O_2–N_2 mixture at 100°–400° F. for at least 4 hr. The O_2–N_2 mixture has a composition of 1–25% O_2 and 75–99% N_2. Air makes a good regenerating gas. The regeneration may be done in situ. 4 United States patents cited.

2501. NASH, A. W., BOWEN, A. R., AND ELVINS, O. C. Olefins From Carbon Monoxide and Hydrogen. British Patent 291,867, Mar. 9, 1927. Chem. Abs., vol. 23, 1929, p. 1136.

Mixture of H_2 with an excess of CO is passed at atmospheric pressure and at a temperature of 280°–300° over a catalyst comprising a mixture of the reduced oxides of Co, Cu, and Mn. Gives various details.

NATIONAL COKE & OIL CO., LTD. *See* abs. **3659.**

NATIONAL INDUSTRIEL DE L'AZOTE. *See* abs. **206.**

2502. NATTA, G. [Alcohols.] French Patent 683,320, Oct. 15, 1929. Chem. Abs., vol. 24, 1930, p. 4519.

Alcohols higher than MeOH are prepared from mixtures of CO and H_2 using alkali salts of fatty acids on porous supports as catalysts, such as HCOOK or AcOK. MeOH may be added to the CO and H_2, or a catalyst favoring the production of MeOH from CO and H_2 may be added to the other catalyst.

2503. ———. [Alcohols.] Swiss Patent 147,151, Oct. 15, 1929. Chem. Abs., vol. 26, 1932, p. 2198.

Alcohols containing more than 1 C atom are prepared by the reaction of CO with H_2 under raised temperature and pressure, with intermediate formation of MeOH. A catalyzer for the synthesis of MeOH is present together with an alkali salt of a fatty acid. Thus, the CO and H_2 form CH_3OH, which then with KOH forms CH_3OK. This, with more CO forms CH_3COOK and this, finally with H_2 forms C_2H_5OH and KOH. Process is continuous.

2504. ———. Catalyst Suitable for Use in Producing Methanol From Carbon Oxides and Hydrogen. United States Patent 2,193,464, Mar. 12, 1940; appl. filed June 9, 1937, Serial No. 147,253, in Italy June 10, 1936; 8 claims (*Cl. 23–237*). Chem. Abs., vol. 34, 1940, p. 4746.

ZnO catalyst is prepared by decomposing by heat a molten anhydrous organic Zn salt having a decomposing temperature above its melting point, such as Zn acetate.

2505. ———. [Catalysts.] French Patent 822,818, Jan. 8, 1938. Chem. Abs., vol. 32, 1938, p. 5166.

Catalyst for chemical reactions in which oxides of C participate contain ZnO prepared by heating to decomposition organic salts of Zn, the freezing point of which are below decomposition point. Thus, the ZnO may be prepared by decomposition of $Zn(OAc)_2$ and may be used for the preparation of MeOH.

2506. ———. [Catalysts and Their Use in Reactions in Which Carbon Monoxide Occurs.] Italian Patent 342,930, June 10, 1936. Chem. Zentralb., 1938, I, p. 431.

Catalysts are given for production of MeOH by the hydrogenation of CO and CO_2 or of water gas, of ketone from organic acids containing at least 2 C atoms, of aldehydes from a mixture of HCOOH and other volatile organic acids. Catalysts are obtained by the partial or total pyrogenetic decomposition of organic salts of Zn, such as Zn acetate whose melting point is lower than its decomposition temperature, at the lowest possible temperature and increased pressure with exclusion of air and in a reducing or inert gas atmosphere.

2507. ———. [Catalytic Process for Alcohols.] Austrian Patent 158,416, Apr. 10, 1940 (*Cl. 12 e*). Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 208; Chem. Abs., vol. 36, 1942, p. 2270.

See United States Patent 2,193,464 (abs. **2504**).

2508. ———. Ethanol and Other Alcohols Produced Synthetically. British Patent 340,656, Oct. 16, 1929. Chem. Abs., vol. 25, 1931, p. 4894.

In the synthesis of EtOH and higher alcohols from CO and H_2 mixtures under pressure, with or without addition of MeOH, there are employed as catalysts alkali salts of aliphatic acids such as formates, acetates, or propionates of K; Rb or Cs mixed with porous supports such as ZnO, pumice, magnesite, or silica; or MeOH–synthesis catalysts such as calcined Smithsonite. A temperature of 400°–420° and pressure of 250–300 atm. are suitable. Synthetic MeOH may be used for washing the reaction gases to remove CO_2.

See also French Patent 683,320 (abs. **2502**) and Swiss Patent 147,151 (abs. **2503**).

2509. ———. [Gas.] German Patent 614,928, June 25, 1935 (*24 e–1.07*). Chem. Abs., vol. 29, 1935, p. 8297.

Solid fuel is gasified by O_2, H_2O vapor, and heat to give a mixture of CO, H_2, and CO_2 suitable for the synthesis of alcohols, especially MeOH. The temperature of the gas producer is kept <750°, and the proportions of O_2 and steam are not more than 1 vol. of O_2 to 2 vol. of steam.

2510. ———. [Gas Mixtures.] Swiss Patent 141,827, Mar. 7, 1929. Chem. Abs., vol. 25, 1931, p. 2273.

Gas mixture of CO, H_2, and CO_2 containing at least 2 times as much H_2 as oxide of C, is obtained by passing an O_2 and steam current, containing at least 2 times as much steam as O_2, over C at about 700° and not over 750°.

See also British Patent 330,918 (abs. **2511**).

2511. ———. Hydrogen and Carbon Monoxide Mixtures for Synthesis of Organic Compounds. British Patent 330,918, Mar. 11, 1929. Chem. Abs., vol. 24, 1930, p. 5765.

Mixture of O_2 and H_2O vapor, not >1 vol. of O_2 to 2 vol. of H_2O vapor, is passed over C at a temperature not exceeding 750° and CO_2 is removed to obtain a mixture containing H_2, 2 and CO, 1 vol. By preheating the O_2 and H_2O vapor and using a temperature <700°, a mixture of H_2, 3 and CO, 1 vol. is obtained. Pressures up to 20 atm. may be used, and the gas mixtures obtained may be used for the synthesis of hydrocarbons, MeOH, and other O-containing organic compounds.

2512. ———. [Methanol.] French Patent 670,763, Mar. 4, 1929. Chem. Abs., vol. 24, 1930, p. 1869.

Mineral smithsonite previously heated to 400°–450° is used as catalyst in the production of MeOH from CO and H_2.

2513. ———. [Methanol.] French Patent 681,147, Feb. 7, 1929. Chem. Abs., vol. 24, 1930, p. 4305.

Hydrocarbons, alcohols, and other compounds, particularly MeOH, are made from gaseous mixtures of CO, H_2, and CO_2, which contain at least 2 vol. of H_2 for 1 vol. of CO, obtained by passing a mixture of 1 vol. of O_2 with at least 2 vol. of steam over charcoal heated to about 700°.

See also French Patent 670,763 (abs. **2512**).

2514. ———. [Methanol.] Swiss Patent 140,093, Mar. 9, 1929. Chem. Abs., vol. 25, 1931, p. 715.

See French Patent 670,763 (abs. **2512**).

2515. ———. [Methanol Catalyst.] Italian Patent 267,698. no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 208.

Before use, smithsonite is heated to 400°–450° at 300 atm.

See also German Patent 612,267 (abs. **2519**) and United States Patent 1,815,677 (abs. **2518**).

2516. ———. (Deutsche Gold- u. Silber-Scheideanstalt vorm. Roessler). [Methonal Synthesis.] German Patent 646,928, July 16, 1937; appl. filed Aug. 1, 1934. Chem. Zentralb., 1937, II, p. 2432.

Conversion of CO and H_2 is carried out in an apparatus in which the parts in contact with the gases are made of Cu–Ni alloys containing preferably 2–75% of Ni.

2517. ———. [Methanol Synthesis.] Italian Patent 283,343, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 208.

Catalyst of solid solutions of bivalent metal oxides with an ion radius 0.6–0.9 Å. (Zn, Mg, Ni, Co, Fe, Mn).

2518. ———. Methanol Synthesis. United States Patent 1,815,677, July 21, 1931; appl. filed Mar. 7, 1929. Chem. Abs., vol. 25, 1931, p. 5436.

MeOH and other oxygenated organic compounds are formed by subjecting a mixture of CO and H_2 to the catalytic action of mineral smithsonite.

2519. ———. [Oxygenated Organic Compounds From Carbon Monoxide and Hydrogen.] German Patent 612,267, Apr. 18, 1935 (*Cl. 12 o–5.01*). Chem. Abs., vol. 29, 1935, p. 4771.

This corresponds to French Patent 670,763 (abs. **2512**) but gives additional details.

2520. ———. [Oxygen-Containing Products.] Swiss Patent 102.236, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 208.

Fatty acid Zn salts are decomposed above their melting points, especially Zn acetate.

See United States Patent 2,193,464 (abs. **2504**).

2521. ———. Preparation of Catalysts for the Synthesis of Methanol. British Patent 492,073, June 10, 1937. British Chem. Abs., B, 1938, p. 1389.

Reduction of CO to MeOH by H_2 or H_2+steam is catalyzed by ZnO prepared by decomposing an organic salt of Zn of which the melting point is < the decomposing point, $(Zn(OAc)_2)$, preferably in an inert atmosphere at >1 atm.

2522. ———. [Synthesis Gas.] Italian Patent 356,468, Nov. 3, 1937. Chem. Zentralb., 1942, I, p. 141.

To produce a N_2-poor synthesis gas, gases from the low-temperature treatment of organic substances are converted with a mixture of O_2 and about 5–6 times the quantity of steam.

2523. NATTA, G., AND BEATI, E. Production of Aldehydes. British Patent 646,424, Nov. 22, 1950. Chem. Abs., vol. 45, 1951, p. 5714.

Aliphatic and cycloaliphatic aldehydes are obtained from olefins and cycloalkenes (boiling not below the reaction temperature), H_2 and CO at a temperature above 80° and at a pressure of 10–50 atm. in the presence of a Co-containing catalyst. A preferred catalyst is partly reduced CoO activated with up to 2% Fe_2O_3 and supported on a carrier. Thus, to $Me(CH_2)_{15}CH:CH_2$ 1 and catalyst 0.1 kg. (obtained by partial reduction of basic carbonates of Co 98% and Fe 2% with H_2 at 350°) in a 3-l. tank are added CO and H_2 at a pressure of 12 atm. The mixture is heated at 100°–110° and the addition of CO and H_2 continued until absorption ceases, to yield mainly $Me(CH_2)_{16}CHMeCHO$ and $Me(CH_2)_{18}CHO$ containing small quantities of the corresponding alcohols. Gives other examples.

2524. NATTA, G., AND FALDINI, M. [Methanol.] French Patent 658,788, July 18, 1928. Chem. Abs., vol. 23, 1929, p. 5196.

MeOH is obtained by passing a mixture of CO and H_2 at high pressure over a mixture of FeO or CoO and oxides of other bivalent metals such as Mg, Mn, Cr, Zn, and Be with or without small amounts of oxides of tervalent metals.

2525. NAUMANN, F. K. (F. Krupp A. G.). [Reaction Kettles of Decarbonization-Resisting Alloy.] German Patent 692,226, May 16, 1940 (*Cl. 18 d–2.20*). Chem. Abs., vol. 35, 1941, p. 4340.

Such vessels, of great importance in hydrogenation and synthetic-ammonia works, are made of steels containing Ti fourfold the amount of C. These steels contain also 1 or more metals, for example, Si, Mn, Ni, Co, Cr, W, Mo, or V.

NEIMAN, P. E. *See* abs. **330.**

2526. NELLY, H. M., JR., AND HOTTEL, H. C. (M. W. Kellogg Co.). Combined Regenerator and Catalyst Chamber Suitable for use in Producing Carbon Monoxide and Hydrogen From Carbon Dioxide and Methane. United States Patent 2,230,467, Feb. 4, 1941; appl. filed July 12, 1939, Serial No. 284,031; 7 claims (*Cl. 12–128.1*). Chem. Abs., vol. 35, 1941, p. 3399.

Gives various structural and operative details.

2527. NELLY, H. M., JR., KEITH, P. C., JR., AND WILSON, D. W. (M. W. Kellogg Co.). Liquid Hydrocarbons From Hydrocarbon Gases. Canadian Patent 411,292, Mar. 23, 1943. Chem. Abs., vol. 37, 1943, p. 3589.

Hydrocarbon gas is burned in a catalyst contact zone, the temperature rising to 1,800°–2,200° F.; the CO_2 is recovered, mixed with hydrocarbon gas and steam, and subjected to catalytic conversion to form CO and H_2, and the mixture of CO and H_2, is converted into liquid hydrocarbons in the presence of a catalyst at elevated temperature. Describes an apparatus.

NELSON, K. J. *See* abs. **828, 829.**

NENRYO, KENKYUZYOTYO, DIRECTOR OF. *See* abs. **124, 3763.**

NEWCOMBE, J. *See* abs. **1111.**

NEWELING, H. *See* abs. **647.**

NEWNS, J. E. *See* abs. **888, 889, 890.**

2528. NIELSON, H. Destructive Distillation of Coal, Wood or Similar Materials. United States Patent 1,605,761, Nov. 2, 1926; appl. filed Nov. 27, 1922. Chem. Abs., vol. 21, 1927, p. 168.

Formic acid is made from CH_4 or gas containing it by passing the gas over a metallic catalyst such as Cu suboxide. The reaction is as follows: $CH_4+O_2=CO+H_2O+H_2=HCOOH$. It may also be made from CO in the presence of H_2O vapor and the catalyst.

2529. NIELSEN, H., AND LAING, B. Distilling Solid Fuels of Coking Character. British Patent 292,060, Dec. 4, 1926. Chem. Abs., vol. 23, 1929, p. 1248.

Material treated is subjected to the action of hot gases containing a controlled quantity of O_2 (2–8%) or an oxidizing constituent to oxidize some of the coking constituents and influence their coking power, and, after carbonization, the solid residue is treated with steam to effect gasification. Carbonizing may be effected at 600° or lower, followed by a high-temperature treatment up to 1,200°. A free-burning residue is obtained, which is not coated with a graphitic C and is easily oxidized by the O of ores such as oxides of Cu or Fe or by steam in a water-gas producer. Gives various details.

2530. ———. Hydrogen From Water Gas. British Patent 342,817, Nov. 22, 1929. Chem. Abs., vol. 25, 1931, p. 4388.

Water gas, obtained as described in British Patent 292,060 (abs. **2529**) or by gasifying coke obtained by high-temperature distillation from fuel of 0.03- to 2.0-in. cube, may have its CH_4 content converted by steam in the presence of a catalyst to CO and H_2, or its CO converted to CO_2 with production of H_2. Water gas from low-temperature distillation semicoke may be catalytically converted to obtain higher paraffin hydrocarbons, and CH_4 formed may be removed and converted to H_2, CO, and CO_2.

2531. NIENBURG, H. (Badische Anilin- u. Soda-Fabrik). [Organic Compounds Containing Oxygen.] German Patent 800,400, Nov. 2, 1950; appl. filed Oct. 2, 1948 (*Cl. 12 o–7.03*). Chem. Abs., vol. 45, 1951, p. 1625.

Process of preparing organic compounds containing O by reaction of CO and H_2 with diolefins in the presence of hydrogenation catalysts is improved by using dimerized diolefins as reactants. The dimerization is effected by heating the diolefins several hours at 200°–250°. Treating dimerized butadiene thus in presence of a Co-kieselguhr catalyst with a CO–H_2 mixture (1:1) at 120° and 200 atm. for 60–80 min., replacing the CO–H_2 mixture by H_2 (100 atm.), heating the mixture 1 hr. at 120° to decompose the Co carbonyl compounds, and distilling the reaction product in vacuo yields a cyclic singly unsaturated C_9–aldehyde, $b._{18}$ 93°–98°. The analogous treatment of dimerized isoprene yields a cyclic C_{11}–aldehyde, colorless oil, $b._{14}$ 130°–135°, and small quantities of the corresponding C_{11}–alcohol.

NIENBURG, H. *See* abs. **1846.**

2532. NIENBURG, H., AND FRIEDRICHSEN, W. (I. G. Farbenindustrie A. G. "In Auflösung"). [Primary Alcohols.] German Patent 844,891, July 24, 1952 (*Cl. 12 o–5.02*). Chem. Abs., vol. 47, 1953, p. 5422.

Treating *m*–dioxanes with H_2 in the presence of hydrogenation catalysts at elevated temperature (preferably 200°–280°) and pressure (preferably >100 atm.), sometimes in the presence of inert solvents or diluents gives primary alcohols; 2 moles H_2 are consumed per mole of the dioxane derivative, and the cleavage of the dioxane nucleus results in the formation of 1 mole each of MeOH and the higher-molecular alcohol. Heating 4,4–dimethyl–*m*–dioxane 100 and a Cu–Cr oxide catalyst 5 parts by weight in an autoclave with H_2 at 200 atm. and 260° gives, after removal of the catalyst and distillation, 80–90% iso-AmOH, b. 131°, besides MeOH. Similarly are prepared: 2,3–dimethyl–1–butanol, b. 145°, from 4,4,5–trimethyl–*m*–dioxane; 2,2,3–trimethyl–1–butanol, b. 156°, from 4,4,5,5–tetramethyl–*m*–dioxane; BuOH, b. 117°, from 4–methyl–*m*–dioxane.

2533. NIPPON CHEMICAL INDUSTRIES CO. [Catalysts for Synthesizing Isobutanol.] Japanese Patent 157,787, July 20, 1943. Chem. Abs., vol. 44, 1950, p. 1127.

ZnO, CuO, MnO, or Cr_2O_3 or hydroxides, alone or mixed after adding an alkali complex salt of the single or mixed metals and then heating, forms a long-lasting active catalyst for making iso-BuOH from H_2 and CO. For example, H_2 and CO (2:1) passed at 40° and 150 atm. over $Zn(OH)_2$ and $Cu(OH)_2$ [precipitated together from $Zn(NO_3)_2$ 2 and $Cu(NO_3)_2$ 1 molecule with NaOH, dried at 400°, and powdered], heated 100°–400° with 1 molecule $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ gave 30% iso-BuOH and only 15% higher alcohols.

NIPPON FATS & OILS CO. *See* abs. **2554, 3227.**

NIPPON SYNTHETIC PETROLEUM CO. *See* abs. **604.**

NISSAN CHEMICAL INDUSTRIES CO. *See* abs. **1053.**

NISSIN CHEMICAL INDUSTRIES CO. *See* abs. **1809.**

NITROGEN ENGINEERING CORP. *See* abs. **2780.**

NITTO CHEMICAL INDUSTRIES CO. *See* abs. **2400.**

NIWA, A. *See* abs. **3705.**

2534. NOBLEE & THÖRL G. M. B. H. [Fatty Acids.] German Patent Appl. N 44,653, no date (*Cl. 12 o–11*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 283.

High-molecular aliphatic hydrocarbons are oxidized on catalysts consisting of Mn compounds and of compounds of elements of group 4 of the periodic system.

2535. ———. [Fatty Acids.] German Patent Appl. N 44,666, no date (*Cl. 12 o–11*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 283.

Fatty acids are obtained by oxidizing high-molecular aliphatic hydrocarbons b. <360° in the presence of heavy metal catalysts with compounds of group 4 of the periodic system as promoters. The process leads to a fatty acid content of at most 15% in the oxidation mixture.

———. *See* abs. **2577, 2578, 2579.**

NON-POISONOUS GAS HOLDING CO., LTD. *See* abs. **393.**

2536. NYSTRÖM, E. H. R. [Ferromagnetic Iron Hydroxides and Oxides.] Swedish Patent 134,706, Mar. 4, 1952. Chem. Abs., vol. 47, 1953, p. 236.

Ferromagnetic Fe hydroxides obtained by precipitation of an Fe salt in a known manner is powdered by spraying the precipitate after washing out soluble salts into a drying atmosphere at a temperature not >350° but high enough to dehydrate the hydroxide. Preferably an oxidizing atmosphere is used to oxidize the Fe to a higher valence.

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2537. OBERFELL, G. G. (Phillips Petroleum Co.). Synthesis of Hydrocarbons. United States Patent 2,490,463, Dec. 6, 1949; appl. filed Oct. 22, 1945, Serial No. 623,799; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 2205.

Thermal control in synthesis of hydrocarbons with more than 1 C atom per mol. from H_2 and an oxide of C is achieved by introducing liquid Hg into the upper portion of a vertical reaction chamber. The Hg flows downward over the catalyst in direct heat exchange with the reacting gases. When the excess exothermic heat of reaction is removed primarily by removal as sensible heat of the liquid Hg, it is preferable to have countercurrent flow of gases and Hg. When the temperature is so high that a large portion of the Hg will be vaporized, thus removing the exothermic heat as latent heat of vaporization of the Hg, it is preferable to introduce the synthesis gas near the upper portion of the reaction chamber resulting in concurrent flow of reacting gases and Hg. I foreign patent and 6 United States patents cited.

2538. OBLAD, A. G., AND MESSENGER, J. U. (Socony-Vacuum Oil Co., Inc.). Catalytic Isomerization of Olefinic Hydrocarbons. United States Patent 2,471,647, May 31, 1949; appl. filed Mar. 4, 1946, Serial No. 651,990; 3 claims (*Cl. 260–683.2*). Chem. Abs., vol. 43, 1949, p. 5939.

Straight-chain olefins containing 4–6 C atoms per mol. are converted to branched-chain olefins by subjecting the former to temperatures of 500°–950° F. in the presence of an alumina catalyst impregnated with HF. A light naphtha cut from Fischer-Tropsch synthetic hydrocarbon product containing pentenes and hexenes can be converted to an equilibrium mixture containing high % of branched-chain olefins.

2539. OCON, E. A. Manufacture of Branched-Chain Aliphatic Compounds. United States Patent 2,299,844, Oct. 27, 1942; appl. filed Jan. 2, 1940, Serial No. 312,027 (*Cl. 44–54*). Chem. Abs., vol. 37, 1943, p. 1722.

Method is employed for converting low-boiling, straight-chain, oxygenated derivatives of normal aliphatic hydrocarbons, such as are obtained by synthesis from CO and H_2, into higher boiling isoaliphatic compounds of higher antiknock value suitable for motor fuel, which involves bringing a mixture of such oxygenated derivatives, normally gaseous olefins, and a reducing gas composed primarily of CO and containing <25% of H_2, the combined CO and olefin content of the gaseous material being at least equal to the volume

of oxygenated derivatives, into contact with a dehydrating catalyst, such as a dehydrated Cu–U phosphate, at a temperature in the range of 400°–1,100° F. while maintaining the H_2O vapor content of the reactants <8% by volume.

2540. ———. [Synthesis Gas.] French Patent 50,928, no date. Kainer, p. 130.

Gas mixtures occurring in the reforming of heavy benzine are used for the production of synthesis gas. Addition to French Patent 849,312.

2541. ODELL, W. W. (Columbia Engineering & Management Corp.). Combustible Gas. United States Patent Reissue 18,382, Mar. 8, 1932; appl. filed Nov. 25, 1931. Chem. Abs., vol. 26, 1932, p. 2851.

Describes preparation from a hydrocarbon gas of a H_2–CO mixture of about 2–3 parts H_2 to 1 part CO. Reissue of original United States Patent 1,762,100 (abs. **2542**).

2542. ——— (Columbia Engineering & Management Corp.). Combustible Gas. United States Patent 1,762,100, June 3, 1930; appl. filed Mar. 4, 1927. Chem. Abs., vol. 24, 1930, p. 3633.

Hydrocarbon gas is introduced into a mass of solid fuel heated to a temperature high enough to decompose the hydrocarbon gas, and steam is simultaneously introduced in quantity sufficient to effect substantially complete reaction with the hydrocarbon gas, thus producing a gas comprising essentially H_2 and CO and in which the ratio of H_2 : CO is substantially from 2 : 1 to 3 : 1. Describes an arrangement of apparatus.

2543. ——— (Columbia Engineering & Management Corp.). Combustible Gas. United States Patent 1,930,442, Oct. 10, 1933; appl. filed Apr. 11, 1930. Chem. Abs., vol. 28, 1934, p. 293.

Mixture of steam and hydrocarbon gas comprising chiefly C_3H_8 and C_4H_{10} is introduced into a highly heated fuel bed to produce a gas comprising essentially H_2 and CO in the ratio of 2 : 1 to 3 : 1, respectively, and the resulting gas is enriched by at least partly reforming hydrocarbon material of normally liquid character in a chamber containing refractory material. Describes apparatus.

2544. ——— (Columbia Engineering & Management Corp.). Combustible Gas. United States Patent 1,930,443, Oct. 10, 1933; appl. filed May 22, 1930. Chem. Abs., vol. 28, 1934, p. 293.

Relates to the manufacture of gas by air-blasting an ignited fuel bed to bring it to incandescence, separately introducing a hydrocarbon material into a stream of superheated steam, and thoroughly mixing and heating the steam and hydrocarbon material to > 540°, introducing the heated gaseous product into the incandescent fuel bed from above, and removing the resulting gas from beneath. The gas generated contains 2.0–3.5 times as much H_2 as CO and is substantially free from suspended C resulting from pyrolysis of the hydrocarbon material. Describes apparatus.

2545. ———. Combustible Gas. United States Patent 2,052,149, Aug. 25, 1936; appl. filed June 13, 1930. Chem. Abs., vol. 30, 1936, p. 6926.

Combustible gas having a relatively low calorific value is made in a repeated cycled process; 1 cycle comprises first heating a confined porous bed of solid refractory material to incandescence by conducting combustion in contact with the surface of the material then discontinuing the heating operation and making a prolonged gasmaking run with introduction of suitably proportioned amounts of steam, air, and fluid hydrocarbon material such as a petroleum refinery gas, which react to form a gas substantially free from suspended C and which is mainly composed of CO and H_2. The volume of air used is > the vapor volume of the fluid hydrocarbon material but insufficient for the complete combustion of the latter, and the amount of steam used is lower than that at which appreciable amounts of C appear suspended in the generated gas. Describes apparatus.

2546. ——— (Columbia Engineering & Management Corp.). Combustible Gas From Hydrocarbon Gas and Steam. United States Patent 1,841,201, Jan. 12, 1932; appl. filed Mar. 4, 1927. Chem. Abs., vol. 26, 1932, p. 1758.

Gas substantially free from suspended C resulting from hydrocarbon decomposition is produced by introducing a hydrocarbon gas into a mass of noncombustible checker material heated to a degree sufficient to decompose the hydrocarbon gas, and simultaneously introducing steam to effect reaction and formation of a gas comprising essentially H_2 and CO in the proportion of 2 : 1 to 3 : 1. Describes apparatus.

2547. ———. Effecting Chemical Reactions Such as Heat Treatments of Hydrocarbons, Oil Shale. United States Patent 1,984,380, Dec. 18, 1934; appl. filed Dec. 17, 1929. Chem. Abs., vol. 29, 1935, p. 918.

Gaseous stream initially containing a plurality of gaseous fluids such as CH_4 and steam capable of reacting with each other, as for the production of CO and H_2, is passed upward through a mass of granular catalytic material of considerable depth, such as 1 containing Ni, Co, or Al_2O_3, at such a rate that the layer of catalytic material is maintained in a state of motion presenting the appearance of a boiling liquid, while a suitable reaction temperature is maintained. Describes apparatus which is suitable for various other reactions also.

2548. ———. Process for Promoting Reactions in a Fluidized Bed Comprising a Plurality of Catalysts. United States Patent 2,503,291, Apr. 11, 1950; appl. filed Mar. 14, 1945, Serial No. 582,692; 31 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 5500.

Gives process for fluidizing solids in a reaction chamber. The catalyst may be uniformly sized and of the same composition, or a number of catalysts may be used so selected and graded that they remain largely in separate layers, although each layer is a part of a common fluidized mass. An Fe oxide or an Fe–Al oxide may be used as the lower layer catalyst with or without Si and a catalyst of lower specific gravity such as Al phosphate, $3NaF \cdot AlF_3$ may be used in the upper layer. When the particles are the same size in each layer the lower gravity particles will remain in the upper level and only a relatively thin layer will be mixed with those of the lower layer at an intermediate level. When the particles are all the same density, a double layer can be maintained only when the particles in the lower layer are larger than those in the upper. By adjusting the relative particle size and selecting catalysts of predetermined relative densities, any number of different layers may be maintained. Escape of the top particles may be prevented by making the upper portion of the reactor wider than that adjacent the bottom layer of catalyst. The process may be applied to the Fischer-Tropsch synthesis. 23 United States patent cited.

2549. ——— (Standard Oil Development Co.). Process for Treating Hydrocarbon Synthesis Tail Gas. United States Patent 2,554,264, May 22, 1951; appl. filed Oct. 26, 1948, Serial No. 56,632; 5 claims (*Cl. 260–449.6*).

Tail gas from the hydrocarbon synthesis plant is prepared for recirculation by passing it in countercurrent contact with finely divided hot carbonaceous solids while the solids and gas are flowing through a pebble stove. A 1-way fluid flow with a gradient temperature from a maximum at 1 end to a minimum at

the opposite end is continuously maintained in the pebble stone. This treatment destroys tail-gas constituents deleterious to the synthesis catalyst and reconverts CO_2 to CO. 3 United States patents cited.

2550. Oesterreichisch Amerikanische Magnesit A.-G. [Reaction of Carbon Monoxide and Steam.] French Patent 770,608, Sept. 17, 1934. Chem. Abs., vol. 29, 1935, p. 533.

CO and steam are caused to react under increased pressure, a catalyst composed of MgO and C or MgO, C, and K_2CO_3 is used. The reaction may be carried out in 2 or more steps, the 1st at 400°–500° and the 2d or last at 320°–400°.

2551. Office National Industriel de l'Azote. [Catalytic Reactions.] French Patent 700,034, Nov. 16, 1929. Chem. Abs., vol. 25, 1931, p. 3415.

In exothermic catalytic gas reactions the temperature is kept down by the introduction at points of equal distance in the catalyst of the gaseous mixture not yet combined at a temperature below the optimum temperature of reaction.

2552. ———. [Hydrogen and Carbon Monoxide From Methane.] French Patent 976,553, Mar. 20, 1951. Chem. abs., vol. 47, 1953, p. 2463.

CH_4 and air or O_2 are caused to react together to give steam and CO_2; the mixture of gases then combine in the presence of a catalyst to give CO and H_2. Unheated CH_4 (1,000 $m.^3$ per hr.) and 520 $m.^3$ O_2 are passed into the conical bottom of a reactive vessel of 2-in. diameter containing porcelain pieces surmounted by a layer of a heated oxidation catalyst, such as Pt gauze, on the top of which lies 1 $m.^3$ of a Ni catalyst. The mixture of CO and H_2, 3,000 $m.^3$ per hr., contains 0.5% CH_4.

2553. Ogorzaly, H. J. (Standard Oil Development Co.). Hydrogenation of an Oxide of Carbon. United States Patent 2,458,870, Jan. 11, 1949; appl. filed Maq 29, 1946, Serial No. 673,189; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 3175.

Waxy and oily deposits formed on the catalyst during Fischer-Tropsch synthesis can be removed in a hydrogenation zone by treatment with H_2-containing gas at 600°–900° F. This treatment will remove deposits not removable by conventional washing with solvents. The advantages of the use of a 2d vessel are: Optimum temperature and pressure can be established; additional H_2 and products of hydrogenation are not mixed with the synthesis product; and the $CO:H_2$ ratio in the reaction zone will not be affected by the hydrogenation of the deposits on the catalyst. 3 United States patents are cited.

See also United States Patent 2,414,276 (abs. **3329**).

———. *See* abs. **2169.**

2554. Ohashi, T., and others. (Dai Nippon Fats & Oils Co.). [Nickel Oxide Catalyst for Hydrogenation.] Japanese Patent 871 (1951), Feb. 23, 1952. Chem. Abs., vol. 46, 1952, p. 11,513.

$Ni(OH)_2$ or $NiCO_3 \cdot 2(\text{or } 3)Ni(OH)_2$ is prepared by precipitation of an aqueous Ni salt containing the carrier with aqueous alkali or its carbonate, dried, ground, reduced by H at 450°–500°, cooled to 200°, the H replaced by N, and the N gradually replaced by air.

2555. Ohlendieck-Dolge, J. S. [Partial Combustion of Hydrocarbons.] German Patent 514,394, May 4, 1928. Chem. Abs., vol. 25, 1931, p. 1536.

This relates to the manufacture of mixtures containing CO and H_2 by treating hydrocarbons with air or other oxidizing gas at a raised temperature in the presence or absence of catalysts. The improvement consists in using an alloy of Fe, Cr, and Ni, which has been fused in vacuo, for constructing the parts of the reaction chamber that come into contact with the gases.

Ohsol, E. O. *See* abs. **347.**

Oil & Gas Research, Inc. *See* abs. **3929.**

2556. Olin, J. F., and Deger, T. E. (Sharples Chemicals, Inc.). Aliphatic Amines and Acid Amides. United States Patent 2,422,631, June 17, 1947. Chem. Abs., vol. 41, 1947, p. 5892.

An olefin of formula $RR^1C:CR^2R^3$ (I), CO or CO_2, an aminating agent R^4R^5NH (II), and H react to give aliphatic amines and acid amides. R, R^1, R^2, and R^3 are H or alkyl radicals, and R^4 and R^5 are H or aliphatic, cycloaliphatic, heterocyclic, or aromatic radicals. The reactions proceed as follows: (I)+CO+(II)+2 $H_2 \rightarrow RR^1CHCR^2R^3CH_2NR^4R^5$ (III)+H_2O. (I)+CO_2+(II)+3$H_2 \rightarrow$(III)+2H_2O. (I)+CO+(II)$\rightarrow$ $RR^1CHCR^2R^3CONR^4R^5$ (IV). (I)+CO_2+(II)+$H_2 \rightarrow$ (IV)+H_2O. A mixture of primary, secondary, and tertiary amines is formed. The 3d equation represents an intermediate reaction for the 1st equation. Where the olefin contains between 2–10 C atoms, the reaction is carried out in the vapor phase. The reaction mixture is preheated and then passed through a reactor at 250°–450° but preferably at 325°–375°. A pressure of 500–20,000 p. s. i. is desirable. A mixture of dehydrating and dehydrogenating catalysts or a single catalyst promoting the amide formation and the hydrogenation is desirable. Single catalysts of this type are $ZnCrO_4$, $ZnWO_4$, $MnCrO_4$, $Mn_3(PO_4)_2$, or MnO mixed with phosphates, sulfates, or halides of metals of groups (I) and (II) of the periodic system. Thus a 2-cu. ft. stainless-steel chamber is filled with a mixture of 10% MnO and 90% $ZnCrO_4$ activated by heating at 350° 5 hr. in a H_2–NH_3 atm. A mixture of CO, H_2, NH_3, and C_2H_4 in 30:5:3:1 mol. ratio is pumped into the preheater at a space velocity of 2,000 and then passed into the reactor kept at 350° and 8,700 p. s. i. The crude product is passed through a gas-liquid trap under 1,000 p. s. i. where the excess CO and H_2 are bled off and recirculated. From the crude mixture pure propylamine is obtained. Similarly, there are obtained a mixture of $AmNH_2$ and iso–$BuNH_2$, iso–BuNHMe, b. 67°–70°, d^{20} 0.735, and PrNHMe b. 62°–65°, d^{20} 0.717.

2557. ——— (Sharples Chemicals, Inc.). Aliphatic Amines and Acid Amides. United States Patent 2,422,632, June 17, 1947. Chem. Abs., vol. 41, 1947, p. 5892.

Amides are produced by the reaction of an olefin having 2–10 C atoms with CO and an aminating agent: $RR^1C:CR^2R^3 + Co + R^4R^5NH \rightarrow RR^1CHCR^2R^3CONR^4R^5$, where R, R^1, R^2, and R^3 may be H or alkyl and R^4 and R^5 may be H or aliphatic, cycloaliphatic, heterocyclic, or aromatic radicals. By subsequent reduction with H_2, amines may be formed. The primary amides formed may be dehydrated to nitriles as a byproduct reaction. The reaction may take place in the liquid or vapor phase and may be a batch or continuous operation. The preferred temperature is 325°–375° and pressures of 500–20,000 p. s. i. or higher are preferred. Dehydrating catalysts (for example, H_3PO_4 and its metallic salts and oxides of metals of Group II and III of the periodic system) are desired for the amide formation, and hydrogenation catalysts (for example, Ni, Pt, Pd) are desired for the reduction to the amine. Best results are obtained when the CO is present in a molecular ratio to the olefin of at least 10 : 1 and in a molecular ratio to NH_3 of at least 10 : 2. The preferred space velocity is 1,000–7,000 cu. ft. reactant gas per cu. ft. catalyst per hr. Thus a mixture of CO, NH_3, and C_2H_4 in molecular proportions 2 : 6 : 1 is fed through an activated C catalyst at 360°–370° at a space velocity of 1,500 and a pressure of 1,500 p. s. i. From the crude product, $EtCONH_2$, b_{17} 110°–120°, is obtained.

Similarly, EtCONHMe and $Me_2CHCONH_2$, b. 219°–223°, are obtained with the appropriate olefin.

OLSON, L. E. *See* abs. **3739.**

ORCHIN, M. *See* abs. **3897, 3898.**

2558. OSHEROVA, M. M. [Catalyst of the Iron Group.] Russian Patent 47,287, June 30, 1936. Chem. Abs., vol. 33, 1939, p. 3548.

Catalyst, especially suitable for the synthesis of gasoline, is prepared by reducing metal oxides and hydroxides (formed by precipitation of nitrates with K_2CO_3) in an atmosphere of H_2 and CO, and cooling in a current of CO_2.

———. *See* abs. **503.**

ÖSTERREICHISCH-AMERIKANISCHE MAGNESIT A. G. *See* abs. **934.**

ÖSTERREICHISCHE STICKOFFWERKE A. G. *See* abs. **3889.**

2559. OTTO, C., & Co. G. M. B. H. [Device for the Neutralization of Acid Components Contained in Gases Which Had Been Treated Catalytically for the Production of a Synthetic Fuel.] French Patent 846,605, Sept. 21, 1939. Chem. Zentralb., 1940, II, p. 2419. Chem. Abs., vol. 35, 1941, p. 4579.

Neutralization is effected by means of basic liquids and by subsequent refrigeration of the gases under pressure.

2560. ———. [Gas for Synthesis Fuels.] French Patent 846,588, Sept. 20, 1939. Chem. Abs., vol. 35, 1941, p. 1208.

Gas for the production of fuels according to Fischer-Tropsch method is prepared by transforming hydrocarbons in coke furnaces into H_2 and CO and adding blast-furnace gas in such a quantity that the ratio of H_2 : CO is 2 : 1. The blast-furnace gas and the distillation gas are desulfurized before the mixing.

———. *See* abs. **2694, 3296.**

OVERSEAS FINANCE & COMMERCE, LTD. *See* abs. **3634.**

2561. OWEN, J. J. (Standard Oil Development Co.). Aldehydes. United States Patent 2,509,878, May 30, 1950; appl. filed Jan. 2, 1947, Serial No. 719,725; 3 claims (*Cl. 260–604*). Chem. Abs., vol. 44, 1950, p. 8363.

Presence of the product alcohol or aldehyde inhibits gelation of the Co soap catalyst in the synthesis of aldehydes from an olefin, H_2, and CO. Diisobutylene, 1% Co stearate, 4% nonylalcohol, at 300° F., 3,000 p. s. i., and a 1.2 : 1 vol. ratio of H_2 : CO at a rate of 8,920 cu. ft./per bbl. of feed gave 61% conversion to oxygenated product, mainly nonylaldehyde.

2562. ——— (Standard Oil Development Co.). Pretreatment of Gases for the Synthesis of Hydrocarbons. United States Patent 2,468,510, Apr. 26, 1949; appl. filed Dec. 14, 1945, Serial No. 635,099; 4 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 7214.

Feed stock of impure CO and H_2 is contacted under suitable conditions with a solid desulfurization agent, such as Cu carried on Al or Mo, which does not form a metal carbonyl under these conditions. The purified feed gas is thereafter directly treated under hydrocarbon synthesis conditions in the presence of a fluidized synthesis catalyst while preventing the entry of desulfurizing agent into the synthesis zone. 1 literature ref. and 5 United States patents cited.

2563. ——— (Standard Oil Development Co.). [Synthesis of Aldehydes and Secondary Alcohols.] French Patent 962,947, June 23, 1950; appl. filed Mar. 8, 1948, in United States May 9, 1947. Chem. Zentralb., 1950, II, p. 2369.

Olefins are reacted with CO and H_2 in the presence of a catalyst consisting of Fe on an inert support. Aldehydes are formed in the 1st stage of the process and then these are catalytically hydrogenated to the corresponding secondary alcohols. The synthesis catalyst consists of 20–40% Fe, 0.3–3.0% Cu, 50–75% kieselguhr and 0.05–1.0% K_2CO_3. Diisobutylene is converted at 135° and at 210 atm. pressure with CO and H_2. The product has the following constants: Carbonyl number 257, hydroxyl number 41, saponification number 13, and acid number 0.7. It is hydrogenated with Ni on a support at 177° and 189 atm. pressure. The same constants for the hydrogenation products are 186, 1, 32, and 0.2, respectively.

2564. ——— (Standard Oil Development Co.). [Synthesis of Oxygenated Organic Compounds.] French Patent 960,314, Apr. 17, 1950; appl. filed Oct. 15, 1947. Chem. Zentralb., 1951, I, p. 1070.

Olefins, CO, and H_2 are reacted in the presence of metallic soaps such as Fe-, Co-, or Ni stearate, oleate, linoleate, or naphthenate. Example: Di-isobutylene (b. 101.7°–102.8°) is reacted with 1.2% Co stearate and 4.8% nonylalcohol and the mixture treated in presence of a catalyst consisting of Co and Cu oxide on pumice with synthesis gas at 162° and 210.9 atm. pressure. Mainly nonylaldehyde with other oxygenated compounds is obtained.

———. *See* abs. **2220, 3852.**

2565. OWEN, J. J., AND FASCE, E. V. (Standard Oil Development Co.). Utilization of Oxo Bottoms. United States Patent 2,594,341, Apr. 29, 1952; appl. filed Sept. 13, 1949, Serial No. 115,432; 11 claims (*Cl. 260–418*). Chem. Abs., vol. 47, 1953, p. 3330.

High-boiling mixtures of oxygenated organic compounds, produced as still bottoms in a 2-stage oxo process, are selectively oxidized by means of a O_2-containing gas at temperatures 100°–300° F. and in presence of a metallic soap oxidation catalyst, whereby a mixture of fatty acids and alcohols is obtained.

2566. OWEN, J. J., AND SUMERFORD, S. D. (Standard Oil Development Co.). Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen With an Iron Type Catalyst. United States Patent 2,610,975, Sept. 16, 1952; appl. filed May 12, 1948, Serial No. 26,538; 4 claims (*Cl. 260–449.6*). Chem. Abs., vol. 47, 1953, p. 848.

It is found that the molecular weight of the product obtained by the reaction of CO with H_2 over an Fe catalyst can be controlled by adding unreduced catalyst to the hydrocarbon synthesis reactor. The gas mixture is passed at about 625°–725° F. and 400–600 p. s. i. in contact with a catalyst consisting of a major amount of metallic Fe and Fe oxides promoted with a minor amount of a K compound. The synthesis reaction is started with a fluidized mass of substantially reduced catalyst, and fresh unreduced Fe oxide catalyst is added continually in amounts sufficient to maintain the O_2 content of the total catalyst > the equilibrium range. About 2–10% per day is needed, depending on the desired molecular weight of the product.

2567. OWEN, J. R. (Phillips Petroleum Co.). Catalyst. United States Patent 2,606,159, Aug. 5, 1952. Chem. Abs., vol. 47, 1953, pp. 799–800.

A catalyst of superior activity is obtained when the minor component or promoter is concentrated at or near the surface of the catalyst pellet, with the inner part of the pellet substantially free of the minor component. Active Al_2O_3, obtained by precipitating hydrous Al_2O_3 gel and drying, or by other methods, is finely ground, mixed with a volatile or combustible binder, and pelletted. The pellets are then calcined in such a manner that a predetermined amount of the binder, preferably 50–75% is removed. This may be accomplished by heating the pellets in air at 204°–593°

for 3–15 min. The cooled pellets are impregnated with a solution of a metal salt that is converted to the desired minor component by ignition. When Cr_2O_3 is desired, aqueous solutions of CrO_3 and $Cr(NO_3)_2$ are suitable. The impregnated pellets are finally ignited at 204°–593°, ordinarily in an oxidizing atmosphere, to convert the dissolved salt to the oxide and to remove substantially all the remaining binder. Instead of combustion, solvent extraction may be used to remove the binder from the outer parts of the pellets, and finally the residual solvent is evaporated. The process is particularly applicable to the preparation of hydrogenating-dehydrogenating catalysts, which consist of metals, metal oxides, and mixtures of metals and oxides. In an example, 2 catalysts consisting of Ni_2O_3 were deposited on Al_2O_3, 1 completely impregnated and the other shell-impregnated, but both containing 9.0% Ni_2O_3. After impregnation, the catalysts were calcined in air for several hours at 538°. They were then reduced at 343° and tested before exposure to air in the hydrogenation of C_2H_4 with a 1:1 ratio of C_2H_4: H_2 and a space velocity of 10,000 vol. (standard conditions) total gas per catalyst vol. per hr. The extent of hydrogenation was measured by comparing the thermal condition of the charge and effluent gas in a thermal-condition cell, previously calibrated with known mixtures of H_2 and C_2H_4 during each test. After reducing for 4 hr., the completely impregnated catalyst showed −1.0% average hydrogenation in 60 min. at 0°. The shell-impregnated catalyst, after reducing for 4 hr., had an average hydrogenation of 74.1% in 60 min. at 0°.

2568. Oxley, H. F. (Celanese Corp. of America). Aliphatic Acids and Esters from Carbon Monoxide and Primary Aliphatic Alcohols. United States Patent 1,927,414, Sept. 19, 1933; appl. filed Aug. 5, 1930, Serial No. 473,287 in Great Britain Aug. 22, 1929; 21 claims (*Cl. 260–116*). Chem. Abs., vol. 27, 1933, p. 5755.

Products such as MeOAc and HOAc are formed by causing CO to react upon a primary aliphatic alcohol such as MeOH in the presence of an inorganic acidic catalyst such as pyrophosphoric acid, which contains at least 1 acidic hydroxyl group directly linked to a nonmetallic element in the presence of a promoter such as Fe or Mn formate.

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Page, B. S. *See* abs. **2641, 2642.**

Page, R. *See* abs. **891, 892, 893.**

2569. Page, R., and Thomas, E. B. (Celanese Corp. of America). Catalyst for Methane Production From Carbon Monoxide and Hydrogen. United States Patent 2,151,329, Mar. 21, 1939; appl. filed Oct. 20, 1936 (*Cl. 23–237*). Chem. Abs., vol. 33, 1939, p. 5002.

Catalyst is prepared by precipitating Ni and Al hydroxides from a solution of their nitrates containing 4 times as much Ni nitrate as Al nitrate, the washed precipitate is formed into a shaped mass and dried, all these operations being conducted at a temperature < 30°, and the Ni hydroxide is subsequently reduced at a temperature of about 250°. Example: A mixture of CO and coal gas is treated for removal of S. The resulting gas consisting mainly of CO, H_2, and CH_4 in proportion of 1:2:1, still containing about 45 mg. S per l. is passed over the catalyst at about 350°. The resulting gas contains over 50% CH_4.

2570. Page, R., Thomas, E. B., and British Celanese, Ltd. Catalyst for the Production of Methane From Carbon Monoxide and Hydrogen. British Patent 465,157, Apr. 29, 1937. Chem. Abs., vol. 31, 1937, p. 7883.

Catalyst is made by co-precipitating in the cold Ni oxide and Al_2O_3, shaping the precipitate, and reducing the Ni oxide. The Al_2O_3 may be partly or wholly replaced by another dehydrating or dehydrogenating oxide, for example, ThO_2, blue oxide of W, TiO_2, MgO. The catalyst may be prepared as described in British Patent 354,351. The CH_4 reaction is preferably effected at 330°–400° and at atm. or slightly increased pressure.

2571. Pallemaerts, F. A. F. [Underground Gasification of Solid Fuels.] Belgian Patent 469,188, May 1947. Chem. Abs., vol. 43, 1949, p. 1170.

Gasification is effected by means of a combustive fluid rich in O_2 (air containing over 30% O_2, commercial O_2, or pure O_2), which fluid may contain O_2, H_2O vapor, and/or CO_2. The proportions of O_2, H_2O, and/or CO_2 are such that the total gasification reaction is thermally virtually neutral.

2572. ———. [Underground Gasification of Solid Fuels.] Belgian Patent 470,772, February 1947. Chem. Abs., vol. 43, 1949, p. 1170.

Steam required for catalytic conversion of the CO is generated under high pressure in a boiler embedded in the catalyst mass of the converter. The mean temperature of the catalyst is regulated by the pressure at which the steam is generated.

2573. ———. [Underground Gasification of Solid Fuels.] Belgian Patent 471,877, April 1947. Chem. Abs., vol. 43, 1949, p. 1170.

Completion of the reaction is effected using a liquid fuel, such as fuel oil, gas oil, or other mineral, synthetic, vegetable, or animal oils, to produce CO or $CO+H_2$ with a view to subsequent conversion into industrial H_2 or to the production of a hydrocarbon gas.

2574. Palm, J. W., and King, J. A. (Cities Service Oil Co.). Solvent Extraction of Organic Acids. United States Patent 2,563,739, Aug. 7, 1951; appl. filed Sept. 4, 1948, Serial No. 47,952; 6 claims (*Cl. 260–450*).

Patent relates to the recovery of organic acids from dilute aqueous solutions such as those obtained in the oxygenated compounds fraction of Fischer-Tropsch products. Recovery of such acids by solvent extraction is specifically described. An aqueous solution of lower aliphatic acids derived from the Fischer-Tropsch synthesis and containing less than about 5% acids is introduced into the top of an extraction tower and passes countercurrent to an upward stream of isopropyl ether and methyl-ethyl ketone to the bottom of the tower. The solvents are present in the ratio of 75 parts ketone to 25 of isopropyl ether, a solvent to feed ration of 2:1 is maintained. It was found that 94.9% of the acid present in the Fischer-Tropsch water was removed with a loss of only 3.4% of the ketone in the raffinate.

Palmer, G. H. *See* abs. **14.**

2575. Palmer, J. S. (Standard Oil Development Co.). Means for Distributing Solids in Gases in Catalytic Apparatus. United States Patent 2,586,705, Feb. 19, 1952; appl. filed Feb. 14, 1948, Serial No. 8,336; 3 claims (*Cl. 23–288*).

Method and apparatus for dispersing finely divided catalyst particles to form a suspension and for maintaining this suspension in a gaseous fluid.

2576. Pape, W. (Henkel & Cie G. m. b. H.). [Soap for Drawing Wires.] German Patent 745,919, Dec. 23, 1943 (*Cl. 23 c–1.04*). Chem. Abs., vol. 40, 1946, p. 754.

Soap of an aliphatic carboxylic acid with 6–10 C atoms is used as aid in wire drawing and similar operations.

2577. PARDUN, H. (Noblee & Thörl G. m. b. H.). [Method and Apparatus for the Continuous Preparation of Fatty Acids by Oxidation of Hydrocarbons.] German Patent 714,489; appl. N 41,215, filed Oct. 5, 1937 (*Cl. 12 o–11*). Bib. Sci. Ind. Repts., vol. 2, No. 12, p. 913; Chem. Abs., vol. 38, 1944, p. 1753.

Quality and quantity of yield of fatty acids produced through oxidation of aliphatic or cycloaliphatic hydrocarbons is improved by adoption of a continuous process.

2578. ——— (Noblee & Thörl G. m. b. H.). [Process for Separating Unsaponifiable Components From Their Mixtures With Saponifiable Components.] German Patent Appl. N 43,538, Aug. 23, 1939 (*Cl. IV a–23 e*). FIAT Reel K–20, frames 452–457; PB 70,211.

This method provides for the H_2O-containing saponification product being injected into the already melted soap at temperatures of 275°–325°. By this means, the H_2O and part of the unsaponifiable substance is eliminated. The remaining unsaponifiable substance is then distilled off in a high vacuum under pressures <2 mm. Hg. Two stills have to be passed, the 2d preferably acting as film evaporator.

2579. ——— (Noblee & Thörl G. m. b. H.). Separating Mixtures of Compounds of Unsaponifiable and Saponifiable Matter Such as Oxidation Products of Hydrocarbons. United States Patent 2,283,456, May 19, 1942. Chem. Abs., vol. 36, 1942, p. 6169.

Mixture such as one formed by oxidizing hydrogenation products of CO is saponified with an aqueous solution of a basic agent such as NaOH, and the resulting aqueous saponification product is injected into melted anhydrous soap, so that H_2O and a portion of unsaponifiable matter are removed by volatilization and the molten soap becomes again anhydrous, and the remainder of the unsaponifiable matter is distilled from the soap in a high vacuum.

2580. PARK, J. R. (Imperial Chemical Industries, Ltd.). Removing Iron Compounds From Crude Synthetic Alcohols. United States Patent 1,833,331, Nov. 24, 1931. Chem. Abs., vol. 26, 1932, p. 993.

Distillation fractions obtained by catalytic hydrogenation of oxides of C are subjected to prolonged treatment with an alkali (as by use of NaOH) and then distilled.

2581. PARK, J. R., AND IMPERIAL CHEMICAL INDUSTRIES, LTD. Synthetic Methanol and Formaldehyde. British Patent 344,796, Dec. 10, 1929. Chem. Abs., vol. 26, 1932, p. 156.

Fe compounds present in synthetic alcohols such as crude synthetic MeOH are removed by subjecting the crude material to prolonged treatment with alkali (suitably by flowing over NaOH into a steel tank, aerating, allowing to stand for several days and then distilling). CH_2O is made by passing MeOH vapor mixed with air over Ag gauze heated to redness (preliminary purification of the MeOH giving longer life to the catalyst).

See also United States Patent 1,833,331 (abs. **2580**).

2582. PARKER, P. T. (Standard Oil Development Co.). [Oxygenated Organic Compounds.] French Patent 963,334, July 5, 1950; appl. filed Mar. 16, 1948. Chem. Zentralb., 1951, I, p. 3418.

CO, H_2, and olefins are reacted to form aldehydes and ketones, which are themselves hydrogenated to alcohols. Catalysts consist of the Co-, Fe-, and Ni-salts of high molecular fatty acids obtained as the byproducts in the catalytic synthesis of hydrocarbons from CO and H_2. The initial olefins may be ethylene, propylene, hexene, butadiene, pentadiene, diisobutylene, triisobutylene, and polypropylene.

2583. ——— (Standard Oil Development Co.). Synthesis of Alcohol From Olefins, Carbon Monoxide, and Hydrogen. United States Patent 2,595,096, Apr. 29, 1952; appl. filed May 20, 1948, Serial No. 28,256; 5 claims (*Cl. 260–638*).

Oxo process, as usually performed, is carried out in contact with a Co catalyst and at pressures <4,500 p. s. i. g. to produce oxygenated reaction products comprising organic carbonyl compounds, which are reduced to alcohols and aldehydes by hydrogenation and then distilled. The process is improved by hydrolyzing the residues from the alcohol distillation process in a neutral medium at temperatures >300° F. and then hydrogenating a portion of the products thus obtained to increase the overall yield of alcohols.

2584. ——— (Standard Oil Development Co.). Synthesis of Oxygenated Organic Compounds. United States Patent 2,530,989, Nov. 21, 1950; appl. filed June 5, 1947, Serial No. 752,800; 9 claims (*Cl. 260–632*). Chem. Abs., vol. 45, 1951, p. 1752.

In producing oxygenated organic compounds from olefins, CO, and H_2, the total product from the oxygenation stage of a 2-stage process is distilled to separate unreacted olefins from oxygenated products. The olefins are recycled to the oxygenation stage. Aldehyde condensation is suppressed by carrying out the distillation at reduced pressure 5–500 mm. Hg, depending on the boiling range of the olefins originally charged.

See abs. **2221.**

2585. PARKER, P. T., AND HILLARD, G. O. (Standard Oil Development Co.). Oxo Synthesis Process. United States Patent 2,571,160, Oct. 16, 1951; appl. filed Oct. 25, 1946, Serial No. 705,706; 4 claims (*Cl. 260–638*).

In carrying out the oxo process utilizing a Co catalyst, considerable losses of catalyst substance occur in the formation of Co carbonyl and its subsequent removal from the reaction zone. This disadvantage is now overcome by utilizing 2 fixed-bed reaction zones in series, each reactor being packed with a supported Co-type catalyst. In operation, olefins are fed to the initial reactor through which synthesis gas is preferably recycled. The liquid oxo product thus obtained is passed to a 2d reactor through which H_2 is recycled. Co carried from the initial reactor as Co carbonyl is deposited on the catalyst support in the 2d reactor. After the Co in the 1st reaction zone is depleted, the flow of the streams is reversed thus making it possible to operate continuously with a fixed-bed catalyst with substantially little loss of Co from the system. Small Co losses may be compenated for by introducing Co carbonyl or a Co salt of a fatty acid into the olefin feed. Also describes procedure whereby a single reactor may be employed for both the oxo and hydrogenation steps.

2586. ——— (Standard Oil Development Co.). [Oxygenated Compounds From Synthesis Gas and Olefins.] French Patent 954,563, Dec. 28, 1949; appl. filed Oct. 22, 1947, in United States Oct. 25, 1946. Chem. Zentralb., 1950, II, p. 340.

Oxygenated compounds, particularly alcohols, with 2–18 C atoms are produced from $CO+H_2$ and olefins in presence of a Fe, Co, or Ni catalyst. The operation is performed in 2 reaction zones whereby the reaction product from the 1st zone, which contains the metal catalysts in the form of carbonyl compounds, is carried over into the 2d zone, where it is treated with H_2, thus regenerating the metal catalyst. The olefin mixture is heated with a synthesis gas, which contains about 44% CO and 55% H_2, in the 1st reaction zone in the presence of a Co catalyst to 121°–204° at a pressure of 100–300

atm. The conversion mixture is separated into a gaseous and a liquid product by cooling, the liquid product being passed into the 2d reaction zone where it meets a stream of H_2. Both components, the liquid mixture and the H_2, are passed from bottom to top of the Co catalyst located herein. The temperature here is 121°–204°, the pressure 100–200 atm., and the time of contact 15–60 min. or more. In the 2d chamber, the aldehydes, produced in the 1st chamber as an intermediate product, are converted into alcohols by contact with the H_2.

2587. PARKHURST, G. L. (Standard Oil Co. of Indiana). Processing Fluids From Distillate Wells or the Like. United States Patent 2,324,172, July 13, 1943; appl. filed Oct. 31, 1940, Serial No. 363,737; 3 claims (*Cl. 44–50*). Chem. Abs., vol. 38, 1944, p. 474.

Describes arrangement of apparatus, and a method is employed for maximum recovery from a high-pressure petroleum reservoir and preparing liquid hydrocarbons from high-pressure well fluids recovered therefrom, which involves simultaneously generating O_2 and a byproduct of the O_2 generation at about the pressure of high-pressure reservoir, injecting this high-pressure byproduct gas into a high-pressure petroleum reservoir to effect maximum recovery of high-pressure well fluids, separating these well fluids at a high pressure into at least 1 fraction rich in normally gaseous hydrocarbons and at least 1 fraction rich in distillate motor-fuel hydrocarbons, generating a synthesis gas comprising CO and H_2 by treating the normally gaseous hydrocarbons at an elevated temperature in the presence of the generated O_2, subjecting the synthesis gas to an exothermic hydrocarbon synthesis step, and fractionating the resulting product into at least 1 gas fraction and at least 1 liquid fraction, the liquid fraction being rich in motor-fuel hydrocarbons.

2588. PARRY, V. F. Distilling Carbonaceous Material. British Patent 630,142, Oct. 6, 1949. Chem. Abs., vol. 44, 1950, p. 3702.

Coal descends by gravity through a vertically arranged, elongated retort through annular passageways where it is distilled by stage-heating by indirect heat exchange between the material and gases ascending through passageways in the center of annular spaces and around them. In the uppermost stage the material is preheated, in the center it is carbonized, and in the lower it gives up heat to ascending gases. Using the process it is possible to gasify 1 ton of natural subbituminous coal, containing about 22% H_2O and having a heating value of only 9,300 B. t. u. per lb., to produce 45,000 cu. ft. of net synthesis gas. When distilling carbonaceous materials for recovery of primary tar oils and gases, the solid material, such as coal, is heated to about 600°, but when distilling oil shale for recovery of maximum oil, it is unnecessary to heat the shale higher than 370°–510°.

2589. ———. Method for Conducting an Endothermic Chemical Reaction Involving both Gaseous and Solid Feed Materials. United States Patent 2,572,051, Oct. 23, 1951; appl. filed Apr. 20, 1945, Serial No. 589,450; 2 claims (*Cl. 48–203*).

Describes process and equipment for the production of synthesis gas and fuel gas from subbituminous coal or other noncaking carbonaceous materials in a vertically ranging externally heated annular retort. A comminuted noncaking, subbituminous coal containing about 22% moisture is charged into the top of the apparatus and directed downward by gravity through annular preheating and reaction zones. Steam (0.2–2 lb. per lb. of coal) is mixed with the coal, and reaction begins at progressively increasing temperature 700°–2,000° F. Products of reaction are removed from the interior of the annular reaction zone while giving up a substantial portion of their sensible heat to incoming reactants. Solid materials not combined with reactants in the upper zone are then directed downward where they contact cooling gases which transfer heat from the solids back toward the center of the system, and the spent solids are discarded at low temperature. In the continuous process described, 1 ton of natural subbituminous coal containing 22% H_2O and having a heating value of only 9,300 B. t. u. per lb., is gasified continuously to produce 45,000 cu. ft. of net synthesis gas in a single-stage, automatic process. The process is also applicable to the distillation of oil shales.

2590. ———. Process for Carrying Out Endothermic Chemical Reactions. United States Patent 2,539,466, Jan. 30, 1951; appl. filed Apr. 20, 1945, Serial No. 589, 450, divided and this appl. filed Oct. 7, 1946, Serial No. 701,632; 1 claim (*Cl. 23–1*).

Describes method and apparatus for producing synthesis gas by complete gasification of lignite or other noncaking carbonaceous material. For example, 1 ton of natural subbituminous coal containing about 22% H_2O and having a heating value of only 9,300 B. t. u. per lb. is gasified continuously to produce 45,000 cu. ft. of net synthesis gas in a single stage process that operates automatically. High conversion ranging 60–75% is accomplished. Coal mixed with steam is passed downward through an externally heated, vertically arranged, elongated, annular reaction zone, from which the gaseous products are withdrawn near the zone of maximum reaction temperature and discharged upward in indirect heat exchange to the descending reactants, the spent solids being discharged from a lower annular reaction zone countercurrent to ascending gases, this reaction zone being maintained in indirect heat exchange relation with incoming gaseous reactants. The process is also applicable to the distillation of oil shale.

PASSINO, H. J. *See* abs. **2013, 2015, 2199, 2200, 2201.**

2591. PATART, G. Alcohols. Canadian Patent 273,983, Sept. 20, 1927. Chem. Abs., vol. 21, 1927, p. 3908.

Method for the synthetic production of higher molecular organic compounds containing O consists in reducing CO by H_2 in the presence of a catalyzer and under high pressure. The products thus obtained are condensed, and the MeOH and other compounds having a lighter molecular weight than the higher compounds to be produced are separated from the condensates. The MeOH and other compounds are again subjected to a catalytic reduction under high pressure.

See also British Patent 250,563 (abs. **2593**).

2592. ———. Alcohols. Canadian Patent 273,984, Sept. 20, 1927. Chem. Abs., vol. 21, 1927, p. 3908.

Method of synthesizing higher alcohols consists in subjecting a mixture of C oxides and H_2 at a high pressure and temperature to the action of a catalyzer formed of a very intimate mixture of 30% ZnO and 70% neutral K_2CrO_4 by weight.

See also British Patent 250,563 (abs. **2593**).

2593. ———. Alcohols and Other Products From Oxides of Carbon and Hydrogen. British Patent 250,563, Apr. 9, 1925. Chem. Abs., vol. 21, 1927, p. 1128.

Conditions are employed that produce mainly higher alcohols and their ethers and ketones. A cyclic process is employed in which CO_2 is eliminated, and the products are separated in a condenser system. The catalyst used may be formed of Ag, Cu, Zn, Mn, Mo, U, and V and a combination of an alkali or alkaline earth oxide and a metallic oxide of acid character, for example, chromates, manganates, molybdates, tungstates, uranates, and vanadates of Na, K, Rb, and Ba. Gives numerous details of operations and describes an apparatus.

2594. ———. [Apparatus for Carrying Out Catalytic Gas Synthesis Under Pressure.] French Patent 598,966, May 25, 1925. Chem. Zentralb., 1926, I, p. 2029.

See British Patent 252,362 (abs. **2595**).

2595. ———. Apparatus for Catalytic Production of Methanol. British Patent 252,362, May 25, 1925. Chem. Abs., vol. 21, 1927, p. 2274.

One or more tubes containing the catalyst are arranged horizontally, and the flow of gases within each tube is in a single direction. Gives various details.

2596. ———. Apparatus for Subjecting Gases to Catalytic Synthesis Under Pressure. British Patent 227,853, Jan. 17, 1924. Chem. Abs., vol. 19, 1925, p. 2579.

2597. ———. [Catalysts for Methanol Synthesis.] Swiss Patent 120,509, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, pp. 208, 215.

Basic chromates, wolframates, molydbates, manganates, and zinc salts are contained in horizontal catalyst tubes. Heat exchange takes place through the catalyst tube.

See British Patent 252,362 (abs. **2595**).

2598. ———. Catalytic Production of Alcohols. British Patent 247,177, Feb. 7, 1925. British Chem. Abs., B, 1927, p. 347; Chem. Abs., vol. 21, 1927, p. 592.

To produce higher oxygenated organic compounds, especially alcohols of higher molecular weight than MeOH, CO and H_2 are caused to react under pressure in the presence of a catalyst and the products of low molecular weight are separated and resubjected to the catalytic treatment or to an auxiliary catalytic treatment of different character. Pressures of 100–500 atm. may be used and mixtures of ZnO with K_2O, Cu oxide, or Cu may be used as catalysts.

2599. ———. [Catalytic Production of Organic Compounds.] Swiss Patent 119,470, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 227.

See United States Patent 1,770,165 (abs. **2600**).

2600. ——— (Du Pont Ammonia Corp.). Catalytic Production of Organic Compounds, Such as Higher Alcohols. United States Patent 1,770,165, July 8, 1930; appl. filed Jan. 29, 1926. Chem. Abs., vol. 24, 1930, p. 4519.

In the production of higher molecular organic compounds containing O such as the higher alcohols, a gas containing CO and H_2 is catalyzed together with an alcohol such as MeOH with use of heat and pressure, suitably by a catalyst such as K_2O with ZnO or Cu oxide or Cu.

2601. ———. [Extracting Oils.] British Patent 249,519, Mar. 21, 1925. Chem. Abs., vol. 21, 1927, p. 973.

In the hydrogenation or extraction of byproducts from organic substances at high temperatures and pressures, the gases or liquids, or both, used are those that are already heated and compressed during industrial operations such as exothermic synthesizing reactions; for example, production of MeOH from H_2 and CO in a catalytic process. Gases from this reaction may be passed upward through a digester packed with pine wood while liquid from the same catalytic process is passed downward through the material. Petroleum oils and coal or similar materials may be similarly treated.

2602. ———. [Heating of Catalysts for Pressure-Synthesis of Gas Mixtures.] French Patent 618,439, July 2, 1926. British Chem. Abs., 1928, p. 886.

To secure uniform temperature the catalyst is mixed with a conducting material and heated electrically; for example, for NH_3 synthesis silica, asbestos, magnesia, or alumina is added to the Fe catalyst; for alcohols and acids from CO and H_2, Cu, Ag, Al, coal, coke, or graphite is added to the $ZnO–Cr_2O_3$ catalyst.

2603. ———. [Hydrocarbon Synthesis.] French Patent 550,720, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 177.

$CO+H_2+C_2H_2$ is converted in 2 steps. Catalysts are: Coke, wood charcoal, Al_2O_3, ThO_2, SiO_2, $Al_2(SO_4)_3$, bleaching earth, alumina, with or without promoters Ni, Pt, Pd.

2604. ———. Methane Utilization. Canadian Patent 264,600, Sept. 28, 1926. Chem. Abs., vol. 21, 1927, p. 916.

Incomplete combustion of CH_4 is effected so as to obtain a gaseous mixture containing 2 H_2 mol. for 1 CO mol., and the combination of the H_2 and CO is effected to produce hydro-oxygenated compounds of C.

2605. ———. Methanol. British Patent 247,932, Feb. 23, 1925. Chem. Abs., vol. 21, 1927, p. 592.

Mixture of water gas of usual composition and gas from the distillation of coal or like fuel is passed over a catalyst to form MeOH and liquid hydrocarbons. Pressures of 150–250 atm., a temperature of about 300° and a catalyst comprising oxides of Zn and Cr may be used. Refers to the use of pressures of 800–1,000 atm. and gives various details.

2606. ———. [Methanol.] French Patent 605,530, 1925.

Distillation products from coal are mixed with CO and treated under pressure with catalysts for the production of MeOH.

2607. ———. Methanol and Hydrocarbons. British Patent 247,178, Feb. 7, 1925. Chem. Abs., vol. 21, 1927, p. 592.

In the catalytic production of MeOH from CO and H_2 at high temperature and pressure, unsaturated hydrocarbons such as C_2H_4, C_2H_2, C_6H_6, or toluene are used with the reaction gases and liquid hydrocarbons are formed along with MeOH. The condensed product separates into 2 layers: an upper fluorescent layer containing hydrocarbons and a lower MeOH layer. The hydrocarbon product is suitable for use as a fuel for internal-combustion engines.

2608. ———[Methanol and Liquid Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 593,648, Feb. 7, 1925. British Chem. Abs., B, 1927, p. 347.

Gas mixtures containing H_2 and CO and C_2H_4 or its higher gaseous homologs are submitted to the action of the catalysts used in the synthesis of MeOH. Thus a mixture of 23% C_2H_4, 22% CO, 49% H_2, 1.2% CO_2, 0.5% O_2, and 4% N_2 was passed over a basic Zn chromate catalyst at 300° and 150–250 atm. pressure; the cooled reaction product formed 2 layers of which the upper consisted of hydrocarbons $d.^{15}$ 0.735 and possessed the fluorescence characteristic of some petroleum hydrocarbons. The lower layer was almost pure MeOH, $d.^{15}$ 0.805, b. p. 66°–68°.

2609. ———. [Methanol and Liquid Hydrocarbons From Water Gas.] French Patent 594,121, Feb. 23, 1925. British Chem. Abs., B, 1927, p. 346.

Mixture of equal volumes of illuminating gas and water gas is passed over a catalyst cosisting of ZnO and Cr_2O_3 at 300° and 150–250 atm. pressure. On cooling, under the same pressure, a liquid product is formed, which separates into 2 layers, the upper containing hydrocarbons and the lower MeOH. The gaseous product is returned to the initial reaction mixture. In the last hour of the reaction the amount of MeOH produced is scarcely diminished, the pressure having fallen meanwhile to only 34 atm. It is better, there-

fore, to work at very high pressures (800–1,000 atm.). CH_4 is separated by refrigeration under pressure and submitted to the process of French Patent 593,650 (abs. **2617**). The residual gas mixture consists of H_2, N_2, and CO. It is, therefore, possible to carry out the process without water gas, using coal gas or coke-oven gas only. The liquid product may be used directly for heating or carburization purposes or the hydrocarbons may be separated after the addition of H_2O and pure MeOH obtained from aqueous solution for distillation.

2610. ———. Methanol; Hydrogen; Carbon Monoxide. British Patent 247,176, Feb. 7, 1925. Chem. Abs., vol. 21, 1927, p. 592.

Mixtures of CO and H_2 for the catalytic production of MeOH and other oxygenated organic compounds are obtained by the incomplete combustion of CH_4, which may be mixed with about ½ its volume of O_2 and the mixture injected into a mass of coke maintained at about 1,000°.

2611. ———. Methanol Synthesis. British Patent 252,361, May 25, 1925. Chem. Abs., vol. 21, 1927, p. 2,274.

Catalysts for synthesis of MeOH and other oxygenated organic compounds comprise basic combinations of ZnO with metallic oxides of an acid character, the compounds containing at least 2 mol. proportions of ZnO to 1 of the acidic oxide. Basic chromates, vanadates, tungstates, and manganates of Zn may be used. With chromates, 3 mol proportions of ZnO to 1 of Cr oxide are preferably used. "Zn yellow" containing sulfate may be used as catalyst; and the catalyst used is preferably agglomerated with a binder such as gum tragacanth. When S compounds accumulate in the catalyst they are eliminated by heating to redness in an open crucible or by slow circulation through an oxidizing flame; this treatment regenerates the catalyst.

2612. ———. [Methonol Synthesis.] Swiss Patent 119,979, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 213.

Cracked gases or water gas are used as synthesis gas.

See British Patent 247,932 (abs. **2605**) and French Patent 594,121 (abs. **2609**).

2613. ———. [Methanol Synthesis.] Swiss Patent 119,980, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 213.

Synthesis gas produced by incomplete oxidation of CH_4.

See British Patent 247,176 (abs. **2610**) and French Patent 593,650 (abs. **2617**).

2614. ———. [Methanol Synthesis Catalysts.] Swiss Patent 121,809, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 208.

See French Patent 618,439 (abs. **2602**).

2615. ———. [Production and Regeneration of Catalysts.] French Patent 599,588, May 25, 1925. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 208; Chem. Zentralb., 1926, I, p. 2030.

See British Patent 252,361 (abs. **2611**).

2616. ———. [Production of Alcohols, Aldehydes, and Acids.] French Patent 540,543, July 12, 1922; appl. filed Aug. 19, 1921. Ind. Eng. Chem., vol. 17, 1925, p. 431; Chem. Zentralb., 1923, II, p. 631.

Mixtures of gaseous hydrocarbons are reacted with CO, H_2, or O_2 in presence of catalysts under high pressure. The heat evolved can be used to preheat the gases. The process serves for the production of MeOH from CH_4 and O_2 or CO and H_2.

2617. ———. [Production of Alcohols From Methane.] French Patent 593,650, Feb. 7, 1925. British Chem. Abs., 1927, B, p. 346.

CH_4 mixed with ½ its vol. of O_2 is passed over coke or other combustible fuel at 800°–1,000°. The gas mixture is preheated to avoid any condensation or any fluctuation in temperature. The gaseous product, consisting of about 2 vol. H_2: 1 vol. CO, is then converted into alcohols by the action of suitable catalysts at high temperatures and under pressure. CH_4 formed as byproduct is separated and utilized.

2618. ———. Simultaneous Synthesis of Methanol and Hydrocarbons. United States Patent 1,836,085, Dec. 15, 1931; appl. filed Jan. 29, 1926, Serial No. 84,770. Chem. Abs., vol. 26, 1932, p. 999.

Gas mixture containing H_2, C oxides, and unsaturated hydrocarbons is subjected to the action of a MeOH-forming catalyst, such as oxides of Zn and Cr, under a temperature and pressure suitable for the catalytic production of MeOH.

2619. ———. [Synthesis Catalysts.] French Patent 25,371, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, pp. 208, 213.

Ni, Ag, Cu, Fe, and other hydrogenation and oxidation catalysts.

See French Patent 540,543 (abs. **2616**).

2620. ———. [Synthesis of Higher Alcohols.] French Patent 593,649, Feb. 7, 1925. British Chem. Abs., 1927, B, p. 347.

The hydrocarbons produced in the process of French Patent 594,121 (abs. **2609**) is passed over the same catalyst, the gases and reaction chambers being heated to avoid condensation or temperature fluctuations. Higher alcohols are thereby produced in greater quantity than MeOH.

2621. ———. [Synthesis of Higher Alcohols.] Swiss Patent 119,717, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 227.

MeOH catalysts impregnated with alkali or alkaline earths; gas recycle with separation of CO_2 and alcohols.

See also British Patent 250,563 (abs. **2593**) and United States Patent 1,859,244 (abs. **2623**).

2622. ———. [Synthesis of Higher Aliphatic Alcohols and Their Separation.] French Patent 598,447, Apr. 9, 1925. British Chem. Abs., B, 1927, p. 347.

Catalysts for reduction of CO or CO_2 by H_2 under pressure at higher temperatures consist of an intimate mixture of alkali or alkaline-earth oxides with other metallic oxides. For example, ZnO is mixed with K chromate or MnO_2 with neutral B or tungstate, the mixture pasted with 10% of a 10–20% dextrin solution, granulated, and dried at <320°. Suitable gas mixture contains 50 vol. H_2: 40 vol. CO. During the reduction, performed at 330°–400°, the CO_2 and CH_4 formed are removed by refrigeration under high pressure. The liquid product separates into 2 layers which can be further separated. The main fraction (about 60%) consists of PrOH, BuOH, and AmOH, higher alcohols are also formed.

2623. ———. Synthesis of Methanol and Higher Alcohols. United States Patent 1,859,244, May 17, 1932; appl. filed Mar. 26, 1926, Serial No. 97,548. Chem. Abs., vol. 26, 1932, p. 3808.

Mixture of C oxides, and H_2 is subjected, at a high pressure and a temperature of 300° or higher, to the action of a mixed catalyzer formed of a very intimate mixture of alkali metal salts of metal oxides of an acid nature such as ZnO and K chromate, and the gases produced are cooled under pressure to condense CO_2 and MeOH and the remaining gases are re-treated. Describes apparatus.

2624. PATTERSON, W. S. (Combustion Engineering-Superheater, Inc.). Gas and Steam Generator for

Systems for Obtaining Fuel Gases and Other Products From Natural Gas and the Like. United States Patent 2,603,559, July 15, 1952; appl. filed June 23, 1948, Serial No. 34,678; 10 claims (*Cl. 48–196*).

Apparatus for containing a high-pressure exothermic synthesis-gas generating reaction and for extracting waste heat therefrom.

2625. PATTERSON, W. S., AND ARMACOST, W. H. (Combustion Engineering-Superheater, Inc.). Synthesis-Gas Generator and Waste-Heat Boiler. United States Patent 2,631,932, Mar. 17, 1953; appl. filed Aug. 8, 1947, Serial No. 767,550; 11 claims (*Cl. 48–196*).

Describes apparatus such as given in United States Patent 2,603,559 (abs. **2624**) in which the gas generator is associated with a waste heat boiler. This invention has to do particularly with the gas-collecting dome and the bundle and parts directly associated with it. These may be fabricated in the shop as a unit or assembled on the ground. 13 United States patents cited.

PAVLIC, A. A. *See* abs. **149, 150.**

2626. PECK, E. B. (Standard Oil Development Co.). Controlling Exothermic Reactions Such as Synthetic Production of Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,161,974, June 13, 1939; appl. filed January 21, 1937. Chem. Abs., vol. 33, 1939, p. 7528.

Method of controlling the temperature of gases undergoing exothermic catalytic reactions within the desired temperature limits comprises passing the reacting gases through a reaction zone in contact with a solid catalyst capable of effecting the desired reaction maintained in suspension within a fluid medium of sufficient quantity to absorb excess heat resulting from the exothermic reactions and then withdrawing the fluid medium from the reaction zone, removing the excess heat of the reaction from the fluid medium so withdrawn, and returning the same to the reaction zone.

2627. ——— (Standard Catalytic Co.). Physiologically Inert Paraffinic Oil Suitable for Medicinal Use. United States Patent 2,354,540, July 25, 1944. Chem. Abs., vol. 38, 1944, p. 6501.

Method of production is employed that involves passing H_2 2 and CO 1 part by vol. over a skeleton alloy catalyst containing Ni together with 5–20% as much Co, at a temperature in the range of 360°–500° F. and under a pressure of from about atmospheric pressure to about 20 atm. pressure, segregating normally liquid hydrocarbons, b. about 400° F., and further purifying them, as by use of NaOH solution and clay.

———. *See* abs. **1101, 2438.**

PEOPLES GAS BY-PRODUCTS CORP. *See* abs. **906.**

PERSIEL, H. *See* abs. **3959.**

2628. PETERS, E. F. (Standard Oil Co. of Indiana). Catalytic Polymerization of α–olefins. United States Patent 2,552,508, May 15, 1951. Chem. Abs., vol. 45, 1951, p. 9555.

Liquid-phase polymerization of tertiary α–olefins, preferably isobutylene, to dimers and trimers principally, by utilizing 5–40% O to prevent the formation of higher polymers with the formation of minor amounts of oxygenated compounds and employing a BF_3 catalyst (0.05–30% by weight, based on the olefin) at 70°–250° F. for enough time to effect substantial polymerization. The liquid polymerization products and a liquid catalyst layer are separated, the oxygenated compounds and the BF_3 separated from the liquid catalyst layer, and the BF_3 is recycled to the polymerization zone.

———. *See* abs. **628.**

PÉTROLE SYNTHETIC. *See* abs. **23, 24.**

2629. PEUKERT, E., AND HILBERATH, F. Production of Alcohols. United States Patent 2,621,202, Dec. 9, 1952; appl. filed Aug. 1, 1949, and in France Sept. 19, 1947, Serial No. 107,888; 6 claims (*Cl. 260–449.5*).

Alcohols, especially MeOH, can be produced from CO and H_2 at 250° C. and pressures of 300–600 atm. in Fe apparatus without damage to the apparatus if the partial pressure of CO is kept at 15–20 atm. Virtually no Fe carbonyl is formed. The low partial pressure is necessary only at the parts of the apparatus with temperatures favorable for formation of carbonyl. Partial pressures equal to those ordinarily used may be maintained in the zones with temperatures above that favorable for the formation of Fe carbonyl. To fulfill these conditions, fresh synthesis gas, richer in CO than the recycled gas, is introduced at a temperature $<100°$ C. into the 2d and succeeding layers of catalyst in an amount sufficient to increase the partial pressure of the CO at the points the fresh gas is added to >20 atm. 2 literature refs., 1 foreign patent, and 3 United States patents are cited.

2630. ——— (Union rheinische Braunkohlen Kraftstoff A. G.). [Production of Alcohols, Particularly Methanol From Carbon Monoxide and Hydrogen.] German Patent 819,854, Nov. 5, 1951; appl. filed Oct. 2, 1948 (*Cl. 12 o*). Chem. Zentralb., 1952, I, pp. 1403, 1568.

Synthesis is performed in Fe autoclaves at CO pressures so low that only nonessential amounts of Fe carbonyl are formed. For example, at a total pressure of 300 atm. the CO pressure is kept at 20 atm. It is sufficient if this partial pressure is maintained in the cooler parts (up to 250°), whereas in the actual reaction zone the operation can be carried out at higher CO pressures of 30 atm.

2631. ——— (Union rheinische Braunkohlen Kraftstoff A. G.). [Production of Alcohols, Particularly Methanol From Carbon Monoxide and Hydrogen.] Swedish Patent 130,726, Feb. 6, 1951; appl. filed May 13, 1949. Chem. Zentralb, 1952, I, pp. 1403, 1568.

See German Patent 819,854 (abs. **2630**).

2632. PEVERE, E. F., HATCH, G. B., AND SENSEL, E. E. (The Texas Co.). Synthesis of Motor Fuel by Hydrogenation of Carbon Oxides. United States Patent 2,418,899, Apr. 15, 1947; appl. filed Oct. 24, 1945, Serial No. 624,292; 9 claims (*cl. 260–449.6*). Chem. Abs., vol. 41, 1947, p. 4634.

Branched chain hydrocarbons, which are in vapor state under hydrogenation conditions, are added to the H_2 and C oxide. Isobutane, isobutylene, isopentane, the methylbutenes and methylpentenes, 2,2–dimethylbutane, and 2,3–dimethylbutane are examples of hydrocarbons of the preferred volatility range. A mixture may be used, but recycling of the unreacted branched-chain hydrocarbon in substantial absence of straight-chain hydrocarbons is simplified if only a single branched hydrocarbon has been used. It is believed that the branched-chain hydrocarbon reacts with the methylene radicals at the catalyst surface to produce branched chain hydrocarbons of higher molecular weight rather than essentially straight chain hydrocarbons such as are produced from CO and H_2 alone. It is desirable to use at least 5 mol. percent of isobutane, based on the C oxide in the reaction mixture and corresponding amounts of other branched chain hydrocarbons amounts of 5–15 mol. percent are suitable for obtaining a substantially modified reaction product. However, a large excess of the branched-chain hydrocarbons, such as, 100–1,000 mol. percent may be used to minimize the formation of the usual C oxide hydrogenation products. The usual hydrogenation procedure is used.

PEXTON, S. *See* abs. **912.**

2633. PFANNMÜLLER, W., AND REICHART, J. (I. G. Farbenindustrie A. G.). [Process and Equipment for Carrying Out Catalytic Gas Reactions.] German Patent 744,075, Jan. 8, 1944; appl. I 65,343, Aug. 3, 1939 (*Cl. 12 g–4.01*). FIAT Reel E 29, frames 607–609; PB 70,432.

Describes process and apparatus for carrying out exothermic gas reactions in a converter with tube bundles and with regulated heat exchange between the catalyst mass and the incoming fresh gas with drawings.

2634. PFIRRMANN, T. W. High-Quality Benzine and Diesel Motor Fuels. United States Patent 2,232,673, Feb. 18, 1941; appl. filed Aug. 23, 1938, Serial No. 226,243, in Germany Aug. 30, 1937; 1 claim (*Cl. 196–62*). Chem. Abs., vol. 35, 1941, p. 3418

Brown coal tar is mixed with an equal amount of Kogasin middle oil obtained by reduction of CO with H_2, causing a separation into 2 layers of different specific gravity. This separation permits high yields since each layer can be hydrogenated under the most favorable conditions.

———. *See* abs. **3766, 3767, 3768, 3769, 3770.**

2635. PHILIPON, H. [Gas Producers.] French Patent 803,293, Sept. 26, 1936. Chem. Abs., vol. 31, 1937, p. 2791.

Gas rich in CO and H_2 is obtained by blowing a mixture of O_2 and steam superheated to 400°–600° into a gas producer in which the ash is fused in the presence of a suitable amount of fused materials.

2636. PHILLIPS, I. H., AND HUMPHREYS & GLASGOW, LTD. Removing Hydrogen Sulfide From a Gas Mixture With a Purification Material and Then Revivifying That Material. British Patent 681,551, Oct. 29, 1952. Chem. Abs., vol. 47, 1953, p. 5667.

H_2S as in coke-oven gas is removed with a material containing $Fe(OH)_3$. This material is revivified by passing air or other O_2-containing gas through the material.

2637. PHILLIPS PETROLEUM CO. Catalyst for Synthesis of Hydrocarbons. British Patent 669,831, 1952. Fuel Abs., 1952, abs. 4969.

Improved catalyst for the Fischer-Tropsch synthesis is prepared by reducing a mixture of ferroso ferric oxide, small amounts of K_2O and Al_2O_3 (which may be in the form of thermally decomposable salts) and 1–10 wt. % of CaO in an atmosphere of H_2 at 450°–550° to form metallic Fe in which is incorporated small amounts of K_2O and Al_2O_3 and 1.3–12 wt. % of CaO.

2638. ———. Hydrocarbon Synthesis. British Patent 635,219, Apr. 5, 1950. Chem. Abs., vol. 44, 1950, p. 7516.

See United States Patent 2,497,761 (abs. **388**).

———. *See* abs. **46, 121, 374, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384, 385, 386, 387, 388, 389, 390, 447, 448, 449, 715, 716, 717, 718, 745, 748, 749, 750, 751, 752, 753, 754, 822, 907, 948, 1076, 1077, 1078, 1079, 1109, 1780, 1784, 1960, 1992, 1993, 2157, 2172, 2173, 2174, 2175, 2176, 2177, 2178, 2179, 2180, 2181, 2182, 2395, 2537, 2567, 2747, 3641, 3642, 3793, 3958.**

2639. PHINNEY, J. A. (Stanolind Oil & Gas. Co.). Method and Apparatus for Making Hydrogen-Carbon Monoxide Mixtures. United States Patent 2,532,514, Dec. 5, 1950; appl. filed Aug. 14, 1945, Serial No. 610,845; 4 claims (*Cl. 48–196*). Chem. Abs., vol. 45, 1951, p. 1326.

Air, natural gas or CH_4, and recycle CO_2 are separately preheated by heat exchange with hot synthesis gas combined and reacted over a catalyst at 1,900° F. The temperature before the preheating by heat exchange is 850° F., increased in the heat exchange tubes to 1,625° F. The gaseous product leaves the exchanger at about 1,000° F. and is supplied to a hydrocarbon synthesis zone after cooling to about 400° F. Co or Fe fluidized catalyst is used. Coke produced in the preheating of CH_4 is oxidized by the air and each zone is purged by CO_2 before and after the introduction of air. Describes apparatus. 1 foreign patent and 10 United States patents cited.

2640. ——— (Stanolind Oil & Gas Co.). Production of Carbon Monoxide and Hydrogen. United States Patent 2,482,866, Sept. 27, 1949; appl. filed Nov. 1, 1944, Serial No. 561,352; 1 claim (*Cl. 252–373*). Chem. Abs., vol. 44, 1950, p. 823.

Natural gas or CH_4 and O_2-containing gas such as air are contacted with a fluid group VIII metal in a gas generator at approximately 30 p. s. i. gage pressure. 0.6 mol. of O_2 per mol. of CH_4 is supplied to attain an equilibrium reaction temperature of 1,530° F. favoring conversion of CH_4 to 92% H_2 and CO in molal ratio 2:1. 6 United States Patents cited.

See abs. **2313.**

2641. PHINNEY, J. A., PACE, B. S., AND AYTON, G. R. (Stanolind Oil & Gas Co.). Hydrogen–Carbon Monoxide Synthesis. United States Patent 2,527,846, Oct. 31, 1950; appl. filed Jan. 14, 1947, Serial No. 722,065; 3 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 334.

N_2 content is reduced by using relatively pure O_2 in the synthesis gas production. The O_2 and CH_4 are separately preheated to 1,000° F. Then direct partial combustion takes place under a pressure of 200–300 p. s. i., temperature at least 2,200° F. by using 10% excess O_2 in combustion step a synthesis gas is produced, 90–95% H_2: CO=1.8:1–2:1. The remainder is unconverted CH_4 and CO_2. If the CO content of the gas charged to the synthesis step is properly limited, the catalyst does not become defluidized. The limiting is done by mixing inert gas diluents such as tail gas with the make gas. The total gas charged at the base of the reactor should contain less than 15 mol. %, preferably not more than 12 mol. % of CO during normal operation. The H_2: CO: CO_2 ratio in the reactor charge should be approximately 3:1:2 and a Z number 3–9, where Z is the quotient of mol. % H_2 multiplied by mol. % CO_2 and divided by the square of the mol. % CO. 11 United States patents cited.

2642. ——— (Stanolind Oil & Gas Co.). [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 959,599, Mar. 31, 1950; appl. filed Jan. 14, 1948. Chem. Zentralb., 1951, I, p. 280.

Synthesis is carried out in the presence of CO_2 with a suspended Fe catalyst. The gases are contained in the reaction mixture in the following relative amounts: H_2, CO, and CO_2=1–6:1:0.5–3. The gas mixture entering the reaction zone contains H_2, CO and CO_2 in molecular proportions $(H_2)(CO_2)$ per $(CO)^2$=2–9 at a reaction temperature 288°–399° and a pressure above 10.5 atm. The O-containing compounds obtained in the synthesis as byproducts are converted into hydrocarbons by treatment with a catalyst of SiO_2 and Al_2O_3 from bauxite at 371°–426° and 3.5 atm.

2643. PICCONI, C. [Appliance for Catalytic Reactions.] German Patent Appl.—, filed Nov. 13, 1940; APC 365,412.

Apparatus for NH_3 and MeOH synthesis has a catalyst zone surrounded by a nest of tubes serving as the heat exchanger of the recuperator. These tubes are provided with electric resistors to raise the preheated reacting gases to the optimum temperature. The heat exchanger tubes may be arranged in 1 or more layers around the catalytic zone and may be straight or coiled.

PICHLER, H. *See* abs. **672, 673, 674, 675, 676, 677, 678, 679, 680, 681, 682, 683, 684, 685, 686, 687, 688, 689, 690, 691, 710, 711, 712.**

2644. PICTET, R. P. Making Carbon Monoxide and Hydrogen. United States Patent 1,228,818, June 5, 1917. Chem. Abs., vol. 11, 1917, p. 2275.

Mixture of CO and H_2 is formed by simultaneously admitting steam, O_2, and petroleum oil, in vaporized form, into a horizontal pipe heated externally in a furnace to a temperature high enough to decompose the steam and hydrocarbon, preferably about 1,300°–1,500°.

2645. PIER, M. (Standard-I. G. Co.). Catalytic Hydrogenation of Mineral Oils. United States Patent 1,845,058, Feb. 16, 1932. Chem. Abs., vol. 26, 1932, p. 2312.

Catalyst particles such as Mo, Cr catalyst are maintained in a state of suspension and eddying motion within the reaction space by means of H_2 charged with the vapors of mineral oil undergoing destructive hydrogenation and blown in at sufficient speed but not at such a high speed as would carry away the bulk of the catalyst from the reaction space; any catalyst particles that may be carried along are separated from the reaction gas before condensation takes place by contact with cooler parts of the apparatus. Describes various details of apparatus.

See also French Patent 638,109 (abs. **1242**) and British Patent 274,904 (abs. **1225**).

2646. ——— (I. G. Farbenindustrie A. G.). Methanol Synthesis. United States Patent 1,823,468, Sept. 15, 1931; appl. filed Feb. 16, 1924, Serial No. 693,372. Chem. Abs., vol. 26, 1932, p. 156.

Synthesis of MeOH and other O-containing organic compounds by catalytic reduction of CO is effected in an apparatus having the inner surface of both hot and cold parts formed of steel containing a high percentage of Cr.

See also Austrian Patent 116,055 (abs. **88**).

2647. ——— (I. G. Farbenindustrie A. G.). [Oxygenated Hydrocarbons.] German Patent 614,975, June 25, 1935 (*Cl. 12 o–5.01*). Chem. Abs., vol. 29, 1935, p. 7999.

Oxides of C are treated with H_2 under high temperature and pressure in the presence of a catalyst. The deposition of solid high-molecular products on the catalyst during the reaction is prevented by the presence of a high-boiling solvent, which does not change or vaporize under the conditions of the reaction. Thus, a catalyst obtained by fusing ZnO and $CaCr_2O_7$ is used in treating CO with H_2 at 400° and 200 atm. to give a mixture of higher alcohols. The catalyst is rinsed with anthracene oil to prevent inactivation by deposition of solid products.

2648. ——— (I. G. Farbenindustrie A. G.). [Oxygenated Organic Compounds.] German Patent 484,166, Sept. 16, 1923. Chem. Abs., vol. 24, 1930, p. 860.

In the catalytic manufacture of MeOH and other oxygenated organic compounds from H_2 and oxides of C, undesired byreactions, such as the formation of CH_4 and the consequent overheating of the catalyst, are avoided by injecting the liquid reaction product or a constituent thereof directly into the contact mass continuously or from time to time.

2649. ——— (Standard-I. G. Co.). Production of Valuable Liquid Hydrocarbons. United States Patent 1,921,478, Aug. 8, 1933. Chem. Abs., vol. 27, 1933, p. 5182.

In the reaction of CO with H_2 over a catalyst such as Zn oxide and Ca bichromate, to produce alcohols, the catalyst is kept clean by passage of 1 kg. anthracene and 7 $m.^3$ mixed gas per hr. per kg. of catalyst through the reactor. Similarly, an equal volume of anthracene oil is passed with heavy tar over the molybdic acid, chromic acid, and manganese carbonate catalyst employed for hydrogenation, to give a net charge rate of 1 kg. mixed oil per kg. catalyst per hr. Building up of heavy carbonaceous material upon the catalyst surface with consequent lowering of its activity is thus prevented.

2650. ——— (I. G. Farbenindustrie A. G.). [Reducing Oxides of Carbon.] German Patent 630,824, June 6, 1936; appl. I 35,544, filed Sept. 18, 1928 (*Cl. 12 o–1.03*). FIAT Reel AA 88, frame 3,710; PB 70,273; Chem. Abs., vol. 31, 1937, p. 227.

In the catalytic reduction of C oxides, enough hydrocarbons that are liquid under the conditions of the reaction are added to ensure that the process is completely carried out in the liquid phase. Thus, a kieselguhr–Ni–Al catalyst is suspended in heavy oil freed from S and a CO–H_2 mixture led in, the CO being reduced mainly to CH_4.

———. *See* abs. **1945, 1996, 2350, 2351, 2352, 2353, 2354, 2355, 2356, 2362, 2363, 2364, 2365, 2366, 2367, 2368, 2369, 2370, 2371, 2374.**

2651. PIER, M., AND CHRISTMANN, F. (I. G. Farbenindustrie A.-G.). Cracking Hydrocarbon Mixtures. United States Patent 2,203,470, June 4, 1940; appl. filed July 21, 1937, Serial No. 154,752, in Germany July 29, 1936; 2 claims (*Cl. 196–39*). Chem. Abs., vol. 34, 1940, p. 7102.

CO and H_2 in the ratio of 1 : 2 are passed at 200° C. over a catalyst containing Co, Th, and bleaching earths. The fraction b. above 320° C. is then treated with H_2SO_4. The oil thus prepared is cracked at 550°–600° C., while returning products of high boiling point.

2652. ——— (I. G. Farbenindustrie A. G.). [Hydrocarbon Polymerization Products.] German Patent 594,167, Mar. 13, 1934 (*Cl. 12 o–1.01*). Chem. Abs., vol. 28, 1934, p. 3576.

Difficulty fusible or infusible solids of high molecular weight, with or without lubricating oils, are obtained by dehydrogenating solid or semisolid paraffin hydrocarbons, or mixtures consisting mainly thereof, and treating the products with a condensing or polymerizing agent; for example, $AlCl_3$, $ZnCl_2$ or BF_3. The dehydrogenation may be effected by introducing substituents such as Cl, O_2, or S into the starting materials and then removing the substituents, suitably in the form of their H compounds. The solid products are useful as insulating materials or components of rubber mixtures. Gives examples and numerous details. Addition to German Patent 556,309 (abs. **2657**).

2653. ——— (Alien Property Custodian). Liquid Lubricating Oils from Paraffin Wax. United States Patent 2,318,625, May 11, 1943. Chem. Abs., vol. 37, 1943, p. 6449.

Oils are produced by subjecting a straight-chain paraffin wax to the action of a halogenating agent such as Cl, under conditions adapted to convert it into halogen derivatives of substantially the same number of C atoms, and subjecting the resulting product to the action of a chemical condensing agent, such as $AlCl_3$, in the presence of a bleaching earth to make oils of high viscosity index.

2654. ——— (I. G. Farbenindustrie A. G.). [Lubricant.] German Patent 726,885, Sept. 17, 1942 (*Cl. 23 c–1.01*). Chem. Abs., vol. 37, 1943, p. 6884.

Lubricant is a mixture of high-molecular polymers of polymerizable double-bond compounds containing an aromatic group and cracking or dehydrogenation products of hydrocarbons or substances containing unsaturated components such as are obtained in the hydrocarbon synthesis from CO and H_2. The polymers

are obtained with the aid of acid halides or materials of large surface area.

2655. ——— (Attorney General of the United States). Lubricant. United States Patent 2,421,082, May 27, 1947. Chem. Abs., vol. 41, 1947, p. 5299.

Certain polymerization products if added to lubricating oils will improve the viscosity index. These products are obtained by polymerizing compounds having a polymerizable double linkage, which, when polymerized by themselves with the aid of acid-reacting inorganic halides, yield products with over 1,000 molecular weight in admixture with cracked or dehydrogenation products of hydrocarbons or hydrocarbons obtained by synthesis from CO and H_2, if they contain unsaturated constituents. Gives 4 examples of preparation. In 1 instance 5% of the additive increases the viscosity index of an oil from 5 to 49.

2656. ———. [Lubricants.] German Patent Appl. —, filed Mar. 8, 1941; APC 382,394.

A relatively small amount of aromatic polymer (mol. wt. >1,000), such as styrene, alkyl-styrene, cumarone or indene is catalytically interpolymerized with unsaturated products from cracking, dehydrogenation, or catalytic hydrogenation of CO.

2657. ——— (I. G. Farbenindustrie A. G.). [Lubricating Oils.] German Patent 556,309, Oct. 1, 1929. Chem. Abs., vol. 27, 1933, p. 1160.

Solid or semisolid paraffin hydrocarbons or mixtures consisting mainly thereof are halogenated and then subjected to condensation, either in the presence of a condensing agent or under the influence of silent electric discharge. Aromatic hydrocarbons, for example, $C_{10}H_8$, or liquid olefins or other liquid hydrocarbons may be added before condensation. Gaseous olefins may be led into the mixture during condensation. The starting materials or the condensation products may be hydrogenated. Gives examples and numerous details.

2658. Pier, M., and Donath, E. (Alien Property Custodian). Hydrocarbons From Hydrogen and Carbon Monoxide. United States Patent 2,318,626, May 11, 1943; appl. filed Sept. 24, 1938, Serial No. 231,612, in Germany Sept. 30, 1937; 2 claims (*Cl. 260–449*). Chem. Abs., vol. 37, 1943, p. 6112.

Process is employed that involves passing a gas mixture containing < 2 parts by volume of H_2 for each part by volume of CO into the inlet end of a reaction chamber, adding further H_2 to the reaction mixture at spaced points along the reaction chamber in such amounts that there are < 2 parts by volume of H_2 for each part by volume of CO in every part of the reaction chamber, the total volume of H_2 supplied to the chamber being substantially 2 times the volume of CO supplied to it.

2659. ——— (I. G. Farbenindustrie A. G.). Lubricating Oil. United States Patent 2,063,623, Dec. 8, 1936. Chem. Abs., vol. 31, 1937, p. 852.

Paraffin wax composed of materials of a molecular weight of at least 250 is heated under pressure (suitably about 40–140 atm.) and in the presence of a dehydrogenating and condensing catalyst such as molybdic acid, C and $ZnCl_2$ to a temperature of about 400° to produce a reaction product containing a substantial proportion of constituents b. >200° in vacuo and of only slightly less H content than the initial material.

2660. Pier, M., and Free, G. (W. E. Currie). Antiknock Motor Fuels. United States Patent 2,242,321, May 20, 1941; appl. filed Aug. 24, 1939, Serial No. 291,670, in Germany Aug. 31, 1938; 11 claims (*Cl. 196–50*). Chem. Abs., vol. 35, 1941, p. 6104.

Process for the production of nonknocking motor fuels involves catalytically cracking hydrocarbons obtained from CO by reaction with H_2 mixed with a paraffin-base petroleum oil.

2661. ——— (W. E. Currie). Antiknock Motor Fuels. United States Patent 2,245,157, June 10, 1941; appl. filed Aug. 12, 1938, Serial No. 224,488, in Great Britain July 15, 1937; 3 claims (*Cl. 196–50*). Chem. Abs., vol. 35, 1941, p. 6433.

Describes arrangement of apparatus and a process for producing safety fuels stable to knocking, which comprises subjecting to cracking higher boiling mainly aliphatic hydrocarbon oils, in particular those having a high content of paraffinic constituents, such as higher boiling fractions of CO reduction products, and further cracking in the vapor phase at a temperature 400°–700° and in a separate reaction zone. The fraction of the resulting product b. about 150°–300° and consists mainly of unsaturated aliphatic hydrocarbons in the presence of > about 10% of an added cyclic hydrocarbon, which under the reaction conditions is vaporous but in the absence of a substantial amount of added H_2 or of a gas supplying H_2.

2662. ——— (I. G. Farbenindustrie A. G.). [Process for Producing Antiknock Gasoline From the Hydrocarbon Oils Obtained by the Reduction of Carbon Monoxide.] German Patent Appl. I 63,924, Feb. 25, 1939 (*Cl. 23 b–1.04*). TOM Reel 41, bag 2,744, item 22, 5 pp.

Before subjecting the raw material to cracking in the presence of catalysts at temperatures 200°–450° under pressures of 5–150 atm., it is given a very mild dehydrogenating and isomerizing treatment in the presence of catalysts so that virtually no cracking into low boiling products results. Example: A heavy gasoline b. 100°–200° obtained through the reduction of CO is passed over a catalyst consisting of active alumina with 10% of molybdenum oxide at 430° and normal pressure. The product has virtually the same boiling range as the raw material. It contains about 50% of olefins and has an octane number of 60. It is then passed over artificial Al silicate at 460° at a flow rate of 1 kg. oil per l. of catalyst per h., whereby 80% by weight of the raw material is converted into a gasoline b. up to 200° (38% up to 100°) and having an octane No. of 72 motor method.

2663. ———. [Use of Aromatics in Vapor-Phase Oil-Hydrogenation Feed Stock.] German Patent Appl. —, filed Apr. 26, 1941; APC SN 390,534.

20–50% of benzol or toluene is mixed with vapor phase feed, catalytic cracking feed, or synthesis gas for Fischer-Tropsch process.

2664. Pier, M., and Kleine, J. (I. G. Farbenindustrie A. G.). [Oxygenated Organic Compounds From Carbon Monoxide and Hydrogen.] German Patent 587,818, Nov. 11, 1933 (*Cl. 12 o–5.01*). Chem. Abs., vol. 28, 1934, p. 1354.

Cold or warm parts of the apparatus that comes into contact with CO may be made of Fe, Ni, or Co, provided that the gases used are dry. Addition to abs. **1377, 1378, 1996, 2672,** and **2679.**

2665. Pier, M., and Kroenig, W. (I. G. Farbenindustrie A. G.). Production of Nonknocking Motor Fuels. United States Patent 2,116,081, May 3, 1938; appl. filed Jan. 29, 1936. Chem. Abs., vol. 32, 1938, p. 5200.

Nonknocking motor fuels are made by converting CO and H_2 in presence of a Co–Mn catalyst on kieselguhr into hydrocarbons boiling at least in part in the gasoline range, separating these hydrocarbons into higher and lower boiling constituents by compression, and polymerizing the lower boiling constituents in presence

of a condensing agent, such as bleaching earth impregnated with H_3PO_4.

2666. PIER, M., AND KUPPINGER, O. (I. G. Farbenindustrie A.-G.). [Synthetic Organic Oxycompounds.] Russian Patent 9,349, May 31, 1929; appl. filed Aug. 28, 1926. Chem. Zentralb., 1931, I, p. 2672.

Synthesis takes place by catalytic pressure hydrogenation of CO, whereby for the purpose of obtaining higher aliphatic alcohols, such as isobutyl alcohol, the CO gases are freed as far as possible from CO_2.

2667. PIER, M., AND MÜLLER, C. (Badische Anilin- und Soda-Fabrik.). Oxygenated Organic Compounds. Canadian Patent 251,483, July 7, 1925; appl. filed Nov. 7, 1923. Chem. Zentralb., 1926, I, p. 2508; Chem. Abs., vol. 19, 1925, p. 3272.

Methanol is produced by passing a mixture of C oxides, 1 vol., with more than 1 vol. of H_2 over a catalyst at elevated temperature and pressure. The catalyst may be a metal oxide nonreducible under the conditions of working.

2668. PIER, M., AND MÜLLER-CUNRADI, M. (Badische Anilin- u. Soda-Fabrik). [Methanol.] Austrian Patent 101,331, Oct. 26, 1925; appl. filed Sept. 26, 1923.

See British Patent 229,714 (abs. **91**).

2669. ——— (Badische Anilin- u. Soda-Fabrik.). [Methanol.] Swiss Patent 107,200, Oct. 16, 1924; appl. filed Sept. 26, 1923. Chem. Zentralb., 1926, I, p. 2508.

See British Patent 229,714 (abs. **91**).

2670. ——— (Badische Anilin- u. Soda-Fabrik). [Production of Methanol.] French Patent 571,354, May 16, 1924; appl. filed Oct. 1, 1923.

See British Patent 229,714 (abs. **91**) and Canadian Patent 251, 483 (abs. **2667**).

2671. PIER, M., AND RINGER, F. (Standard-I. G. Co.). Nonknocking Motor Fuel. United States Patent 1,979,841, Nov. 6, 1934. Chem. Abs., vol. 29, 1935, p. 334.

Process for the production of a nonknocking motor fuel comprises catalytically reducing compounds such as aldehydes and alcohols of 3 or more C atoms in the molecule, obtained from the catalytic reduction of CO with H_2 and which on reduction produces hydrocarbons of branched chain structure boiling in the motor-fuel range.

2672. PIER, M., AND RUMPF, W. (I. G. Farbenindustrie A. G.). [Oxygenated Organic Compounds From Carbon Monoxide and Hydrogen.] German Patent 568,627, Sept. 16, 1923. Chem. Abs., vol. 27, 1933, p. 2691.

Parts of the apparatus that come into contact with CO are coated with Cr, Mn, Mo, W, or U. This is an addition to German Patents 490,248 and 548,434 (abs. **2679** and **1378**).

See also German Patent 559,892 (abs. **1377**).

2673. PIER, M., AND SIMON, W. Cracking or Pressure Hydrogenation of Hydrocarbons. United States Patent 2,224,003, Dec. 3, 1940; appl. filed Mar. 24, 1939, Serial No. 263,908, in Germany Apr. 1, 1938; 4 claims (*Cl. 196–50*). Chem. Abs., vol. 35, 1941, p. 2312.

In cracking oils rich in H, such as Kogasin, gas formation is reduced by the use of a hydrogenation catalyst previously partly spent by use in destructive hydrogenation of oils poor in H. W disulfide was used to hydrogenate a coal tar oil for 3 days, reducing its activity by 25%. It was then used without revivification to crack a 200°–325° C oil from CO to a 70% yield of gasoline with only 6% yield of hydrocarbon gas.

2674. PIER, M., AND WIETZEL, G. (I. G. Farbenindustrie A. G.). Methanol Synthesis. United States Patent 1,788,170, Jan. 6, 1931; appl. filed Oct. 27, 1925. Chem. Abs., vol. 25, 1931, p. 715.

For production of organic compounds such as MeOH there is passed over a suitable catalyst such as Fe oxide, in a circulating system, a gas mixture containing a large proportion of inert gas, such as a "power-gas", which has been scrubbed to remove CO_2 and then contains CO about 15.3%, H_2 about 30.6%, CH_4 about 2.8%, and N_2 about 51.3%, and part of the residual gas mixture is removed and continuously replaced by fresh gas to constantly maintain a proportion of about 12% CO and 24% H_2 in the circulating gas. Temperatures of 200°–500° and pressures above 50 atm. are suitable for the process. It is stated that as good yields may be obtained as when employing gases richer in reacting constituents.

2675. PIER, M., AND WINKLER, K. (Standard-I. G. Co.). Conversion of Waste Gases From the Destructive Hydrogenation of Fuels. United States Patent 1,-919,857, July 25, 1933. Chem. Abs., vol. 27, 1933, p. 4908.

Gas containing 30–40% CH_4 is mixed with CO_2; the product contains, in percent: CO_2, 23.6; H_2, 52; CH_4, 22.5; N_2, 1.3; and CO, 0.6. It is passed at about 1,100° C. through a furnace filled with refractory masses on which metals with catalytic properties such as Ni have been deposited. The gas mixture leaving the furnace contains in percent: CO, 31.4; H_2, 66.2; CO_2, 1.1; and N_2, 1.3.

2676. PIER, M., DONATH, E., AND MICHAEL, W. (I. G. Farbenindustrie A. G.). [Regenerating Catalysts.] German Patent 736,528, May 13, 1943 (*Cl. 12 g–4.01*). Chem. Abs., vol. 38, 1944, p. 3100.

The catalyst is treated with a gas containing a high but limited volume of O_2. Ordinarily such a concentration of O_2 would overheat the catalyst. However, the gas is put through at such a velocity that it carries off the generated heat without raising its own (gas) temperature excessively. The gas leaving the catalyst room is divided into 2 parts. Of these, the larger is cooled and recycled. Fresh gas is admixed periodically or continuously.

2677. PIER, M., MICHAEL, W., AND JAECKH, W. (I. G. Farbenindustrie A. G.). Hydrocarbon Production From Carbon Monoxide and Hydrogen. United States Patent 2,167,004, July 25, 1939; appl. filed Dec. 16, 1936. Chem. Abs., vol. 33, 1939, p. 8624.

CO and H_2 are passed at a reacting temperature, which may be about 200°–450°, over a catalyst such as Fe with 5% Al_2O_3 while trickling over the catalyst a medium such as paraffin oil, which is at least partly liquid under the conditions employed, and while avoiding formation of a liquid level in the catalyst space. Describes apparatus.

2678. PIER, M., RUMPF, W., AND SCHAPPERT, H. (I. G. Farbenindustrie A. G.). [Liquid Hydrocarbons From Carbon Monoxide and Hydrogen.] German Patent 703,101, Jan. 30, 1941; appl. I 53,873, filed Dec. 14, 1935 (*Cl. 12 o–1.03*). FIAT Reel AA 88, frames 3,544–3,547. PB 70,273; Chem. Abs., vol. 36, 1942, p. 251.

Excess exothermic heat is removed as usual by indirect heat exchange of the reacting material with steam. In this case the steam is passed into the cooling chamber in a wet state saturated with H_2O up to 60% and 80% of its capacity. It is advantageous to maintain the wet steam under such pressure that the saturation temperature lies only slightly below the reaction temperature.

2679. PIER, M., RUMPF, W., AND STEIN, G. (I. G. Farbenindustrie A. G.). [Oxygenated Organic Compounds.] German Patent 490,248, Feb. 25, 1923. Chem. Zentralb., 1930, I, p. 3133; Chem. Abs., vol. 24, 1930, p. 2137.

In the manufacture of oxygenated organic compounds by the catalytic interaction of CO and H_2 at a raised temperature and under high pressure, the reaction vessel is made of, or lined with, Cu or Ag or their alloys, and the other parts of the apparatus coming in contact with CO are constructed similarly or made of, or lined with, more fusible metals, for example, Al, Sn, Zn, or Pb or their alloys. Contamination of the contact mass with Fe is so avoided.

See also French Patent 575,913 (abs. **99**).

2680. PIER, M., SIMON, W., AND JACOB, P. (I. G. Farbenindustrie A. G.). [Catalysts.] German Patent 693,985, June 27, 1940 (*Cl. 12 g–4.01*). Chem. Abs., vol. 35, 1941, p. 4926.

Very effective catalysts are produced by converting thio salts, such as the S compounds of Cu, Zn, Sb, As, Mo, W, Cr, Re, Ge, with heavy metal compounds, such as halides, sulfates, nitrates, carbonates. The conversion can take place in aqueous or preferably organic solutions or suspensions. The 2 participating metals should preferably be different. Good solvents that can be used are acid amides, for example, formamide, acid chlorides, for example, acetyl chloride, amino acids, ketonic acids, esters, nitriles, amines, aldehydes, ketones, or nitro compounds. In an example, 0.5 mol. $TiCl_4$ in C_6H_6 is slowly added to 1 mol. NH_4 thiotungstate in cyclohexylamine, while cooled by H_2O. The brown precipitate is filtered, and the solvents adhering to it are extracted with low-boiling solvents, for example, acetone or alcohol. It is then treated with H_2 with a slight admixture of H_2S at 300°–400°. The resulting gray-black compound is pressed and used.

2681. ——— (I. G. Farbenindustrie A. G.). [Synthesis Catalysts.] German Patent 695,925, no date. Kainer, p. 34.

Discusses kieselguhr catalyst.

2682. PIER, M., WIETZEL, R., AND WINKLER, K. (I. G. Farbenindustrie A. G.). Oxygenated Organic Compounds From Oxides of Carbon and Hydrogen. United States Patent 1,917,323, July 11, 1933; appl. filed Feb. 14, 1929, Serial No. 340,001. Chem. Abs., vol. 27, 1933, p. 4538.

Compounds such as MeOH are obtained by reaction of C oxides and H_2 at 320°–500° under 200–800 atm. pressure in the presence of a catalyst such as oxides of Fe, Zn, and Cr together with S, Te, P, Si, B, As, Sb, or Bi.

See also United States Patent 1,917,323 (abs. **2684**).

2683. ——— (I. G. Farbenindustrie A. G.). [Synthesis of Methanol.] German Patent 510,302, Feb. 8, 1924. Chem. Abs., vol. 25, 1931, p. 972.

See British Patent 254,760 (abs. **114**).

2684. ——— (I. G. Farbenindustrie A. G.). Synthesis of Oxygenated Organic Compounds, Such as Alcohols, Acetone, Acids. United States Patent 1,841,910, Jan. 19, 1932; appl. filed Feb. 6, 1925, Serial No. 7,391. Chem. Abs., vol. 26, 1932, p. 1617.

Reaction is effected between C oxides and H_2 under 200–800 atm. pressure and at temperatures of 320°–500° in the presence of a catalytic mass comprising Fe in combined condition such as $Fe(OH)_3$ and a difficultly reducible oxide such as that of W, Cr, or Mn. ZnO also may be used.

2685. PIER, M., MÜLLER-CUNRADI, M., WIETZEL, G., AND WINKLER, K. (I. G. Farbenindustrie A. G.). Catalytic Methanol Production. United States Patent 1,766,763, June 24, 1930; appl. filed Sept. 15, 1923. Chem. Abs., vol. 24, 1930, p. 4053.

In the production of MeOH and other oxygenated organic compounds by catalysis under pressure of H_2 and C oxides, volatile compounds of Fe are removed from the gases before they come into contact with the catalyst, suitably by passing through a layer of active C.

2686. ——— (Badische Anilin- u. Soda-Fabrik). [Methanol From Carbon Oxides.] French Patent 571,285, May 14, 1924; appl. filed Sept. 29, 1923.

See British Patent 228,959 (abs. **90**).

2687. ——— (Badische Anilin-u. Soda-Fabrik). [Oxygenated Organic Compounds.] Austrian Patent 116,054, no date. Chem. Zentralb. 1930, I, p. 3628.

See Canadian Patent 251,485 (abs. **2688**).

2688. ——— (Badische Anilin-u. Soda-Fabrik.). Oxygenated Organic Compounds. Canadian Patent 251,485, July 7, 1925; appl. filed Nov. 7, 1923. Chem. Abs., vol. 19, 1925, p. 3272.

Mixture of C oxides and H_2 is passed through active C to remove volatile S and Fe compounds from the mixture and then subjected to the action of a catalyst under pressure.

2689. PIER, M., RUMPF, W., LAPPE, F., AND STERN, G. Methanol and Other Oxygenated Organic Compounds. Canadian Patent 254,987, Oct. 27, 1925. Chem, Abs., vol. 20, 1926, p. 210.

In the manufacture of MeOH by the catalytic reduction of CO at elevated temperature and pressure, the apparatus used is lined with a metal or alloy resistant to CO at the temperature of working. Cu, Ag, Al, and their alloys or special steel containing Cr, Mn, W, Mo, or V are specified.

2690. PIERCE, J. A. (Standard Oil Development Co.). [Catalysts for the Synthesis of Hydrocarbons and Oxygenated Compounds by the Fluidization Process.] French Patent 945,103, Apr. 26, 1949; appl. filed Apr. 15, 1947. Chem. Zentralb., 1950, I, p. 2395.

Fe_2O_3 or another Fe oxide is converted with 10–20% by weight of powdered Al and the hard, brittle product pulverized. If the materials are present in stoichiometric amounts a fused mixture of Al_2O_3 and metallic Fe is obtained. If Al is in excess, a homogeneous mixture of Al, Al_2O_3 and alloys is formed; with less Al a mixture of Al_2O_3, Fe, and Fe oxide (magnetite) is obtained. Activating substances such as K compounds, Mn, and Cu can be added. In similar way as the oxides of Fe, the oxides of Cr, Co, Th, Ni, and Cu can be treated; instead of Al pulverized amorphous Si is suitable. Example: 40 parts Fe_2O_3 and 6 parts, or about 13%, of Al powder are mixed in an earthenware vessel, and the mass is ignited with an acetylene burner. The vigorous exothermic reaction is quickly ended, and a hard, porous, strongly magnetic mass, with the appearance of lava, is obtained.

2691. ——— (Standard Oil Development Co.). Magnetite Containing Catalyst for the Synthesis of Hydrocarbons. United States Patent 2,537,699, Jan. 9, 1951; appl. filed Sept. 12, 1946, Serial No. 696,627; 7 claims (*Cl. 260–449.6*).

Gives preparation for an alumina-Fe metal-magnetite catalyst. In an example 40 parts by weight of Fe_2O_3 and 6 parts of powdered Al (13%) were mixed in a clay receptacle. The mixture was ignited. A violent exothermic reaction occurred, which was completed in a relatively short time. The product was cooled to room temperature. It was a hard, porous mass and was strongly magnetic. In another example, 10 parts by weight of CuO and 1 part MnO were mixed with 77 parts Fe_2O_3 and 13 parts Al powder. In the 3d example

6 parts of Al powder were mixed with 95 parts magnetic Fe_3O_4. 10 United States patents cited.

———. *See* abs. **3856, 3857.**

2692. PIERCE, J. A., AND RICHARDSON, R. W. (Standard Oil Development Co.). Catalyst for the Synthesis of Hydrocarbons. United States Patent 2,541,663, Feb. 13, 1951; appl. filed Nov. 15, 1946, Serial No. 710,232; 1 claim (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 3966.

Hydrocarbon synthesis is carried out and hydrogenation catalysts are prepared by plating Al with Fe, Co, or Ni with or without promoter. The Al is reacted with a salt of the metal. When using a 20% solution of $FeCl_3.6\ H_2O$ and 8 to 10-mesh Al, the time of contact is 15–30 min. During this time approximately 10–15% of the Fe is deposited on the Al. The preferred temperature is 125°–135° F. In using powdered Al, not over 2 l. of solution is used and it is added to the Al. In this case, the time of contact should be <5 min. Sulfates, nitrates, or chlorides are satisfactory salts. Under certain conditions an Fe carbonyl solution may be used. 5 United States patents cited.

2693. ——— (Standard Oil Development Co.). Process of Preparing a Group VIII Metal-on-Aluminum Catalyst. United States Patent 2,481,238, Sept. 6, 1949; appl. filed Sept. 24, 1947, Serial No. 775,975; 3 claims (*Cl. 252–466*). Chem. Abs., vol. 44, 1950, p. 824.

Al is plated with Fe, Co, or Ni, with or without addition of a promoter, by reacting it with a salt of the metal. Example: A 20% solution of $FeCl_3 \cdot 6\ H_2O$ was prepared. 1 l. of this solution was mixed with 160 gm. of granular Al. During the course of the reaction, H_2 was evolved. After 15–20 min. the ferric chloride solution was drained off the metal, which was rinsed and the H_2O removed. The catalyst is preferably preserved under iso-octane or other volatile, nonreactive hydrocarbon solvent. The granular Al cores were plated with a porous, active coating of metallic Fe. 1 literature ref. and 1 United States patent cited.

PIEROH, K. *See* abs. **2086.**

2694. PIETERS, H. A. J. (50% each to C. Otto & Co. G. m. b. H. and Staatsmijnen in Limburg). Purifying Gases Such as Those From Coal Distillation. United States Patent 2,169,282, Aug. 15, 1939. Chem. Abs., vol. 33, 1939, p. 9601.

Describes arrangement of apparatus and a method of separating H_2S from gases, which involves washing the gases with an aqueous ammoniacal solution initially containing Fe ferrocyanide in suspension and having an ammonium-salt content required to stabilize said ferrocyanide suspension against decomposition, regenerating the solution following its use and preparatory to its reuse in the washing operation by aerating the same, and compensating for the wastage of Fe ferrocyanide from the solution by adding to it finely divided material from the group consisting of (1) Fe ferrocyanide and (2) cyanides and Fe salts.

2695. PINE, P. R., AND RAY, E. C. (The Harshaw Chemical Co.) Preparation of Extruded Iron Oxide Catalysts. United States Patent 2,457,719, Dec. 28, 1948; appl. filed Apr. 3, 1947, Serial No. 739,267; 4 claims (*Cl. 252–259*). Chem. Abs., vol. 43, 1949, p. 3162.

Paste is formed consisting of ferrous carbonate, a compound of a catalytic metal of atomic number 22–30, excluding Fe, capable of yielding the oxide on calcination, a compound of an alkali metal capable of yielding the oxide on calcination, and H_2O. The proportions of the product after calcination shall be, 2–30% oxide of the catalytic metal, up to 28% oxide of the alkali metal, and not less than 70% Fe oxide, percentages based on total weight of final product. H_2O shall be present in proportion suitable for extrusion. The paste is extruded, shaped, and sized. The catalyst is heated to 110°–150° C. to remove H_2O and then calcined at 900°–950° C. for 2–6 hr. 2 United States patents cited.

2696. PINES, H. (Universal Oil Products Co.). Alkylation of Isoparaffins. United States Patent 2,594,-343, Apr. 29, 1952. Chem. Abs., vol. 47, 1953, p. 1179.

Describes an improved method for the production of saturated branched-chain hydrocarbons by the alkylation of isoparaffins with olefins. The olefin is treated under isomerizing conditions to convert a substantial portion into an olefin having a more centrally located double bond and then alkylating the isoparaffin with a HF catalyst.

PING, P. *See* abs. **3445.**

2697. PINTIAUX, O. (Société de Produits Chimiques et Engrais d'Auby). Contact Tower for Conversion of Carbon Monoxide Under Pressure. United States Patent 2,530,314, Nov. 14, 1950; appl. filed Mar. 16, 1945, Serial No. 583,122, in France June 9, 1943; 5 claims (*Cl. 23–288*).

Tower is made up of a series of superposed baskets receiving the catalyst and is also provided with a double series of heat exchange tubes. It is chiefly characterized by an inner lining that may be dismantled and removed. 4 United States patents cited.

2698. ——— (Société de Produits Chimiques & Engrais d'Auby). [Contact Tower for Conversion Under Pressure of Carbon Monoxide and the Like Applications.] Swedish Patent 128,900, Aug. 1, 1950; appl. filed Apr. 6, 1944. Chem. Zentralb., 1951, II, p. 118.

See United States Patent 2,530,314 (abs. **2697**).

2699. PINTSCH, J., KOM.-GES. [Continuous-Operation Water-Gas Generator Operating On Solid Fuel.] German Patent 742,154, Oct. 14, 1943 (*Cl. 24 e–1.05*). Chem. Abs., vol. 40, 1946, p. 445.

Part of the generated gas is diverted for use in the generator. The diverted gas is highly preheated in 1 of 2 heat accumulators, the hot gas is mixed with steam, and the mixture fed into the generator. Meanwhile the other accumulator is reheated. For this purpose is used an extraneous gas supplied through the top and part of the originally diverted generator gas fed through the bottom. The volume of the latter is such as to supply enough pressure to prevent the combustion gases from entering the generator.

2700. ———. [Motor Fuel.] French Patent 871,499, Apr. 27, 1942; appl. filed Apr. 11, 1941. Chem. Zentralb., 1942, II, p. 2109.

Lead susceptibility of motor fuels from the Fischer-Tropsch process can be increased by adding 10–30% of liquid propane or butane.

2701. ———. [Synthetic Gasoline.] French Patent 871,999, no date.

Pb susceptibility of synthetic gasoline can be increased by the addition of 10–20% of liquid propane or butane.

See abs. **504, 2071.**

2702. PIRKLE, L. E. (Jasco, Inc.). Purified Soaps From Synthetic Fatty Acids. United States Patent 2,287,128, June 23, 1942. Chem. Abs., vol. 37, 1943, p. 277.

Describes arrangement of apparatus, and a process is employed that may involve subjecting a petroleum wax to limited catalytic oxidation in liquid phase to produce a crude oxidation product containing fatty acids, neutralizing these fatty acids with aqueous alkali to produce an aqueous solution having a soap content of about 20–40%, separating unsaponified and unsaponifiable matter from the resulting aqueous solu-

tion of crude soaps, heating the remaining aqueous solution of crude soaps in liquid phase to a temperature of about 275°–325°, and then subjecting the heated solution to flash vaporization to vaporize about 25–75% of H_2O in the heated solution together with impurities therein, separately withdrawing the resulting vapors and recovering as the flash vaporization residue a concentrated aqueous solution of purified soaps.

2703. Pittsburgh Consolidation Coal Co. Gasification Process. British Patent 673,170, June 4, 1952. Chem. Abs., vol. 47, 1953, p. 296.

Gas is produced by passing steam into a mixture of carbonaceous solid fuel and CaO, in which process the steam is introduced into the reactor at 777°–982° and under a pressure that is at least $3.40–1.89 \times 10^{-2}$ $(t–1{,}430) + 4.48 \times 10^{-4} (t–1{,}430)^2$ atm., where t is the temperature in ° F. The amount of CaO is sufficient to convert substantially all the CO_2 produced to carbonate. The process also includes the use of mixtures consisting of 120–300 parts, by weight, CaO per 100 parts C in the fuel. After completion of the steam–C reaction, air is circulated at atmospheric pressure through the solid residue to regenerate the CaO. Under the above conditions the overall reaction will be at least thermoneutral and preferably exothermic. To produce a gas rich in CH_4 with a heating value in excess of 400 B. t. u. per ft.^{3}, the minimum pressure in atmospheres can be expressed by $5.0 + 4.2 \times 10^{-2} (t–1{,}430) + 2.7 \times 10^{-4} (t–1{,}430)^2$. The yield of CH_4 can be increased by carrying out the steam–C reaction at 910°–966° and then passing the products in contact with carbonaceous solids at 777°–871°. The steam–C–CaO reaction may be accelerated by impregnating the CaO with a small amount of a catalyst, such as an oxide of Fe, Ni, Co, or Mn.

2704. ———. Hydrogen. British Patent 673,332, June 4, 1952. Chem. Abs., vol. 47, 1953, p. 7744.

Quite pure H is produced by passing steam and a hydrocarbon such as CH_4 through a reaction zone packed with enough BaO to absorb all the CO_2 formed, the zone is held at 1,750°–2,300° F. and at least 1 atm. absolute pressure. At least 8 parts by weight of BaO for each part of C in the hydrocarbon gas is provided. The BaO is regenerated by heating in a fluidized bed at 2,300°–2,350° F. The best results are obtained when the reaction is carried out at 1,750°–2,050° F. and 20–50 atm. and when the steam : hydrocarbon ratio is 2 : 1 to 4 : 1.

2705. ———. Hydrogen. British Patent 673,333, June 4, 1952. Chem. Abs., vol. 47, 1953, p. 7744.

H_2 is produced by passing steam and CH_4 in a ratio of 2–4 : 1 over granular CaO in an amount equal to 2½ times the weight of the C in the CH_4. The reaction zone is held 1,500°–1,650° F. and 20–50 atm.; and the inlet temperature should be at least 100° F. above the outlet temperature. The CaO is regenerated by heating to 1,750°–1,800° F.

———. *See* abs. **827, 2760.**

2706. Pizzighelli, R., and Societa anon. carburanti italiani sintetici. [Hydrocarbons.] French Patent 707,607, Dec. 16, 1930. Chem. Abs., vol. 26, 1932, p. 838.

Liquid hydrocarbons, such as, benzine are synthesized by passing a gaseous mixture of CO and H_2 over a catalyst composed of metals of the Fe group activated by oxides of Zn or Al (up to 30%) with the addition of Cu, the oxide of which is reducible at 180°–200° and acts as a reducing catalyst for the Fe. By this means the usual preliminary reduction of the Fe by H_2 at 400° is avoided. Describes a suitable electrical heating tube for the gas passing to the catalyst.

2707. Plathner, G. [Water-Gas Generator.] German Patent 809,334, Oct. 8, 1951 (*Cl. 24 e–1*$_{06}$). Chem. Abs., vol. 47, 1953, p. 6637.

Steam passed through a luminous arc between C electrodes is allowed to react with them to produce water gas.

2708. Plauson, H. Use of Beta-rays and X-rays in Synthesizing Liquid Hydrocarbons From Gaseous Compounds. British Patent 309,002, Dec. 30, 1927. Chem. Abs., vol. 24, 1930, p. 299.

Liquid hydrocarbons are synthesized by subjecting gaseous C compounds such as are contained in water gas, coke-oven gas, natural gas, and gases produced by cracking heavy oils, to the action of rapidly moving electrons (β-rays) or to the joint action of β-rays and X-rays. The reaction may be facilitated by rotating electric or electromagnetic fields and by a catalyst in suspension in the reacting gases. In addition to hydrocarbons, other products such as ketones and alcohols may be obtained, especially when the gases contain water vapor. Higher boiling hydrocarbons may be obtained by subjecting those of lower boiling point to the radiations. Water gas may be subjected to the radiations and then compressed to 800–1,000 atm. The hydrocarbon products are mainly saturated.

Plauth, E. *See* abs. **2335.**

2709. Plummer, W. B. (Standard Oil Co. of Indiana). Catalyst Regeneration. United States Patent 2,248,196, July 8, 1941; appl. filed Sept. 13, 1939. Chem. Abs., vol. 35, 1941, p. 7172.

Powdered catalysts used in the cracking, aromatization of vaporizable hydrocarbons, such as those from the synthesis of CO and H_2, are regenerated by the oxidation of the carbonaceous deposits thereon with utilization of the exothermic heat therefrom for supplying the endothermic heat of cracking of reforming.

Porter, C. E. *See* abs. **316.**

2710. Porter, F. (Atmospheric Nitrogen Corp.). Catalyst for Promoting Reactions of Hydrocarbons With Steam. United States Patent 2,067,729, Jan. 12, 1937. Chem. Abs., vol. 31, 1937, p. 1564.

Catalyst suitable for promoting reactions such as H_2 production from CH_4 and steam at 500°–900° comprises oxides of Cr and Mo and contains substantially no Ni, Fe, or Co.

2711. Potts, H. E. Conversion of Carbon Monoxide Into Hydrocarbons. British Patent 526,465, Sept. 18, 1940. Chem. Abs., vol. 35, 1941, p. 7156.

Ratio of 2 parts or less of H_2 to 1 part of CO is employed and when the activity of the catalyst has decreased below a certain degree, the catalyst may be reactivated with a gas containing at least 2.5 parts of H_2 : 1 part of CO. The reactivated catalyst may be even more active than the original catalyst. It is advantageous to work in 2 or more reaction vessels in order to switch over for the activation. Known catalysts can be used.

2712. ——— (International Hydrocarbon Synthesis Co.). Process and Apparatus for the Production of Hydrocarbons by Reduction of Carbon Monoxide With Hydrogen. British Patent 567,609, Feb. 23, 1945; appl. filed May 12, 1941. Chem. Abs., vol. 41, 1947, p. 2559.

Gives process and apparatus for the production of hydrocarbons with more than 1 C atom in which the distance in the vertical tubes is at least 5 m. between the inlet and outlet openings. The tubes are surrounded by a boiling cooling medium. H_2O, diphenyl, glycerin, paraffin oil, and tricresyl phosphate may be used as the cooling medium. The invention allows the gases to be passed through the catalyst tubes at a

higher linear velocity, thereby effecting a better transmission of the reaction heat to the cooling wall.

2713. ———. Synthesis of Hydrocarbons From Mixtures of Carbon Monoxide and Hydrogen. British Patent 526,814, Sept. 26, 1940; appl. filed Mar. 11, 1939. Chem. Abs., vol. 35, 1941, p. 7155.

Synthesis gas consisting of a mixture of CO and H_2, if desired together with other gases, is passed at 1,000°–1,250° over bauxite in such a way that the gas remains 0.5 sec. in the hot zone. The gas is then freed from H_2S by means of an Fe oxide purification mass and after cooling passed over a Co–Th oxide catalyst at ordinary pressure and at about 180°. The yield of liquid hydrocarbons produced amounts to 115 cc. per $m.^3$ of CO–H_2 mixture. Quartz can be used instead of bauxite.

2714. Powell, A. R. (Koppers Co.). Catalytic Synthesis of Hydrocarbons. British Patent 638,087, May 31, 1950; appl. filed July 29, 1947. Chem. Abs., vol. 44, 1950, p. 8093.

CO is hydrogenated by passing a synthesis gas mixture containing CO : H_2=1 : 1 to 1 : 2 parts by volume into a synthesis catalyst bed, preheating the gas mixture entering the bed to a synthesis temperature, and adding enough H_2O to the gases passing through the catalyst bed to absorb the exothermic heat of the synthesis reaction by evaporation of the H_2O. When the process is operated with an Fe catalyst and a synthesis gas pressure between 20 and 30 atm. with a synthesis gas composed of approximately equal portions of CO and H_2 and a temperature of about 240° in the catalyst bed, the following equation corresponds very closely to the type of products made: 45 CO+48 H_2=3 C_8H_{16}+C_3H_6+3 CH_4+15 CO_2+15 H_2O. When a Co catalyst and a synthesis gas pressure of approximately 10–15 atm. are used at a temperature of about 200° with a synthesis gas composed of about 1.75 parts H_2 : 1 part CO, the following products are formed: 40 CO+68 H_2=$C_{20}H_{42}$+C_8H_{18}+C_3H_8+3 CH_4+6 CO_2+28 H_2O. With the Fe catalyst approximately 62 B. t. u. are evolved per cu. ft. of gas; with the Co catalyst, 67 B. t. u. per cu. ft. Not more than 1% of liquid H_2O should leave the catalyst bed with the reaction products.

Power-Gas Corp., Ltd. *See* abs. **886.**

2715. Pranschke, A. (Braunkohle-Benzin, A.-G.). [Deacidification of Products Synthesized From Carbon Monoxide and Hydrogen.] German Patent 716,836, Jan. 8, 1942; appl. B 179,863, filed Sept. 9. 1937 (*Cl. 23 b–1.05*). Chem. Abs., vol. 38, 1944, p. 2478.

Fractions b. 175°–320° are treated at 120°–150° with masses containing Fe_2O_3 or $Fe(OH)_3$. The masses are regenerated by treatment with steam or hot H_2O at about 175° C.

Pratt, R. S. *See* abs. **195, 2014.**

Prickett, T. B. *See* abs. **1096.**

Pring, P. *See* abs. **3938, 3939.**

2716. Process Management Co., Inc. [Liquid Hydrocarbons.] French Patent 834,686, Nov. 29, 1938. Chem. Abs., vol. 33, 1939, p. 4011.

Normally liquid hydrocarbons obtained by synthesis from CO and H_2 and containing constituents forming a motor fuel, are mixed with normally gaseous hydrocarbons and are also capable, by polymerization, of giving normally liquid products. The mixture is maintained at a high temperature to form a motor fuel having a high antiknock value. Describes apparatus.

2717. ———. Motor Fuels. British Patent 513,674, Oct. 19, 1939; appl. filed Jan. 5, 1938. Chem. Abs., vol. 35, 1941, p. 2303.

In producing hydrocarbon motor fuels by causing CO and H_2 to react to produce normally liquid hydrocarbons including motor fuel constituents and normally gaseous hydrocarbons, the normally liquid hydrocarbons thus obtained are admixed with normally gaseous hydrocarbons containing 2, 3, or 4 C atoms per mol., and the temperature of the resulting mixture is maintained at 750°–1,500° F. to effect conversion thereof to motor fuel of high antiknock value.

———. *See* abs. **51, 57.**

2718. Prudhomme, E. A. Catalytic Production of Liquid Fuels From Water Gas. British Patent 238,931, May 23, 1924. Chem. Abs., vol. 20, 1926, p. 2063.

In producing a liquid fuel generally suitable for the same uses as gasoline, water gas or Dowson gas is mixed with a gas rich in hydrocarbons, especially those of the C_2H_2 series, and the mixture is passed first over a hydrogenation catalyst, then over a dehydrogenation catalyst, and finally over catalysts to effect polymerization of the C_2H_2 hydrocarbons. Numerous details specified.

2719. ——— (L. H. Roman). Formaldehyde. United States Patent 2,000,096, May 7, 1935; appl. filed July 20, 1931, Serial No. 551,976. Chem. Abs., vol. 29, 1935, p. 4029.

Current of gas containing essentially H_2 and CO is passed, at a temperature of 130°–200°, through a hydrogenation catalyst of the Ni group of the periodic system until the catalyst becomes polarized by polymerization of aldehydes formed; depolarization is effected with a current of N_2.

2720. ———. [Hydrocarbon Synthesis.] Austrian Patent 109,706, 1925. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 167; Chem. Zentralb., 1928, II, p. 1959.

See British Patent 238,931 (abs. **2718**).

2721. ———. [Liquid Fuel.] French Patent 601,163, Oct. 21, 1924. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 167; Chem. Zentralb., 1926, I, p. 3196.

CO+H_2 is first passed through glowing coke and then after purifying used for the synthesis.

See also British Patent 238,931 (abs. **2718**).

2722. ———. [Liquid, Petroleumlike Fuel.] French Patent 554,529, June 12, 1923; appl. filed July 28, 1922. Chem. Zentralb., 1924, I, p. 605.

Mixture of CO and H_2, after removal of CO_2 by washing with K_2CO_3, is passed over a Ni catalyst on pumice at 180°–250°. By using a mixture of 3 vol. H_2 to 1 vol. CO, almost pure CH_4 is obtained. The CH_4 with or without addition of CO and H_2 is passed over a catalyst of BF_3, colloidal Pd, $SbCl_3$, and $AlCl_3$. The liquid obtained thus contains toluol, xylol, cyclohexane, and heptane. If the CH_4 is passed through a tube heated to 390° over a Ni or V catalyst, a mixture of C_2H_2 and H_2 is obtained, and over a Ni, Co, or Fe catalyst at 200°–300° a petroleum liquid distilling mostly up to 150°.

2723. ———. Regenerating Metal Catalysts Contaminated With Sulfur. United States Patent 1,640,668, Aug. 30, 1927. Chem. Abs., vol. 21, 1927, p. 3431.

S-contaminated catalysts, for example, those used in synthesis of light hydrocarbons, are treated with HOAc, formic acid, or other suitable organic acid to eliminate the S as H_2S.

Pryde, D. R. *See* abs. **38.**

2724. Puig, J. J., and Sunen-Beneded, R. [Hydrocarbons and Alcohols.] French Patent 784,742, July 23, 1935. Chem. Abs., vol. 30, 1936, p. 484.

Alkali, alkaline earth, or earth carbonate or bicarbonate is partly reduced by a metal or carbonaceous reducing agent to obtain a gas rich in CO, which is caused to react with H_2 in the presence of catalysts to produce hydrocarbons or alcohols as desired. The H_2 may be obtained by reduction of steam with a part of the CO formed.

2725. PUKIREW, A. G. [Refining Methanol.] Russian Patent 58,217, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 219.

Refining by double fractionation distillation.

2726. PUNGS, W. (I. G. Farbenindustrie A. G.). Cleansing and Emulsifying Agent. United States Patent 1,757,441, May 6, 1930. Chem. Abs., vol. 24, 1930, p. 3332.

Describes composition containing oily hydrogenation products of oxides of C substantially insoluble in H_2O, comprising mainly O-containing organic compounds, a soap, an aliphatic alcohol of low boiling point such as EtOH, and a hydrocarbon b. $>20°$.

2727. ——— (I. G. Farbenindustrie A. G.). Oxidation Products of Paraffin Wax. German Patent 467,930, Aug. 30, 1922. Chem. Abs., vol. 23, 1929, p. 1748.

Oxygenated products obtained by oxidizing solid hydrocarbons, for example, paraffin wax, with gaseous oxidants are separated from unaltered hydrocarbon by careful warming so that the oxidation products separate in liquid form from the solid hydrocarbon. Gives example.

2728. ——— (I. G. Farbenindustrie A. G.). [Oxygenated Organic Compounds.] German Patent 489,280, Jan. 29, 1924. Chem. Abs., vol. 24, 1930, p. 2137.

Oxygenated organic compounds prepared by the catalytic hydrogenation of oxides of C are improved in color and smell by treatment in the liquid state with H_2 at a temperature low enough to avoid decomposition and in the presence of a hydrogenating catalyst. The products to be treated may be preliminarily distilled and treated with an adsorbent. Gives examples.

2729. PUSTOVOIT, B. V. [Ammonia Synthesis.] Russian Patent 44,240, Sept. 30, 1935. Chem. Abs., vol. 32, 1938, p. 3102.

In the synthesis of NH_3 the heat of reaction is removed by introducing into the apparatus an amount of gases only a part of which passes through the catalyst tubes.

2730. PUTNEY, D. H. (Stratford Engineering Corp.). Gas-Liquid Contact Apparatus. United States Patent 2,579,203, Dec. 18, 1951; appl. filed Nov. 10, 1948, Serial No. 59,274; 2 claims (*Cl. 261–3*). Chem. Abs., vol. 46, 1952, p. 2783.

Apparatus used for the synthesis of hydrocarbons from CO and H_2 in the presence of pulverized Fe catalyst suspended in heavy hydrocarbon oil.

2731. PYZEL, E. (Shell Development Co.). Catalytic Converter Suitable for Use in the Synthesis of Ammonia, and Methanol. United States Patent 2,006,078, June 25, 1935. Chem. Abs., vol. 29, 1935, p. 5316.

Apparatus suitable for use under high pressure comprises a converter shell containing at least 3 alternate layers of coarsely divided uniform catalyst and finely divided uniform catalyst of the same chemical composition arranged transverse to the gas flow through the converter and in contact with each other.

2732. PYZEL, E. D. (Shell Development Co.). Hydrogenation of Olefinic Polymers. United States Patent 2,147,268, Feb. 14, 1939. Chem. Abs., vol. 33, 1939, p. 3810.

Multistage continuous process for effecting the catalytic hydrogenation of an olefin-polymer material to the corresponding saturated material by reaction with free H_2 in the presence of an active hydrogenation catalyst when the polymer material contains more than a critical concentration of a catalyst-poisoning impurity capable of poisoning the hydrogenation catalyst used, which comprises passing the polymer material together with less than a stoichiometrical amount of free H_2 into contact with the hydrogenation catalyst in the 1st stage under such conditions that only a part of the polymer material is hydrogenated, separating normally gaseous constituents from the treated material leaving the first hydrogenation stage, and then passing the partly hydrogenated material, which has been substantially freed of catalyst-poisoning impurities by treatment in the 1st hydrogenation stage, together with more than a stoichiometrical amount of free H_2 into contact under hydrogenation conditions with the hydrogenation catalyst in a subsequent hydrogenation stage, whereby substantially complete hydrogenation of the polymer material is effected with substantially no decrease in activity of the catalyst in any hydrogenation stage subsequent to the first. Describes arrangement of apparatus.

2733. PYZEL, R. (M. W. Kellogg Co.). Synthesis of Organic Compounds. United States Patent 2,596,434, May 13, 1952; appl. filed Aug. 20, 1947, Serial No. 769,568; 3 claims (*Cl. 260–449.6*).

In a Fischer-Tropsch synthesis process wherein synthesis gas is passed upward through a suspended finely divided hydrogenation catalyst, a reaction effluent is cooled and condensed to form a liquid phase comprising relatively high boiling and relatively low boiling organic compounds. This liquid phase is stripped of the organic compounds boiling below the initial boiling point of the cooling medium. A small part (about 5 vol. %) of the stripped liquid phase is fractionated to remove the organic compounds boiling above the end boiling point of the cooling medium. The low-boiling portion of the fractionated liquid phase is combined with stripped liquid and the mixture injected into the catalyst as a cooling medium.

PYZHEV, V. M. *See* abs. **3735.**

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2734. RADTKE, M. (Koppers Co.). Gases for Hydrocarbon Synthesis. United States Patent 2,266,989, Dec. 23, 1941; appl. filed Sept. 30, 1938, Serial No. 232,476; in Germany, Oct. 1, 1937; 1 claim (*Cl. 48–75*). Chem. Abs., vol. 36, 1942, p. 2393.

Describes apparatus for producing gases containing CO and H_2 in the proportions of about 1:1–2 vols., respectively, comprising a gas heater having a checkerbrick section side by side with an unobstructed checkerless combustion section and connected at their tops for flow of combustion gases up through the combustion section and down through the checkerbrick section and reactant gas reversely; waste-gas offtake means for offtake of waste combustion gases from the base of the checkerbrick section; inlet means for introducing gas to be treated into the base of the checkerbrick section; partial waste-gas-withdrawal means for withdrawing part of the waste gas from the waste gas-offtake means; a cooler, a pressure washer, and a storage chamber, connected in series with the partial waste-gas-withdrawal means for recovery and storage of CO_2 from the part of the waste combustion gas withdrawn from

the waste-gas-offtake means; adjustable means for introducing CO_2 gas from the storage means into the inlet means for introducing gas to be reacted into the base of the checkerbrick section; and means for withdrawing the reacted gas from the lower part of the checkerless combustion section.

2735. ——— (Koppers Co.). Water Gas. United States Patent 2,175,613, Oct. 10, 1939; appl. filed Mar. 11, 1937, Serial No. 130,354; in Germany, Mar. 10, 1936; 3 claims. (*Cl. 48–202*). Chem. Abs., vol. 34, 1940, p. 874.

Describes arrangement of apparatus and gives a process for the continuous production, from distillable bituminous fuel, of water gas virtually free from hydrocarbons from subsequent synthesis to hydrocarbons for motor fuel. A gaseous heat carrier comprising a highly heated water gas and steam mixture in cycle is circulated through a gasification step. The distillable fuel is distilled by the heat of the gaseous heat carrier to liberate hydrocarbons from the fuel and is also caused to react with the steam in the heat carrier to form water gas. From the gasification step the carrier goes through a reheating step in which the liberated hydrocarbons in the carrier are caused to react to water gas. The reheated carrier returns to the gasification step. The newly generated water gas flows through the gasification step, together with the heat carrier and with the hydrocarbons distilled off in the gasification step. The final and product water gas is withdrawn from the reheated carrier before it reenters the gasification step.

2736. ——— (Koppers Co.). Water Gas. United States Patent 2,204,001, June 11, 1940; appl. filed Sept. 30, 1937, Serial No. 166,486; in Germany, Oct. 1, 1936; 3 claims (*Cl. 48–207*). Chem. Zentralb., 1941, I, p. 988; Chem. Abs., vol. 34, 1940, p. 7092.

Describes apparatus and gives a method for generating water gas containing CO and H_2 in the ratio 1 : 2 from solid carbonaceous fuel poor in hydrocarbons of tarry constituents in a water-gas generator. Fuel is supplied at the top, and ash is discharged at the bottom of the bed; air is blasted upward from the bottom through the ash in the lower zone of the fuel bed, and the resultant gases are withdrawn from the top. Alternately, steam is passed down through the fuel bed, and water gas generated is withdrawn through the ash in the lower zone of the bed; concurrently, secondary steam is introduced into the ash in the lower zone to convert part of the CO of the downrun water gas to CO_2 in the presence of minerals in the ash. CO : H_2 mixture in the proportion of 1 : 2 is produced in the final downrun water gas, leaving the ash zone in the lower part of the fuel bed.

2737. RAMAGE, A. S. Aromatic Hydrocarbons. British Patent 335,353, Sept. 3, 1929. Chem. Abs., vol. 25, 1931, p. 1259.

Hydrocarbons such as benzene, toluene, and xylene are produced by contact of a mixture containing unsaturated hydrocarbons, such as may be obtained by dehydrogenating light weathered products and casinghead gasoline vapors over ferric or cupric oxide, with CO and H_2, suitable water gas, with metallic Fe, at atmospheric pressure and a temperature of about 540°–815°, the catalyst being maintained active by the presence of an excess of the hydrocarbon and the reacting gases being, if necessary, freed from saturated hydrocarbons by passage over cupric or ferric oxide. Describes arrangement of apparatus.

2738. ——— (Coals & Chemicals, Ltd.). Aromatic Hydrocarbons From Olefinic Gases. United States Patent 1,812,372, June 30, 1931; appl. filed May 18, 1928, Serial No. 278,916. Chem. Abs., vol. 25, 1931, p. 4889.

See British patent 335,353 (abs. **2737**).

2739. ——— (Coals & Chemicals, Ltd.). Converting Olefinic Hydrocarbons Into Aromatic Hydrocarbons. United States Patent 2,242,836, May 20, 1941; appl. filed June 7, 1937, Serial No. 146,895 (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 5509.

Describes arrangement of apparatus and a process of converting hydrocarbons of the olefinic series into hydrocarbons of the aromatic series and low-boiling alcohols, which involves successive dehydrogenation of the olefinic hydrocarbons in the vapor phase by treating them, at substantially atmospheric pressure and at a temperature of about 1,100°–1,300° F., with steam in an amount equal to about 10–30% of that of such olefinic vapors and with CO in an amount approximately equal to the combined amounts of such vapors and steam in the presence of finely divided Fe.

2740. ——— (Merlin Wiley and Ora L. Smith as trustees). Vapor-Phase Treatment of Unsaturated Hydrocarbons to Produce Alcohols. United States Patent 2,035,189, Mar. 24, 1936. Chem. Abs., vol. 30, 1936, p. 2985.

CO_2 is introduced into hydrocarbon vapors, and the resulting mixture is heated to about 540°–815° in the presence of metallic Fe and steam, at substantially atmospheric pressure. Describes arrangement of apparatus.

2741. RANCHON, F. L. [Dry Distillation of Wood.] Norwegian Patent 77,199, 1950. Chem. Zentralb., 1951, II, p. 1837.

Predried wood is heated so rapidly that the generated organic vapors attain temperatures of 800°–900° and are cracked into gaseous fractions. The H_2 contained therein can be used for increasing the cracking or for gasification of the coke. The gases are either detoxicated by methanizing to CO and CO_2 contained therein or the steam can be employed for converting the CO into H_2 and CO_2. The gases are then suitable for synthesis gas for MeOH synthesis or Fischer-Tropsch hydrocarbon synthesis.

2742. RANEY, M. [Catalysts.] French Patent 729,357, Jan. 7, 1932. Chem. Abs., vol. 26, 1932, p. 6171.

Catalyst such as Ni for the hydrogenation of oils, fats, and waxes is allowed with a noncatalyst metal such as Al, the alloy is treated with NaOH, in amount insufficient to remove all the Al, and the product is washed and treated with H_2 under raised temperature and pressure.

2743. ———. Catalytic Material Suitable for Use in Hydrogenation of Oils. United States Patent 1,915,473, June 27, 1933. Chem. Abs., vol. 27, 1933, p. 4362.

Ni is alloyed with Al, and the alloy is powdered, treated with heated H_2O or steam under pressure to produce a voluminous catalyzer, heated in air to drive off substantially all H_2O, and then heated in H_2.

See also French Patent 729,357 (abs. **2742**).

2744. ———. Catalytic Nickel. United States Patent 1,563,587, Dec. 1, 1925. Chem. Abs., vol. 20, 1926, p. 515.

Pulverized alloy of Ni 50 and Si 50% is treated with NaOH to convert the Si into Na silicate, and the finely divided catalytic material is separated from the solution. It is suitable for use in hydrogenating oils.

2745. ———. Finely Divided Nickel. United States Patent 1,628,190, May 10, 1927. Chem. Abs., vol. 21, 1927, p. 2116.

In preparing a catalytic material, Ni is alloyed with Al and the Al is then dissolved from the alloy, for example, by NaOH.

RAPASKY, F. *See* abs. **2393**.

2746. RATCLIFF, W. F. (Standard Oil Development Co.). Production of Alcohols and Gasoline by the Oxo Process. United States Patent 2,623,074, Dec. 23, 1952; appl. filed Aug. 19, 1948, Serial No. 45,038; 9 claims (*Cl. 260–638*).

Process is given for production of high antiknock gasoline. CO, H_2, and olefins are reacted in presence of a carbonylation catalyst at 250°–450° F. and pressures of 1,500–4,500 p. s. i. g. The bottoms from this carbonylation process, after the alcohols have been removed by distillation, are used as feed stock to a catalytic reforming process. The bottoms represent 20–30% of the total hydrogenation product. Exceptionally high-octane motor fuel consisting almost entirely of olefinic material and containing <0.1% O is obtained. 2 foreign patents and 5 United States patents cited.

RAY, E. C. *See* abs. **2695**.

2747. RAY, G. C. (Phillips Petroleum Co.). Hydrogenation of Acetylene. United States Patent Appl. 32,541, no date. Official Gaz., vol. 652, 1951, p. 891; Chem. Abs., vol. 47, 1953, p. 1725.

Effluent from hydrocarbon cracking is passed over a catalyst consisting of at least 1 of the group of a Mo, a Ni, or a W sulfide at 150°–350°, 1–50 atm. pressure, and space velocity of 300–500 vol. gas per catalyst vol. per hr., to selectively hydrogenate the 5% or less of C_2H_2 present.

2748. REBS, H. (K. Herberts & Co.). [Varnishes, Air-Drying Lacquers, and Paints.] German Patent 742,666, Oct. 21, 1943 (*Cl. 22 h–3*). Chem. Abs., vol. 40, 1946, p. 478.

Distillation residues of oxidation products obtained when CO is hydrogenated by the Fischer-Tropsch method are mixed with siccatives and used in the production of varnishes.

RECONSTRUCTION FINANCE CORP. *See* abs. **169**.

2749. REDCAY, A. K. (Standard Catalytic Co.). Temperature Control in Fischer Synthesis. United States Patent 2,406,851, Sept. 3, 1946; appl. filed Aug. 15, 1941, Serial No. 406,947; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 40, 1946, p. 7226.

To maintain temperature control in exothermic reactions, such as Fischer-Tropsch synthesis, a cooling liquid is injected into the reaction zone at a plurality of stages. A portion of the product may be recycled, the fluid catalyst may be recirculated, or another liquid such as H_2O may be introduced into the reaction zone. In the Fischer synthesis the temperature is controlled within 10° in the reaction zone by recirculating a suspended powdered catalyst and injecting a cooling fluid at a number of stages. Higher boiling constituents of the hydrocarbons boiling in the motor-fuel range are returned to the reaction chamber where they vaporize almost completely at the temperature prevailing at their point of entry.

2750. REED, F. C. Carbon Black and Carbon Monoxide–Hydrogen Gas Mixtures From Natural Gas, etc. United States Patent 2,173,695, Sept. 19, 1939; appl. filed July 9, 1934, Serial No. 734,435; 8 claims (*Cl. 23–212*). Chem. Abs., vol. 34, 1940, p. 597.

Describes arrangement of apparatus and a process that comprises alternating the periods of combustion and dissociation of hydrocarbons within closed retorts, separating CO_2 from the gases of combustion, subjecting hydrocarbons to dissociating temperatures during said dissociating periods for producing a gas mixture of CH_4 and H_2, utilizing said CO_2 to cool the products of dissociation by heat exchange therewith, catalyzing any unsaturated compounds present to CH_4, then adding said CO_2 to said CH_4 and H_2 and subjecting the resultant mixture to high temperatures to produce said CO_2–H_2 gas mixtures.

2751. ———. Catalytic Production of Compounds Such as Alcohols, Aldehydes, and Organic Acids. United States Patent 1,959,219, May 15, 1934; appl. filed Sept. 8, 1932, Serial No. 632,199 (*Cl. 260–116*). Chem. Abs., vol. 28, 1934, p. 4430.

H_2 and an oxide of C in suitable proportions are passed over a suitable catalyst at an elevated temperature and pressure, compounds formed are removed at a lower temperature, a portion of the residual gases is again passed over the same catalyst and another portion of the residual gases is similarly passed over a 2d catalyst, and compounds formed by each such treatment are removed at lower temperatures. Describes apparatus.

2752. REED, H. C., AND BERG, C. H. O. (Union Oil Co. of California). Hydrogen. United States Patent 2,635,947, Apr. 21, 1953. Chem. Abs., vol. 47, 1953, p. 6637.

H is produced in a 4-stage process, which comprises: (1) Coking a hydrocarbon oil in the presence of fluidized particles of a higher oxide of Fe at 371°–649° to form a distillate and a deposit of coke on the particles; (2) separating the particles from the distillate and, while still in a fluidized state at about 538°–816°, treating them with a gas containing O_2 to burn the C and to heat and reduce the particles of Fe oxide with the formation of a gas containing CO and coke-free, reduced Fe-containing particles; (3) fluidizing the particles thus obtained in steam at 427°–816° to form H_2 and reform the higher oxide of Fe; and (4) separating the H_2 and recirculating the oxide to treat more oil. When the process is applied to a hydrocarbon fraction with a low A. P. I. gravity and containing S compounds, Fe sulfides are formed with desulfurization of the fraction. To prevent undue concentration of Fe sulfides in the catalyst, a side stream of catalyst is removed from the H_2 generator and is oxidized in an O_2 regenerator with the formation of SO_2 and higher Fe oxides, mostly Fe_2O_3 at temperature 538°–1,093°.

2753. REED, H. C., AND BOLT, B. M. (Union Oil Co. of California). Azeotropic Distillation of Toluene. United States Patent 2,413,245, Dec. 24, 1946; appl. filed Oct. 6, 1943, Serial No. 505,150; 11 claims (*Cl. 202–42*).

Substantially pure toluene can be obtained from mixtures such as Fischer-Tropsch synthesis products by azeotropic distillation with methylethyl ketone in the presence of H_2O.

2754. REED, R. M. (Girdler Corp.). Method and Apparatus for Removing Carbon Monoxide From Gaseous Mixtures. United States Patent 2,487,981, Nov. 15, 1949; appl. filed Apr. 19, 1946, Serial No. 663,354; 6 claims (*Cl. 23–213*).

Gaseous mixture is treated with steam at a high temperature to convert part of the CO to CO_2. The CO_2 is removed at low temperature. A 2d high temperature stage converts additional CO to CO_2. The process may be used for complete removal of CO or for preparation of a synthesis gas from a mixture high in CO for gasoline or methanol synthesis. 1 foreign patent and 2 United States patents cited.

2755. REES, H. V. (Texaco Development Corp.). Process for Synthesis of Hydrocarbons and the Like. United States Patent 2,521,538, Sept. 5, 1950; appl. filed June 20, 1945, Serial No. 600,473; 3 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 11067.

Thin continuous layer of catalyst, 1/64 in. to 1.0 in. in thickness, lies on a porous surface through which the reactant gases diffuse by application of pressure differential great enough to cause diffusion without fracture or channeling of the catalyst. A cooling fluid

is applied to either the exposed surface of the catalyst layer or to the surface of the supporting member opposite from that upon which the catalyst layer rests and out of contact with the catalyst. 1 foreign patent and 10 United States patents cited.

2756. ——— (Texaco Development Corp.). Synthesis Gas. United States Patent 2,552,737, May 15, 1951; appl. filed May 25, 1945, Serial No. 595,710; 6 claims (*Cl. 48–214*). Chem. Abs., vol. 45, 1951, p. 6824.

Mixture of CO and H_2 for synthesis purposes is made from a hydrocarbon feed gas by mixing a portion of the hydrocarbon gas with sufficient O_2 or O_2-containing gas for substantially complete combustion to CO_2 and H_2O; this combustion takes place at the internal surface of the porous refractory tubes and heats them to incandescence. The balance of the hydrocarbon gas is passed through the tubes, in intimate mixture with the products of combustion, so that the hydrocarbons are caused to react with the combustion products to give a CO and H_2 mixture. Steam may be added if desired. This process offers a simple and effective means for converting hydrocarbons into synthesis gas at temperatures of 3,000°–3,600° F. and higher. When a Fe catalyst is used in the synthesis process, the excess CO_2 may be separated and returned to the refractory tube; other tail gases may also be recycled through the process.

2757. Rees, H. V., and Ludeman, C. G. (Texaco Development Corp.). Manufacture of Hydrocarbons and the Like. United States Patent 2,486,879, Nov. 1, 1949; appl. filed Mar. 31, 1945, Serial No. 586,004; 9 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 1675.

Stream of gaseous hydrocarbons, mainly CH_4 is split into streams of approximately 6.29 and 93.71 mol. %. The minor stream is passed to a combustion zone at a rate of about 12.32 lb. per hr. O_2 and CO_2 recycled from a later stage of the process are supplied. Combustion forms CO_2 and H_2O at a temperature not exceeding 3,500° F. The gas mixture is passed to a reversion zone to which is supplied the major hydrocarbon stream at about 183.64 lb. per hr. Synthesis gas is formed. The synthesis gas is passed into contact with an Fe catalyst for production of products having at least 2 C atoms per molecule. CO_2 is stripped from the tail gas and recycled. Only enough CO_2 to effect quenching is returned to the combustion zone. The tail gas is divided into 2 streams, 1 of which is discharged and the other is recycled. The portion discharged keeps the accumulation of N_2 below 20 mol. % of the synthesis gas passing to the converter. The exothermic heat generated in the 1 zone balances the endothermic heat of reaction in the other zone. 2 literature refs. and 12 United States patents cited.

Reichart, J. *See* abs. **2633.**

2758. Reichl, E. H. (Stanolind Oil & Gas Co.). Catalytic Reactor. United States Patent 2,585,274, Feb. 12, 1952; appl. filed Dec. 22, 1944, Serial No. 569,413; 1 claim (*Cl. 23–288*).

Various structural and operative details are presented. The major objects of the invention are the removal of heat and the control of temperature in the catalytic reactor. In general the objects are attained by employing a fluidized catalyst reaction system and a plurality of bayonet-type cooling tubes extending into the reaction zone.

2759. ——— (Stanolind Oil & Gas Co.). Process for the Manufacture of Synthesis Gases. United States Patent 2,529,630, Nov. 14, 1950; appl. filed Apr. 25, 1947, Serial No. 743,889; 1 claim (*Cl. 48–215*). Chem. Abs., vol. 45, 1951, p. 1327.

Method for producing synthesis gas consists of preheating H_2O vapor, CO_2, and CH_4 in the presence of a catalyst, and then conducting the hot gas mixture thus formed to a combustion zone where O_2 and more CH_4 are added so as to achieve a high enough temperature to cause a substantially complete conversion of CH_4 and CO_2 to H_2 and CO. 6 United States patents cited.

2760. Reichl, E. H., and Safford, R. V. (Pittsburgh Consolidation Coal Co.). Gasification of Carbonaceous Solids. British Patent 658,542, Oct. 10, 1951. Chem. Abs., vol. 46, 1952, p. 4203.

Carbonaceous solids are completely gasified to yield a H_2–CO mixture suitable for use as synthesis gas in the Fischer-Tropsch process. In the 1st stage, pressurized steam from the product-gas heat exchanger is used to fluidize a bed of low-temperature coke, which is kept at 1,400°–1,800° F. by partially burning in a combustion zone a portion of the coke with air, also preheated by heat exchange. The unburned coke is removed from the flue gas by an internal cyclone and returned to the fluidized bed. In the 2d stage, the temperature of the heated coke is further raised by partly burning with O_2 in a powdered-fuel burner. The coke is finally gasified with the heated steam from the fluidizer. The temperature of the burner is maintained at 1,900°–2,500° F. for the nonslagging operation and 2,500°–3,000° F. for slagging.

2761. Reichle, L., and Wegerich, A. (Badische Anilin- u. Soda-Fabrik). [Production of Isobutyl Alcohol.] German Patent 824,793, Dec. 13, 1951; appl. filed Dec. 10, 1949 (*Cl. 12 o*). Chem. Zentralb., vol. 123, 1952, p. 4529.

CO is reacted with H_2 at raised temperature and under pressure. The gases and vapors issuing from the reaction vessel are dissociated without pressure release in a distillation column. As reflux, a condensate is used, which is separated from the gases and vapors without expansion. Further, a condensate obtained from the gases and vapors leaving the distillation column, together with the uncondensed portions still remaining, is wholly or partly returned to the reaction chamber.

Reid, J. A. *See* abs. **121.**

Reid, L. S. *See* abs. **1116.**

2762. Reiff, O. M., Andress, H. J., Jr., and Kozacik, A. P. (Socony-Vacuum Oil Co., Inc.). Synthetic Lubricants. United States Patent 2,500,203, Mar. 14, 1950; appl. filed May 11, 1949, Serial No. 92,744; 17 claims (*Cl. 260–666*).

Preparation is given of a viscous oil with low pour point and cloud point. A mono-olefin, 8–18 C atoms per molecule, and a vinyl aromatic compound are heated with a catalyst consisting of silica and an amphoteric metal oxide until condensation. The temperature is 300°–600° F. The charge is 1–2 molar proportions of mono-olefin per molecule vinyl aromatic compound. The process may be applied to mixtures from cracking of paraffin waxes and paraffin products from the Fischer-Tropsch synthesis. 4 United States patents cited.

Reisinger, —. *See* abs. **3901, 3902, 3904, 3905.**

2763. Reisinger, —, Wenzel, —, and Wintzer, —. (I. G. Farbenindustrie A. G.). [Process for Converting Carbon Monoxide With Hydrogen.] German Patent Appl. I 70,282, OZ 12,948, filed Aug. 20, 1941 (*Cl. IV d–12 o*). TOM Reel 19, item 136, frames 1,596–1,607; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, ch. 100, 1948, p. 77.

Catalytic conversion of CO with H_2 to oxygenated organic products and hydrocarbons is carried out at moderately increased temperatures in the presence of multibranched hydrocarbons, such as those obtained by the cracking of kogasin or by the extraction of the

high-boiling fraction of the synthesis product. The yield of oxygenated compounds can be greatly increased by adding olefins to the mixture. They appear to enter into indirect reaction with the CO. When operating by stages, only the higher boiling fractions are removed from the reaction mixture of the preceding step, and the unconverted gases, together with the low-boiling fractions, are conducted to the next step. The hydrocarbons with 3 and 4 C's and the benzine hydrocarbons are left in the gas for further treatment.

2764. REITLINGER, O. Catalytic Contact Masses. British Patent 640,455; appl. filed Feb. 20, 1947. British Abs., 1950, B, I, p. 1013.

Oxidation catalyst suitable for use at atmospheric pressure and relatively high-space velocities is prepared by applying a metal bonding substance (Fe_2O_3) to a preferably porous carrier (nonmetal, metal without reducing action on the catalyst, or powdered catalyst), drying in air or O_2 and HCl at 200°–750° and giving a number of coats of a powdered catalyst, for example, Mn_2O_3, Cr_2O_3 (Fe_2O_3), in the presence of H_2O and/or an organic liquid (limited to the amount completely adsorbed by the metal bonding substance without affecting packing of the powder) until the carrier is completely covered by layers of firmly held catalyst. Examples are given, including one of similarly prepared Fischer-Tropsch catalysts showing markedly increased activity at atmospheric pressure.

2765. ———. Structure of Contact Masses. United States Patent 2,488,560, Nov. 22, 1949; appl. filed Nov. 25, 1946, Serial No. 712,047; 38 claims (*Cl. 252–472*). Chem. Abs., vol. 44, 1950, p. 1628.

Adhesive property of the catalyst support is increased by a pretreatment in which it is impregnated with hydrophilic material or an intermediate layer of catalytic material is precipitated upon the support. The impregnating ground layer and the surface layer may consist of ferric oxide or one or both layers may be another metal oxide. The catalytic material adheres more firmly and more uniformly than when impregnation alone is used. The efficiency of the catalyst is controlled by the size of the particles of catalytic powder, by the thickness of the outer layer formed by this powder, and by the size of the grains of carrier material. Example: Pumice, 20- to 60-mesh, stood in ferric chloride solution for 24 hr. It is separated and dried at 180° C. The grains are filled into a tube through which gaseous ammonia is passed slowly for 1 hr. Then the grains are brought into concentrated ammonia and left for 24 hr. The aqueous ammonia is decanted and the grains washed until red litmus remains red and the H_2O suspended ferric hydroxide precipitate has been removed. The grains are dried at 200° C. and filled into a reactor tube and subjected, at 490° C. for 2 hr., to action of a gas stream 10 parts air and 4 parts by volume of HCl, space velocity 3.25 per min. After cooling, the impregnated grains are shaken with ferric oxide in ratio 60 parts grains and 40 parts ferric oxide, 95% 325-mesh. The powder is gradually added to the grains in a humid atmosphere. The grains absorb some H_2O and hold the ferric oxide firmly upon their surface. 145.5 gm. of catalyst contained 58% impregnated pumice grains, 39% ferric oxide in powder form, and 3% H_2O. 5 United States patents cited.

2766. REITSTÖTTER, —. (Metallgesellschaft A. G.). [Process for the Recovery of Alcohols.] German Patent Appl. M 147,073. PA 98,309, filed Feb. 13, 1940 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 310–314; PB 83,253.

In separating mixtures of primary aliphatic alcohols and hydrocarbons obtained from the Fischer-Tropsch synthesis, there is added an excess, preferably up to 5 times the amount of alcohols in the mixture, of dehydrated $CaCl_2$, which forms crystallized addition products of the alcohols, from which the hydrocarbons can be separated by means of solvents, by centrifuging, or by filtration. Example: 100 parts of a mixture, obtained by the hydrogenation of CO at temp. >220° and pressure >15 atm. in presence of a Co catalyst and consisting of 40% alcohols and 60% hydrocarbons, are stirred with 200 gm. of powdered, dehydrated $CaCl_2$ and allowed to stand for 5 hr. After the portion b. >300° is separated and the temperature brought down to 45°, 50 parts of the original raw material is added and the crystallized addition product separated by centrifuging. The alcohols are then recovered therefrom by washing in an equal amount of warm H_2O. A yield of 38 parts of alcohol having an OH number of 230 is obtained.

2767. REITSTÖTTER, J. [Carboxylic Acids.] German Patent Appl. M 134,467, no date (*Cl. 12 o–11*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 267.

Aliphatic carboxylic acids are made by gasifying fuels, hydrogenating the products, and oxidizing.

2768. ———. [Carboxylic Acids.] German Patent Appl. M 158,940, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 281.

Aliphatic carboxylic acids are obtained by oxidation of hydrocarbon mixtures from the hydrogenation of CO and fractionation of the hydrogenation mixture. Mixtures are used which b. 250°–400°. The oxidation temperature is about 115°.

2769. ———. [Fatty Acids.] German Patent Appl. M 132,610, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 266.

Fatty acids are mode from thep roducts of CO hydrogenation, particularly from hydrocarbons by oxidation with air or O_2 in the presence of catalysts at 60°–160°.

2770. ———. [Reduction of High-Molecular Hydrocarbons.] German Patent Appl. M 140,004, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 270.

Hydrocarbons b. 300°–420° are obtained from high-molecular hydrocarbons, such as those from the hydrogenation of CO, by cracking distillation, if desired, under addition of cracking agents, in an atmosphere of H_2.

2771. REPPE, W., AND MAGIN, A. Ketones. United States Patent 2,562,393, July 31, 1951. Chem. Abs., vol. 46, 1952, p. 2566.

Hydrocarbons or functionally substituted compounds containing an acetylenic linkage are treated with CO and H_2O in the presence of an alkali metal-Ni cyanide catalyst, for example, $K_2Ni(CN)_4$ (I) at 60°–200° and at least under 10 atm. pressure. At 60°–100°, insoluble polyketones and poly (keto carboxylic acids) (II) are obtained, while at 100°–200°, the primary products are low molecular weight and include monoketones and monocarboxylic and dicarboxylic acids; in both cases, cyclic saturated and unsaturated ketones are formed. A preferred reaction consists of charging C_2H_2 10 gm. and CO 10 atm. at room temperature to a vessel containing (I) 240 and H_2O 1,200 gm. and heating 40 hr. at 100°; equimolar amounts of C_2H_2 and CO are added to maintain the pressure at 25 atm. The filtrate from the resulting mixture may be extracted with Et_2O to give the low-molecular products; the residue consists mainly of the K salts of (II), from which the free acids are obtained by treatment with H_2SO_4.

REYNOLDS, B. *See* abs. **594.**

2772. RHEINMETALL-BORSIG, A. G. Werk Borsig Berlin-Tegel. Expansion Device, Particularly for Gases or Liquids Under High Pressure as Used in the

Synthetic Production of Benzine and Ammonia. British Patent 484,369, May 4, 1938. Chem. Abs., vol. 32, 1938, p. 7315.

RHENANIA-OSSAG MINERALÖLWERKE A.-G. *See* abs. **3992.**

2773. RIBLETT, E. W. (M. W. Kellogg Co.). Converting Methane and Carbon Dioxide Into Hydrogen and Carbon Monoxide. United States Patent 2,220,849, Nov. 5, 1940; appl. filed Aug. 29, 1938, Serial No. 212,702; 15 claims (*Cl. 252–53*). Chem. Zentralb., 1941, I, p. 2206; Chem. Abs., vol. 35, 1941, p. 1587.

Describes apparatus and a method of operation that involves flowing a mixture of CH_4 and CO_2 through a conversion zone where it is brought into contact, at a temperature of about 1,700°, 1st with a Co catalyst and then with a Ni catalyst, both catalysts promoting the formation of H_2 and CO and the time of contact with the Co catalyst being of sufficient length substantially to remove S and S-containing compounds from the incoming gases.

2774. ——— (Hydrocarbon Research, Inc.). Generation of Synthesis Gas. United States Patent 2,491,518, Dec. 20, 1949; appl. filed Apr. 11, 1947, Serial No. 740,836; 5 claims (*Cl. 252–373*). Chem. Abs., vol. 44, 1950, p. 2206.

Normally, gaseous hydrocarbons are reacted in vapor phase with O_2 (98% purity) in such proportions that the resulting synthesis gas contains less than 2.0% CO_2 and less than 0.2% residual hydrocarbon. The temperature is 2,100°–2,500°, pressure 200–300 p. s. i. Contact time is preferably 3–10 sec. O_2 content of the synthesis gas is rarely as much as 0.01% by volume. 2 United States patents cited.

2775. ——— (Hydrocarbon Research, Inc.). Process for Catalytic Conversion. United States Patent 2,616,914, Nov. 4, 1952; appl. filed May 11, 1946, Serial No. 669,007; 2 claims (*Cl. 260–449.6*).

Invention prevents catalyst particles from being entrained and carried out of the reaction zone by the gaseous effluent by using large catalyst particles, such as 40- to 100-mesh, mixed with smaller particles of inert material, such as sand, silica, or glass, having a smaller settling rate and adapted to assume good fluidization in the prevailing flow of reactant gases. The proportion of inert fines to catalyst particles may be 1–2 parts inert fines to 1 part catalyst, although such proportion may fall as low as 0.1 part or be as great as 5 or 10 parts per part of catalyst. The process is particularly adaptable to Fischer-Tropsch synthesis, using Fe catalyst containing 1–2% K oxide and 2–3% alumina. 10 United States patents cited.

2776. ——— (Hydrocarbon Research, Inc.). Producing Hydrocarbons by the Catalytic Reduction of Carbon Monoxide by Hydrogen. United States Patent 2,525,827, Oct. 17, 1950; appl. filed July 19, 1947, Serial No. 762,020; 6 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 334.

Stripping gas, after removing absorbed hydrocarbons from the synthesis catalyst, is passed through a conventional plant for recovering natural gasoline, and the residual gases are converted by partial oxidation to synthesis gas to be used in the reaction zone. Catalyst is removed and stripped in a separate zone with additional wet natural gas, which is treated for recovery of liquid products and then used to supplement the synthesis gas feed. 7 United States patents cited.

2777. ——— (Hydrocarbon Research, Inc.). Synthesis Gas. British Patent 646,532, Nov. 22, 1950; appl. filed in United States, Apr. 11, 1947. Petroleum, vol. 14, 1951, p. 81.

Object of this invention is the production of synthesis gas at high pressure, with efficient use of the hydrocarbon and O_2 and almost complete elimination of C formation. Normally, gaseous hydrocarbons are reacted with O_2 of 98% purity in such proportions that the resulting gas contains less than about 2% of CO_2 by volume, in a reaction zone maintained at 2,100°–2,500° F. and under a pressure of more than 200 p. s. i. The contact time is 3–10 sec. Under these conditions, the O_2 is practically all used, and unwanted side reactions with formation of C are virtually eliminated. The O_2 content in the product is rarely more than 0.01%. The reacting gases may be previously heated to about 600° F. before entering the reacting zone.

See also United States Patent 2,491,518 (abs. **2774**).

2778. ——— (M. W. Kellogg Co.). Synthesis of Liquid Hydrocarbons From Gas Mixtures Containing Carbon Monoxide and Hydrogen. United States Patent 2,250,421, July 22, 1941; appl. filed May 7, 1938, Serial No. 206,602; 15 claims (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 7155.

Describes arrangement of apparatus and a method that may involve passing CO over Ni, Co, or Fe to form the metal carbonyl, introducing the carbonyl into a body of inert liquid, such as a hydrocarbon oil, maintained at a temperature (suitably about 200°) high enough to decompose the metal carbonyl, introducing a mixture of CO and H_2 into the inert liquid in the presence of the finely divided metal formed from the carbonyl, and recovering the liquid hydrocarbons formed by fractionation of the products withdrawn.

———. *See* abs. **771, 1765, 1766, 1824, 2840.**

2779. RICARD, E. (Usines de Melle). Process of Manufacturing Formaldehyde by Electrosynthesis From Carbon Monoxide and Hydrogen. United States Patent 2,205,542, June 25, 1940; appl. filed Dec. 24, 1936, Serial No. 117,614; in France, Dec. 24, 1935; 4 claims (*Cl. 204–31*). Chem. Abs., vol. 34, 1940, p. 7187.

HCHO may be prepared by introducing CO and H_2 into an electric glow discharge zone while maintaining a gas pressure of less than 0.15 atm. A charge of 0.05–0.3 milliamps. per $cm.^3$ of cross-sectional area of the reaction tube is advantageous.

2780. RICHARDSON, R. S. (Nitrogen Engineering Corp.). Methanol. United States Patent 1,921,776, Aug. 8, 1933; appl. filed Dec. 12, 1928. Chem. Abs., vol. 27, 1933, p. 5086.

In producing MeOH by passing a gaseous mixture containing CO and H_2 under pressure over a catalyst at high temperature, the gas is introduced in predetermined amounts to separated portions of different content of the catalyst mass while maintaining a continuous circulation to effect desired temperature control. Describes apparatus.

RICHARDSON, R. W. *See* abs. **2692, 2693.**

RIDER, C. A. *See* abs. **3786.**

RINCKHOFF, J. B. *See* abs. **2782.**

RINGER, F. *See* abs. **2671.**

RITTER, G. *See* abs. **595.**

2781. RJABOW, N. N. [Removing the Heat of Reaction.] Russian Patent 58,699, no date. Kainer, p. 173.

Hot mineral oil, which has been used for removing the reaction heat, on leaving the reactor is used to evaporate the synthesis products.

2782. ROBERTS, E. S., RINCKHOFF, J. B., AND CUNNINGHAM, F. C. (Chemical Construction Corp.). Method for the Production of Water Gas. United States Patent 2,502,670, Apr. 4, 1950; appl. filed June 4, 1946, Serial No. 674,198; 4 claims (*Cl. 48–206*). Chem. Abs., vol. 44, 1950, p. 5569.

Method is given for producing N_2 free water gas from coal. The coal is reacted with steam at water-gas reaction temperatures in a gas producer to form a hot water gas consisting of H_2 and CO. Part of the hot water gas is recovered as product gas, and the rest is mixed with steam and used with movable heat-exchange solids in a gas-heating zone to bring the mixture to a water-gas reaction temperature. The hot mixture is passed to the water-gas producer. The heat-exchange solids had been heated above the desired temperature by the hot products of combustion in a solids heating zone. The partly cooled water gas is further cooled in heat exchange with preheated H_2O to generate steam. The water gas is divided into 2 streams. 1 is mixed with a portion of the generated steam and recycled through a gas-heating zone to the gas producer. The 2d stream is scrubbed and further divided into 2 streams. 1 is withdrawn as product gas. The other is mixed with preheated air, and the mixture is burned in the solids heating zone. A gas suitable for Fischer-Tropsch synthesis is produced. Describes apparatus. 2 United States patents cited.

2783. ROBERTS, G., JR. (M. W. Kellogg Co.). Apparatus for Endothermic Catalytic Reactions Such as Carbon Monoxide and Hydrogen Production From Methane, Carbon Dioxide, and Water. United States Patent 2,355,753, Aug. 15, 1944; appl. filed Mar. 20, 1940, Serial No. 324,899; 4 claims (*Cl. 23–288*). Chem. Abs., vol. 39, 1945, p. 164.

Apparatus is employed for use of a porous catalytic mass, such as one containing Ni on fire clay or alundum, at elevated temperature, such as 1,800°–2,200° F., for the production of CO and H_2 from gaseous reactants, such as CH_4, CO_2, and H_2O, and adapted to operate on alternating conversion and heat-regenerative cycles, that comprises a chamber having a contact mass in loose aggregate form disposed in the interior and openings in the side wall of the chamber for introducing a fuel gas into it, conduits imbedded in and supported by this mass in substantially horizontal planes and having apertures at suitably spaced intervals throughout their length for the introduction of the fuel gas into the mass, the ends of these conduits being abutted against the side walls of the chamber and arranged in fluid-intercommunicating relationship with the wall openings and being non-rigidly and movably associated with the wall of the chamber, so that the conduits are capable of limited movement relative to the wall without interruption of the flow of fuel gas through the conduits.

2784. ——— (M. W. Kellogg Co.). Catalyst Adapted for Use in the Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,244,573, June 3, 1941; appl. filed July 18, 1938, Serial No. 219,931; 4 claims (*Cl. 252–253*). Chem. Abs., vol. 35, 1941, p. 5660.

Method of preparing a Co-on-kieselguhr catalyst associated with a Th oxide promoter involves forming a solution of Co nitrate from HNO_3 and Co, simultaneously forming Th hydroxide by the reaction or Th sulfate with NH_3, treating Th hydroxide and HNO_3 to form Th nitrate, agitating the solution of Co nitrate and Th nitrate with kieselguhr, precipitating Co carbonate and Th carbonate from the agitated mixture upon the kieselguhr, forming a corresponding amount of KNO_3 by addition of K_2CO_3, separating the kieselguhr and Co and Th carbonates precipitated thereon, passing the KNO_3 solution to a HNO_3-recovery operation, returning the HNO_3 to the process, drying the kieselguhr-Co carbonate-Th carbonate precipitate, heating it to decompose the Th and Co carbonates to form oxides, and subjecting the mixture of oxides on the kieselguhr to reduction to reduce the Co but not the Th. Describes arrangement of apparatus.

2785. ——— (Stanolind Oil & Gas Co.). Method for Producing Reducing Gas Mixtures. United States Patent 2,625,470, Jan. 13, 1953; appl. filed Aug. 8, 1946, Serial No. 689,151; 2 claims (*Cl. 48–196*).

H_2–CO mixtures of desired ratio are obtained from hydrocarbon gases, CO_2 and steam in suitable proportions in a multistage, multitemperature, multipressure reforming system. Reforming of the hydrocarbon gases takes place in a series of stages, with each stage maintained at successively higher temperature level. The stage of maximum temperature can be located in the radiant zone of a furnace, and the prior stages of lower temperature located in the convection section of the furnace where they are heated by the hot combustion gas from the radiant zone. 13 United States patents cited.

2786. ——— (M. W. Kellogg Co.). Preparing Mixtures of Carbon Monoxide and Hydrogen Suitable for Use in Catalytic Synthesis. United States Patent 2,185,989, Jan. 2, 1940; appl. filed Aug. 19, 1938, Serial No. 225,755; 6 claims (*Cl. 23–212*). Chem. Abs., vol. 34, 1940, p. 2862.

Describes arrangement of apparatus and a method of preparing a mixture of CO and H_2 for catalytic synthesis, including the steps of desulfurizing CH_4 to remove objectionable S compounds, subjecting a CO_2-bearing gas to absorption by an absorption menstruum selective to CO_2 in an absorption zone, stripping the absorbed CO_2 from the absorption menstruum by means of the CH_4 removed from the desulfurizing zone and thereby forming a mixture of CO_2 and CH_4, generating the desired synthesis gas comprising CO and H_2 by heating the mixture of CO_2 and CH_4 in a synthesis-gas generating zone at temperatures above 815° in the presence of a catalyst.

2787. ROBERTS, G., JR., WILSON, D. W., AND KEITH, P. C. (M. W. Kellogg Co.). Use of Carbon Monoxide and Hydrogen in the Synthesis of Liquid Hydrocarbons. United States Patent 2,198,553, Apr. 23, 1940; appl. filed Apr. 8, 1938, Serial No. 200,930; 7 claims (*Cl. 23–7*). Chem. Abs., vol. 34, 1940, p. 5853.

Describes arrangement of apparatus used and a method of producing a synthesis-gas mixture of CO and H_2 in a catalytic contact zone, in which a mixture of hydrocarbon gas, steam, and CO_2 is converted into synthesis gas in the presence of a catalyst at temperatures 2,200°–1,800° F., simultaneously converting, by the water-gas reaction, a gaseous mixture containing CO and H_2 into CO_2 and H_2, separating the H_2 from the CO_2 and employing the separated CO_2 in the catalytic contact zone.

2788. ROBERTS, G., JR., MARSHALL, W. H., JR., WILSON, D. W., AND KEITH, P. C. (M. W. Kellogg Co.). Synthesis Gas Containing Carbon Monoxide and Hydrogen. United States Patent 2,270,897, Jan. 27, 1942; appl. filed Feb. 17, 1938, Serial No. 190,948; 8 claims (*Cl. 252–373*). Chem. Abs., vol. 36, 1942, p. 3346.

Describes arrangement of apparatus and a method in which a mixture of a hydrocarbon gas, such as CH_4, steam, and CO_2, is converted into synthesis gas in the presence of a Ni catalyst between temperatures of 1,800°–2,200° F., which involves bleeding a portion of the synthesis-gas mixture, subjecting the bled portion to oxidation by means of an easily reducible metal oxide to form CO_2 and steam, and introducing the CO_2 and steam to the catalytic zone as the CO_2 and steam used during the conversion step.

2789. ROBERTS, J. K. (Standard Oil Co. of Indiana). Synthesis of Liquids From Carbon Monoxide and Hydrogen. United States 2,461,570, Feb. 15, 1949; appl. filed May 3, 1947, Serial No. 745,744; 9 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 3175.

Describes method for producing liquid hydrocarbons and oxygenated organic compounds with catalyst of the Fe type, fluidized catalyst of small particle size (2–200μ), and for conditioning synthesis catalyst. The synthesis gas, that contains H_2 62 and CO_2 33%, is mixed with diluent gas H_2 20, CO 1, CO_2 35%, and the rest CH_4) and charged into 1 of the 2 reactors (I). The H_2 : CO : CO_2 ratio of the synthesis-gas stream should be 2–6 : 1 : 1–3. The gasiform effluent is introduced into a product recovery system. The residual gas, that leaves the product recovery system, is not introduced for the conditioning of the fresh catalyst in the other reactor (II). The catalyst is ready to go onstream with the total synthesis gas charge as soon as the catalyst activity in reactor (I) is inactive. At this point, another batch of fresh catalyst starts to be conditioned in reactor (II).

ROBERTSON, N. C. *See* abs. **316, 814.**

ROBEY, R. F. *See* abs. **2405.**

2790. ROBINSON BINDLEY PROCESSES, LTD. [Catalytic Treatment of Carbonaceous Material.] Czechoslovak Patent 64,264, Apr. 25, 1939; appl. filed Apr. 16, 1932. Chem. Zentralb., 1940, II, p. 1386.

The catalytic treatment of a gaseous hydrocarbon in the presence of H_2 takes place on a catalyst that is treated with an easily hydrolyzable ester, such as a methyl, ethyl, or propyl ester. Example: 30 vol. % of pure CO and 70 vol. % of H_2 is passed over a catalyst consisting of Co and Mn. The reaction takes place at 208°–230°. The yield amounts to 270 gm. of hydrocarbon oil from 2.83 $m.^3$ of gas mixture.

———. *See* Synthetic Oils, Ltd.

2791. ROELEN, O. [Catalytic Conversion of Carbon Oxides Into Hydrocarbons of Higher Molecular Weight by Hydrogenation.] German Patent 748,287, Oct. 31, 1944; appl. R 95,118, filed Jan. 1, 1936 (*Cl. 12 o–1.03*). FIAT Reel J–5, frames 369–370; PB 70,145; FIAT Reel AA–90, frames 1,587–1,588; PB 70,275; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. V, 1949, ch. 157, p. 38.

Process of German Patent 701,846 (abs. **2810**) for regenerating the catalyst after short periods of use by treatment with H_2 is improved by using H_2 free from CO_2. It is also advantageous to regenerate under increased pressure.

2792. ——— (Ruhrchemie A. G.). [Contact Catalysts for Synthesizing Benzine.] German Patent 729,060, Nov. 12, 1942; appl. R 99,888, R 356, filed July 23, 1937 (*Cl. 12 o–1.03*). FIAT Reel AA–90, frames 1,578–1,580; PB 70,275; Chem. Zentralb., 1943, I, p. 1741; Meyer transl. PC–S–II, Fischer-Tropsch, vol. V, 1949, ch. 143, p. 1; Chem. Abs., vol. 38, 1944, p. 462.

The contracts contain Co or Co and Ni, which are precipitated on carriers from parent materials containing also Fe, Cu, Al, and Ca. In the solution from which the active metals are precipitated, the total amount of Fe, Cu, Al, and Ca is up to 1% of the active metals.

2793. ——— (Studien- und Verwertungs-G. m. b. H.). Desulfurizing Gases. United States Patent 2,110,241, Mar. 8, 1938; appl. filed Oct. 31, 1935. Chem. Abs., vol. 32, 1938, p. 3588.

Describes multistage process for removing S in organic combination from a gas mixture containing CO and H_2, which comprises treating such gas mixtures with Fe oxide to remove any substantial quantity of H_2S present, treating the gas mixture for the decomposition of part of the organic S compounds at a temperature 300°–450° with the mixture of sulfurized Fe oxide and alkali metal carbonate, which results in another stage of the process, thereupon treating the gas mixture with Fe oxide to remove part of the H_2S formed in this treatment and passing the partly desulfurized gas mixture at a temperature of 150°–300° in contact with a mixture of Fe oxide and a comparatively large % of an alkali-metal carbonate.

2794. ——— (Ruhrchemie, A. G.). [Distributing Water-Containing Masses.] German Patent 718,509, Feb. 19, 1942 (*Cl. 12 g–1.01*). Chem. Abs., vol. 37, 1943, p. 1629.

Masses, that in spite of a high H_2O content have a stiff consistency and under pressure separate into a liquid and a solid phase, are pressed through thin perforated plates. Immediately upon their passing the perforations, the threadlike mass is further treated in a manner preventing the separation into a liquid and a solid.

2795. ———. [Molding of Mixtures of Solid and Liquid Matter Into Filaments.] German Patent Appl. —, filed Sept. 17, 1938; APC 230,512.

Molding a solid-liquid paste, for example, a precipitate suspended in H_2O to form thin filaments or threads; catalyst-carrier systems may be treated in this way. Catalysts for synthetic production of gasoline from CO and H_2 are prepared by precipitation of metal salt solutions. By filtration, the solid residue of such solutions still retains 70–80% H_2O, but can be extruded into thin filaments 1–3 mm. in diameter.

2796. ——— Ruhrchemie A. G.). [Oxo Process.] French Patent 860,289, Jan. 10, 1941; appl. filed Sept. 18, 1939. Chem. Zentralb., 1941, II, p. 536; Kainer, no date, pp. 267–268.

Reaction takes place under pressure, at least 20 atm., at raised temperature 50°–200° in presence of a solvent.

$$R{-}CH{=}CH{-}R + CO + H_2 \rightarrow R{-}CH_2{-}\underset{\displaystyle CHO}{\underset{|}{CH}}{-}R$$

$$2R{-}CH{=}CH{-}R + CO + H_2 \rightarrow R{-}CH_2{-}CRH{-}CO{-}CRH{-}CH_2R$$

By passing C_2H_4 over a Co–Th catalyst at 90°–100° and 100 atm. pressure 40% propionaldehyde 40%, diethylketone 20% and higher boiling aldehydes and ketones and oxygenated compounds are obtained.

2797. ———. (Ruhrchemie A.-G.) [Oxo Process.] Netherlands Patent 55,463, Nov. 15, 1943. Chem. Zentralb., 1944, I, p. 1462.

See French Patent 860,289 (abs. **2796**).

2798. ———. [Oxygenated Carbon Compounds.] Norwegian Patent 64,344, Jan. 26, 1942.

See United States Patent 2,327,006 (abs. **2803**).

2799. ——— (Hydrocarbon Synthesis Corp.). Paraffin From Hydrogen and Carbon Oxides. United States Patent 2,225,487, Dec. 17, 1940; appl. filed July 3, 1937, Serial No. 151,835; in Germany, July 3, 1936; 5 claims (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 2304.

Describes arrangement of apparatus and a method for the production of paraffin by acting on a C oxide in the presence of a catalyst that is suitable for forming hydrocarbons, with gases containing free H_2, that are practically free from other reactants, at an elevated temperature below that at which CH_4 would normally be exclusively formed with the use of the same gases and the same catalyst, involving periodically removing from the catalyst by extraction with a solvent for paraffin the nonvolatile reaction products, that have settled on the catalyst, at a temperature not materially above the reaction temperature, each time before the proportion of paraffin formed is appreciably diminished in comparison with the other products simultaneously formed.

2800. ——— (Ruhrchemie A. G.). [Process for Preparing Valuable Oxo Compounds.] German Patent Appl. R 103,362, R 402, filed Sept. 19, 1938. FIAT Reel K–20, frames 225–228; PB 70,211; TOM Reel 37, bag 3,451, item 35, 3 pp.; Meyer Transl. PC–S–V, Oxo, vol. II, 1949, ch. 35, p. 12.

In preparing valuable Oxo compounds by the condensation of unsaturated hydrocarbon compounds with CO, the unsaturated compounds such as olefins are converted at elevated pressures and moderately increased temperatures in the presence of catalysts with CO, gases which contain CO or such gas mixtures which also contain H_2 as well as CO. The reaction is carried out at pressures of 50 atm. or higher and temperatures <100°. Example: Through a reaction tube, which is filled with a Co–Th catalyst of the composition 100 parts Co : 15 Th : 200 kieselguhr, is passed at a temperature of 80° and under a pressure of 100 atm., a mixture of C_2H_4, CO, and H_2 in the ratio of 1 : 1 : 1 up to 2 : 1 : 1. There are obtained per $m.^3$ of the gas mixture, depending upon the velocity of flow, 200–700 gm. of liquid product. From this can be separated by simple fractionation about 20% of a fraction b. 50° which consists of pure propionaldehyde. Higher aldehydes and ketones are present, as well as small amounts of oxygenated byproducts such as carboxylic acids. Gaseous byproducts do not occur in notable amounts.

See also United States Patent 2,327,066 (abs. **2803**).

2801. ———. Production of Oxygenated Carbon Compounds. Australian Patent 113,828, no date.

See United States Patent 2,327,066 (abs. **2803**).

2802. ———. [Production of Oxygenated Carbon Compounds.] Swedish Patent 101,547, no date.

See United States Patent 2,327,066 (abs. **2803**).

2803. ———. Production of Oxygenated Carbon Compounds. United States Patent 2,327,066, Aug. 17, 1943; appl. filed Apr. 15, 1939, Serial No. 268,024; in Germany, Sept. 19, 1938; 8 claims (*Cl. 260–598*). British Chem. Abs., 1945, B, II, p. 331. Chem. Abs., vol. 38, 1944, p. 550.

Process of producing organic carbonyl compounds that comprises passing a gaseous mixture of CO, H_2, and an organic substance selected from the group consisting of the aliphatic and cyclic olefins at a temperature of about 40°–200° C. and under a pressure of about 20–300 atm. into contact with a hydrogenation catalyst, separating the compounds formed in the reaction and returning the remaining mixture into contact with the catalyst. The catalysts are from the 8th group. The products may be used for the production of fatty acids.

2804. ———. [Production of Oxygenated Organic Compounds.] German Patent Appl. —, filed Apr. 15, 1939, APC SN 268,024.

Treatment of olefins with H_2 and CO at 50°–150° C. and 20–300 atm. in presence of Fischer-Tropsch catalysts yields aldehydes, ketones, and alcohols. The yield is 300–400 gm. per $m.^3$ of $2C_2H_4 : 1CO : 1H_2$ gas per pass of 100 l. of gas per l. of catalyst per hr.

2805. ——— (Ruhrchemie A. G.). [Removing Sulfur Compounds From Gases.] German Patent 659,407, May 3, 1938 (*Cl. 26 d–8.04*). Chem. Zentralb., 1938, II, p. 811; Chem. Abs., vol. 32, 1938, p. 6038.

Granular composition for desulfurizing gases is made from a mixture of Fe oxides and/or hydroxides with more than 5% of an alkali carbonate by making the mixture into a paste with H_2O at a moderately raised temperature, partly drying the mixture, allowing it to cool, and crushing the product. Alternatively, the partly dried mixture may be molded by extrusion while still hot, and then further dried and crushed.

2806. ———. [Sulfonates From Fischer-Tropsch Synthetic Olefins.] German Patent Appl. —, filed Dec. 10, 1940; APC 369,507.

To prepare sulfonates free from impurities, alcohols prepared from synthetic olefins, for example, undecene, are used. Catalysts for making the alcohols are finely divided metals (Fe, Ni, Co) mixed with an oxide of Th, Mg, or Al. The high-pressure conversion takes place at 50°–200° C. Only primary alcohols are formed, and about 50% have ramified chains, since the olefins are prepared from CO and H_2, and are hydroxylated (while adding 1 C atom) with CO and H_2. A complete series can be made, for example, 10 C–20 C, starting with the olefin from 9 C–19 C.

2807. ——— (Ruhrchemie A. G.). [Tubular Heat-Exchange Apparatus for Effecting Catalytic Gas Reactions.] German Patent 675,182, May 2, 1939 (*Cl. 12 g–4.02*). Chem. Abs., vol. 33, 1939, p. 5240.

See abs. **647, 648, 692, 693, 950, 951, 952, 1989, 1990, 1991, 2138, 2139, 2144, 2145, 3240.**

2808. Roelen, O., and Feisst, W. Catalysts for Benzine Synthesis. United States Patent 2,447,029, Aug. 17, 1948. Chem. Abs., vol. 42, 1948, p. 9126.

Improved catalytic materials for reaction of CO and H_2 are provided. Also means of regenerating these catalysts following a material reduction in activity. In large-scale benzine synthesis from CO and H_2 the catalysts employed are metals of the Fe group (Fe, Co, Ni), whose active constituents have been precipitated on kieselguhr. It has been found that certain drawbacks are eliminated by use of CO_2 compounds of Mg as carrier substances insoluble in alkaline solutions for precipitating catalysts of the Fischer-Tropsch benzine synthesis, more particularly for the production of catalysts containing Mg, it having been found that basic $MgCO_3$ is particularly suitable. Method of preparing catalysts involves addition of the carrier mass, that consists of 1 of the Mg compounds previously referred, immediately after precipitation of the metal catalysts, and this is stirred with the precipitant. Advantage of using $MgCO_3$ as carrier substance consists in the facility of procuring raw materials. Furthermore, it is advantageous to work up spent catalysts produced from $MgCO_3$. Use of the carrier substances, according to the invention, is particularly advantageous because no other chemicals are required to dissolve them except the cheap CO_2 that is available in large quantities as waste gas and which, moreover, may be used in circulation. Unlike kieselguhr, Mg can be used as often as desired, so that there is practically no loss in carrier mass. Furthermore, no foreign substances find their way into the catalyst or into the solution from which the catalyst is precipitated.

2809. ——— (Ruhrchemie A. G.). Catalysts for Benzine Synthesis From Water Gas. Australian Patent 103,630, May 5, 1938; appl. filed Apr. 1, 1937. Chem. Zentralb., 1938, II, p. 4345.

Care must be taken in making up the catalyst that the kieselguhr base contain no harmful impurity in solution as in working up used catalysts. Therefore, these should be made insoluble first by igniting. Furthermore, no harmful material should be allowed to be adsorbed from the catalyst solution on to the carrier base. One must therefore use catalyst solutions that do not contain such impurities or must remove them from the solution before depositing the catalyst constituents upon the carrier, for example, by precipitating with alkali and separating the precipitate.

2810. ——— (Ruhrchemie A. G.). [Catalytic Conversion of Carbon Monoxide Into Higher Hydrocarbons.] German Patent 701,846, Dec. 24, 1940 (*Cl. 12 o–1.03*). Chem. Abs., vol. 35, 1941, p. 8259.

In synthesizing higher hydrocarbons from CO and H_2 a nonvolatile product deposits on the catalysts. The deposit is periodically removed by passing H_2 or steam or a suitable solvent without lowering the temperature appreciably and without removing the catalysts.

2811. ——— (Studien- u. Verwertungs-G. m. b. H.). Desulfurizing Gases. United States Patent 2,110,240, Mar. 8, 1938; appl. filed Jan. 23, 1935. Chem. Abs., vol. 32, 1938, p. 3588.

See German Patent 651,462 (abs. **2812**).

2812. ——— (Studien- u. Verwertungs-G. m. b. H.) [Purifying Gases Containing Carbon Monoxide and Hydrogen.] German Patent 651,462, Oct. 15, 1937 (*Cl. 26 d–8.04*). Chem. Abs., vol. 32, 1938, p. 1434.

Gases containing CO and H_2, after removal of H_2S, are freed from organic S compounds by passing them at 150°–300° over a catalyst comprising Fe_2O_3 or $Fe(OH)_3$ mixed with at least 10% of an alkali carbonate.

2813. ——— (Ruhrchemie A. G.). [Regenerating Contact Catalysts.] German Patent 705,311, Apr. 24, 1941; appl. R 95,984, filed Apr. 2, 1936 (*Cl. 12 o–1.03*). FIAT Reel AA 88, frames 3,473–3,474; PB 70,273. Chem. Zentralb., 1941, II, p. 839; Chem. Abs., vol. 36, 1942, p. 2100.

When the contact catalysts used in CO+H reactions cannot be regenerated by ordinary means, they are dissolved in an acid. The solution is filtered to remove the carrier, and then by partial precipitation with, for example, Na_2CO_3, the contaminants are removed. After filtering, the catalyzing substance is precipitated, care being taken that the carrier is added toward the end, lest the carrier, usually SiO_2 be attacked by the alkali.

2814. ——— (Hydrocarbon Synthesis Corp.). Synthesizing Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,261,184, Nov. 4, 1941; appl. filed Mar. 23, 1937, Serial No. 132,595; in Germany, Apr. 1, 1936; 5 claims (*Cl. 260–449*). Chem. Abs., vol. 36, 1942, p. 1167.

Catalysts such as Co, Ni, or Fe deposited on carrier substances, which may be formed of kieselguhr and which are pretreated by heating their soluble constituents to render them insoluble, are used, the catalysts being precipitated from their salt solutions with alkaline-reacting agents and applied to the pretreated carrier substances, so as substantially to prevent soluble components from entering the solution from which precipitation is effected.

2815. Roelen, O., and Hanisch, F. (Hydrocarbon Synthesis Corp.). Cobalt Recovery From Spent Catalysts. United States Patent 2,215,885, Sept. 24, 1940; appl. filed Sept. 17, 1938, Serial No. 230,510; in Germany Sept. 25, 1937; 3 claims (*Cl. 23–238*). Chem. Abs., vol. 35, 1941, p. 861.

Method of recovering Co values from catalysts prepared by precipitating compounds of Co onto kieselguhr, that have been used in the synthetic production of benzine from CO and H_2, by which a paraffinic deposit has been formed on the catalysts, involves treating the catalyst with a solution containing HNO_3 until the Co is dissolved, the solution containing, throughout the process, a concentration of about 3–5% HNO_3 and separating the resulting solution from the kieselguhr.

2816. ——— (Ruhrchemie A. G.). [Reviving Cobalt Catalysts Used for Synthesizing Benzine.] German Patent 717,693, Feb. 5, 1942; appl. R 100,354 filed Sept. 1937 (*Cl. 12 o–1.03*). Chem. Abs., vol. 38, 1944, p. 2478.

See British Patent 504,700 (abs. **3173**).

2817. Roelen, O., and Lochmann, K. (Ruhrchemie A. G.). [Coldproof Mixtures of Benzine and Lactic Acid Ethyl Ester.] German Patent 727,750, Oct. 8, 1942 (*Cl. 22 h–3*). Chem. Abs., vol. 37, 1943, p. 6675.

Aliphatic alcohols with at least 5 C atoms per molecule are used to facilitate solution of the reactants.

2818. Roelen, O., and Schaller, P. (Ruhrchemie A. G.). [Diesel Fuel.] German Patent 683,927, Oct. 26, 1939 (*Cl. 46 a⁶–7*). Chem. Abs., vol. 36, 1942, p. 4318.

See United States Patent 2,243,760 (abs. **2145**).

2819. Roelen, O., Heckel, H., and Hanisch, F. [Catalytic Conversion of Carbon Oxides to Hydrocarbons of Higher Molecular Weight by Hydrogenation.] German Patent 748,374, Nov. 1, 1944; appl. filed Nov. 8, 1938 (*Cl. 12 o–1.03*). FIAT Reel J–5, frames 545–546; PB 70,145; FIAT Reel AA–90, frames 1,573–1,574; PB 70,275; Meyer transl. PC–S–II, Fischer-Tropsch, vol. 6, 1949, ch. 168, p. 13.

Process of German Patent 701,846 (abs. **2810**) for the regeneration of synthesis catalysts is improved by carrying out the treatment with H_2 by gradually raising the temperature above the synthesis temperature or up to about 450°.

2820. ——— (Hydrocarbon Synthesis Corp.). Reactivation of Catalysts for Hydrogenation of Carbon Monoxide. United States Patent 2,289,731, July 14, 1942; appl. filed Nov. 7, 1939, Serial No. 303,312; in Germany, Nov. 7, 1938; 5 claims (*Cl. 252–243*). Chem. Abs., vol. 37, 1943, p. 515.

Process is employed for the reactivation of spent catalysts, such as those containing Co, ThO_2, and MgO, from a process in which low-boiling hydrocarbons are synthesized by passing CO and H_2 through a catalytic chamber filled with the catalyst and heated to about 185°–192°, that involves increasing the temperature of the catalytic chamber and passing H_2 therethrough in contact with the catalyst until the paraffins are removed from the catalyst, then continuing the treatment at still higher temperatures approaching but not substantially exceeding 450° for a time sufficient to restore the catalyst substantially to the activity of a fresh catalyst.

2821. ——— (Ruhrchemie A. G.). [Regenerating Catalysts Used for Synthesizing Benzine.] German Patent 722,706, July 27, 1942; appl. R 103,714, R 418, filed Nov. 8, 1938 (*Cl. 12 o–1.03*). FIAT Reel K–20, frames 326–331; PB 70,211; FIAT Reel AA–89, frames 501–503; PB 70,274; TOM Reel 37, bag 3,451, item 35, 3 pp.; Meyer transl. PC–S–II, Fischer-Tropsch, vol. 4, ch. 138, 1949, p. 28; Chem. Abs., vol. 37, 1943, p. 5574.

Catalysts are cleaned of paraffin, then treated at an elevated temperature with H_2. The H_2 is passed at a rate at least of 1,000 cc. per hr. per $m.^2$ cross section. H_2 can be recirculated if the CO and CO_2 content is kept <2.5 gm. per $m.^3$ and $H_2O<1$ gm. per $m.^3$

2822. Roesner, G., Ley, H., and Wegener, E. (Metallgesellschaft A. G.). [Gas Purification Agent.] German Patent 745,242, Dec. 2, 1943; (*Cl. 26 d–8.04*). Chem. Abs., vol. 40, 1946, p. 1990.

Nonsintered Fe_3O_4 obtained by any of the known methods is used for purifying gas. The mass is revivified by heating at 600°–1,000° in a neutral atmosphere and is granulated by mixing 3 pt. revivified Fe_3O_4 with 1 pt. H_2O.

Roessler & Hasslacher Chemical Co. *See* abs. **201, 3648, 3649, 3650, 3651, 3652, 3653, 3654.**

2823. Rogers, D. C. (G. D. Buckley, F. S. B. Jones, W. J. Levy, and Imperial Chemical Industries Ltd.). Ketenes, Carboxylic Acids, and Their Derivatives. British Patent 668,309, Mar. 12, 1952. Chem. Abs., vol. 47, 1953, p. 1183.

C_2H_2 derivatives are oxidized with N_2O at 200°–300° and 100–500 atm. pressure. Oxidation in the presence

of N_2O alone gives ketenes, usually in the form of dimers of uncertain constitution; in the presence of H_2O, NH_3 or primary or secondary amines, carboxylic acids, alcohols, or phenols; in the presence of mercaptans or H_2S, carboxylic acids, amides, acid anhydrides, esters, thio esters, or thio acids. 1-Hexyne 10 parts and EtOH 40 parts are placed in a reactor double the volume of the reactants, the air is replaced by N_2O, the reactor heated to 300°, N_2O pumped in to 500 atm., and the mixture stirred 1 hr., yielding 15 parts $AmCO_2Et$. C_2H_2 15 parts and EtOH 30 parts at —40° similarly treated yield an azeotrope 12 parts, boiling 71°, containing EtOAc 70% and EtOH 30%. $HOCH_2CH_2C:CH$ 5 parts in cyclohexane 35 parts gives γ-butyrolactone 5 parts; $PhC:CH$ 10 parts in H_2O 30 parts gives $PhCH_2CO_2H$.

ROHM & HAAS Co. *See* abs. **1854, 1855, 2206, 2207, 2208, 2209.**

2824. ROLLMAN, W. F. (Standard Oil Development Co.). Contacting Fluid Solids With Gases. United States Patent 2,491,135, Dec. 13, 1949; appl. filed Apr. 27, 1948, Serial No. 23,590; 4 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 1764.

Subdivided catalyst in a fluid solids hydrocarbon synthesis reactor is withdrawn continuously through a series of vertical tubes near the periphery near the bottom of the reactor. The tubes connect with a corresponding number of inclined tubes manifolded together at the center of the bottom of the reactor through which the synthesis gases enter the reactor. The catalyst, thus withdrawn, is picked up by incoming gases and returned to the reactor. The incoming mixture passes into the reactor through a cone. The turbulent fluid bed condition is arrived at a lower vapor inlet velocity than when catalyst is not recycled without any tendency to fixed bed formation at the extreme bottom of the vessel. Overheating is prevented and attrition is reduced. 3 United States patents cited.

2825. ——— (Standard Oil Development Co.). Method of Producing a Carbon Monoxide and Hydrogen-Gas Mixture From Carbonaceous Materials. United States Patent 2,527,197, Oct. 24, 1950; appl. filed Feb. 17, 1945, Serial No. 578,436; 4 claims (*Cl. 48–206*). Chem. Abs., vol. 45, 1951, p. 334.

Mixture of CO and H_2 is produced, and a fuel is burned to supply the heat for the reaction in the same enlarged confined space, but in different adjacent zones. Solid material may be transferred from one zone to another without using conduits or valves. The cylindrical sectors are arranged about a common axis within the same general confined space. The zones are in continuous open communication. Some are burning zones, some water-gas generating zones, and the remainder neutral zones. The carbonaceous material is fluidized with air, partly burned in the 1st burning zone. The partly burned material is withdrawn from a point above the bottom of the 1st burning zone and passed to the top of an adjoining neutral zone, down through the neutral zone as a dense suspension, then to an adjoining water-gas generation zone. The water gas is not contaminated with flue gas from the burning zone. 3 foreign patents and 3 United States patents are cited.

2826. ———(Standard Oil Development Co.). Process and Apparatus for Contacting Fluid Solids With Gases. United States Patent 2,575,297, Nov. 13, 1951; appl. filed Apr. 30, 1949, Serial No. 90,588; 9 claims (*Cl. 260–449.6*).

Process and apparatus are described for converting CO and H_2 to liquid hydrocarbons and oxygenated products by contacting CO and H_2 under synthesis conditions, with a fluidized catalyst, in a vertically elongated reaction chamber having a bottom section in the form of a truncated inverted cone. A part of the catalyst is withdrawn continuously in vertical downwardly flowing streams from the periphery of the lower portion of the reaction zone, while separate streams of the catalyst suspended in the synthesis gas are passed upward along inclined paths equal in number to the vertical streams with which they are united from the bottom portion of the reaction zone. The improvement in the process comprises passing the last named streams tangentially into the lower portion of the reaction zone, thus imparting to the gases suspension a cyclonic flow pattern within the reaction zone.

See also United States Patent 2,491,135 (abs. **2824**).

2827. ROMAN, L. H. [Aldehydes.] French Patent 734,065, July 19, 1930. Chem. Abs., vol. 27, 1933, p. 992.

Aldehydes such as CH_2O are obtained by passing purified water gas, blast-furnace gases, etc., at 130°–200° and normal pressure over a catalyst composed of Ni, Fe, Co, Cu, Pt, or their oxides, the catalyst being regenerated by gases such as Cl, Br, I, N_2, and NO. The CH_2O may be converted to alcohols, etc. by luminous energy, the rays of which are caused to pass through color filters to eliminate the useless or harmful rays for the desired transformation.

2828. ———. [Formaldehyde.] German Patent 590,433, Jan. 4, 1934; (*Cl. 12 o–7.01*). Chem. Abs., vol. 28, 1934, p. 2019.

See French Patent 734,065 (abs. **2827**).

2829. ———. Formaldehyde From Gas Containing Hydrogen and Carbon Monoxide. British Patent 371,377, Oct. 14, 1930. British Chem. Abs., 1932, B, p. 763.

Gas is passed at atmospheric pressure and 130°–200° over a catalyst comprising Ni, Fe, Co, Cu, Pt or Pd, or oxides of these, the catalyst being regenerated by substituting a stream of N_2 or N oxides; the gas flows for 80–100 sec. and the regenerating stream 25–35 sec. in alternation.

———. *See* abs. **2719.**

2830. ROSSINSKY, J. [Synthesis of Formaldehyde.] Belgian Patent 225,027, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 230.

From CO and H_2 in the absence of CO_2 over pumice and Pt black.

2831. ROTTIG, W. (Ruhrchemie A. G.). Catalytic Hydrogenation of Carbon Monoxide With Iron Catalysts. United States Patent 2,620,347, Dec. 2, 1952; appl. filed Apr. 26, 1950, Serial No. 158,320; in Germany, May 7, 1949; 12 claims (*Cl. 260–449.6*). Chem. Abs., vol. 47, 1953, p. 5666.

Synthesis gas is passed over Fe catalyst that has been activated by continuous contact with synthesis gas for at least 96 hr. The temperature is maintained at 150°–195° C., and the paraffin is extracted from the catalyst with a solvent at that temperature. The treatment is repeated at least once more with synthesis gas for 100–200 hr. at atmospheric pressure. The temperature throughout the major part of the catalytic material is kept at 190°–200° C. The catalyst thus prepared by repeated solvent extraction may be used for a considerable period of time before any appreciable drop in efficiency. H_2 reduction of the Fe particles is carried out preferably at 200°–250° C. and a gas velocity of 100–200 cm. per sec. until at least 25% by weight of the total Fe is obtained in the reduced form. 3 United States patents cited.

2832. ——— (Ruhrchemie A. G.). Iron Catalysts for the Hydrogenation of Carbon Monoxide. United States Patent 2,628,969, Feb. 17, 1953; appl. filed Sept.

30, 1949, Serial No. 118,993; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 47, 1953, p. 5099.

Catalyst produced by precipitation of an Fe salt with an alkali compound is washed only to a point where the resulting catalyst still contains alkali compounds within the limit of 3–20% (preferably 5–10%) calculated for K_2O, of the Fe present, calculated as metallic Fe. 100–200 l. of H_2O will be sufficient to wash a catalyst mass containing 8 kg. Fe. The highest yield of oxygenated compound is obtained with this catalyst when the hydrogenation of CO is carried out under pressure of 3–20 atm. Synthesis gas rich in CO is used. Beside the conventional activators the catalyst may contain elements such as V, Ce, or W favoring formation of O-containing compounds. The entire product obtained by this process contains 30–40% O-containing compounds, mostly alcohols. 7 United States patents cited.

2833. ——— (Ruhrchemie A. G.). [Process for the Aromatization of Hydrocarbons.] German Patent 736,839, May 20, 1943; appl. R 104,540, R 433, filed Feb. 14, 1939 (*Cl. 23 b–1.04*). TOM Reel 37, bag 3,451, item 35; TOM Reel 41, bag 2,744, item 14, 3 pp.; Chem. Abs., vol. 38, 1944, p. 2965.

Aliphatic mixtures with 6–12 C atoms in the molecule, such as the synthetic gasoline produced by the reduction of CO by H_2 at normal pressure, are aromatized by being passed at elevated temperatures over catalysts consisting of Al_2O_3, Cr_2O_3, and Mn and Th compounds as activators.. The catalyst contains about 30% of Cr_2O_3 and in additional small amounts of Co, Ni, or both. These catalysts have greater mechanical stability and higher activity than those consisting of 30–50% Cr_2O_3 on MgO described in German Patent 763,831 (abs. **3004**).

2834. ——— (Ruhrchemie A. G.). Process of Extracting Oxygen Compounds From Hydrocarbon Mixture. United States Patent 2,581,712, Jan. 8, 1952; appl. filed Aug. 8, 1949, Serial No. 109,226; in France, Aug. 12, 1948; 2 claims (*Cl. 260–450*).

Treatment of mixtures of aliphatic hydrocarbons, such as result from the catalytic hydrogenation of CO, for removing the oxygenated compounds is discussed. The mixtures are treated in 2 stages: 1st with polyvalent alcohol such as glycol and then with a mixture of polyvalent alcohol and a low-molecular-weight monovalent alcohol such as MeOH in the proportion of 1 : 2 parts. This is followed with a water wash to remove any residual alcohols. The extracted oxygenated compounds are separated from the solvent by simple distillation.

———. *See* abs. **1914.**

2835. Rottig, W., Gross, H. W., Royen, P., and Schenk, K. (Ruhrchemie A. G. and Lurgi Gesellschaft für Waermetechnik). Preparation of an Iron Silica-Gel Fischer-Tropsch Catalyst. United States Patent 2,617,774, Nov. 11, 1952; appl. filed Sept. 9, 1950, Serial No. 184,114; 3 claims (*Cl. 252–451*).

Process consists of precipitating a hot solution of Fe nitrate, while intensively stirring, with a hot caustic soda solution in such a manner that the *pH* value after precipitation is 6.8–7.2. The precipitated mass is washed to a K_2O calculated content of no more than 0.5 part by weight of K_2O for every 100 parts by weight of Fe content, stirring at first with a small amount of H_2O, then converting into a suspension by addition of further amounts of H_2O. Enough K-water-glass solution is added to this suspension to give 20–25 parts by weight of SiO_2 for every 100 parts by weight of Fe contained in the catalyst. Then enough nitric acid is added to give for the catalyst mass remaining after filtration a K_2O : SiO_2 ratio of 1 : 4–1 : 5. The catalyst is dried, molded, and reduced at 260°–300° C. to a point at which the catalyst contains 30–50% of its total Fe content in the form of free Fe. High gas velocity of 1–2 m. per sec. is used during reduction. 3 United States patents cited.

Royen, P. *See* abs. **2835.**

2836. Ruben, S. Promoting Reactions Between Gases by High-Frequency Currents. United States Patent 1,431,047, Oct. 3, 1922. Chem. Abs., vol. 16, 1922, p. 3818.

Gases, for example, CO and H_2 to produce CH_2O, which are to react upon each other, are brought into contact with each other in a conductive liquid, for example, an aqueous electrolyte, through which a high-frequency current is passed.

2837. Rubin, L. C. (M. W. Kellogg Co.). Synthesis of Organic Compounds. United States Patent 2,448,279, Aug. 31, 1948; appl. filed Aug. 23, 1944, Serial No. 550,799; 3 claims (Cl. 260–449.6). Chem. Abs., vol. 42, 1948, p. 9123.

Powdered catalyst such as one of the composition Co : 0.15 MgO : 2.0 Superfiltrol was used in a reactor sufficiently large to allow 2 distinct phases, the one having a density ordinarily not less than ½ that of the settled mass and the other a diffuse phase large enough to allow disengagement of catalyst by settling. After the catalyst was raised to reaction temperature, the preheated feed gas was introduced. Conversion started and the operation continued for some time, with the temperature controlled by H_2O bath in jacket. The H_2O was withdrawn from the jacket, and the temperature controlled by the vaporization of a light naphtha introduced into the reaction zone through nozzles. The naphtha b. 126°–360° F. had been produced in the process. An example using H_2O as the injected coolant and 1 using the injection method in combination with indirect heat exchange are given. Conditions and results are given in tabular form. 6 United States patents and 2 foreign patents cited.

2838. ——— (M. W. Kellogg Co.). Synthesis of Organic Compounds. United States Patent 2,576,858, Nov. 27, 1951; appl. filed May 5, 1948, Serial No. 25,256; 14 claims (*Cl. 260–449.6*).

This is a continuation of United States Patent 2,448,279 (abs. **2837**). A C oxide is hydrogenated by passing the reactants upward through a reaction zone containing a catalyst at such a velocity that the catalyst is kept in suspension. The upward linear velocity of the gaseous mixture and the bulk of the catalyst material are so limited as to form a lower dense phase consisting of the greater part of the catalyst mass, in which the catalyst particles circulate at a relatively high rate, and an upper dilute phase, the 2 phases forming an interface between. The upward velocity of the gaseous mixture is kept at a higher rate than the free settling rate of the particles comprising the greater part of the dense phase, whereby catalyst particles are entrained in the gaseous reaction mixture passing from the dense phase to the dilute phase. A liquid, substantially free from solids and completely vaporizable at the reaction conditions, is injected into the dilute phase adjacent to the interface, cooling the reaction gases and disengaging a substantial proportion of the entrained catalyst material which falls back into the dense phase. Gaseous reaction mixture and vaporized liquid from the reaction zone are withdrawn to recover the reaction products. The catalyst may comprise Co or Fe supported on acid treated bentonite and promoted with MgO, for example, Co : 0.15 MgO : 2.0 Superfiltrol.

———. *See abs.* **291, 2197, 2198, 2199, 2200, 2201.**

2839. Rubin, L. C., and McGrath, H. G. (M. W. Kellogg Co.). Synthesis of Organic Compounds. United

States Patent 2,620,346, Dec. 2, 1952; appl. filed Sept. 24, 1948, Serial No. 50,966; 6 claims (*Cl. 260–449.6*).

Finely divided catalyst is fluidized and heated to 350° F. or higher before contact with synthesis gas. The use of synthesis gas as the fluidizing gas in the starting-up procedure conveniently heats the catalyst mass to operating temperature. There should be < 15 parts by weight of CO per part by weight of the reduced catalyst. The heat is supplied by the exothermic reaction of H_2 and CO. 4–6 lb. CO (using $2:1=H_2:CO$ gas) is enough to raise each lb. catalyst mass from 300° to 360° F. The main purpose is to assure proper fluidization and to preheat the catalyst mass to operating temperature without excessive formation of wax upon the catalyst during startup. In main operating run, the temperature should be maintained >350° at all times. At 350°–450° F., space velocities of 50–2,000 vol. reactants per hr. per vol. of fluidized dense phase are satisfactory; higher velocities being associated with higher temperatures. For catalysts comprising about ⅛ by weight of hydrogenating metal, the above range corresponds to 0.2–8 l. per hr. per gm. of hydrogenating metal. Such operation gives maximum yield of liquid products and a minimum production of solids. The liquid product contains a valuable diesel fuel fraction. 5 United States patents cited.

2840. Rubin, L. C., Riblett, E. W., and McGrath, H. G. (M. W. Kellogg Co.). Liquid Hydrocarbons. United States Patent 2,615,035, Oct. 21, 1952. Chem. Abs., vol. 47, 1953, p. 2966.

Liquid hydrocarbons are formed at least in 50% yield by passing H_2 and CO in molar ratios of 2–5 : 1 upward in a reaction zone through a Co-containing catalyst in suspension at 440°–500° F. and at 45 p. s. i. g. pressure or less. The product is suitable for diesel fuel. In an example, gas containing CO 30.9%, H_2 61.4%, and inerts 7.7% is introduced at a rate of about 40 cu. ft. per hr. per lb. of Co catalyst at an average temperature of 440° F. Of the CO charged, 47.5% was converted to liquid hydrocarbons containing >3 C atoms per molecule and end b.p. 670° F.; 11% was converted to liquid hydrocarbons containing 1–2 C atoms per molecule; and 6% to CO_2. Liquid product was 131 cc. per $m.^3$ gas charged.

2841. Ruble, R. J. (Texaco Development Corp.). Preparation of Gas Mixtures. United States Patent 2,484,249, Oct. 11, 1949; appl. filed Mar. 19, 1947, Serial No. 735,597; 3 claims (*Cl. 48–212*). Chem. Abs., vol. 44, 1950, p. 2207.

Gas mixtures, such as H_2 and CO, are prepared from hydrocarbons, such as natural gas, by controlled combustion in an engine of the internal-combustion type, but the carburetion of the feed gases has proved difficult because of the danger of preignition and flashback. These difficulties are avoided in the present invention by feeding the reactants into the cylinder separately; this prevents them from mixing throughout the combustion space and causes them to mix in a predetermined zone at a predetermined time by controlled increments, so that the advance of the flame front compresses only a incombustible reactant of mixture of reactants. For example, 1 of the reactants, such as the O_2-containing gas, preferably consisting of 90–99% O_2, is introduced through the usual intake valve and compressed on the compression stroke. The hydrocarbon is then introduced in the compressed gas containing O_2 at a point of piston travel and under such conditions that a combustible mixture is formed only at the point of ignition or near it. If preignition occurs, it can only be at or near the desired point of ignition and can do no harm. The injection of the hydrocarbon is continued into zones of the combustion chamber immediately in advance of the reaction front in its direction of burning. A mixture of H_2 and CO is released through the exhaust valve, and power is produced by the engine.

2842. Ruhl, O. (I. G. Farbenindustrie A. G.). [Equipment for Catalytic Synthesis of Gases With Automatic Removal of Side-Reaction Products or Gases Not Participating in the Reaction.] German Patent 703,562, Feb. 6, 1941 (*Cl. 12 g–4.01*). Chem. Abs., vol. 36, 1942, p. 6.

2843. Ruhrchemie A. G. [Active Iron Catalyst for the Synthesis Process.] German Patent Appl. R 106,554 R 469, filed Dec. 9, 1939 (*Cl. IV d–12 o*). FIAT Reel K–20, frames 232–240; PB 70,211; TOM Reel 177, frames 1,695–1,703; Meyer transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 50, 1948, p. 124.

Highly active Fe catalysts are obtained by promotion with at least 5% of the oxides of Ca or Mn and by precipitation from mixtures of Fe salt solutions with Ca or Mn salt solutions by means of alkali hydroxide. The catalysts are preferably deposited on granular carriers such as kieselguhr, CaO, MgO, or diatomite. After the precipitates are washed they are impregnated with solutions of alkali hydroxide. To speed up the induction time small amounts (2–5%) of Ni, Co, Cu, or mixtures of these metals are added. Maximum gas contractions and oil yields per $m.^3$ of synthesis gas are reported with greatly increased active catalyst life.

2844. ———. [Alcohols From Hydrocarbons.] German Patent Appl. R 105,067, Apr. 19, 1939 (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 298; FIAT Reel K–20, frames 229–231; PB 70,211.

Alcohols are obtained from hydrocarbons containing olefinic double bonds by conducting the hydrocarbons over a catalyst under a pressure up to 100 atm., at a temperature of 200° in the presence of gases containing CO and H_2. Addition to German Patent Appl. R 103,362 (abs. **2800**).

2845. ———. [Aldehydes.] German Patent 722,707, June 4, 1942 (*Cl. 12 o–7.03*). Chem. Abs., vol. 37, 1943, p. 5077.

Aldehydes are produced from ethylene or its homologs by oxidation with O_2-containing gases. The gaseous mixture flows in a circuit and is periodically and for short periods only heated to the reaction temperature of approximately 225°. The O_2 supply is periodically interrupted. Activated C is used as catalyst.

2846. ———. [Alkalinity of the Catalyst as a Regulator of the Consumption Ratio of Carbon Monoxide to Hydrogen.] German Patent Appl. —, R 537, no date. FIAT Reel K–20, frames 268–273, Sept. 11, 1940; PB 70,211.

Dependent on the alkalinity of the catalyst ready for use, a definite consumption ratio $CO:H_2$ can be obtained. An increased alkali content raises the consumption of CO, whereas a decreased alkalinity raises the proportion of H_2. The alkali content of the catalysts is adjusted to 2–6% in the form of hydroxides or carbonates.

2847. ———. Antidetonating Fuels. British Patent 469,044, July 19, 1937. Chem. Abs., vol. 32, 1938, p. 763.

In producing the fuels by the thermal treatment of a mixture of hydrocarbons poor in H with hydrocarbons rich in H, the latter comprise hydrocarbons produced by the hydrogenation of CO at normal or slightly increased pressures. The former may comprise tar, coals, liquid phase hydrogenation products, emulsions of pit coals or brown coals, and pitch coals. H_2 and other gases may be present during the treatment, which is conducted at 300°–650°. In examples, (1) hydrocarbons produced in the hydrogenation of oxides of C are fractionated to remove products that b. <110° and are

then mixed with 0.2 their weight of tar, the mixture, being heated to 430°–450° under 60 atm. The products are distilled, and the residues of high boiling point are re-treated with further CO hydrogenation products. (2) Coal extract 10 and benzine obtained by hydrogenation of CO 90 parts are similarly treated at 450°–500° in presence of MoO_3.

2848. ———. [Antiknock Gasoline Made From Hydrogenated Carbon Monoxide.] German Patent 726,197, Oct. 13, 1942; appl. filed Oct. 25, 1935 (*Cl. 23 b–1.04*). Chem. Zentralb., 1943, I, p. 358; Chem. Abs., vol. 37, 1943, p. 6880.

Approximately 10% of coal extracts is added to the gasoline, and the mixture is treated thermally under pressure in the presence of catalysts.

See also German Patent 725,000 (abs. **2949**).

2849. ———. [Antiknock Motor Fuel.] French Patent 800,735, July 17, 1936. Chem. Zentralb., 1937, I, p. 260; Chem. Abs., vol. 31, 1937, p. 250.

Hydrocarbons rich in H resulting from the hydrogenation of CO with bituminous products poor in H such as tars and mineral oils, are subjected to a transformation by heat treatment.

2850. ———. [Antiknock Motor Fuel.] German Patent 766,110, Aug. 19, 1940; appl. R 108,161. R 525 (*Cl. 23 b–1.04*). TOM Reel 36, bag 3,454, item 20.

Hydrocarbon mixture obtained by the hydrogenation of CO, using the regular water gas under recycle conditions, is fractionated, and the fraction b. <200° and containing a high % of olefins is treated in the vapor phase with bleaching earth ("Tonsil Optimum" or "Granosil"). If desired the isomerizing effect may be heightened by adding borylphosphate or the like to the catalyst. By such treatment the octane number of the gasoline product can be raised from 40 to 48, about 25 points.

2851. ———. [Apparatus for Carrying Out Gas Reactions at High Temperature.] German Patent 558,745, Mar. 10, 1929. Chem. Abs., vol. 27, 1933, p. 453.

2852. ———. Apparatus for Catalytic Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. German Patent 703,225, Mar. 4, 1941; appl. R 96,525, R 315, filed June 11, 1936 (*Cl. 12 o–1.03*). TOM Reel 37, bag 3,451, item 35, 2 pp.; FIAT Reel AA–88, frames 3,541–3,543; PB 70,273; Ind. chim., vol. 32, 1945, p. 149; Chem. Abs., vol. 36, 1942, p. 251.

Heat of reaction is removed using H_2O. Its heat is used in a steam boiler, and then the H_2O is returned to the contact furnace. All furnaces can thus be kept at the same reaction temperature.

2853. ———. [Apparatus for the Regulation of One Temperature in Relation to Another Temperature.] German Patent Appl. —, R 610, filed May 6, 1942. FIAT Reel K–30, frames 7,698–7,701; PB 73,587; TOM Reel 36, bag 3,454, item 36, 5 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, chap. 84, 1948, p. 24.

In an apparatus for the regulation of one temperature in relation to another, the controlling temperature as well as the one to be regulated is measured with a gas thermometer, whereby the pressure difference occurring as a result of the difference in the temperatures is used to operate a switch, which in its turn connects or disconnects a heating device with the result that the temperature becomes equalized. In applying the device to the operation of distilling columns, particularly to laboratory columns, the controlling air thermometer is located inside the distillation column, and the air thermometer required for measuring the temperature to be regulated is in the insulating jacket of the distillation column. This jacket can be heated. The apparatus is illustrated.

2854. ———. [Carboxylic Acids.] German Patent Appl. R 109,773, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 306.

Polybasic carboxylic acids are obtained from carboxylic acids containing olefinic double bonds, with use of suitable hydrogenation catalysts, by converting at elevated pressure and temperature gas mixtures containing CO and H_2 and by oxidizing the aldehyde-, keto-, or alcohol-carboxylic acids produced thereby.

2855. ———. Catalyst. British Patent (Provisional) 8,643, filed 1937.

$MgCO_3$ is claimed as a support in place of kieselguhr or a similar material. Regeneration of catalysts supported on $MgCO_3$ is easy. The spent mass is mixed with H_2O and blown with CO_2 when the $MgCO_3$ goes into solution as bicarbonate. After filtration the basic $MgCO_3$ is reprecipitated by blowing with steam.

2856. ———. [Catalyst Carrier.] Austrian Patent 160,467, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 154.

See British Patent 498,007 (abs. **2873**), French Patent 819,701 (abs. **3198**), and Italian Patent 349,478 (abs. **2859**).

2857. ———. [Catalyst Chamber.] Netherlands Patent 49,555, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 163.

See United States Patent 2,148,545 (abs. **505**).

2858. ———. [Catalyst for Benzine Synthesis.] Austrian Patent 158,997, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 154.

See British Patent 500,182 (abs. **2870**), French Patent 819,701 (abs. **3198**), and United States Patent 2,261,184 (abs. **2814**).

2359. ———. [Catalyst for Synthesis of Gasoline From Carbon Monoxide and Hydrogen.] Italian Patent 349,478, Mar. 31, 1937. Chem. Zentralb., 1938, II, p. 3774.

Basic Mg carbonate is used as the carrier for the known Co-Th-Mg catalysts. The catalysts are highly active and can be easily regenerated. After extraction of the paraffin they are washed out with cold H_2O and CO_2, whereby all of the Mg goes into solution as Mg $(CO_3)_2$. From this the basic salt is again precipitated by heating the solution and flowing steam therethrough. The other constituents are dissolved in HNO_3 and precipitated with NaOH, and the hot precipitate is again mixed with the precipitated basic Mg carbonate.

2860. ———. [Catalyst Furnace.] French Patent 844,575, no date. Schmidt, J., by Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 163.

2861. ———. [Catalyst Preparation.] German Patent Appl. R 103,450, filed Oct. 1, 1938 (*Cl. 12 o–1.03*). PB Report 412, May 15, 1945.

Reducing catalysts for hydrogenation of CO with H_2 containing <2.5 gm. oxides of C and <1 gm. H_2O vapor per $m.^3$ to get faster reduction and a more active catalyst.

2862. ———. [Catalyst Protection.] Belgian Patent 430,870, Oct. 29, 1938. Chem. Zentralb., 1939, II, p. 3160.

To protect the catalyst from the action of air, it is treated with CO_2 at temperatures <30°.

2863. ———. [Catalyst Regeneration.] Austrian Patent 155,807, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 157.

See French Patent 812,883 (abs. **2920**), German Patent 701,846 (abs. **2810**), Indian Patent 23,662 abs. **2884**), Italian Patent 346,389 (abs. **2885**), and United States Patent 2,225,487 (abs. **2799**).

2864. ———. [Catalyst Regeneration.] French Patent 899,044. Kainer, no date, p. 264.

Deposit of C on the catalyst in the catalytic cracking of synthetic oils over bleaching-earth catalysts is avoided by subjecting the catalyst to a periodic oxidizing regeneration. The cracking and regenerating periods are so arranged that a thermal equilibrium exists and the heat requirement in the cracking period is equal to the heat of oxidation set free during the regeneration.

2865. ———. [Catalyst Regeneration.] Indian Patent 24,309, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 157.

See United States Patent 2,238,726 (abs. **647**).

2866. ———. [Catalyst Regeneration.] Netherlands Patent 46,377, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 157.

See United States Patent 2,225,487 (abs. **2799**).

2867. ———. [Catalyst Support.] Swedish Patent 104,645, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 154.

See United States Patent 2,261,184 (abs. **2814**).

2868. ———. [Catalyst Treatment.] Italian Patent 367,118, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 154.

Reduced catalysts are cooled in N_2 to 30° and then stored in CO_2.

See French Patent 845,301 (abs. **3163**) and German Patent 720,107 (abs. **2137**).

2869. ———. [Catalyst Treatment With Hydrogen.] Austrian Patent 159,016, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 157.

See United States Patent 2,238,726 (abs. **647**).

2870. ———. Catalysts. British Patent 500,182, Feb. 1, 1939; appl. filed May 1, 1937. Chem. Abs., vol. 33, 1939, p. 5645.

In the preparation of catalysts suitable for benzine synthesis, etc., by precipitating a compound of the Fe group upon a carrier consisting of kieselguhr, powdered asbestos, Cr oxide, or steatite, the carrier is previously heated to incandescence to reduce the solubility of constituents soluble in the acid and alkaline reagents used in the preparation and regeneration of the catalyst. To obtain a fine distribution of the carrier material, it may be mixed with finely divided combustible material, such as wood pulp, before being heated. An extraction with acid may follow the heating. As a further precaution against solution of constituents of the carrier the latter may be added to the catalyst solution only when the precipitation of the latter is almost completed. When the exhausted catalyst is dissolved from the carrier by means of acid and reprecipitated, any impurities that have also been dissolved may be removed by a preliminary precipitation followed by filtration.

2871. ———. Catalysts. British Patent 665,218, 1952. Fuel Abs., vol. 11, No. 4, abs. 3121.

Fe catalyst for CO hydrogenation at approximately atmospheric pressure, in which the Fe is in the form of Fe and Fe oxides in proportions relative to each other of 25–35% of metallic Fe, 50–61% of ferrous oxide, and 25–4% of ferric oxide, the catalyst being impregnated with 0.5–5%, preferably 1–3%, of an alkali metal, calculated as the monoxide, relative to the total Fe content of the catalyst.

2872. ———. [Catalysts for Aromatization or Dehydrogenation.] German Patent Appl. —, R 687, filed Aug. 20, 1943 (*Cl. IV d–23 b*). FIAT Reel K–30, frames 7,896–7,902; PB 73,587; TOM Reel 36, bag 3,454, item 20, 7 pp; TOM Reel 37, bag 3,451, item 36.

In making catalysts for aromatization or dehydrogenation in accordance with German Patent Appl. R 114,653, use is made of Al hydroxide, which is quickly precipitated with acids under definite concentration and temperature conditions from Na or K aluminate solution and freed directly from its alkali content up to a definite limit by washing. It is then calcined under strictly regulated duration and temperature producing a starchy product, which is plasticized with Cr nitrate containing definite amounts of H_2O and acid under addition of regulated amounts of alkali, shaped and then strongly calcined at a definite temperature after a slow heating to an initial temperature. There may also be used a starchy Al hydrate, which has been obtained by precipitating the hydroxide using CO_2 from an aluminate solution containing about 5% NaOH at about 25°–35°, whereby the Na is present in excess, preferably about 80%, above the amount represented by the formula $NaAlO_2$.

2873. ———. Catalysts for Benzine Synthesis. British Patent 498,007, Dec. 28, 1938. Chem. Abs., vol. 33, 1939, p. 5645.

$MgCO_3$ is used as a carrier for Fe-group catalysts for benzine synthesis. The carrier can be separated from the spent catalyst, before regeneration of the latter, by treatment with H_2O and CO_2 to produce soluble $Mg(HCO_3)_2$.

See also British Patent 500,182 (abs. **2870**).

2874. ———. [Catalysts for Benzine Synthesis.] German Patent 741,998, no date; appl. R 100,408 (*Cl. 12 g–1.01*). Auszüge deut. Patent-Anmeldungen, vol. 7, p. 220.

Granular pieces from very wet material, especially for the production of catalysts for the benzine synthesis, are made by dividing the material into threads or strings and then drying for a short time by hot gases.

2875. ———. Catalysts for Synthesis of Hydrocarbons. British Patent 518,334, Feb. 23, 1940. Chem. Abs., vol. 35, 1941, p. 7413.

Very effective catalysts of Co and Mg are produced by precipitating simultaneously or successively the Mg and Co contained in a solution of their nitrates or chlorides while using a Mg solution having a larger content of Mg than that corresponding to the stoichiometric ratio of Mg to Co in the catalyst to be produced.

2876. ———. [Catalysts for Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Indian Patent 22,776, Sept. 19, 1936; appl. filed Apr. 15, 1936. Chem. Zentralb., 1937, I, p. 427.

To reduce the too high initial activity of catalysts, they are pretreated with liquid or fused synthetic or natural hydrocarbons; especially suitable are the hydrocarbons synthetically obtained by the aid of such catalysts. The catalyst can be broken up in a mixture of oil and benzine, the benzine evaporated so that it retains only the oil, or the reduced catalyst can be cooled in a stream of inert gas then treated with a hydrocarbon mixture. Since it is heavily charged with gas, it will take up only a small amount of hydrocarbons.

2877. ———. [Catalysts for the Carbon Monoxide Hydrogenation.] German Patent Appl. —, no date. FIAT Reel K–20, frames 279–285, Jan. 14, 1941; PB 70,211.

Draft of a patent specification. The Fe-containing residues from the production of Al are treated with alkaline solutions and mixed with kieselguhr. For raising the activity, an Fe, Cu, and/or Ca salt solution may be added before, during, or after the treatment with the alkaline solution.

2878. ———. [Catalytic Apparatus.] British Patent 460,017, Jan. 19, 1937. Chem. Abs., vol. 31, 1937, p. 4542.

Apparatus for the treatment of gases comprises a tower containing superimposed pairs of catalyst containers, the lower edge of each pair fitting into a U-shaped rim of the pair below. The spaces in the rims are filled with finely divided catalyst of the same composition as that in the containers.

2879. ———. Catalytic Apparatus British Patent 496,718, Dec. 1, 1938; appl. filed June 1, 1937. Chem. Abs., vol. 33, 1939, p. 3213.

Reaction chamber for the catalytic synthesis of benzine from CO and H_2 is traversed by tubes connected in parallel by headers in a circuit comprising a boiler, so that cooling H_2O is circulated by thermosyphonic action. A number of reaction vessels may be connected to the same boiler.

2880. ———. [Catalytic Cracking of Hydrocarbons.] German Patent 759,895, Sept. 13, 1940; appl. R 108,-321, R 536 (*Cl. 23 b–1.04*). TOM Reel 37, bag 3,451, Item 35; TOM Reel 177, frames, 1,609–1,611; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 34, 1948, p. 84.

Catalytic cracking of hydrocarbon vapors, such as paraffinic Kogasin, takes place in 3 stages:

1. Cracking, accompanied by formation of C deposits.
2. Removal of hydrocarbons from catalyst.
3. Regeneration of the catalyst by oxidation of the C deposit.

Particularly high quality products were obtained by addtion of H_2O vapor to stage (1) (30–70 wt. % of initial hydrocarbons) and by flushing with pure H_2O vapor in (2), but serious fluctuations in temperature were observed. This was eliminated by addition of an amount of H_2O vapor corresponding to a saturation temperature of 50°–70° C. in stage (3) to the oxidizing gas. The process was especially suited to Al silicate catalysts (activated fuller's earth). It ensured unifom operation of the converter and a constant operating temperature. 40% cracking gasoline was obtained. C deposits amount to 1.2–2.5 wt. %.

2881. ———. Catalytic Hydrogenation of Carbon Monoxide. British Patent 672,405, 1952. Fuel Abs., 1952, abs. 520.

Small quantities, preferably 0.5–5 vol. % of NH_3 and/or its derivatives such as methylamine are added to the synthesis gas.

2882. ———. Catalytic Hydrogenation of Carbon Monoxide. British Patent 680,241, Oct. 1, 1952. Chem. Abs., vol. 47, 1953, p. 5099.

Describes apparatus for maintaining the inlet of a reactor cooler than the outlet. A fluid cooling agent (I) is passed through a reactor in indirect heat transfer with the catalyst. (I) passes through 2 or more cooling zones in series, the cooling zones being connected to each other through a throttling valve so as to produce a progressive decrease in pressure from 1 cooling zone to the next in the direction of flow of (I).

2883. ———. Catalytic Hydrogenation of Carbon Monoxide. British Patent 680,281, Oct. 15, 1952. Chem. Abs., vol. 47, 1953, p. 5099.

Cooling systems for the different reactor zones are kept separate, although 1 system may be used for the same zone in several different reactors.

2884. ———. [Catalytic Hydrogenation of Carbon Monoxide.] Indian Patent 23,662, July 17, 1937; appl. filed Feb. 9, 1937.

See French Patent 812,883 (abs. **2920**).

2885. ———. [Catalytic Hydrogenation of Carbon Monoxide.] Italian Patent 346,389, Nov. 16, 1936.

See French Patent 812,883 (abs. **2920**).

2886. ———. [Catalytic Reaction of Carbon Monoxide and Hydrogen.] Italian Patent 352,319, July 7, 1937. Chem. Zentralb., 1938, I, p. 3735.

See French Patent 824,216 (abs. **2928**).

2887. ———. [Catalytic Syntheses.] French Patent 802,536, Sept. 7, 1936. Chem. Abs., vol. 31, 1937, p. 1820.

In the catalytic synthesis of organic compounds, particularly the formation of hydrocarbons from CO and H_2, the high initial activity of the catalyst is reduced by adding natural or synthetic liquid hydrocarbons thereto, during or after its manufacture. The products of the reaction are most suitable for addition. The added liquid is gradually removed by the gases traversing the reaction chamber.

2888. ———. [Cobalt Catalysts.] German Patent Appl. R 95,985, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 294.

Co catalysts for the hydrocarbon synthesis from CO and H_2 are made by precipitation from solutions of Co salts on $MgCO_3$ as support. The used catalysts are regenerated by dissolving the Mg as Mg bicarbonate with H_2O and CO_2, separation of the Co compounds, and renewed precipitation as basic carbonate.

2889. ———. [Cobalt-Magnesium Catalyst for Conversion of Carbon Monoxide-Hydrogen Mixtures Into Hydrocarbons.] Belgian Patent 430,164, Mar. 22. 1939; appl. filed Sept. 13, 1938, in Germany Sept. 27, 1937. Chem. Zentralb. 1940, I, p. 325.

See French Patent 843,305 (abs. **2966**).

2890. ———. [Combining City-Gas Production and Gasoline Synthesis.] German Patent Appl. R 111,103, R 594, filed Sept. 23, 1941 (*Cl. IV d–12 o*). TOM Reel 36, bag 3,454, item 36, 6 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, chap. 79, 1948, p. 10.

City-gas production is combined with gasoline synthesis by CO hydrogenation using Fe catalysts. The catalyst load is greater than in the normal synthesis operation. Temperature and pressure are increased. Chiefly, a once-through operation is used. The synthesis gas contains more H_2 in proportion to the CO than is usually used with Fe catalysts in the synthesis of gasoline. Tabulated data are presented for 4 different types of operation showing the factors that contribute to the production of a better residual gas for city gas use without seriously interfering with the normal yield of liquid products.

2891. ———. [Condensation of Aldehydes of High Molecular Weight.] German Patent Appl. —, R 526, filed Aug. 17, 1940. FIAT Reel K–20, frames 254–257; PB 70,211.

Aldehydes formed in the CO hydrogenation by action of water gas on olefinic hydrocarbon mixtures can be transformed into aldehydes of high molecular weight by condensation in presence of a strong caustic alkali solution at temperature of 50°–75°. After separation of the reaction products, the condensing agents can be used for further condensation.

2892. ———. [Condensation of Higher Aldehydes.] German Patent Appl. R 108,162, no date (*Cl. IV d–12 o*). Auszüge deut. Patent Anmeldungen, vol. 6, p. 302.

Higher aldehydes are condensed by means of alkaline condensing agents in higher concentration and at elevated temperature.

2893. ———. [Conversion of Olefins From Sources Other Than Carbon Monoxide Hydrogenation Into Fatty Acids.] German Patent Appl. R 110,167, R 573,

filed May 23, 1941 (*Cl. IV d–12 o*). TOM Reel 36, bag 3,454, item 36, 3 pp.; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 1, 1948, p. 1.

Olefins or products containing them, from sources other than CO hydrogenation such as the reaction products from the catalytic or thermal cracking of carbonaceous substances, from gas production by thermal means or the like, or from the reaction between CO and H_2 in presence of catalysts at ordinary or increased pressures and temperatures, are treated at pressures and temperatures in the range of about 100 atm. and 50°–200°, respectively, after which the resulting mixture is subjected to a mild oxidation and the fatty acids obtained thereby separated. Example: 1 kg. of olefinic cracked oil obtained by the thermal cracking of high-molecular hydrocarbons from the hydrogenation of CO and containing 40% of olefins is mixed with 45 gm. of Co in the form of a finely pulverized catalyst (Co 110 : ThO_2 5 : MgO 10 : kieselguhr 200 parts), and stirred at about 140° and 200 atm, with water gas (CO : H_2=1 : 1). After about 4 hr. the olefins have adsorbed 1 mol. of CO and H_2. The liquid reaction products are freed from catalyst by filtration and then oxidized with air at 70°–80°. The crude fatty acids obtained in this manner are saponified in the usual manner with alcoholic caustic liquor and finally freed from neutral oil by extraction with light benzine. The fatty acids amount to 300–350 gm.

2894. ———. [Conversion of Water-Containing Masses Into Thin Threads.] French Patent 843,306, June 30, 1939; appl. filed Sept. 12, 1938. Chem. Zentralb., 1940, I, p. 1458.

Mass, which in spite of its H_2O content is of stiff consistency, is thoroughly mechanically worked until a paste is obtained and then forced through a perforated plate. The process serves for the production of Co–Th catalysts for the benzine synthesis.

2895. ———. [Converter for Carrying Out Exothermic Gas Reactions Particularly Those for the Catalytic Hydrogenation of Carbon Monoxide.] German Patent Appl. R 113,200, R–619, filed June 8, 1942 (*Cl. IV b–12 g*). FIAT Reel K–30, frames 7,668–7,672; PB 73,587; TOM Reel 177, frames 1,523–1,526; TOM Reel 36, bag 3,454, item 36; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 14, 1948, p. 35.

Describes cooling arrangement with aid of diagrams.

See also German Patent Appl. R 113,201 (abs. **2973**) and R 113,202 (abs. **2980**).

2896. ———. Cooling Reactors for the Hydrogenation of Carbon Monoxide. British Patent 677,470, Aug. 13, 1952. Chem. Abs., vol. 47, 1953, p. 295.

Synthesis gas flowing downward through the catalyst bed of a Fischer-Tropsch reactor is cooled, and a positive temperature gradient is maintained in the direction of gas flow by indirect heat transfer to a solution having a solvent component, which is a single liquid compound or an azeotropic mixture that vaporizes under the conditions in the reactor. The boiling point of the solution should vary with relatively small changes in concentration so that the boiling point of the lower layers is 5°–20° higher than the boiling point of the upper layers of solution in the reactor. Aqueous solutions of $CaCl_2$, $MgCl_2$, or NaOH are particularly well suited for use as the solution.

2897. ———. [Cutoff Valve for Storage Containers Especially for Catalysts.] German Patent Appl. —, R 645, filed Nov. 28, 1942. FIAT Reel K 30, frames 8,028–8,032. PB 73,587; TOM Reel 36, bag 3,454, item 36, 2 pp.; Meyer Transl. PC–S–2, F–T, vol. 2, chap. 86, p. 30.

Cutoff valve arrangement for storage containers consists of a preferably rectangular or square discharge passage in which sliding rods are mounted close to the side walls and on these rods the cutoff valve slides. Gives 3 diagrams.

2898. ———. [Dehydrogenation of Cyclic Hydrocarbons.] German Patent Appl. R 115,223, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 314.

Cyclic hydrocarbons are dehydrogenated by treating with Cl and/or Br at elevated temperatures and by the use of Al oxide and/or catalysts containing silicic acid.

2899. ———. [Dehydrogenation of Saturated Hydrocarbons.] German Patent Appl. R 109,613, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 305.

Saturated aliphatic hydrocarbons are dehydrogenated by addition of Br and by splitting off the H bromide at elevated temperatures, 300°–500°.

2900. ———. [Dehydrogenation of Saturated Hydrocarbons.] German Patent Appl. R 112,917, no date (*Cl. 12 o–19.01*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 310.

Saturated hydrocarbons with 6 or more C atoms in the molecule are catalytically dehydrogenated to olefins by utilizing the hydrocarbons admixed with such O_2-containing gases that H_2O is able to form on the strongly cyclic-acting catalysts.

2901. ———. [Dehydrogenation of Saturated Hydrocarbons.] German Patent Appl. R 113,825, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 312.

Saturated aliphatic hydrocarbons are dehydrogenated by simultaneous catalytic Br addition and splitting-off at 300°–500° and subatmospheric pressure. To avoid undesirable diolefin or polyolefin formation especially high catalyst burdens are used amounting per hour to >10 l., preferably >20 l., of liquid hydrocarbons per l. of catalyst. Addition to German Patent Appl. R 109,613 (abs. **2899**).

2902. ———. Diesel Fuel. British Patent (provisional) 5,877 filed 1937.

Diesel-oil fraction from the Fischer-Tropsch process has a cetene number of approximately 100 and is therefore valuable for blending with tar oils, which, when used alone, are unsuitable for high-speed diesel engines.

2903. ———. [Diesel Oil.] German Patent Appl. R 107,891, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 302.

Diesel oil is produced by carrying out the hydrogenation of CO with suspended Co–ThO_2–MgO–kieselguhr catalyst, the hydrocarbon mixture used as the dispersion medium being recycled after it is purified using alkali liquor.

2904. ———. [Diesel Fuel.] German Patent 726,894, Sept. 17, 1942; appl. R 95,973, filed Apr. 1, 1936 (*Cl. 46 a^6–7*). Chem. Abs., vol. 37, 1943, p. 6439.

Medium or heavy oils, such as are obtained by catalytic hydrogenation of CO are mixed with H-poor hydrogenation products, for example, mildly hydrogenated coal extracts. The H-poor products are hydrogenated only to a degree that prevents flocculation when they are mixed with the paraffinic substances. The mixture is freed of solids and used as diesel fuel.

2905. ———. [Dissipation of Heat of Reaction in Synthesis of Gasoline From Carbon Monoxide.] Indian Patent 24,210, Dec. 18, 1937; appl. filed July 12, 1937. Chem. Zentralb., 1938, I, p. 3736.

See French Patent 822,636 (abs. **3200**).

2906. ———. [Dissipation of Heat of Reaction in Synthesis of Gasoline From Carbon Monoxide.]

Italian Patent 351,470, May 26, 1937. Chem. Zentralb., 1938, I, p. 3736.

See French Patent 822,636 (abs. **3200**) and Indian Patent 24,210 (abs. **2905**).

2907. ———. [Experimental Apparatus for Carrying Out Chemical Reactions, Particularly Reactions Under High Pressure.] German Patent Appl. —, R 659, filed Jan. 21, 1943. FIAT Reel K–30, frames 7,992–7,995; PB 73,587; TOM Reel 36, bag 3,454, item 36, 4 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, chap. 87, p. 32.

Detailed description with diagram of an apparatus for carrying out chemical reactions in which gases and/or liquids are caused to react under high pressures as in hydrogenation or water-gas reactions.

2908. ———. [Fatty Acids.] German Patent Appl. R 106,746, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 300.

Fatty acids are obtained from the hydrocarbons b. >200° and produced by the hydrogenation of CO by cracking to olefins b. 180°–300°. These are converted with CO and H_2 and then catalytically oxidized with air.

2909. ———. [Fatty Acids.] German Patent Appl. R 107,858, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 302.

High-molecular fatty acids are made by oxidizing paraffin hydrocarbons, especially hard paraffins, obtained from the hydrogenation of CO, with sulfuric and solutions of alkali bichromates in the fused state.

2910. ———. [Fatty Acids From Carbon Monoxide Hydrogenation Products.] Belgian Patent, 440,117, Aug. 23, 1941; appl. filed Dec. 23, 1940. Chem. Zentralb., 1942, I, p. 1054.

CO is so hydrogenated that as far as possible aliphatic hydrocarbons boiling >200° are obtained. These are separated into fractions 180°–300°. These mixtures are treated with water gas and converted through oxidation into fatty acids.

2911. ———. [Fuel for Diesel Engines.] French Patent 818,056, Sept. 17, 1937. Chem. Abs., vol. 32, 1938, p. 2325.

Paraffinic oils, obtained in known manner by the catalytic hydrogenation of CO at about atmospheric pressure, are mixed with liquid or solid carbonaceous materials of lower H content, such as tar oils or oils obtained by the extraction or hydrogenation of coal. Gives examples and various details.

2912. ———. [Gas Purification.] German Patent Appl. R 101,389, filed Jan. 25, 1938 (*Cl. IV b–26 d*). PB Report 412, May 15, 1945.

Organic S compounds in gases are converted to H_2S by heating the gas, preferably with added O_2 and steam rapidly to >400° C. and digesting at this temperature in the absence of a catalyst for a considerably longer time than required for heating. Final heating is preferably accomplished by partial combustion to prevent trouble owing to deposition of solids on indirect heating surfaces.

2913. ———. [High-Boiling Hydrocarbon Oils.] German Patent 721,929, June 27, 1942; appl. R 95,052, filed Dec. 21, 1935 (*Cl. o–1.01*). FIAT Reel AA 88, frames 4,227–4,230; PB 70,273; Chem. Abs., vol. 37, 1943, p. 5578.

Oils are condensed from low-boiling hydrocarbon mixtures, such as the various fractions of a gasoline obtained by synthesis from CO and H_2, containing unsaturated components. The condensation agent, such as $AlCl_3$, is reused repeatedly. Each time a fraction with a higher content of olefins is used and the working temperature is increased accordingly.

2914. ———. [Highly Ignitible Fuel and Process for Producing It.] German Patent Appl. —, R 616, filed May 28, 1942. FIAT Reel K–30, frames 8,098–8,101; PB 73,587.

Highly ignitible fuel with cetane number >100 consists of higher alkylnitrates alone or admixed with up to 80% of hydrocarbons wholly or partly b. < 200°, if desired < 100°. To produce this fuel, alcoholic hydrocarbon mixtures are converted into hydrocarbon mixtures containing alkylnitrates by treatment with nitrating acids. Oxygenated primary products of the catalytic hydrogenation of CO may also be nitrated after previous addition of H_2. Also the alcoholic hydrocarbon mixtures obtained by the reaction between water gas and olefins and subsequent hydrogenation are nitrated. Example: An alcoholic heavy oil, produced from an olefinic fraction b. 150°–340°, which had reacted with water gas and was subsequently hydrogenated, had an OH number of 138. 900 gm. of this heavy oil were stirred into 3,600 gm. of nitrating acid (40% HNO_3 and 60% H_2SO_4). The reaction temperature was maintained at —5° by means of dry ice. After addition of the heavy oil was completed, the mixture was allowed to stand for 30 minutes at 10°. The nitrated mixture was then treated in the usual manner with H_2O and a solution of bicarbonate whereby 975 gm. of nitrated product was obtained whose OH number was 0 and the neutralization number 0.5, while the solidifying point was established at —16°. The product showed a calculated cetane number of 460.

2915. ———. [High-Molecular Fatty Acids.] French Patent 872,069, May 28, 1942; appl. filed May 10, 1941, in Germany June 28 and 29, 1940. Chem. Zentralb., 1942, II, p. 1853.

Hard paraffins from the CO hydrogenation are oxidized in the molten state by means of sulfuric acid solutions of alkali bichromate or other O_2-evolving salts. Example: 200 gm. of hard paraffins, 95°, are oxidized within 4 hr. at 125° with 2,500 gm. of 55% H_2SO_4 and 250 gm. $Na_2Cr_2O_7$ in solution. After drawing off the oxidation solution, the oxidation is repeated 3 times. The yield is 150 gm. of fatty acids.

2916. ———. [High-Molecular Hydrocarbons.] German Patent Appl. R 95,051, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 294.

High-molecular hydrocarbon oils are obtained by the catalytic hydrogenation of CO and condensation of the resulting products with rising temperature. Addition to German Patent Appl. R 94,081 (abs. **3152**).

2917. ———. [High-Molecular Hydrocarbons.] German Patent Appl. R 97,688, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 295.

High-molecular hydrocarbon oils are obtained by catalytically hydrogenating CO, splitting and condensing the constituents b. >150°, which show at a mean boiling temperature of 50°–220° densities of 0.6510–0.7555. Addition to German Patent Appl. R 94,081 (abs. **3152**).

2918. ———. [High-Molecular Hydrocarbons.] German Patent Appl. R 105,033, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 298.

High-molecular hydrocarbon oils are obtained from hydrocarbons produced by the catalytic hydrogenation of CO by cracking and condensing the cracked product under continuous addition of small amounts (about 0.5%) of condensing agents to produce oils of lower viscosity and greater amounts (about 1.3%) to produce oils of higher viscosity. Addition to German Patent Appl. R 95,050 (abs. **3148**).

2919. ———. Hydrocarbon Synthesis. British Patent 690,432, Apr. 22, 1953. Chem. Abs., vol. 47, 1953, p. 8996.

Hydrocarbons and O-containing organic compounds are synthesized by the hydrogenation of CO at atmospheric pressure in the presence of an Fe catalyst, in which the catalyst is used at 170°–200°, and in such manner that in the course of the 1st 500 hr. of operation, the catalyst is extracted 4–7 times to remove high-boiling synthesis products therefrom; the synthesis is thereafter continued at 170°–200°. Before its use, the catalyst is impregnated with an alkali metal salt of a nonvolatile acid, such as K silicate or K phosphate, and is reduced with H_2 at a high rate of flow and 200°–350°. The extractions are generally effected with hydrocarbon mixtures at the synthesis temperature in use at the time. While up to the 1st extraction the conversion remains quite unsatisfactory at 30–40%, an improved conversion is obtained after the 1st extraction. After 4–7 extractions of the catalyst within the 1st 500 hr. of operation, the normal CO plus H_2 conversion of 72% is attained. Thereafter the catalyst can be used generally for 2,000–4,000 operational hr. before its activity is reduced. Owing to the low synthesis temperature, the CH_4 formation remains considerably lower than in usual processes for hydrogenating CO, in spite of a high total conversion. The life of the catalyst is also considerably lengthened. In an example, an Fe catalyst containing Fe 100, Cu 5, and CaO 10 parts was precipitated with Na_2CO_3 from a mixed solution of the corresponding materials at pH 7. The precipitate was separated by filtration, washed, dried, and finally impregnated with K silicate. The reduction was carried out for 60 min. in H_2 at 225°. The catalyst was then put on stream at 160° with 100 l. water gas per l. catalyst per hr. In 498 hr. the temperature was raised to 195°, to give a CO plus H_2 conversion of approximately 39%, which fell to 30% in the next 48 hr. of use, owing to the deposition of paraffin on the catalyst. The catalyst was then extracted with 4 times its volume of a diesel-oil fraction boiling 220°–300°. Immediately after the extraction the CO plus H_2 conversion rose to 48%.

2920. ———. [Hydrocarbon Synthesis.] French Patent 812,883, May 19, 1937. Chem. Abs., vol. 32, 1938, p. 951.

In the catalytic transformation of oxides of C to higher hydrocarbons by means of H_2, the nonvolatile reaction products are withdrawn from the catalytic mass at frequent intervals without appreciably increasing the reaction temperature above its original value and before these products have had time to have a harmful effect. The removal may be effected by means of H_2 or steam or solvents.

2921. ———. [Hydrocarbon Synthesis.] Italian Patent 340,547, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 177.

See United States Patent 2,127,127 (abs. **2144**).

2922. ———. [Hydrocarbon Synthesis.] Netherlands Patent 43,369, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 177.

See United States Patent 2,127,127 (abs. **2144**).

2923. ———. Hydrocarbons. British Patent 471,595, Sept. 7, 1937. Chem. Abs., vol. 32, 1938, p. 1276.

In the catalytic conversion of C oxides and H_2 into hydrocarbons, the catalysts are charged, before, during, or after their preparation, with hydrocarbons in liquid, molten, or dissolved state, which are carried away after the reaction has begun. The high initial activity of the catalyst is thus reduced. In examples, (1) equal parts of kieselguhr and $CoCO_3$ with activating additions are treated with a benzine solution of solid paraffin so that, after evaporation of benzine, 5% of paraffin remains in the catalyst, which is shaped and reduced with H_2 at 200°, surplus paraffin draining off; CO and H_2 are introduced, the reaction beginning slowly but increasing in intensity as the gas stream carries off the paraffin, and (2) $NiCO_3$ is precipitated on kieselguhr from a solution of Ni and Al nitrates, the product granulated, reduced with H_2 at 450° and introduced into melted paraffin, O_2 being excluded; surplus paraffin is removed. The granules harden on cooling and are unaffected by air.

2924. ———. Hydrocarbons. British Patent 486,928, June 9, 1938. Chem. Abs., vol. 32, 1938, p. 9095.

See French Patent 812,883 (abs. **2920**).

2925. ———. [Hydrocarbons From Carbon Dioxide and Hydrogen.] Belgian Patent 418,230, Apr. 30, 1937; appl. filed Nov. 4, 1936. Chem. Zentralb., 1937, II, p. 4101.

Catalyst whose efficiency is reduced by the deposition thereon of solid substances is activated during the course of the synthesis and the rise in temperature with H_2, steam, or solvents.

2926. ———. Hydrocarbons From Carbon Monoxide and Hydrogen. British Patent 502,880, no date. Chem. Zentralb., 1939, II, p. 4662.

Addition to French Patent 812,883 (abs. **2920**).

See also United States Patent 2,238,726 (abs. **647**).

2927. ———. Hydrogenation of Carbon Monoxide. British Patent 504,910, Apr. 27, 1939. Chem. Abs., vol. 33, 1939, p. 7814.

Solid paraffin hydrocarbons are produced from CO and H_2 with a Co catalyst at or near atmospheric pressure and at 160°–175°, the reaction gases being passed at not more than 20 l. per hr. per l. of catalyst, which results in a yield of 50% or more of solid paraffins. The catalyst preferably contains no catalytic metal other than Co and is activated by ThO_2 or MgO. The products are especially suitable as ingredients of polishing wax.

See also French Patent 824,216 (abs. **2928**).

2928. ———. [Hydrogenation of Carbon Monoxide.] French Patent 824,216, Feb. 4, 1938. Chem. Abs., vol. 32, 1938, p. 5852.

In the catalytic conversion of mixtures of CO and H_2 under ordinary or slightly raised pressure, the proportion of hydrocarbons having higher boiling point or solid hydrocarbons is increased by using lower temperatures (165°–170°) than those used in the production of hydrocarbons of lower boiling point. The catalyst may be Co, activated by addition of Th and Mg.

See also Italian Patent 352,319 (abs. **2886**).

2929. ———. [Hydrogenation of Carbon Monoxide.] German Patent Appl. R 96,684, no date (*Cl. IV b–12 i*). Auszüge deut. Patent-Anmeldungen, vol. 7, p. 310.

Catalysts are used consisting of Fe oxides or hydroxides and at least 20% alkali carbonate.

2930. ———. [Hydrogenation of Carbon Monoxide.] German Patent Appl. R 102,909, filed July 20, 1938 (*Cl. IV d–12 o*). PB Report 412, May 15, 1945.

Making relatively light products from the hydrogenation of CO by using a catalyst containing not more than 33% by weight of active metal and operating at relatively high temperatures, 235°–240° C. with Co, and high space velocities, up to 9 $m.^3$ synthesis gas per kg. Co per hr.

2931. ———. [Hydrogenation of Carbon Monoxide.] German Patent Appl. R 104,584, filed Feb. 20, 1939 (*Cl. IV d–12 o*). PB Report 412, May 15, 1945; Auszüge deut. Patent-Anmeldungen, vol. 6, p. 297.

To make products of lower molecular weight and higher olefin content the hydrogenation of CO is carried out with recycling of the product gas after separation of condensables by cooling and charcoal absorption.

With a Co catalyst at 200°–230° C., a recycle ratio of 3 : 1 to 10 : 1 is preferred. A relatively high pressure, 3–10 atm. and high temp. 200°–230° C., can be used. The resulting gas and gasoline is stated to be about 75% olefinic and 55% of the product is in the C_2–C_4 range.

2932. ———. [Hydrogenation of Carbon Monoxide.] German Patent Appl. R 104,876, filed Mar. 28, 1939 (*Cl. IV d–12 o*). PB Report 412, May 15, 1945; Auszüge deut. Patent-Anmeldungen, vol. 6, p. 298.

Hydrogenation of CO is carried out by passing synthesis gas into a suspension of finely divided catalyst in a suitable oil, preferably with mechanical agitation to distribute the gas, and simultaneously introducing a liquid such as H_2O, which vaporizes under the reaction conditions to control the temperature. For example, 1,270 gm. of Co–ThO_2–MgO–kieselguhr catalyst containing 400 gm. Co is suspended in 15 l. of oil b. 240°–300° C. Synthesis gas containing 1 Co : 2 H_2 is introduced at a rate of 2.5 l. per gm. Co per hr., and a pressure of 10 atm, is maintained in the reaction. The synthesis begins at 190° C., and the temperature is gradually raised to 210° C. as H_2O is introduced to maintain this temperature. The contraction of synthesis gas amounts to 85%, and the yield of liquid and solid hydrocarbons amounts to 172 gm. per $m.^3$. The liquid product contains 90% boiling up to 300° C and having an olefin content of 20%.

2933. ———. [Hydrogenation of Carbon Monoxide.] German Patent Appl. R 105,297, filed May 24, 1939 (*Cl. IV d–12 o*). PB Report 412, May 15, 1945.

Increasing production of high-molecular-weight hydrocarbons by using a catalyst on a support of very low bulk density. Low temperatures, 160°–180° C., low space velocity, 4 l. per hr. per kg. catalyst, elevated pressure, 10–20 kg. per $cm.^2$ and high Co content, over 100 gm. Co per l. of catalyst, are recommended with a catalyst support consisting of uncalcined Mg or low density kieselguhr.

2934. ———. [Hydrogenation of Carbon Monoxide.] German Patent 752,475, no date; appl. R 100,505 (*Cl. 12 g–4.02*). Auszüge deut. Patent-Anmeldungen, vol. 7, p. 220.

Describes arrangement of the cooling pipes in the reaction furnace for the hydrogenation of CO to gasoline.

2935. ———. [Hydrogenation of Carbon Oxides.] German Patent Appl. R 96,036, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 294.

In the catalytic hydrogenation of CO to higher hydrocarbons, the greater part of the gases used for regeneration is recycled to the synthesis furnace. Addition to German Patent Appl. R 94,946.

2936. ———. Improvements in and Relating to Apparatus for Carrying out Catalytic Gas Reactions Sensitive to Changes in Temperatures. British Patent Appl. 29,546, filed 1938.

Refers specifically to catalyst masses in annular containers that are disposed concentrically with respect to the reaction furnace, the container being formed by hollow bodies that are disposed concentrically with respect to the reaction furnaces at suitable distances apart and traversed by a heating or cooling medium and in which the annular container through which passes the heating or cooling medium is formed by separate closure parts provided with supply and discharge pipes for the heating and cooling medium.

2937. ———. Improvements Relating to Catalytic Production of Hydrocarbons. British Patent Appl. 15,166, filed 1937.

Deals with a method of regulating the reaction temperature of the Fischer synthesis. Tubes containing superheated H_2O pass through the catalyst from a H_2O chest at one end of the converter to another H_2O chest at the other end. H_2O from a boiler enters the 1st chest at the bottom, passes through the tubes and returns to the boiler from the top of the other chest. No pumps are used, the circulation being maintained by thermosyphon action alone. The converter is inclined in order to help circulation and to free steam bubbles. The flow of H_2O through each tube is thus automatically regulated by the amount of reaction heat evolved locally, and efficient temperature regulation is claimed. Several converters may be connected to a common steam boiler and several boilers connected to equalize the pressure.

2938. ———. [Improving Antiknock Properties of Gasoline.] German Patent 749,424, July 3, 1938; Appl. R 102,756, R 396 (*Cl. 23 b–1.05*). TOM Reel 37, bag 3,451, item 35, 3 pp.; TOM Reel 177, frames 1,562–1,564.

Octane number of benzine from the hydrogenation of CO is improved, from 5–10 points, by passage over material of high surface area such as silica gel, active C, acid treated clay, at 180°–200° C, apparently as a result of isomerization.

2939. ———. Improving Liquid Hydrocarbons. British Patent 464,393, Apr. 12, 1937. Chem. Abs., vol. 31, 1937, p. 7243.

Hydrocarbons, for example, lubricating oils, benzines, gas oils, lignite-tar oils, hydrogenation oils, and oils synthesized from CO and H_2, are improved by adding polymerization products obtained by treating mixtures of propylene and ethylene, or gases containing such mixtures, with polymerizing agents, for example, BF_3, $ZnCl_2$, $FeCl_3$, $AlCl_3$, at $< 0°$. Reaction accelerators, for example, $HgCl_2$, or retardants, for example, H_2O, Al_2O_3, ZnO, may be present. In examples, (1) 30, 50, or 80% of polymer is added to a refrigerator oil and (2) 100 lb. of mixed C_3H_6, C_2H_4, C_2H_6, C_3H_8, and CH_4, obtained from coke-oven gas by adsorption and cooling, are fed during 5 hr. into 20 lb. of a paraffin oil containing 10 lb. of twice-used $AlCl_3$, a temperature of —30° and pressure of 9.5 atm. being maintained; after 10 hr. the temperature is allowed to rise to atm., the pressure is relieved, and the hydrocarbons are dissolved in petroleum ether, purified by 30% H_2SO_4 and 30% NaOH and freed from solvent.

2940. ———. Improving Liquid Hydrocarbons. British Patent 464,468, Apr. 12, 1937. Chem. Abs., vol. 31, 1937, p. 7243.

In a process similar to that described in British Patent 464,393 (abs. **2939**), the added polymers are obtained by treating C_3H_6, or gases containing C_3H_6 but no C_2H_4, $< 0°$ with the polymerizing agents. In an example, 10, 20, 30, or 40% of polymerized C_3H_6 is added to a refrigerator oil.

2941. ———. [Increasing the Antiknock Property of Gasolines.] Italian Patent 375,265, June 27, 1939. Chem. Zentralb., 1942, I, p. 2354.

Gasolines obtained by the hydrogenation of CO are treated with activated bleaching earth or other adsorption agents at raised temperature. In general temperatures of 100°–450° are used. The method can also be used advantageously with cracked gasoline from the higher synthetic oils or with polymerization gasoline.

2942. ———. [Increasing the Antiknock Property of Motor Gasoline.] French Patent 866,308, July 28, 1941; appl. filed June 26, 1939. Chem. Zentralb., 1942, I, p. 2959.

Octane number of olefinic hydrocarbons, such as cracked or synthetic gasoline, is improved by treatment at 150°–400° with activated fuller's earth or silica gel. Especially suitable are earths that have been activated with HCl or H_2SO_4 as "Granosil" or "Tonsil", or those

to which $AlCl_3$, BCl_3, $FeCl_2$, H_3PO_4 have been added. As the activity of the earths decrease in operation, the temperature is raised.

2943. ———. [Increasing the Yield of Oxygenated Products in the Catalytic Hydrogenation of Carbon Monoxide.] German Patent Appl. —, no date. FIAT Reel K–30, frames 7,633–7,634, Aug. 25, 1942; PB 73,587.

This is a rough draft to patent application. According to this process, 2–50%, preferably 5–7%, of C_2H_2 are added during the catalytic reaction of gas mixture containing CO and H_2. Addition to German Patent Appl. R 109,774 (abs. **3209**).

2944. ———. Increasing the Yield of Solid Hydrocarbons. British Patent Appl. 19,431, filed 1937.

By using a lower temperature than usual and a diminished rate of reaction the yields of solid hydrocarbons are increased.

2945. ———. [Iron Catalyst for the Production of Predominantly Olefinic and Oxygenated Hydrocarbons by Hydrogenation of Carbon Monoxide.] German Patent Appl. R 115,709, R 667, filed Mar. 19, 1943 (*Cl. IV d–12 o*). FIAT Reel K–30, frames 7,969–7,972; PB 73,587; TOM Reel 177, frames 1,485–1,488; TOM Reel 36, bag 3,454, item 36; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 6, 1948, p. 15.

To increase the % of olefins or oxygenated compounds in the products of CO hydrogenation, the Fe catalysts are promoted with 2% of Ce, V, or Mn and carried on suitable fine-grained carriers such as kieselguhr, CaO, MgO, or diatomaceous earth. To shorten the induction period or to aid the reduction, 1–5% of Cu or Ag may be added. Example: An Fe catalyst of composition 100 Fe, 2 Ag, 10 V_2O_5, 100 kieselguhr and precipitated from potash solution was used in the synthesis process at 230°–245° and 15 atm. pressure. The product consisted of 40% benzine up to 200°, 25% diesel oil up to 320°, 15% soft paraffin up to 320°–460°, and 20% hard paraffin above 460°. The 200° fraction contained 25% alcohols, that from 200°–320°, 26–30% alcohols, and 320°–460°, 15–25% alcohols. These same fractions contained, respectively, 40, 42, and 50% of olefins.

2946. ———. [Iron Catalyst.] German Patent Appl. —, no date. FIAT Reel K–20, frames 232–240, Dec. 8, 1939; PB 70,211.

Highly active Fe catalysts are obtained from a mixture of Fe salt solution and a solution of a Ca or Mn salt by precipitation with alkali hydroxide, the content of Ca or Mn being >5%. Precipitation takes place on fine-grain kieselguhr, CaO, MgO, or diatomite. The precipitate is then impregnated with alkali hydroxide solutions while still moist. For reducing the induction time, 2–5% Ni, Co, or Cu are added.

2947. ———. [Iron Catalysts.] German Patent Appl. R 108,338, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 303.

Catalysts for the conversion of CO with H_2 are made by precipitating them from Fe salts with alkali, the alkali content being increased as the consumption of CO is increased, and decreasing it as the CO consumption is decreased.

2948. ———. [Iron Catalysts for Use in the Hydrogenation of Carbon Monoxide.] German Patent Appl. R 106,876, R 490, filed Feb. 2, 1940 (*Cl. IV d–12 o*). FIAT Reel K–20, frames 305–308 A; PB 70,211; TOM Reel 177, frames 1,704–1,708; Meyer Transi. PC–S–II, Fischer-Tropsch, vol. 1, chap. 51, 1948, p. 129.

Active Fe catalysts are prepared directly from the decomposition residues of natural argillaceous earth (luxmasse, Lautamasse). Reduction of these materials by the usual procedure gave up to 13% contraction with water gas at atmospheric pressure and 245°. Treatment with boiling H_2O, followed by drying and reduction, gave up to 17% contraction. Treatment with complex Cu salts, for example, cuproammonium salts, gave up to 27% contraction. Treatment with boiling alkali hydroxide followed by drying and reduction gave the same value. Catalysts prepared by boiling in a Cu salt solution, for example, Cu nitrate, treating the hot solution with alkali hydroxide, washing with dilute alkali, and reducing as usual, gave 43% and more contraction. In all cases, synthesis at pressures of 10–20 atm. raised contraction values by approximately 30%. The process is of interest because the presence of impurities that ordinarily inhibit catalytic activity, Al, Ti, SO_4-ion, appear to have no inhibiting action in this case.

2949. ———. [Knockproof Gasoline.] German Patent 725,000, June 30, 1942; appl. R 103,969, R 421, filed June 22, 1937 (*Cl. 23 b–1.04*). FIAT Reel K–20, frames 332–336; PB 70,211; TOM Reel 37, bag 3,451, item 36, 3 pp.; TOM Reel 177, frames 1,565–1,569; Chem. Zentralb., 1943, I, p. 358; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 24, 1948, p. 61; Chem. Abs. vol. 37, 1943, p. 6119.

Products of catalytic hydrogenation of CO are separated into 3 fractions according to the b. p. up to 120° light oil, 120°–210° medium oil, and 210°–316° heavy oil. The medium oil is cracked at 500°–700° and 2–11 atm. into olefinic hydrocarbons. The heavy fraction is transformed into aromatic compounds rich in benzene at 500°–700° and 7–15 atm. The gases evolved in the cracking are combined with the olefinic gases evolved in hydrogenating CO. The combined gases are treated with acid and the resulting acid esters are saponified; thus they are transformed into a mixture of alcohols. By mixing the 3 benzine fractions and the alcohol in proportions of 38.5 : 16.5 : 28.5 : 16.5, respectively, a motor fuel of 75 octane no. is obtained.

2950. ———. [Lubricant.] Austrian Patent 160,912, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 185.

Middle oil from synthesis is cracked to olefins and these polymerized to lubricant.

See also French Patent 813,766 (abs. **2951**).

2951. ———. [Lubricant.] French Patent 813,766, June 8, 1937; appl. filed Nov. 19, 1936. Chem. Zentralb., 1938, I, p. 237.

Olefin-containing hydrocarbons are condensed with $AlCl_3$ to lubricating oils. The temperature is raised gradually during the condensation from 0°–30° to 50°–80° and to 100°–130° to produce oils of different viscosity. The reaction temperature is regulated by adding neutral oils such as propane, butane, pentane, or the corresponding olefins, which are vaporized under the reaction conditions. The exhausted catalyst can be removed with fresh catalyst for the condensation at lower temperatures.

2952. ———. [Lubricants.] German Patent Appl. —, R 625, filed Aug. 4, 1942. FIAT Reel K–30, frames 7,645–7,677; PB 73,587; TOM Reel 36, bag 3,454, item 36.

Lubricants are prepared by mixing with them carboxylic acids that have the same or similar structure as the constituents of the original lubricating oils themselves. Such carboxylic acids are made by building up 1 or more carboxyl groups in hydrocarbons or in hydrocarbon mixtures that show pronounced lubricating properties. These so-called lubricant-carboxylic acids can be prepared in various ways. Gas mixtures containing CO and H_2 can be added catalytically to olefinic lubricating oils and the aldehydes converted by oxidation to carboxylic acids. The lubricant- alde-

hydes thus obtained can be reduced to alcohols and thereafter be converted in known manner into the lubricant-carboxylic acids. The raw material for this lubricant can with special advantage be the synthetic lubricant obtained through the polymerization of olefinic hydrocarbons by $AlCl_3$, BF_3, and similar condensation agents.

2953. ———. [Lubricants.] German Patent Appl. R 108,293, no date (*Cl. 21 o–1.01*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 303.

CO hydrogenation products, which were obtained by recycling of the synthesis gas, are used as the raw material for the production of high-grade lubricants by condensation with $AlCl_3$.

2954. ———. Lubricating Oils. British Patent Appl. 22,934, filed 1938.

Thermal stability of the synthetic oils is improved by treatment with Al chloride at temperatures >140°.

2955. ———. Lubricating Oils. British Patent 470,534, Aug. 17, 1937. Chem. Abs., vol. 32, 1938, p. 1087.

See French Patent 809,226 (abs. **3204**).

2956. ———. Lubricating Oils. British Patent 473,935, Oct. 22, 1937. Chem. Abs., vol. 32, 1938, p. 3142.

In the process of British Patent 470,534 (abs. **2955**), the condensation catalyst that has become spent after use in a series of condensation reactions at increasing temperatures is regenerated by adding small quantities of fresh catalyst and is used again for conducting a series of similar condensations in which the reaction temperature is raised from condensation to condensation, the initial temperature being the low-conversion temperature originally employed. Alternatively, the spent catalyst can be further utilized by employment in the conversion of cracked products of different composition and of increasing olefin content.

2957. ———. Lubricating Oils. British Patent 490,930. Aug. 22, 1938. Chem. Abs., vol. 33, 1939, p. 1139.

In the production of these by the condensation with $AlCl_3$ or like condensation agents of benzines rich in unsaturated hydrocarbons produced by the catalytic conversion of mixtures of H_2 and CO, the condensation agent is used in a quantity insufficient for complete conversion in a single temperature stage and the condensation temperatures is raised gradually, continuously, or in stages during the conversion, whereas the conversion agent separated off after the reaction is completed is used for the conversion of a new charge of benzine commencing again in a low temperature. The conversion agent, which is reduced in effectiveness after 1 or more conversions, may be regenerated by adding small quantities of fresh agent, as described in British Patent 473,935 (abs. **2956**). The condensation temperature may be controlled by absorbing the heat generated in the reaction by adding neutral low-boiling hydrocarbons, for example, PrH, BuH, pentane.

2958. ———. Lubricating Oils. British Patent 504,350, Apr. 19, 1939; appl. filed Oct. 19, 1937. Chem. Abs., vol. 33, 1939, p. 7556.

Lubricating oils are produced by the action of condensing agents such as $AlCl_2$ on olefinic benzines obtained by cracking at 450°–550° and about 4–12 atm. hydrocarbons obtained by the Fischer-Tropsch synthesis and boiling above 150°, the fractions of which benzines having a boiling range fo 10° correspond within 1% to a given density curve. The necessary density values for fractions of mean boiling temperatures of 50°–220° are given and vary from 0.6510 to 0.7555. The cracked benzines are used without separation of any intermediate fraction, although the lower and upper boiling limits may vary. The cracking is preferably effected at 460°–510° and 6–8 atm. for 3–15 min.

See also French Patent 827,761 (abs. **2962**).

2959. ———. [Lubricating Oils.] French Patent 47,-814, July 31, 1937; appl. filed Nov. 24, 1936. Chem. Zentralb. 1938, I, p. 237; Chem. Abs., vol. 32, 1938, p. 4774.

Olefin-containing hydrocarbons, such as, those from benzine synthesis by cracking the product, are condensed with $AlCl_3$. The catalyst is renewed from time to time by introducing about 10% of fresh catalyst.

See also French Patent 809,226 (abs. **3204**) and British Patent 473,935 (abs. **2956**).

2960. ———. [Lubricating Oils.] French Patent 791,950, Dec. 19, 1935. Chem. Abs., vol. 30, 1936, p. 4315.

Lubricating oils are improved by mixing them with the polymerization products obtained by treating gases containing C_2H_4 and C_3H_6 with agents such as $AlCl_3$, $FeCl_3$, $ZnCl_2$, BF and, if necessary, accelerators or retarders.

See also British Patent 464,393 (abs. **2939**).

2961. ———. [Lubricating Oils.] French Patent 826,821, Apr. 11, 1938; appl. filed Sept. 16, 1937. Chem. Zentralb., 1938, II, p. 2217.

Olefin mixtures, obtained by cracking the higher boiling portion of the synthetic hydrocarbons from the Fischer-Tropsch process, are polymerized with $AlCl_3$ at increasing temperatures. If highly viscous oils are desired, large amounts of catalyst, low polymerization temperatures, and long polymerization times are employed; for less viscous oils, higher reaction temperatures, shorter contact periods, and smaller amounts of catalyst. The catalyst can be renewed from time to time by adding fresh amounts of $AlCl_3$.

2962. ———. [Lubricating Oils.] French Patent 827,761, May 3, 1938; appl. filed Oct. 11, 1937. Chem. Zentralb., 1938, II, p. 2217; Chem. Abs., vol. 32, 1938, p. 8764.

Mixtures of hydrocarbons are condensed with known condensing agents, for example, $AlCl_3$. The starting material is gasoline, the different fractions of which have the following densities to within 1% above or below, the temperature being the mean boiling temperature of that fraction, 50°=0.6510, 60°=0.6635, 70°=0.6755, 80°=0.6860, 90°=0.6960, 100°=0.7055, 110°=0.7120, 120°=0.7180, 130°=0.7225, 140°=0.7275, 150°=0.7315, 160°=0.736, 170°=0.74, 180°=0.743, 190°=0.7465, 200°=0.75, 210°=0.753, and 220°=0.7555.

2963. ———. [Lubricating Oils.] Italian Patent 344,270, Aug. 16, 1936.

See Belgian Patent 416,717 (abs. **3151**).

2964. ———. [Lubricating Oils.] Italian Patent 389,688, July 9, 1941, in Germany Sept. 9, 1940. Oel u. Kohle, vol. 39, 1943, Sch. 193; Chem. Zentralb., 1943, I, p. 591.

Hydrocarbons obtained from water gas by the Fischer-Tropsch process b. above 150° and preferably above 280° are condensed with $AlCl_3$. It is advantageous to make use of oils that have been obtained by working with Co catalysts with a high content of inert material and with recycling of a synthesis gas with a ratio of fresh gas to recycle gas of 1:3 or 1:5. The lubricating oil has a very low viscosity pole height, 1.75–1.48, and a very low congealing point, about −30°.

2965. ———. Lubricating Oils by Polymerization of Fischer-Tropsch Primary Products. British Patent Appl. 28,479, filed 1937.

This patent application specifies the choice of material for polymerization, the fractions of which have densities within prescribed limits.

2966. ———. [Magnesium and Cobalt Catalysts for the Conversion of Carbon Monoxide and Hydrogen Mixtures.] French Patent 843,305, June 30, 1939. Chem. Abs., vol. 34, 1940, p. 6780.

Method for the preparation of Mg and Co catalysts to be used in the synthesis of hydrocarbons, by precipitation from their nitrate and chloride solutions, consists in using a Mg solution containing a greater amount of Mg then those corresponding to the stoichiometric proportion between the Mg and the Co in the catalyst. Among examples, (1) a solution containing 24.91 gm. Co in the form of nitrate and 3.97 gm. MgO in the form of nitrate is precipitated at the boiling temperature by means of 10% Na_2CO_3 solution; (2) a Mg and Co catalyst is obtained by preparing a Mg $(NO_3)_2$ solution containing 150 gm. MgO in 2 l. H_2O precipitating by means of a b. 10% Na_2CO_3 solution (30 l.), introducing 10 l. $Co(NO_3)_2$ solution containing 1 kg. Co, adding the support material, and filtering while hot.

2967. ———. [Magnesium-containing Catalysts for Gasoline Synthesis.] German Patent Appl. —, filed Mar. 31, 1936. TOM Reel 37, bag 3,451, item 35, 3 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 4, chap. 126, 1949, p. 6.

In producing hydrocarbons by the catalytic reaction of CO and H_2 in the presence of Co catalysts, use is made of catalysts containing no other catalytic metal than Co, the catalysts being activated only through the addition of ThO_2 and MgO. A suitable catalyst is found to consist of 100 parts Co, 5 ThO_2, and 5 MgO.

2968. ———. Manufacture of Products Including Oxygen-Containing Organic Compounds by Hydrogenation of Carbon Monoxide. British Patent 668,419, 1952. Fuel Abs., vol. 11, 1952, abs. 4030.

Hydrogenation is effected in the presence of an Fe catalyst that has been obtained by precipitation from solution by an alkali metal compound, the precipitated catalyst mass obtained having been incompletely washed so that the catalyst contains an alkali metal content of 3–20 wt. % of the Fe present in the catalyst, the alkali metal content being calculated as K_2O and the Fe being determined as metal.

2969. ———. [Metallic Catalysts.] French Patent 842,278, June 8, 1939. Chem. Abs., vol. 34, 1940, p. 5258.

Worn out catalysts used in the synthesis of organic compounds from CO and H_2, that are obtained by precipitating metals acting catalytically in presence of kieselguhr, are renewed by dissolving them in a dilute solution of HNO_3 containing preferably 3–5% free HNO_3 and reprecipitating the components capable of catalytic action.

2970. ———. [Methane From Carbon Monoxide and Hydrogen.] French Patent 956,586, Feb. 2, 1950; appl. filed June 9, 1944. Chem. Zentralb., 1950, II, p. 581.

CH_4 is produced from CO and H_2 in the presence of a Ni catalyst and 5–50 parts of MgO as CO_2 absorbent to 100 of Ni and at temperatures of 170°–190°. Kieselguhr serves as the carrier substance for the Ni. Synthesis gas is passed over the catalyst at a speed of 25–100 l. per 4 gm. Ni per hr. After removal of organic S and H_2S the synthesis gas is heated to 200°–500°, preferably 400°–450°, in the presence of a catalytically active substance such as finely divided Cu.

2971. ———. [Method for Activating Hydrogenation Catalysts.] German Patent Appl. R 104,999, PA 294,891, filed Apr. 15, 1939 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 283–287; PB 83,253; PB Report 412, May 15, 1945; Auszüge deut. Patent-Anmeldungen, vol. 6, p. 298.

Preparation of synthesis catalysts by precipitating from sulfate instead of nitrate solution and activating by washing with alkali carbonate or hydroxide solution. For example, a catalyst containing 100 parts Co, 10 parts MgO, 5 parts ThO_2, and 200 parts kieselguhr is prepared from a solution containing 40 gm. per l. of Co in the form of sulfate. The precipitate obtained by addition of soda is washed first with H_2O, 1 l. per 25 gm. Co, then with $N/20$ $(NH_4)_2CO_3$, 1 l. per 25 gm. Co, and finally with H_2O, 1 l. per 25 gm. Co.

2972. ———. [Method for Making Textiles or Other Fibrous Material Waterproof or Water-Resistant.] German Patent Appl. —, R 647, filed Dec. 14, 1942. TOM Reel 36, bag 3,454, item 36, 5 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, chap. 12, 1948, p. 30.

In H_2O-proofing textiles by impregnation with high molecular fatty acids, those fatty acids are used that are obtained by the oxidation by means of oxidizing agents of the higher aliphatic hydrocarbons. Also, use can be made of the oxidation products that are obtained through treatment with nitrous gases in presence of concentrated H_2SO_4 or nitrosyl H_2SO_4 or through repeated treatment with bichromate H_2SO_4. As raw material for the oxidation, paraffins obtained by the catalytic reduction of CO with H_2 are used.

2973. ———. [Method for Operating an Exothermic Catalytic Converter Especially One for Hydrogenation of Carbon Monoxide.] German Patent Appl. R 113,201, R–620, filed June 11, 1942 (*Cl. IV b–12 g*). FIAT Reel K–30, frames 7,663–7,667; PB 73,587; TOM Reel 177, frames 1,527–1,530; TOM Reel 36, bag 3,454, item 36; TOM Reel 39, bag 3,453, item 1; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 15, 1948, p. 38.

Describes the manner of circulating the cooling medium.

See also German Patent Appl. R 113,200 (abs. **2895**) and R 113,202 (abs. **2980**).

2974. ———. [Method for Purifying Magnesia for Use in Catalyst Manufacture.] German Patent Appl. R 114,640, R 641, filed Nov. 14, 1942 (*Cl. IV b–12 a*). FIAT Reel K–30, frames 8,039–8,041; PB 73,587; TOM Reel 177, frames 1,475–1,477; TOM Reel 36, bag 3,454, item 36, 3 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 3, 1948, p. 9.

Commercial magnesia is purified of its lime and made suitable for the preparation of the Co–MgO–ThO_2–kieselguhr catalyst by washing in the mother liquor remaining from a previous catalyst preparation. The treatment is continued until the magnesia present is converted and removed as the bicarbonate. Likewise the small % of Co present in the mother liquor as bicarbonate is precipitated and recovered as metallic Co.

2975. ———. [Method for Reducing Catalysts.] German Patent Appl. —, R 407, filed Sept. 30, 1938. TOM Reel 37, bag 3,451, item 35, 2 pp.; Meyer Trans. PC–S–II, Fischer-Tropsch, vol. 4, chap. 134, 1949, p. 21.

In preparing catalysts for the conversion of CO with H_2 by the reduction at elevated temperatures of the metal oxide by means of H_2 or gases containing it, a reduction gas is used which contains, per $m.^3$, <2.5 gm. of CO and <1 gm. of H_2O vapor. By such means a shortening of the reduction time is made possible, or with the same reduction time, catalysts of higher catalytic activity are obtained.

2976. ———. [Method for Separating Emulsions of High-Boiling Reaction Products From the Hydrogenation of Carbon Monoxide.] German Patent Appl. R 109,401, R 554, filed Feb. 18, 1941 (*Cl. IV d–23 b*). TOM Reel 177, frames 1,760–1,761; Meyer

transl. PC–S–II, Fischer-Tropsch, vol. I, chap. 60, 1948, p. 153.

These emulsions are decomposed by adding 1–5% of alkali chloride ($CaCl_2$) calculated on the emulsion.

2977. ———. [Method for the Catalytic Performance of Gasoline Synthesis From Carbon Monoxide and Hydrogen.] German Patent Appl. R 110.169, R 574, filed May 23, 1941 (*Cl. IV d–12 o*). TOM Reel 36, bag 3,454, item 36, 3 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, chap. 78, 1948, p. 8.

In catalytically converting a CO–H_2 mixture to aliphatic hydrocarbons which are liquid under normal conditions, the operation is first carried out with the raw gases containing CO_2. The CO_2 is removed by known means after a sufficient concentration is obtained following repeated utilization of the raw gas for the stated reaction and separation of the reaction products. The CO in the residual gas freed from the CO_2 is further used in carrying out the hydrogenation reaction. By this means the yield of useful product per volume unit of useful gas is very much increased. The raw gas mixture with a CO_2 content of 14%, gave 82.7 gm. of useful products per $m.^3$ of useful gas, whereas the residual gas, obtained thereby and having a CO_2 content of 26%, gave 94.8 gm. of useful product per $m.^3$ of useful gas.

2978. ———. [Method for the Comminution With Little Resulting Abrasion of Threadlike Formed Masses, Especially Catalysts.] German Patent Appl. R 113,738, R 626, filed Aug. 10, 1942 (*Cl. III 50 e*). FIAT Reel K–30, frames 7,641–7,644; PB 73,587; TOM Reel 177, frames 1,504–1,508; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 11, 1948, p. 28.

Stringy masses of catalyst material, formed from the moist plastic condition by drying, can be disintegrated very uniformly with little dust formation if the material is thrown by centrifugal force against solid walls. The apparatus and its operation are described by aid of diagrams.

2979. ———. [Method for Transformation of Gaseous Olefins in Liquid Fuels.] German Patent 726,870, Oct. 22, 1942; appl. R 96,288, filed May 12, 1936 (*Cl. 12 o–1.06*). FIAT Reel AA 88, frames 4,170–4,172; PB 70,273; Bib. Sci. Ind. Repts., vol. 2, No. 12, 1946, p. 933.

High-grade liquid fuel may be obtained in the noncatalytic polymerization of olefins if the volume of the reacting gas is reduced as polymer formation proceeds. The cross section of the gas flow is reduced and at the same time the temperature of polymerization increased.

2980. ———. [Method of Filling the Converter With Cooling Medium.] German Patent Appl. R 113,202, R–621, filed June 11, 1942 (*Cl. IV b–12 g*). FIAT Reel K–30, frames 7,656–7,662; PB 73,587; TOM Reel 177, frames 1,518–1,521, 1,531–1,535; TOM Reel 36, bag 3,454, item 36; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 16, 1948, p. 41.

Cooling medium is a fusible material such as paraffin.

See also German Patent Appl. R 113,200 (abs. **2895**) and R 113,201 (abs. **2973**).

2981. ———. [Method of Filling the Converter With Cooling Medium.] German Patent Appl. R 113,316, R 622, filed June 27, 1942 (*Cl. IV b–12 g*). FIAT Reel K–30, frames 7,653–7,655; PB 73,587; TOM Reel 177, frames 1,536–1,538; TOM Reel 36, bag 3,454, item 36; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 17, 1948, p. 46.

Easily fusible paraffin and hot H_2O or a hot salt solution is used.

See also German Patent Appl. R 113,200 (abs. **2895**) and R 113, 201 (abs. **2973**). **2980**).

2982. ———. [Method of Producing Valuable Wax Acids.] German Patent Appl. —, R 646, filed Dec. 2, 1942. TOM Reel 36, bag 3,454, item 36, 7 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, chap. 13, 1948, p. 33.

In producing valuable wax acids by the oxidation of synthetic hard paraffins obtained by the reduction of CO with H_2, the neutralization of the oxidation products obtained, the extraction of the paraffin hydrocarbons present therein, and finally the decomposition of the separated soaps, the oxidation of the hard paraffin takes place with chromic acid or with nitrous gases in the presence of nitrosyl H_2SO_4. This is followed by neutralization with concentrated caustic potash and extraction with a synthetic hydrocarbon fraction, or preferably with a heptane fraction, b. < the softening point of the neutralized reaction product, and finally by a treatment with mineral acid. The advantages of the described method are that, by only a single extraction, high-molecular wax acids can be obtained that are virtually completely free from unsaponificable constituents, contain almost no byproducts, and present a composition and a purity that are not obtainable from the products of paraffin-air oxidation in this molecular range.

2983. ———. Motor Fuel. British Patent 354,215, Nov. 3, 1931; appl. filed Jan. 26, 1930. Chem. Abs., vol. 26, 1932, p. 3904.

Solid fuels are converted into water gas and this into CH_4-containing gases and benzine hydrocarbons by known processes; the CH_4-containing gases are converted into illuminating gas and aromatic hydrocarbons by heating 1 time or repeatedly for a short period to above 1,000°. An antiknock motor fuel is obtained by mixing the benzine hydrocarbons with the subsequently formed aromatic hydrocarbons.

2984. ———. [Motor Fuels.] French Patent 820,576, Nov. 15, 1937. Chem. Abs., vol. 32, 1938, p. 3129.

In transforming gaseous olefins to liquid fuels using high temperatures and pressures and without catalysts, as the polymerization progresses the cross section of flow of the gases is reduced or/and the temperature of polymerization is increased.

2985. ———. [Obtaining High-Molecular Alcohols.] German Patent Appl. R 108,180, no date (*Cl. 12 o–5.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 302.

High-molecular alcohols with at least 6 C atoms in the molecule, and obtained by treating unsaturated hydrocarbons with water gas, are condensed and then hydrogenated.

2986. ———. [Obtaining Lubricants.] Belgian Patent 418,594, Apr. 30, 1937; appl. filed Nov. 25, 1936, in Germany Dec. 20, 1935. Chem. Zentralb. 1938, I, p. 513.

The catalyst used for the condensation can be used again by adding small amounts of fresh catalyst and raising the reaction temperature above that of the previous condensation. Addition to Belgian Patent 416,717 (abs. **3151**).

2987. ———. [Obtaining Olefinic Hydrocarbon Mixtures.] German Patent 764,165, Apr. 17, 1942; appl. R 109,476, R 557 (*Cl. 12 o–1.03*). TOM Reel 39, bag 3,453, item 1.

Hydrocarbon mixtures of a highly olefinic nature may be obtained by the catalytic conversion of gas mixtures containing CO and H_2 and some unsaturated hydrocarbons in the presence of Co catalysts. The conversion is carried out under normal atmospheric pressure and at temperature 185°–225°. The catalysts are preferably diluted with inert material and the synthesis gas may contain up to 50% C_2H_2, preferably 1–2%. Example: A gas mixture consisting of 2 H_2,

1 CO, and 0.3 C_2H_2 by volume is passed under normal pressure at a rate 1 l. per hr. per gm. Co metal over a catalyst consisting of 100 parts Co, 15 ThO_2 and 100 kieselguhr but no inert material. On ordinary cold H_2O condensation of the gases leaving the reactor, a hydrocarbon mixture b. 230° was obtained containing 62 vol. % of olefins. With more severe condensation, a further mixture b. 98° and containing 68 vol. % of olefins is obtained.

2988. ———. [Obtaining Pure Oxygen-Containing Derivatives of Aliphatic Compounds.] German Patent Appl. —, R 489, filed Jan. 24, 1940. FIAT Reel K–20, frames 264–267; PB 70,211.

Olefinic mixtures, especially those with a low-boiling range, 150°–350°, are fractionally distilled, the separate fractions are reacted with water gas, the catalyst is removed, and the reaction mixtures are separated by fractional vacuum distillation. The aldehydes are processed to fatty acids by oxidation or to alcohols by reduction.

2989. ———. [Oxidation of Paraffin to Fatty Acids.] German Patent Appl. R 107,859, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 302.

High-molecular paraffins from the hydrogenation of CO are partly converted into chlorparaffins, the Cl is split off by heating and the Cl-free products are then oxidized in the usual manner, with sulfuric acid solutions of bichromates, to fatty acids.

2990. ———. [Oxidation of Synthetic Paraffin.] Belgian Patent 452,595, Oct. 6, 1943. Chem. Zentralb., 1945, I, p. 490.

Synthetic paraffins with >16 C atoms are converted to fatty acids with nitrous gases in presence of H_2SO_4. The nitrous gases are recycled and again oxidized with pure O_2.

2991. ———. [Oxo Compounds.] German Patent Appl. —, no date. FIAT Reel K–20, frames 225–228, Sept. 16, 1938; PB 70,211.

Draft of a patent specification. Valuable Oxo compounds can be obtained by conducting olefinic hydrocarbons over a catalyst under pressures up to 50 atm. and at temperatures up to 100° in the presence of CO or gases containing it.

2992. ———. [Oxo Compounds.] German Patent Appl. R 108,107, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 302.

Oxo compounds are produced by adding CO and H_2 to olefinic compounds from the hydrogenation of CO, which have undergone an acid-splitting pretreatment.

2993. ———. [Oxo Compounds.] German Patent Appl. R 111,868, no date (*Cl. 12 o–7.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 309.

Oxo compounds, especially aldehydes, are obtained from unsaturated hydrocarbons by reaction with metal carbonyls at increased temperature and pressure. The metal compounds formed in the process are converted into the carbonyls and returned to the process.

2994. ———. [Oxo Reaction.] German Patent Appl. R 105,066, no date (*Cl. 12 o–5.01*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 298.

Alcohols are obtained from olefinic hydrocarbons by the use of catalysts by first effecting reaction between CO and H_2 and finally by reducing with gases containing H_2. Addition to German Patent Appl. R 103,362 (abs. **2800**).

2995. ———. [Oxygenated Hydrocarbon Compounds.] German Patent Appl. R 115,125, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 313.

Oxygenated hydrocarbon compounds are obtained by the catalytic action of water gas on olefins. The conversion is performed <200° in the presence of steam under pressure.

2996. ———. [Oxygenated Hydrocarbons.] German Patent Appl. R 115,133, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 314.

Catalysts for the catalytic reaction of water gas on olefins at elevated pressure and temperature up to nearly 200° are dissolved in mediums which are virtually insoluble in the olefins used for the conversion.

2997. ———. [Paraffin.] German Patent Appl. R 106,698, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 300.

CO is hydrogenated to paraffin with Co catalysts of high Co content (200–300 gm. Co per l.) and an activating addition of Mn.

2998. ———. [Paraffin Emulsions.] German Patent Appl. R 107,860, no date (*Cl. 22 g–6.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 632.

Emulsification of oxidized paraffins, obtained from 2 sources: Hard paraffin from CO hydrogenation partly converted into fatty acids, and soft paraffin mixtures from the primary products of CO hydrogenation. These can be emulsified with alkali hydroxides or carbonates and H_2O into a salvelike mixture.

2999. ———. Polymerizing Hydrocarbons. British Patent 503,206, Apr. 3, 1939. Chem. Abs., vol. 33, 1939, p. 7093.

The viscosity of lubricating oils produced synthetically by the polymerization of benzine (I) hydrocarbons is influenced by varying the quantity of condensation agent, the condensation temperature, and the time of condensation. The temperature limits are 20°–120° and the time limits are 12–20 hr. About 5% of $AlCl_3$ is added to the 1st charge of cracked (I) to be converted, instead of the usual 1%. The contact layer left after separation of the upper layer containing the condensation products serves after reactivation, for the conversion of a new charge of cracked (I) by adding a small quantity, such as, about 0.5–2%, of fresh $AlCl_3$. The original contact layer can be used repeatedly by such reactivation. In an example, 15,000 gm. of dried cracked (I) and a quantity of fresh $AlCl_3$ are added in an autoclave to $AlCl_3$ already used to convert cracked (I) and the contents allowed to react 12 hr.; the amount of $AlCl_3$ added with the (I) and the temperature of the reaction are found to have a direct influence on the viscosity of the resulting oil and by adjustment of the above factors thin or thick oils are produced from the same starting (I) for producing oils of low viscosity about 0.5–0.7% of $AlCl_3$ is used and for oils of high viscosity about 0.7–1% is added, the amount being calculated on the quantity of (I) added.

See also Canadian Patent 375,982.

3000. ———. [Preparation of Iron Catalysts for Use at Low Temperatures.] German Appl. R 116,209, R 670, filed May 21, 1943 (*Cl. IV d–12 o*). FIAT Reel K–30, frames 7,961–7,964; PB 73,587; TOM Reel 177, frames 1,489–1,492; TOM Reel 36, bag 3,454, item 36, 4 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 7, 1948, p. 18.

In making Fe catalysts for carrying out the catalytic hydrogenation of CO at temperatures of 225°–230° and with a consumption of virtually 1 space volume of H_2 or more to 1 space volume of CO, by precipitation from Fe nitrate solutions with the aid of soda and with addition of kieselguhr and subsequent reduction with H_2, the kieselguhr is added in such an amount that the Fe content of the finished catalyst lies 150–350 gm. per l., and the alkalinity of the mass is adjusted in accordance with German Patent appl. R 108,338 (abs. **2947**) by precipitation, washing, or impregnation, whereby reduction takes place at temperatures of about 300° or less.

3001. ———. Pretreatment of Catalyst for Hydrocarbon Synthesis. British Patent 678,963, Sept. 10, 1952. Chem. Abs., vol. 47, 1953, p. 6122.

This invention describes a process for the pretreatment of an Fe catalyst suitable for hydrocarbon synthesis from CO and H_2, in which the catalyst is pretreated in a static layer 100 cm. thick with a gas having a linear velocity of 50–500 cm. per sec. If a catalyst is reduced with a gas mixture of 3 parts H_2 and 1 part N_2 at a gas velocity of 140 cm. per sec. at 300° for 90 min., the catalyst has a reduction value that corresponds to 40% free Fe. When a catalyst pretreated in this manner is used for the synthesis of water gas at a load of 100 l. of gas per l. of catalyst per hr. and 10 kg. per $cm.^2$ pressure, a conversion of 65% is obtained at 209°. The CH_4 formation is 6%. If the same catalyst is reduced in the usual manner, it gives a conversion of 60% at 215°. The CH_4 formation then is 7–8%.

3002. ———. [Process and Apparatus for the Determination of the Oxygen Stability of Lubricating Oils.] German Patent Appl. —, R 716, filed May 18. 1944. FIAT Reel K–30, frames 7,805–7,809; PB 73,587.

Describes electrically heated vessel provided with feed and drain pipes for aging medium and cooling agent. The O_2 stability is determined by the amount of reaction heat, calculated from the amount of cooling agent required to carry it away.

3003. ———. [Process and Apparatus for the Uniform Filling of Catalyst Converter Tubes.] German Patent Appl. R 113,953, R 632, filed Aug. 31, 1942 (*Cl. IV d–12 g*). FIAT Reel K–30, frames 7,628–7,630; PB 73,587; TOM Reel 177, frames 1,509–1,512; TOM Reel 36, bag 3,454, item 36, 4 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch. vol. 1, chap. 12, 1948, p. 31.

Uniform heights of catalyst in reactors equipped with vertical tubes, in which the catalyst is within the tubes, can be established using a suction tube, which is inserted up to a definite depth in the individual catalyst tube. That portion of the catalyst lying above the desired height is suctioned off. The operation is effected by means of gas (especially synthesis gas or residual synthesis gases), which is recycled without injury to the catalyst. The apparatus and the operation are described by aid of a diagram.

3004. ———. [Process for Aromatizing Hydrocarbons.] German Patent 763,831, no date; appl. R 103,240, R 399, filed Aug. 29, 1938 (*Cl. 23 b–1.04*). TOM Reel 41, bag 2,744, item 14; TOM Reel 37, bag 3,451, item 35, 6 pp.

In converting straight-chain hydrocarbons with 6–12 C atoms in the molecule, such as those occurring in the reduction of CO by H_2 at low temperatures, into atomatic hydrocarbons at raised temperatures and under normal or slightly increased pressures, a suitable catalyst therefor consists of calcined magnesite as the carrier substance and Cr oxide as the activator, the amount of Cr oxide being >10%, preferably 30–50%. In forming the catalyst the carrier material may be impregnated in a vacuum with a liquid containing a Cr compound, preferably a solution of ammonium chromate or chromic acid.

3005. ———. [Process for Carrying Out Exothermic Reactions.] German Patent Appl. R 114,104, R 635, filed Sept. 24, 1942 (*Cl. IV b–12 g*). FIAT Reel K–30, frames 7,610–7,616; PB 73,587; TOM Reel 177, frames 1,466–1,474; TOM Reel 36, bag 3,454, item 36, 10 pp.; Meyer transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 2, 1948, p. 3.

Describes process and apparatus with diagrams for regulating the temperature of an exothermic catalytic reaction by means of circulating H_2O under pressure between the reactor and the heat exchanger. The catalyst is arranged in tubes around which the cooling medium circulates.

3006. ———. [Process for Carrying Out the Catalytic Aromatization of Hydrocarbons.] German Patent Appl. R 104,946, R 444, filed April 5, 1939 (*Cl. IV d–23 b*). TOM Reel 41, bag 2,744, item 14, 4 pp., 4 fig.

Describes process and apparatus for maintaining the proper temperature conditions in a catalytic aromatization column so as to avoid the unequal conversion of the gaseous hydrocarbons passing through the catalyst space. The improvement consists in the provision of a segmented heating jacket so arranged that the minimum reaction temperature is maintained at the point where the gases enter the catalyst space and progresses to a maximum at their exit, for example, from about 420° at the entrance to 520° at the exit. By this means the too rapid conversion of the aliphatic hydrocarbons and the resulting deposition of C on the catalyst is prevented locally, and the conversion is spread about equally throughout the entire length of the catalyst space.

3007. ———. [Process for Carrying out the Catalytic Hydrogenation of Carbon Monoxide.] German Patent Appl. R 110,530, R 581, filed July 7, 1941 (*Cl. IV d–12 o*). TOM Reel 177, frames 1,686–1,694; TOM Reel 36, bag 3,454, item 36, 9 pp; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 49, 1948, p. 120.

Catalytic conversion is performed in the presence of a liquid spray and the exothermic heat of reaction is kept at a nearly constant temperature through evaporation of the liquid particles. The conversion may be performed by steps during which the vapors of the mingled liquids are removed in definite amounts together with the reaction products. The described apparatus consists of a converter without cooling tubes and having a condenser through which the gas passes after leaving the converter and is relieved of its condensed vapors after which it is recharged with liquid spray and recirculated.

3008. ———. [Process for Carrying out the Hydrogenation of Carbon Monoxide.] German Patent Appl. R. 110,067, R 571, filed May 12, 1941 (*Cl. IV d–12 o*). TOM Reel 177, frames 1,731–1,733; TOM Reel, 36, bag 3,454, item 36; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 56, 1948, p. 142.

To avert possible damage to the catalyst, particularly young catalysts up to about 2 months old, from the chemical or even the explosive effect of the synthesis gas, immediately after interruption of the synthesis operation when closing down the plant, the converter is flooded with large quantities of N_2 or other inert gas such as the end gas from the process. Resumption of operation is attended with better results when such a procedure is adopted, in fact the same yield and composition of synthesis product is obtained as before the interruption in the operation.

3009. ———. [Process for Carrying Out the Hydrogenation of Carbon Monoxide With Production of a Residual Gas Suitable for City and Grid Gas.] German Appl. R 109,851, R 566, filed Apr. 17, 1941 (*Cl. IV d–12 o*). TOM Reel 177, frames 1,724–1,727; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 54, 1948, p. 138.

In obtaining a residual gas of a composition suitable for city gas in connection with the catalytic conversion of CO and H_2 into hydrocarbons, use is made of alkalized hydrogenation catalysts by means of which the ratio of $CO : H_2$ consumption is so regulated and the reaction gas so converted that the end gas shows the correct content of H_2 and CO as specified by the Ott number for city gas. Example: 100 l. of synthesis

gas of given composition (CO_2, 3.1%; C_mH_n, 0.5%; CO, 31.7%; H_2, 39.8%; CH_4, 22.6%, N_2, 2.3%) per l. of catalyst (100 Fe, 10 Ca, 5 Cu, 100 kieselguhr) was converted at 230°–250° into hydrocarbons and an end gas of composition CO_2, 4.0; C_mH_n, 0.7; CO, 18.6; H_2, 32.4; CH_4, 40.3; N_2, 4.0; 55.90 kg. cal. per N m.^{3}, gas contraction 33%. The conversion of CO into CH_4 amounted to 7% and the total conversion to 65%. Both the increase of CO consumption and the desired maintenance of H_2 enrichment were effected by increasing the alkalinity of the catalyst.

3010. ———. [Process for Catalytically Carrying Out Endothermic Hydrocarbon Reactions.] German Patent Appl. R 104,998, R 446, filed Apr. 14, 1939. TOM Reel 41, bag 2,744, item 14, 5 pp.

Hydrocarbons are converted in the presence of known catalysts and with regenerative utilization of the heat developed by the combustion of the surface-deposited C, by the aid of a converter packing consisting of catalyst substances and refractory heat-storage material, the latter being in granules of the same or nearly the same size as the catalyst and in intimate mixture with it. An especially suitable mixture is one consisting of 40 parts by volume of catalyst in granules of 2–3 mm. in size and of 60 parts of Fe-free refractory chamotte of 3–4 mm. size.

3011. ———. [Process for Combining the Benzine Synthesis With City Gas Production.] German Patent Appl. R 110,396, R 579, filed June 19, 1941 (*Cl. IV d–12 o*). TOM Reel 177, frames 1,738–1,743; TOM Reel 36, bag 3,454, item 36, 6 pp; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 58, 1948, p. 146.

Factors specified for the production of city gas simultaneously with benzine synthesis are: A synthesis gas with the lowest possible N_2 content, preferably made by O_2 pressure gasification; the synthesis converter so heavily loaded that per unit volume of synthesis gas the yield of liquid synthesis products remains below the highest possible yield, the amount of CH_4 greatly increases, and the resulting end gas becomes suitable for use as city gas. The process can also be carried out under gas recycle and under superatmospheric pressure.

3012. ———. [Process for Combining the Production of City Gas With That of the Synthesis of Hydrocarbons.] German Patent Appl. R 110,206, R 576, filed May 27, 1941 (*Cl. IV d–26 a*). TOM Reel 177, frames 1,734–1,737; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 57, 1948, p. 144.

Production of a suitable city gas (4,300 cal. per m.^{3} at 15° and 760 mm. and a d. of 0.5) from the end gas of hydrocarbon synthesis involves the use of a synthesis gas of very low N_2 content and special steps toward CH_4 formation. One way is to use highly active catalysts far beyond the point usually considered efficient for benzine synthesis. This has the result of considerably reducing the formation of liquid hydrocarbons and correspondingly raising the CH_4 content of the end gas. The synthesis can also be performed with less active catalysts, which produce somewhat more CH_4. Also it is advantageous to use active catalysts at atm. pressure, or to perform the synthesis under greater catalyst loads. The end gas can also be subjected to partial methanization.

3013. ———. [Process for Converting Aldehydes Into Carboxylic Acids.] German Patent Appl. R 111,181, R 596, filed Oct. 6, 1941 (*Cl. IV d–12 o*). FIAT Reel K–22, frames 1,219–1,221 A; TOM Reel 36, bag 3,454, item 36, 7 pp.; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 2, 1948, p. 3.

In converting aldehydes into carboxylic acids by oxidation with O_2 or gases containing it, the oxidation takes place in presence of hydrocarbons at normal or increased temperature up to 100°. The aldehydes or the aldehyde mixtures subject to oxidation are diluted with hydrocarbons to 10–30% of aldehydes. The oxidation is performed by thoroughly stirring a mixture of aldehydes, hydrocarbons, and powdered, solid, basic substance, such as calcined soda with air or other O_2-containing gas.

3014. ———. [Process for Converting Aliphatic Hydrocarbons Into Aromatics.] German Patent Appl. R 102,012, R 389, filed Apr. 2, 1938 (*Cl. IV d–23 b*). TOM Reel 41, bag 2,744, item 14, 4 pp.

In converting aliphatic hydrocarbons into aromatics by the use of catalysts at high temperatures, the reaction is carried out under vacuum and/or with increase in temperature. The life of the catalyst is progressively extended. For example, the yield of aromatics when working at 0.1 atm. is the same as when working under 1 atm. and at 40° higher temperature. Also by progressively raising the temperature from 420° to 540° a considerable increase in the life of the catalyst is obtained as well as a greater yield of aromatics. The catalyst, consisting of equal amounts of Cr_2O_3 and ZnO on active C, is the same in either instance.

3015. ———. [Process for Converting Higher Alcohols or Alcohol Mixtures Into the Alkali Salts of Fatty Acids.] German Patent Appl. R 109,564, R 558, filed Mar. 10, 1941 (*Cl. IV d–12 o*). FIAT Reel K–20, frames 241–245; PB 70,211; TOM Reel 39, bag 3,453, item 1.

A metal of the Fe group, a precious metal, or Cu is used as catalyst at 9–11 atm. and 315°–325°. This treatment applies to alcohol mixtures obtained by catalytic addition of water gas to olefins.

3016. ———. Process for Converting Saturated Masses Into Thin Threads. British Patent Appl. 26,624, filed 1938.

Process for converting masses that have a stiff consistency while containing a high % of H_2O, into thin threads by forcing the mass through plates provided with suitable-size holes, in which the mass before being fed to the holes, is subjected to gentle mechanical treatment directly in front of the holes. The process is applicable to the Co–Th–kieselguhr catalysts for hydrocarbon synthesis.

3017. ———. [Process for Converting Unsaturated Hydrocarbon Compounds, Particularly Olefins to Oxo Compounds or Their Reaction Products.] German Patent Appl. —, R 598, filed Dec. 30, 1941. TOM Reel 36, bag 3,454, item 36, 2 pp.; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 3, 1948, p. 7.

Unsaturated hydrocarbons, particularly olefins, are treated at elevated temperature and pressure with metal carbonyls and H_2 or gases containing it. The metal carbonyl before use is dissolved or suspended in the charge and then the H_2 under high pressure and thorough stirring is passed through. The reaction is suitably carried out under 20–200 atm. pressure and at temperatures of about 50°–250°. The reaction takes place rapidly with good yields. If desired, CO can be mixed with the H_2 with a corresponding saving of the carbonyl.

3018. ———. [Process for Dechlorinating the Chlorine Derivatives of High-Molecular Paraffin Hydrocarbons.] German Patent Appl. —, R 701, filed Jan. 25, 1944. TOM Reel 37, bag 3,451, item 36, 4 pp.

In dechlorinating the Cl derivatives of high-molecular paraffin hydrocarbons with 15 C atoms or more in the molecule at elevated temperature in the presence of SiO_2 or Al_2O_3 catalysts, the Cl compounds are passed at temperatures > their polymerization temperature and > their cracking temperature, or at 300°–400°, and at a space-time throughput of 0.2–0.4 (0.2–0.4 l. of liquid Cl derivatives per l. of catalyst per hr.) over the catalysis, which have been previously heated to

or > their sintering temperature. To lower the sintering temperature of the catalysts before the heating, they are treated with a small amount of an alkali, which can be removed after heating by washing.

3019. ———. [Process for Dechlorinating the Chlorine Derivatives of High-Molecular Paraffin Hydrocarbons.] German Patent Appl. —, R 702, filed Jan. 27, 1944. TOM Reel 37, bag 3,451, item 36, 2 pp.

Same method is claimed in this patent application as in R 701 (abs. **3018**), except that the cataylst consists of finely divided metallic Cu or Fe or mixtures of them. Example: A soft paraffin from the catalytic hydrogenation of CO having a solidification point of 25° and distilling 300°–400° was treated at 100° with gaseous Cl until the reaction product contained 26% Cl. The chlorinated product was then passed at 350° and a space-time throughput of 0.2 over Cu turnings. A yield was obtained of 98% olefinic hydrocarbon mixture having an I number of 116 and containing 0.7% Cl.

3020.———. [Process for Dechlorinating the Condensation and Polymerization Products of Olefins Obtained by Cracking the Products From the Hydrogenation of Carbon Monoxide.] German Patent Appl. —, R 723, filed Aug. 3, 1944. FIAT Reel K–30, frames 7,755–7,758; PB 73,587; TOM Reel 37, bag 3,451, item 36, 4 pp.

Olefins before condensation and polymerization are treated with an alkaline agent such as caustic soda and after polymerization with $AlCl_3$ in known manner with dechlorinating agents such as bleaching earth and/or MgO, ZnO or Zn at temperatures of 180°–240°. Such a pretreatment with alkali gives a product with only 14 mg. per kg. Ch as against 350 mg. without such treatment.

3021. ———. [Process for Dehydrating Alcohols.] German Patent Appl. —, R 552, filed Feb. 12, 1941. FIAT Reel K–20, frames 215–218; PB 70,211.

In splitting off the H_2O from alcohols by means of $ZnCl_2$ or other similarly acting Zn halogenide, the latter is first dissolved in alcohols or hydrocarbons before being applied. Example: 2,500 cc. of a hydrocarbon fraction b. 80°–360° and obtained by the catalytic hydrogenation of CO are mixed with a solution of 25 gm. of H_2O-free $ZnCl_2$ in 100 cc. of 80% amyl alcohol and heated for 6 hr. at 300°. The olefins and H_2O are continuousily removed by distillation.

3022. ———. [Process for Dehydrogenating High-Molecular Hydrocarbons.] German Patent Appl. —, R 728, filed Sept. 30, 1944. FIAT Reel K–30, frames 7,736–7,739; PB 73,587; TOM Reel 36, bag 3,454, item 25.

High-molecular hydrocarbons are dehydrogenated in presence of catalysts consisting of materials containing silicic acid, chiefly Al or Mg silicates, deposited on bleaching earth, which has previously been heated for a long time to temperatures >500°, preferably >1,000°. Example: Acid-activated bleaching earth (Tonsil) is heated for 90 min. to 1,100° and then for 3 hr. at this temperature. After cooling, 150 gm. are stirred with 330 gm. $Cr(NO_3)_3$, 200 gm. $Cu(NO_3)_2$, and 30 gm. $NaNO_3$ to a thick syruplike mass, after which the product is heated for different periods and temperatures and then calcined at 600°. Over 200 cc. of this catalyst are passed hourly at 510° and 600 mm. Hg with 80 cc. of the paraffinic hydrocarbon mixture obtained by the hydrogenation of CO and containing up to 90% of C_{17}–C_{18} hydrocarbons. A conversion to lower-molecular olefinic and paraffinic hydrocarbons with 42% of olefins takes place. The product consists of 4% H_2 and CH_4, 9% C_2, and C_3 hydrocarbons with 80% olefins, 9% C_5, and C_6 hydrocarbons with 60% olefins, 24% C_7–C_{10} hydrocarbons with 96% olefins, 21% C_{11}–C_{15} hydrocarbons with 80% olefins, 5% C_{16} hydrocarbons with 25% olefins, 26% olefins with a C number in the raw material boiling range, and 2% C. 60–75% of the olefins obtained have double bonds in the end position.

3022a. ———. [Process for Dehydrogenating Hydrocarbons With Formation of Aromatics.] German Patent Appl. —, R 710, filed Mar. 29, 1944. FIAT Reel K–30, frames 7,826–7,835; PB 73,587.

In the dehydrogenation of hydrocarbons with formation of aromatic compounds, so little C separates and, during the catalyst regeneration, so little heat of reduction generates that the total heat effect from C combustion and from reduction is consumed again during the endothermic course of the reaction. The catalyst serves as a heat accumulator, which exchanges heat directly with the reaction gas.

3023. ———. [Process for Improving Lubricating Oils.] German Patent Appl. —, R415, filed Oct. 31, 1938. TOM Reel 37, bag 3,451, item 35, 2 pp.

Previously the oxidation stability of lubricants obtained by the polymerization of synthetic unsaturated hydrocarbons was improved by the addition of S. It is now found that other elements of group 6 of the periodic system have the same effect. The finished polymerizates are now treated at elevated temperature with Se or Te. Before adding these the lubricating oil is treated with bleaching earth and, if desired, followed by distillation. Besides amounts of about 0.1–1% of Se and Te, various % of vulcanization accelerators and 20–100% of the Se and Te are added. After the reaction is finished the oils are subjected to a vacuum steam distillation up to 180°–245° to remove any volatile Se or Te compounds as well as any unreacted traces of accelerators.

3024. ———. [Process for Improving Lubricating Oils.] German Patent Appl. —, R 432, filed Feb. 11, 1939. TOM Reel 37, bag 3,451, item 35, 2 pp.

Stability to oxidation of lubricants obtained by the polymerization of liquid monoolefins in the presence of $AlCl_3$ is increased by heating the oils, directly after polymerization in the presence of the low-boiling fractions with small amounts (0.5–2.5%) of $AlCl_3$, suitably with addition of 1–5% of the double $AlCl_3$ occurring in the synthesis of the lubricating oils, for several hours at temperatures higher than those used in the synthesis. Suitable temperatures are 170°–180°. By this method higher yields are obtained, the loss of lubricating oil is less, and the resistance to oxidation is improved.

3025. ———. [Process for Improving Lubricating Oils.] German Patent Appl. —, R 434, filed Feb. 10, 1939. TOM Reel 37, bag 3,451, item 35, 3 pp.

Synthetic lubricants obtained by the polymerization of unsaturated hydrocarbons are stabilized against oxidation by treating them as before at 170°–180° with small amounts of fresh $AlCl_3$ and then adding to them an oxidation inhibitor such as β–thionaphthol or β–naphthalamine. Instead of treating with $AlCl_3$, active bleaching earth can be used for 3 hr. at 160°.

(*See also* German patent Appl. —, R. 432 (abs. **3024**).

3026.———. [Process for Improving the Age Stability of Lubricating Oils.] German Patent Appl. —, R 717, filed June 8, 1944. FIAT Reel K–30, frames 7,801–7,804; PB 73,587; TOM Reel 37, bag 3,451, item 36, 4 pp.

In improving the age stability of lubricating oils obtained by the condensation of olefinic hydrocarbon mixtures in the presence of $AlCl_3$ in accordance with German Patent Appl. R 108,370 (abs. **3028**), such oils are treated at about 170° for a long time with small

amounts of $AlCl_3$ and elementary S. Finally they are subjected, at about the same temperature, to the action of bleaching earth and ZnO and/or MgO, after which they are heated for a longer time to about 260° and then vacuum distilled in the usual manner. In this addition to the main patent, the method is so changed that in the 2d step instead of a mixture of bleaching earth and ZnO and/or MgO, a mixture of bleaching earth and Zn or Zn alone is used. When bleaching earth and Zn are used the preferred temperature is about 170°, and when Zn is used alone about 220°–240° is recommended.

3027. ———. [Process for Improving the Quality of Hydrocarbons by Cracking.] German Patent Appl. R 109,371, R 553, filed Feb. 15, 1941 (*Cl. IV d–23 b*). TOM Reel 177, frames 1,612–1,616; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 35, 1948, p. 86.

Catalytic cracking of hydrocarbons b. >200° C. gives low-boiling olefins and gasolines with satisfactory octanes, but low densities. Catalytic cyclization of hydrocarbons is ordinarily limited to the 80°–200° C. fraction. By combined action of cracking catalysts with cyclization catalysts, high-boiling hydrocarbons (diesel oils) may be converted to give a heavy aromatic fraction and a low-boiling olefin fraction (propylene, butylene) unaffected by aromatization. Best results were obtained by passing hydrocarbon vapors, pure or mixed with steam, first through a layer of cracking catalyst (acid activated fuller's earth, with or without addition of metallic oxides) and then through a layer of cyclization catalyst (Al_2O_3, Cr_2O_3, promoted by addition of metallic oxides). The unreacted vapor was recycled.

3028. ———. [Process for Increasing the Age Stability of Synthetic Lubricants.] German Patent Appl. R 108,370, R 539, filed Sept. 21, 1940 (*Cl. IV d–23 b*). TOM Reel 36, bag 3,454, item 20, 3 pp.; TOM Reel 39, bag 3,453, item 1.

Synthetic lubricants, obtained through the condensation of olefinic hydrocarbon mixtures in the presence of $AlCl_3$, are treated for a longer time at about 170° with small amounts of $AlCl_3$ and elementary S. Finally the oil is subjected at about the same temperature to a treatment with a mixture of bleaching earth and ZnO or MgO, then heated for a longer time to about 260° and then finally vacuum-distilled in the usual manner, with a yield of about 97.1%.

3029. ———. [Process for Increasing the Aging Stability of Lubricating Oils.] German Patent Appl. —, R 691, filed Sept. 9, 1943. FIAT Reel K–30, frames 7,884–7,886; PB 73,587; TOM Reel 37, bag 3,451, item 36, 3 pp.

Lubricating oils obtained synthetically or from petroleum are 1st diluted with miscible liquids removable by distillation such as low-boiling saturated hydrocarbons and then passed through layers of highly porous, active material containing silicic acid or Al_2O_3 at normal, sub-, or super-pressure and room temperature. Before using, the adsorbent material is dried for a short time at increased temperature, preferably >150°. Desorption of the absorbates takes place through displacement by H_2O, after which a hot or cold extraction with low-boiling organic solvents such as chloroform or the like is carried out. If necessary, the adsorbent material can be reactivated by acid treatment.

3030. ———. [Process for Increasing the Olefin Content of Hydrocarbon Mixtures.] German Patent Appl. R 115,152, R 657, filed Jan. 16, 1943 (*Cl. IV d–23 b*). FIAT Reel K–30, frames 7,999–8,003; PB 73,587; TOM Reel 36, bag 3,454, item 36, 4 pp.; TOM Reel 177, frames 1,498–1,501; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 7, 1948, p. 14.

Product from the catalytic hydrogenation of CO is subjected to close fractionation, and the narrow molecular fractions thus obtained are distilled further and separated into olefin-rich and olefin-poor fractions, the former being collected into a mixture consisting in general of a high % of olefins.

3031. ———. [Process for Increasing the Yield of Oxygenated Products in the Catalytic Hydrogenation of Carbon Monoxide Under Pressure.] German Patent Appl. R 113,885, R 629, filed Aug. 27, 1942 (*Cl. IV d–12 o*). FIAT Reel K–30, frames 7,633–7,634; PB 73,587; TOM Reel 177, frames 1,464–1,465; TOM Reel 36, bag 3,454, item 36; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 1, 1948, p. 1.

Synthesis gas (1 CO : 2 H_2) containing 5–7% of C_2H_2 is passed over a Co–ThO_2 kieselguhr catalyst under a gas pressure of 5 atm., a temperature of 175°–200° and at a rate of 1 l. of synthesis gas per gm. of Co per hr. The synthesis product has a d_{20} of 0.782, a boiling range up to 175°, I number 50, CO number 63, OH number 69, saponification number 35, distilling 5% at 96°, 50% at 175°, and 90% at 300°. An analysis showed aldehydes and ketones 15 vol. %, alcohols 15, acids 3, esters 2, and hydrocarbons 65. The oxygenated compounds contained virtually no olefins, the 150° hydrocarbon fraction about 35%, and the 150°–300° fraction 23%. Addition to German Patent Appl. R 109,774 (abs. **3209**).

3032. ———. [Process for Making Emulsifiers.] German Patent Appl. R 111,978, R 599, filed Jan. 14, 1942. TOM Reel 36, bag 3,454, item 36, 4 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, chap. 7, 1948, p. 18.

Oxidation products of solid paraffins, particularly those obtained from the catalytic hydrogenation of CO by means of oxidizing agents, especially with nitrous gases in the presence of H_2SO_4 or nitrosyl H_2SO_4 or with bichromates and H_2SO_4, are neutralized in melted condition < 130°, preferably not > 100°, through the action of virtually H_2O-free, strongly alkaline agents. H_2O-free alkali carbonate or organic amines such as triethanalomine may be used until 25–80% of the fatty acids present are saturated. About 50–75% of the paraffin-oxidation products, which are to be partly neutralized, is combined in a 1st step with the whole alkaline agent required, whereupon the remainder of the paraffin-oxidation products are added in a final 2d step. Especially valuable emulsifiers are produced in this manner, particularly when paraffin-oxidation products are used that were produced by help of nitrous gases in the presence of nitrosyl H_2SO_4 or H_2SO_4. These products contain small amounts of organic N compounds, the presence of which has been found to increase the emulsifing power.

3033. ———. [Process for Making High-Antiknock Motor Fuels.] German Patent Appl. R 104,049, R 425, filed Dec. 14, 1938 (*Cl. IV d–12 o*). TOM Reel 37, bag 3,451, item 35, 4 pp.; TOM Reel 177, frames 1,570–1,573; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 25, 1948, p. 64.

High-antiknock fuel, suitable for aviation fuel, is produced from any hydrocarbon fraction, especially the diesel-oil fraction b. 200°–320° and obtained by the conversion of CO by H_2, by cracking in vacuum (about 100 mm. pressure) without a catalyst at temperature of 650°–800° to the gaseous form and then polymerizing in the presence of an Ag-activated H_3PO_4 catalyst at about 100 atm. pressure and increased temp. of 200°–250°, followed by a mild hydrogenation with H_2 in presence of a Co–Th–kieselguhr catalyst and at a temp. of 175°–200°. The product is fractionally distilled, the cut being made at 160°, the lower fraction having an octane number of 74, which can be raised to 89-90 by addition of 0.9 cc. Pb per l.

3034. ———. [Process for Making Smoke-Producing Substances.] German Patent Appl. —, R 504, filed Apr. 24, 1940. FIAT Reel K–20, frames 299–304; PB 70,211.

Chlorinated hydrocarbons containing >2 C atoms to the molecule, such as Fischer-Tropsch paraffin gatsch b. 320°–460°, are mixed and fused with 1 or more finely-divided metals or metal oxides. Freshly burned Ca oxide is suitable. The fused melt is poured into molds and allowed to solidify. It is ignited with thermite or the like and yields a heavy smoke.

3035. ———. [Process for Obtaining Carboxylic Acids or Their Derivatives From Alkaline Liquor Concentrates.] German Patent Appl. —, R 680, filed July 14, 1943 (*Cl. IV a–23 d*). FIAT Reel K–30, frames 7,927–7,928; PB 73,587; TOM Reel 37, bag 3,451, item 36, 2 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 5, chap. 145, 1949, p. 7.

In the further development of the process for obtaining carboxylic acids or their derivatives from soap concentrates obtained by treating the primary products of CO hydrogenation with aqueous alkali liquor, the free alkali in the concentrates is first neutralized by adding the crude carboxylic acids obtained from these concentrates. The mixture is melted and subjected to distillation and finally, in finely divided porous form, to a steam treatment with or without the use of vacuum in accordance with the method of German patent appl. R 115,996 (abs. **3083**). The distillation is discontinued whenever 5–20%, preferably 10%, of the mixture separates out into a thick, oily, upper layer when cooled slowly.

3036. ———. [Process for Obtaining Carboxylic Acids or Their Derivaties From Alkaline Liquor Concentrates.] German Patent Appl. —, R 681, filed July 15, 1943. FIAT Reel K–30, frames 7,925–7,926; PB 73,587; TOM Reel 37, bag 3,451, item 36; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 5, chap. 146, 1949, p. 8.

In the further improvement of the methods of the previous patents for removing the H_2O and the unsaponifiable matter from the soap concentrates, it has now been recognized that the H_2O content of crude soap stock is brought to the desired amount (about 18% for satisfactory milling) if the H_2O to oil ratio therein is maintained at about 5 : 2 up to 2 : 1, or preferably about 3 : 1. The requisite amount of oil to maintain the desired H_2O to oil ratio is best supplied by continuous recycling rather than by single application. Addition to German Patent Appl. R 115,996 (abs. **3083**).

3037. ———. [Process for Obtaining High-Antiknock Motor Fuel.] German Patent Appl. R 105,355, R 455, filed June 2, 1939 (*Cl. 23 b–104*). TOM Reel 177, frames 1,581–1,583; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 28, 1948, p. 70.

High-antiknock motor fuel is obtained from a chiefly aliphatic hydrocarbon mixture, particularly that fraction of the primary product obtained by synthesis from CO and H_2 b. 200°–330°, by cracking in the vapor phase under mild conditions, that is at 500°–550°, and a pressure of 4–20 kg. per cm.^{2}, whereby a gasoline is obtained at a yield of 65–75% with sp. gr. at 15° C. of 0.720–0.726 and containing 70–80% of olefins and aromatics and possessing an octane No. at 200° end point of 59–65. By further treating this cracking product at a somewhat lower temperature, 250°–400°, in presence of a bleaching earth, the octane No. can be raised to 78.

3038. ———. [Process for Obtaining Olefinic Hydrocarbons by the Catalytic Hydrogenation of Carbon Monoxide.] German Patent Appl. —, R–729, filed Dec. 2, 1944. TOM Reel 36, bag 3,454, item 27, 3 pp.

Small amounts (0.5–5 gm. per *N* m.^{3} of synthesis gas) of organic acids such as formic or acetic acids are added to the synthesis gas. Example: 10 *N* l. of a synthesis gas consisting of 4 vol. % N_2; 7, CO_2; 39, CO; and 50, H_2 to which had been added 0.5–1.5 gm. formic acid per *N* m.^{3} were passed hourly at 200°–300° and 9 atm. over 100 cc. of an Fe catalyst consisting of 100 parts Fe; 5, Cu; 10, CaO; and 50, kieselguhr. A $CO+H_2$ conversion of 65% was attained. The CH_4 formation did not exceed 3–5%. 30% of the liquid synthesis products boiled up to 200°, 24% 200°–300° and 46% >320°. 80% of the olefins were in the fraction b. up to 200°, 70–75% in the fraction 200°–320° and only small amounts >320°.

3039. ———. [Process for Obtaining Olefinic Liquid Hydrocarbons.] German Patent Appl. R 108,817, R 545, filed June 1941 (*Cl. IV d–12 o*). TOM Reel 39, bag 3,453, item 1.

CO and H_2 are catalytically converted under pressure and with recycling of part of the reaction product. A Co catalyst is used with synthesis gas, which contains not more than 1.5 parts of H_2 to 1 part of CO, preferably 1.0 CO : 1.3 H_2, a ratio of recycle gas to synthesis gas of about 3 : 1 being used.

3040. ———. [Process for Obtaining Pure Alcohols.] German Patent Appl. —, R 601, filed Jan. 27, 1942. FIAT Reel K–30, frames 7,728–7,729; PB 73,587; TOM Reel 36, bag 3,454, item 36; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 4, 1948, p. 9.

This is an addition to German Patent Appl. R 106,852 (abs. **3158**) for the production of pure oxygenated derivatives of aliphatic hydrocarbons. In direct production of alcohols by catalytic action of water gas on mixtures containing olefins, chiefly those having mean b. ranges 150°–350°, a separation of the mixture into 2 or more fractions takes place before the reaction with water gas begins. The highest boiling fraction has a lower boiling point than the lowest boiling reaction product.

3041. ———. [Process for Obtaining Pure Gasol From Gas Mixtures Containing It.] German Patent Appl. R 111,138, R 595, filed Oct. 1, 1941 (*Cl. IV b–26 d*). TOM Reel 177, frames 1,677–1,683; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 48, 1948, p. 116.

In an improved method for obtaining pure gasol from mixtures containing it, such as the end gases of gasoline synthesis, a CO_2-free product is obtained by first treating the gas mixture with a washing agent for the CO_2, such as solutions of alkylolamines or of alkali carbonates and then completing the gasol extraction in the usual manner by a 2-stage pressure condensation.

3042. ———. [Process for Obtaining Pure Olefins.] German Patent Appl. R 109,144, R 547, filed Jan. 16, 1941 (*Cl. IV d–12 o*). TOM Reel 39, bag 3,453, item 1.

Technical, olefinic mixture obtained by synthesis from CO and H_2 is converted into alcohol by treatment with a $CO–H_2$ mixture at elevated temperature and pressure. The alcohols thus obtained are subsequently dehydrogenated. Before the water-gas treatment, the olefinic mixture is fractionated so that in every fraction the highest boiling portion boils at a lower point than the lowest boiling reaction product. The dehydrogenation of the alcohols then takes place after the further reaction products and the unconverted portions are separated. Example: From an olefinic synthesis product by careful fractionation is obtained a pure C_{11} fraction containing about 35% of olefins. This is treated with water gas at 135°–136° and 150 atm. gage in the presence of a Co catalyst. The aldehydes thus obtained are hydrogenated at 180° and 150 atm. gage H_2 pressure into a mixture of dodecyl alcohol and undecane, which are in turn separated by

vacuum distillation yielding a pure alcohol. This is dehydrogenated whereby a pure olefin is obtained.

3043. ———. [Process for Obtaining Unsaturated Hydrocarbons by the Catalytic Hydrogenation of Carbon Monoxide.] German Patent Appl. R 109,864, R 567, filed Apr. 17, 1941 (*Cl. IV d–12 o*). TOM Reel 177, frames 1,728–1,730; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 55, 1948, p. 140.

The main patent specifies a synthesis gas mixture of 1 vol. each of CO and H_2 and then circulating 1 vol. of fresh gas with 2.5–4.0 vol. of recycle gas, at the same time shortening the period of gas contact with the catalyst as much as possible. This method reduces considerably the quantity of olefins in the reaction gas and has the further disadvantage that the olefins obtained have an unfavorable structure in that the terminal double bonds are replaced by those in the middle position. These disadvantages can be avoided, according to the addition patent, by gradually increasing the CO content in the gas mixture, by starting the operation with water gas and gradually allowing the dilution with inert gas to subside, or by beginning the synthesis with a synthesis gas having a $CO:H_2$ ratio of 1:1 and then gradually increasing the CO content. In these manners it is possible to prevent the reduction in the olefin content and the reversion of the terminal bonds. Furthermore, by increasing the operating time as the $CO:H_2$ ratio is increased (from 1:1 to 1.3:1, for example), a corresponding increase in the olefin content of the product is obtained. Addition to German Patent Appl. R 108,263.

3044. ———. [Process for Performing the Hydrogenation of Carbon Monoxide.] German Patent Appl. R 111,014, R 589, filed Sept. 11, 1941 (*Cl. IV d–12 o*). TOM Reel 177, frames 1,672–1,676; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 47, 1948, p. 112.

Improved apparatus for carrying out the hydrogenation of CO consists of a tube converter the tubes of which, bathed on all sides by H_2O or a similar cooling medium, have an inside diameter of 10–14 mm., a length of 2.0–3.5 m., and are filled with a hydrogenation catalyst, in particular a Co catalyst, of grain size about 0.8–1.5 mm. Such a converter is said to give a considerably increased yield and an improvement in the synthesis operation.

3045. ———. [Process for Preparing Aliphatic Carboxylic Acids of Low Solidifying Point.] German Patent Appl. —, R 703, filed Feb. 4, 1944. FIAT Reel K–30, frames 7,850–7,854; PB 73,587; TOM Reel 37, bag 3,451, item 36, 5 pp.; Meyer Transl. PC–S–V, Oxo, vol. 2, chap. 37, 1948, p. 16.

In preparing carboxylic acids with low solidifying points from the corresponding aldehydes by alkaline fusion and subsequent treatment with mineral acids, the aldehydes or aldehyde mixtures that were obtained by the catalytic reaction of water gas with unsaturated hydrocarbons, especially those containing olefins, are used as raw material. The alkaline fusion is carried out in the presence of thick oils and/or hydrocarbons and/or organic metal compounds, especially those contained in the reaction products of the catalytic addition of water gas to olefins. Example: An olefinic gasoline fraction b. 80°–105° on reacting with water gas under higher pressure gave a crude aldehyde, 60% of which constituted of pure C_8 aldehyde, 22% of C_7 hydrocarbons, 18% thick oil and organic Co addition products. 2,000 gm. were heated for 3 hr. up to 325° with 410 gm. solid NaOH under an initial N_2 pressure of 5 atm. gage and a H_2 pressure of 130 atm. gage. After completion of the reaction, 2,380 gm. of the Na salt of C_8 carboxylic acids were obtained, which after reaction with H_2SO_4 gave 1,980 gm. of crude C_8 acid. On distilling, 2 fractions were obtained—225°–235° and 235°–240° in respective amounts of 1,010 and 280 gm., with solidifying points of —40° and —29°. In comparison with these 2 C_8 carboxylic acids, normal caprylic acid (C_8) solidifies at +16°.

3046. ———. [Process for Preparing Alkali-Free, Salvelike Water-in-Oil Emulsions.] German Patent Appl. —, R 696, filed Jan. 6, 1944. TOM Reel 37, bag 3,451, item 36, 3 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 2, chap. 25, 1948, p. 24.

In preparing emulsions of the above type, the oil phase is emulsified with the addition of high-molecular alcohols, which contain 20 C atoms or more to the molecule. The alcohols as used are obtained through the reduction of the fatty acids, which result from the treatment of the paraffins produced in the catalytic hydrogenation of CO, with nitrous gases in presence of nitrosylsulfuric acid or through oxidation with alkali bichromate-H_2SO_4. Emulsions made by this method have the advantage that they can be prepared completely free from alkali or sulfonate. They are particularly useful in making pharmaceutical or cosmetic preparations.

3047. ———. [Process for Preparing Aluminum Soaps From Wax Acids.] German Patent Appl. —, R 668, filed Apr. 1, 1943. TOM Reel 36, bag 3,354, item 36, 4 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, chap. 18, 1948, p. 44.

In producing Al soaps from wax acids, the latter are heated with addition of an organic solvent with H_2O-free Al-halogen compounds, particularly with H_2O-free $AlCl_3$, and the solvent evaporated after evolution of the halogen hydride has ceased. As the solvent agent, use is made of the product of the catalytic hydrogenation of CO, in particular a synthetic heptane fraction. The raw material consists of wax acids that have been prepared by the oxidation with agents such as alkali bichromate or nitrous gases of paraffins, particularly those high-melting paraffins from the catalytic hydrogenation of CO and nitroslysulfuric acid.

3048. ———. [Process for Preparing Antiknock Hydrocarbon Mixtures.] German Patent Appl. R 109,819, R 565, filed Apr. 7, 1941 (*Cl. IV d–23 b*). TOM Reel 39, bag 3,453, item 1; TOM Reel 177, frames 1,617–1,619; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 36, 1948, p. 89.

Naphthene-free gasolines produced by catalytic cracking of mixtures of heavy hydrocarbons, such as those from the hydrogenation of CO, may be hydrogenated to high antiknock compounds if hydrogenation is preceded by aromatization that affects mainly straight-chain hydrocarbons. Branched chain hydrocarbons are largely saturated by the subsequent hydrogenation, but then antiknock properties undergo little change. Particularly good results are obtained by treating the naphthene-free gasolines with boryl phosphate, fuller's earth, or similar catalysts at 200°–300° C. before aromatization. The final product has an octane number of 87 or more, as against 70 or less for the initial gasolines. Addition to German Patent Appl. R 106,919.

3049. ———. [Process for Preparing Higher Molecular Compounds From Low-Molecular Olefins.] German Patent Appl. —, R 713, filed Apr. 28, 1944. FIAT Reel K–30, frames 7,816–7,817; PB 73,587; TOM Reel 37, bag 3,451, item 36; Meyer Transl. PC–S–V, Oxo, vol. 2, chap. 39, 1949, p. 21.

In preparing higher molecular weight compounds from low molecular weight olefins by the catalytic addition of water gas and subsequent alkaline fusion, the latter is carried out with the amount of alkali calculated from the carbonyl number. The advantage of this method is that the carboxylic acids obtained

from the alkaline fusion of the corresponding aldehydes are not split but can be recovered as such if only the amount of alkali corresponding to the carbonyl number of the crude aldehydes is used.

3050. ———. [Process for Preparing Highly Active Aromatization Catalysts.] German Patent Appl. R 104,875, filed Mar. 24, 1939 (*Cl. IV d–23 b*). TOM Reel 41, bag 2,744, item 14, 3 pp.

In preparing highly active aromatization catalysts, consisting of Al_2O_3 and other metal oxides such as Cr_2O_3, an Al_2O_3 is used. After precipitation the Al_2O_3 is thoroughly and repeatedly washed until the final wash H_2O shows a pH of less than 9, preferably 8.3–8.5. The Al_2O_3 may be precipitated from an alkali-aluminate solution other than Na aluminate. A mixture of aliphatic hydrocarbons b. 80°–200° obtained from the Fischer-Tropsch synthesis was passed in vapor state over a catalyst prepared in this manner consisting of 2 parts Al_2O_3 and 1 part Cr_2O_3 in granules of size 1–3 mm. The temperature was 450°–500°. The reaction product contained as much as 40 vol. % of aromatics.

3051. ———. [Process for Preparing High-Molecular Hydrocarbon Oils by Condensation and Polymerization of Hydrocarbons.] German Patent Appl. —, R 722, filed Aug. 1, 1944. FIAT Reel K–30, frames 7,759–7,762; PB 73,587; TOM Reel 37, bag 3,451, item 36, 4 pp.

Unsaturated hydrocarbons b. 60°–200° obtained by the catalytic hydrogenation of CO are first passed, with heating over a catalyst containing Al_2O_3 for the purpose of converting the hydroxyl impurities contained therein into olefins. The hydrocarbons obtained in this manner are then treated during heating with an alkaline agent such as soda lime and then subjected to condensation and polymerization in known manner. A greatly increased yield of 5–7% or more of lubricating oil is obtained.

3052. ———. [Process for Preparing Iron Catalysts for Use in the Hydrogenation of Carbon Monoxide.] German Patent Appl. R 107,515, R 506, filed May 3, 1940 (*Cl. IV d–12 o*). TOM Reel 177, frames 1,709–1,712; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 52, 1948, p. 131.

Amount of strong hydroxide required for the preparation of precipitated Fe catalysts is reduced considerably by first precipitating the catalyst with a weak hydroxide or carbonate (NH_3, Mg, Ca hydroxide), and then impregnating with a strong alkali (K, Rb, or Cs hydroxide). Results from catalysts prepared in this way are superior to those obtained with catalysts prepared exclusively with strong hydroxide, contraction · 36% against 27–34%.

3053. ———. [Process for Preparing Stable Hard-Paraffin–Water Emulsions Suitable as Polishing Waxes.] German Patent Appl. R 109,184, R 549, filed Dec. 6, 1941 (*Cl. 22 g–6.02*). TOM Reel 39, bag 5,453, item 1, 5 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 2, chap. 23, 1949, p. 17.

Paraffin mixtures with a m. p. of 85° or more, such as are obtained in the catalytic hydrogenation of CO, are emulsified with the addition of alkali salts of carboxylic acids, the free acids of which are obtained from the paraffins m. 40°–65° by oxidation with chromsulfuric acid or nitrosylsulfuric acid or nitrous gases in the presence of nitrosylsulfuric acid. To the emulsion are added free carboxylic acids or esters, the acid components of which are obtained from the paraffins m. >85° by oxidation with chromsulfuric acids, nitrosylsulfuric acids or nitrous gases in presence of nitrosylsulfuric acids.

3054. ———. [Process for Preparing Unsaturated Hydrocarbons.] German Patent Appl. R 106,263, R 531, filed Sept. 2, 1940. TOM Reel 39, bag 3,453, item 1.

In obtaining unsaturated hydrocarbons from the catalytic hydrogenation of CO, use is made of gas recycle or inert-gas addition, with reduction of the gas flow over the catalyst.

3055. ———. [Process for Preparing Water-in-oil Emulsions.] German Patent Appl. —, R 698, filed Jan. 8, 1944. TOM Reel 37, bag 3,451, item 36, 4 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 2, chap 26, 1948, p. 26.

H_2O-in-oil emulsions of salvelike properties are prepared from high-molecular solid hydrocarbons, together if desired with natural or synthetic waxes, by adding Al soaps to the usual emulsifier consisting wholly or partly of saponified wax acids. The fatty acids of paraffin oxidation products used in the production of the Al soaps are made from hard paraffin by treating it with nitrous gases and nitrosylsulfuric acid or with bichromate–H_2SO_4. Also emulsions may be prepared by using an emulsifier, which is made by treating an alkali aluminate with high-molecular wax acids.

3056. ———. [Process for Producing a High-Antiknock Motor Fuel.] German Patent Appl. R 106,921, PA 86,822, filed Feb. 8, 1940 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 809–811; PB 83,253.

Unsaturated hydrocarbons obtained by the catalytic cracking of high-molecular hydrocarbons are treated at high temperature and pressure (up to 300° and 50–200 atm.) with CO and H_2 to convert the olefins into alcohols, which finally are dehydrated and hydrogenated. Previous to the water-gas treatment, a treatment with boryl phosphate, bleaching earth, or other similar agents at temperatures of 200°–300° is carried out for the purpose, in part, to isomerize the unsaturated hydrocarbons and, in part, to shift the double bond toward the middle of the chain. Also, previous to the water-gas treatment, a selective polymerization of the iso-hydrocarbons is introduced. Following the dehydration of the product and previous to its hydrogenation, another isomerization is performed having for its purpose the extensive conversion of the C_3–C_5 hydrocarbons into high-octane aviation gasoline. It is stated that the gasoline product obtained by the dehydration is distributed in such a way that the low-molecular hydrocarbons are the first to be subjected to selective polymerization and the middle-molecular hydrocarbons to water-gas treatment, and the high-molecular hydrocarbons are directly hydrogenated. The process permits virtually complete conversion of the C_3–C_5 hydrocarbons, occurring in considerable amounts in catalytic cracking, to an aviation gasoline of exceedingly high octane no.

3057. ———. [Process for Producing Active Dehydrogenation Catalysts.] German Patent Appl. —, R 700, filed Jan. 15, 1944. FIAT Reel K–30, frames 7,855–7,858; PB 73,587.

In producing highly active, stable dehydrogenation catalysts, compounds of catalytically effective elements, which are decomposed by heat, are precipitated on the carriers by spraying. They are then converted into oxides by steadily increasing the heat from about 200°–700°. The major part of the gases (60–80%) is set free during the decomposition, especially 200°–320°, in the course of about 2 hr.

3058. ———. [Process for Producing Alcohols, Aldehydes, and Ketones From Water Gas or Similar Gas Mixtures.] German Patent Appl. R 106,854, R 488, PA 62,096, filed Jan. 29, 1940 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 876–878; PB 83,253; TOM Reel 36, bag 3,454, item 20, 2 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, chap. 75, 1948, p. 1.

Well-defined oxygenated compounds such as the higher alcohols, aldehydes, and ketones are obtained by contacting water gas or similar gas mixtures with active catalysts consisting of metal of group 8, acti-

vated with oxides of metals from groups 2–7, and suspended in suitable liquid hydrocarbons, such as the paraffins. The working pressure must be > 20 atm., preferably > 100 atm., and the temp. < 300°. The synthesis gas should contain CO and H_2 in the ratio of at least 1.5 : 1 by volume.

3059. ———. [Process for Producing an Antiknock Motor Fuel.] German Patent Appl. R 102,106, R 386, filed Apr. 16, 1938 (*Cl. IV d–12 o*). TOM Reel 37, bag 3,451, item 35, 4 pp.; TOM Reel 177, frames 1,545–1,548; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 19, 1948, p. 50.

In the catalytic polymerization of olefin-rich hydrocarbons, particularly those b. 20°–70°, and in presence of phosphoric acid catalysts, temperature and pressure are so adjusted to each other that the reaction products can be subtracted separately in a liquid condition from the input materials. In the polymerization in the liquid phase, superheated stages are provided between the catalyst layers to convert the input material into the gaseous phase. The input material is mixed with the unreacted, recycled product, the amount used for the recycle being withdrawn and introduced at different points of the reaction system. Polymerization is carried out in several steps, preferably with intensification of the polymerization conditions.

3060. ———. [Process for Producing an Antiknock Motor Fuel.] German Patent Appl. R 102,112, R 388, filed Apr. 16, 1938 (*Cl. IV d–46 a*). TOM Reel 37, bag 3,451, item 35, 6 pp.; TOM Reel 177, frames 1,552–1,557; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 21, 1948, p. 54.

Olefin portion boiling up to 70° of the liquid hydrocarbons obtained by the catalytic conversion of CO and H_2 in the proportion of 1 : 1 and with gas recycle is converted to polymer benzine over a phosphoric acid catalyst. That part of the liquid product of benzine synthesis b. > 200° is cracked under mild conditions, and that part then boiling up to 70° is polymerized as above. The olefins occurring in the cracking with terminal double bonds are then converted by catalytic treatment with activated bleaching earth into olefins with internal double bonds. All of the benzines thus obtained are then mixed to form a motor fuel of excellent quality.

3061. ———. [Process for Producing Antiknock Motor Fuels From Products Obtained by Hydrogenation of Carbon Monoxide.] German Patent Appl. R 107,333, R 501, filed Apr. 8, 1940 (*Cl. IV d–23 b*). TOM Reel 37, bag 3,451, item 35, 4 pp.; TOM Reel 177, frames 1,601–1,604ffi Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 32, 1948, p. 80.

Primary products from CO hydrogenation, b.>200°, are cracked under mild conditions (10 atm., about 500°) to give a maximum yield of monoolefins. The cracking fraction up to 70° is polymerized by action of a catalyst, such as a H_3PO_4 catalyst, under pressure, at about 200°. The cracking fraction >70° is treated in the presence of activated fuller's earth (up to 5 atm., about 200°), resulting in a shift of the terminal double bond. This process raises the octane number of the cracking monoolefins 15–20 units, giving high octane products, which may be mixed with the primary products b. <200° to give maximum yields of high antiknock fuels. This is an addition to German Patent Appl. R 102,112 (abs. **3060**).

3062. ———. [Process for Producing Carboxylic Acids or Their Salts From Esters.] German Patent Appl. —, R 684, filed July 23, 1943. FIAT Reel K–30, frames 7,915–7,917; PB 73,587; TOM Reel 37, bag 3,451, item 36, 3 pp.; Meyer Transl. PC–S–V, Oxo, vol. 2, chap. 36, 1948, p. 14.

Carboxylic acids or their salts are prepared from esters, without the side production of alcohols, by melting the esters with the amount of caustic alkali required for the neutralization of the acid components and for the dehydrogenation of the alcohol components. The reaction is carried out at an initial gas pressure of >1 atm., preferably at 5–20 atm. Suitable raw materials for this purpose are the naturally occurring esters of high molecular weight fatty acids and alcohols or synthetic esters of known composition from products of CO hydrogenation or from the catalytic addition of water gas to olefins. The preparation of carboxylic acids or their salts from esters, in accordance with the invention, offers special advantages for the production of high-grade toilet soaps.

3063. ———. Process for Producing Catalysts for Benzine Synthesis. British Patent Appl. 31,293, filed 1938.

Process for producing catalyst suitable for effecting benzine synthesis from oxides of C and H_2 characterized by the use of $MgCO_3$ as carrier mass. The Mg compounds employed as carrier material are dissolved out from the spent catalyst mass by treatment with H_2O and CO_2, whereupon the Mg solution separated from the insoluble residue is relieved of part of the CO_2 by boiling or by the blowing in of steam and the Mg is precipitated as basic carbonate.

3064. ———. [Process for Producing Catalysts for the Gasoline Synthesis.] German Patent Appl. R 106,936, PA 94,674, filed Feb. 10, 1940 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 887–888; PB 83,253.

In producing a catalyst suitable for the catalytic conversion of CO–H_2 mixtures by precipitation of the catalytically active substance in the presence of a carrier substance, the solution containing the catalyst substance from foreign materials is freed by precipitation with an alkaline precipitating agent such as soda in the absence of the carrier substance, and finally by precipitation of the catalytically active constituents with the residual precipitating agent in presence of the carrier substance. To shorten the time during which the carrier substance is in the solution, it is added only after complete or very nearly complete precipitation.

3065. ———. [Process for Producing Chlorinated Paraffin Hydrocarbons.] German Patent Appl. —, R 699, filed Jan. 13, 1944. TOM Reel 37, bag 3,451, item 36, 3 pp.

In producing chlorinated paraffin hydrocarbons that are virtually free from unreacted paraffin, 1–1.5 mols of Cl are taken up per mol of hydrocarbon, whereby the chlorination is performed in known manner with elementary Cl at temperatures slightly >the melting point of the hydrocarbon. Example: A synthetic table paraffin obtained by the catalytic hydrogenation of CO had an average molecular weight of 380 and a solidifying point of 250°. It was treated with Cl gas at 100°–120° with rapid stirring until the uptake of Cl measured 24.3% or 1.3 mol per mol of paraffin. In the end product only 3.8% of unattacked paraffin was determined by the acetone method.

3066. ———. [Process for Producing Ethers Serving as Solvents or Softeners.] German Patent Appl. —, R 600, filed Jan. 26, 1942. FIAT Reel K–30, frames 7,732–7,735; PB 73,587; TOM Reel 39, bag, 3,453, item 1; TOM Reel 36, bag 3,454, item 36, 4 pp.; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 29, 1948, p. 70.

Alcohols, which have been obtained either through the direct catalytic action of CO and H_2 on olefins containing 1 less C atom or through subsequent reduction of the oxo products formed by the catalytic action of water gas on olefins, are etherified in known manner by heating with one another, or ethers are prepared

in the specified manner by utilizing only 1 of the components derived from the catalytic action of water gas on olefins. By the reaction of CO and H_2 on olefins at temperatures 50°–200° and pressures of about 50 atm. or more in the presence of catalysts containing Fe, Ni, or Co activiated with ThO_2, MgO, or Al_2O_3 and supported on carriers such as kieselguhr, mixtures of oxo compounds, chiefly aldehydes, are formed which are obtained through addition of the carboxyl group and of H_2 to the initial olefins in the branched or unbranched position. These oxo compounds can finally be converted through reduction in the manner described into alcohols. Alcohols, which are used in the formation of ethers, also can be produced directly by the action of CO and H_2 on olefins in presence of the catalysts already mentioned. It is necessary, in this case, when using such catalysts that higher temperatures prevail than in preparing oxo compounds. The process is of special significance since it is the 1st time that the large-scale production of any number of ethers in satisfactory amounts and of a high degree of purity has become possible.

3067. ———. [Process for Producing High-Grade Lubricants From the High-Molecular Paraffins From the Catalytic Hydrogenation of Carbon Monoxide.] German Patent Appl. —, R. 705, filed Feb. 9, 1944. FIAT Reel K–30, frames 7,845–7,847; PB 73,587; TOM Reel 37, bag 3,451, item 36, 3 pp.

In producing high-grade lubricants from high molecular paraffins, the latter are treated at temperatures slightly > their melting point with elementary Cl until the adsorption of Cl amounts to 0.9–1.4 mol. of Cl to each mol. of hydrocarbon. The chlorinated paraffins thus obtained are dechlorinated at 300°–400° over catalysts consisting of SiO_2 and /or Al_2O_3, which before the treatment have been heated to temperatures > the sintering temperature. After the dechlorinated product is polymerized 50°–100° with $AlCl_3$, the layer of polymerisate is diluted with heavy gasoline or other solvent and separated from the catalyst residue. It is finally treated at 100°–120° with bleaching earth, and the heavy gasoline and the fraction b. < 400° are vacuum distilled leaving an end product of viscosity 93° E, a viscosity pole height 1.58, and a solidifying point —22°.

3068. ———. [Process for Producing Highly Active Catalysts for the Hydrogenation of Carbon Monoxide From the Waste Products of Alumina Production.] German Patent Appl. R 109,145, R 548, filed Jan. 16, 1941 (*Cl. IV d–12 o*). FIAT Reel K–20, frames 278–285; PB 70,211; TOM Reel 177, frames 1,714–1,721; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 53, 1948, p. 134.

Suspension of Luxmasse in H_2O is first acidified with HNO_3 to a pH of about 5–6, $Cu(NO_3)_2$ is added and the mixture heated to boiling. There is then added a boiling solution of KOH to which kieselguhr has been added. The mixture is then filtered, shaped, dried, and reduced for 45 min. at 300° with an H_2–N_2 mixture. After or during the alkali treatment, Cu, Ca, or Fe salts may be added. According to 1 example, the reduced catalyst is put on stream at 240°, and 15 atm., the gas consisting of 1 vol. fresh water gas and 2 vol. recycled residual gas. The yield of liquid products amounts to 125 gm, per $m.^3$ of gas and consists of 27.7% benzine b. up to 200°, 22.5% diesel oil b. 200°–320°, 24.3% soft paraffin b. 320°460°, 25.5% hard paraffin b. > 460°. The synthesis products were highly unsaturated—the benzine equals 58.9 vol. % olefins and the diesel oil 47.4 vol. %. The soft paraffin showed an I number of 15.7, the hard paraffin 2.5. The paraffin was pure white. Gives other examples.

3069. ———. [Process for Producing High-Octane Fuel.] German Patent Appl. R 105,615, R 462, filed July 7, 1939, (*Cl. IV d–23 b*). TOM Reel 177, frames 1,584–1,586; PB Report 412, May 15, 1945; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 29, 1948, p. 72.

Preparation of high antiknock fuels by heating a Fischer-Tropsch product with a small quantity, about 10%, of the bituminous components of hard coal or brown coal, freed from ash, and preferably under pressure and in the presence of a catalyst and H_2. Specifically a Pott-Broche coal extract is mixed with Fischer-Tropsch product b. 200°–250° C. and passed over a molybdena catalyst with H_2 at 480°–500° C. under 80 atm. pressure, whereby 70 octane gasoline is obtained. The unconverted kogasin is recycled.

3070. ———. [Process for Producing High-Octane Isoparaffinic Motor Fuels.] German Patent Appl. R 105,623, R 463, filed July 8, 1939 (*Cl. IV d–12 o*). TOM Reel 177, frames 1,587–1,593; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, ch. 30, 1948, p. 74.

Gasol product from the Fischer-Tropsch synthesis is passed in 2 separate stages over a boric acid-phosphoric acid catalyst, the 1st stage operating at virtually atmopheric pressure and 200°–400° with virtually only an isomerization effect, and the 2d stage operating at 5–100 kg. per $cm.^2$ at about 200° with an almost entire polymerization effect. Instead of the above catalyst, the 2d stage may use the H_3PO_4 or the H_2SO_4 polymerization catalyst. The gas is recycled several times in both stages over the catalyst, and the isooctane produced thereby is separated by condensation and the remaining paraffinic gas is subjected to dehydrogenation.

3071. ———. [Process for Producing Hydrocarbon-Nitrocompounds.] German Patent Appl. —, R 644, filed Nov. 28, 1942. TOM Reel 36, bag 3,454, item 36, 3 pp.

Appears to be addition to German Patent Appl. R 114,103 (abs. **3127**) and describes apparatus and method whereby the process of the main patent is carried out.

3072. ———. [Process for Producing Liquid Emulsions.] German Patent Appl. —, R 653, filed Dec. 30, 1942. TOM Reel 36, bag 3,454, item 36, 2 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, ch. 17, 1948, p. 43.

In preparing liquid emulsions, the distillation residues from the oxidation of paraffins are repeatedly treated with alkali bichromate–H_2SO_4 solutions and the refined products used as emulsifier. Example: 3 kg. of the refined distillation residue from paraffin oxidation are mixed with 15 kg. of a synthetic spindel oil which has a viscosity of 1.7° E at 50°. The mixture is heated to 120° and saponified with a solution of 572 gm. KOH in 500 cc. H_2O. Under intensive stirring and at a temperature of 90°–95° about 12 l. H_2O, to which are added 150 gm. KOH, are emulsified into the saponified product. There results a very good, viscous, stable emulsion, which can be diluted in proportion of 1 of emulsion to 10 of H_2O. The product is useful as boring oil, paper-impregnating agent, and disinfectant medium.

3073. ———. [Process for Producing Lubricants.] German Patent Appl. R 113,424, PA 483,418, filed July 8, 1942 (*Cl. IV d–12 o*). FIAT Reel B–196, pp. 56–59; PB 83,253.

In producing high-boiling, viscous products by the polymerization of low-boiling, liquid hydrocarbons of the olefin series or mixtures of liquid hydrocarbons containing these, preferably with the addition of gaseous olefins or gas mixtures containing them in the presence of Al chloride, the polymerization is carried out with the addition of halogens such as Cl. Data are presented concerning the process and the product

obtained by the polymerization of a cracked distillate, obtained by the vapor-phase cracking of the paraffin gatsch from the Fischer-Tropsch synthesis, in the presence of 4% of $AlCl_3$ as catalyst at 25° with varying amounts of halogens.

3074. ———. [Process for Producing Miscible Emulsions.] German Patent Appl. —, R 608, filed Apr. 8, 1942. TOM Reel 36, bag 3,454, item 56, 8 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, ch. 83, 1948, p. 20; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 2, ch. 24, 1948, p. 20.

In producing miscible and stable emulsions with the outer phase H_2O and/or oil, an emulsifier is used made of the paraffins produced in the hydrogenation of CO and oxidized with O-containing agents, particularly with nitrous gases in presence of H_2SO_4 or nitrosylsulfuric acid or with dichromates and H_2SO_4, with final complete or partial saponification. The oxidized product, of which the emulsifier is made, is neutralized to 25–80% by treatment with virtually anhydrous, strongly alkaline agents such as anhydrous alkali carbonates, dry NH_3 gas or organic amines, particularly triethanolamine, at increased temperature but <130°, preferably not over 100°. The emulsifier, or the paraffin oxidation products used for its production, is treated with highly concentrated alkaline solutions or organic amines in such an amount that the degree of saponification is 100% or over and the temperature so high, preferably 100°–120°, that the major part of the H_2O originally present is evaporated during the saponification operation. To obtain from this emulsifier an emulsion containing mainly oil or paraffin as the inner phase, solid or semisolid hydrocarbons or oxygenated compounds are used, while for an emulsion with mainly H_2O as the internal phase, large amounts of liquid compounds, such as mineral oils, heavy benzine, and liquid fats, are used in addition to the emulsifier. Gives several examples of preparation and uses.

3075. ———. [Process for Producing Oxygenated Compounds From the Olefinic Primary Products of Carbon Monoxide Hydrogenation.] German Patent Appl. —, R 522, filed Aug. 8, 1940. FIAT Reel K–20, frames 219–224; PB 70,211.

Before treating the olefinic primary products of CO hydrogenation with CO and H_2 to produce oxygenated compounds, the primary products are subjected to a deoxidizing treatment by passing them in the vapor state at 300°–400° over a H_2O-free, difficultly reducible oxide, such as Al_2O_3, ThO_2, or Cr_2O_3.

3076. ———. [Process for Producing Resins.] German Patent Appl. —, filed May 15, 1944. FIAT Reel K–30, frames 7,814–7,815; PB 73,587; TOM Reel 37, bag 3,451, item 36, 2 pp.; Meyer transl. PC–S–V, Oxo, vol. 2, ch. 38, 1949, p. 19.

Resins can be produced from cyclopentadiene by subjecting it to the action of CO and H_2 mixtures, especially of water gas, at elevated temperatures and under high pressures 125° and 150 atm. gage, respectively. Co or Fe catalysts promoted by Mg, Th, Mn, or Al are suitable.

3077. ———. [Process for Producing Synthetic Soaps.] German Patent Appl. —, R 704, filed Feb. 8, 1944. FIAT Reel K–30, frames 7,848–7,849; PB 73,587; TOM Reel 37, bag 3,451, item 36, 2 pp.; Meyer Transl. PC–S–11, Fischer-Tropsch, vol. 5, chap. 148, 1949, p. 11.

In producing synthetic soap from the alkaline wash liquors occurring in the treatment of the liquid products of the catalytic hydrogenation of CO, the heavy oil fraction b. 220°–380° is separated, alkalized, and the resulting wash liquor, after neutralization with the fatty acids from the same wash liquor, concentrated as far as possible and evaporated to dryness. The product is a highly foaming washing agent of excellent detergent power.

3078. ———. [Process for Producing Valuable Monocarboxylic Acids by Oxidation of High-Boiling Paraffin Hydrocarbons.] German Patent Appl. R 113,913, R 630, PA 602,820, filed Aug. 31, 1942 (*Cl. 12 o–11*). FIAT Reel B–196, frames 331–335; PB 83,253; TOM Reel 36, bag 3,454, item 36; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, chap. 10, 1948, p. 25.

In a process for producing valuable monocarboxylic acids through oxidation of high-boiling paraffins that had been previously dehydrogenated by reaction with halogens, such as Br or Cl, the dehydrogenation is carried out at temperatures of 250°–300°, preferably at atmospheric or subatmospheric pressure in the presence of catalysts, which induce a shift of the existing double bonds. The oxidation takes place in known manner by means of O_2 or O_2-containing gases in the presence of oxidation promoters. Artificial or natural Al or Mg silicates, preferably activated bleaching earths or borates or phosphates, which if desired are activated with metal compounds of groups 3–8 are used as catalysts during the reaction with halogens. Directly combined with the dehydrogenation through cooling to about 100°, the halogen hydrides and the existing cracked products up to and including the C_7 fractions are separated from the higher-boiling fractions by condensation. Then, without further temperature change, the oxidation of the olefinic hydrocarbon mixture takes place.

3079. ———. [Process for Producing Valuable Oxo Compounds.] German Patent Appl. R 106,853, PA 62,092, filed Jan. 29, 1940 (*Cl. 12 o–5.02*). FIAT Reel B–196, frames 873–875; PB 83,253.

In producing valuable Oxo compounds, the reaction between CO and H_2 and olefins is carried out either in the presence of condensing or polymerizing catalysts, or the reaction products obtained thereby are subjected to a polymerizing or condensing treatment. The catalysts consist of metal halogenides such as Al or Zn chlorides or are the usual alkali-containing type used in CO hydrogenation. The activity of the catalysts is increased by raising both the temperature and the pressure. In this manner alcoholic heavy oils are obtained, which are valuable raw materials for the production of detergents and other sulfonated products. It is further specified that in working up olefinic hydrocarbon mixtures, the heavy-oil fraction b. 150°–350° and the olefins separated from the light oil boiling up to about 150° are treated with CO and H_2 and the product is hydrogenated and vacuum distilled. There are obtained a mixture of higher alcohols and ketones and gasoline. The former is a suitable raw material for working up into detergents and other sulfonated compounds. This is an addition to German Patent Appl. R 103,362 (abs. **2800**).

See also United States Patent 2,327,066 (abs. **2803**).

3080. ———. Process for Production of Catalysts. British Patent Appl. 26,276, Sept. 8, 1938.

Process for producing catalysts of Co and Mg for use in the catalytic conversion of mixtures of CO and H_2 by precipitation simultaneously or successively of the Mg and Co contained in a solution of their nitrates or chlorides, in which a Mg solution having a larger content of Mg than corresponds to the stoichiometric ratio of Mg to Co in the catalyst to be produced.

3081. ———. [Process for Purifying Synthetic Fatty Acids.] German Patent Appl. —, R 649, filed Dec. 22, 1942. FIAT Reel K–30, frames 8,019–8,023; PB 73,587; TOM Reel 36, bag 3,454, item 36, 5 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, ch. 15, 1948, p. 39.

In separating nonacid impurities from crude fatty acids through extraction therefrom of prepared soap solutions, if desired in the presence of the lower alcohols, concentrated acid soap solutions, which contain up to 1 mol. of soap to 2 mol. of fatty acids, are extracted with benzine or similar hydrocarbons. The soap solutions under treatment contain 20–35% of total fatty acids and before extraction are made up to the neutral pH point by the addition of acids or the introduction of CO_2. The method affords a considerable saving in alkali for the neutralization of the fatty acids and an increase in the space-time yields. The process is suitable for processing crude fatty acids of any kind and is particularly applicable to the processing of fatty acid mixtures obtained through the reaction of olefins with CO and H_2.

3082. ———. [Process for Raising the Antiknock Value of Benzines Obtained by Working Up the Liquid Primary Products of the Hydrogenation of Carbon Monoxide.] German Patent Appl. R 102,757, R 395, filed July 2, 1938 (*Cl. IV d–23 b*). TOM Reel 37, bag 3,451, item 35, 3 pp.; TOM Reel 177, frames 1,558–1,561; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, ch. 22, 1948, p. 57.

Octane number of benzine obtained by the hydrogenation of CO is improved by treating it with a broad-surface material such as active charcoal or activated bleaching earth at temperatures chiefly at 150°–250°. $AlCl_3$ may be added.

3083. ———. [Process for Recovering Carboxylic Acids or Their Derivatives From Alkaline Liquor Concentrates.] German Patent Appl. R 115,996, R 669, filed Apr. 19, 1943 (*Cl IV a–23 d*). FIAT Reel K–30, frames 7,965–7,968; PB 73,587; TOM Reel 36, bag 3,454, item 36, 4 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, ch. 88, 1948, p. 34.

In recovering carboxylic acids or their derivatives from soap concentrates obtained by treatment of the primary products of CO-hydrogenation with alkali liquor according to German Patent Appl. R 115,143 (abs. **3084**), the free alkali in the concentrates is first neutralized by the addition of crude carboxylic acids obtained from these concentrates, the mixture is melted and by means of distillation, if necessary with the addition of steam, is freed of H_2O and the greater part of the unsaponifiable material, while the balance of the unsaponifiable is expelled from the highly porous comminuted mass by means of heated gases or vapors, such as air, steam, combustion gases, or the like and/or the use of vacuum.

3084. ———. [Process for Recovering Soap-Forming Fatty Acid Concentrates.] German Patent Appl. R 115,143, R 658, filed Jan. 14, 1943 (*Cl. 12 o–11*). FIAT Reel K–22, frames 1,214–1,215; FIAT Reel K–30, frames 7,996–7,998; PB 73,587; TOM Reel, 36, bag 3,454, item 36, 3 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, ch. 104, 1949, p. 90.

In recovering soap-forming fatty acid concentrates by the alkali washing of CO-hydrogenation products, caustic-insoluble hydrocarbon-soap concentrates are separated mainly by cooling, by recycling, and by repeated utilization of the caustic liquor used for the wash, if necessary with the addition of more alkali. The wash treatment is carried out with an approximately 10% alkali solution and the latter is consumed up to about 1% free alkali. For recovering carboxylic acids of definite molecular size, use is made of the corresponding fractions cut from the synthesis products.

3085. ———. [Process for Refining the Distillation Residues From the Oxidation of Paraffin.] German Patent Appl. —, R 652, filed Dec. 30, 1942. TOM Reel 36, bag 3,454, item 36, 4 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, ch. 16, 1948, p. 41.

In working up the distillation residues from the oxidation of paraffin, the so-called oxide pitch, they are treated repeatedly at increased temperatures with H_2SO_4–alkali bichromate solutions. This oxide pitch, before treatment with the alkali bichromate–H_2SO_4 mixture, is saponified with an excess of alkali and again acidified with dilute mineral acid. Example: 100 gm. of a residue from paraffin oxidation are heated to 70° with active stirring with a solution of 125 gm. Na bichromate and 1,250 gm. of 40% H_2SO_4. After the 1st violent reaction, the temperature is raised to 110° and within an hour the reaction is complete. After cooling to room temperature the refined oxide pitch is decanted from the chrome sulfate solution and the treatment repeated with fresh alkali bichromate–H_2SO_4 solution. After a triple oxidation, a product of greenish color, which can be bleached by a H_2O_2 treatment, is obtained. The product is yellowish brown with a neutralization number of 159, a saponification number of 195, and a hardening point of 78°. The yield of refined oxide pitch amounts to 78%.

3086. ———. [Process for Regenerating Catalysts for Hydrogenation of Carbon Monoxide.] German Patent Appl. R 103,713, PA 884,658, filed Nov. 7, 1938 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 427–429; PB 83,253; PB Report 412, May 15, 1945.

Regenerating synthesis catalyst in situ by continuing hydrogenation after completing wax removal but with increasing temperature. For example, treating for 2.5 hr. at 200° C. with a mixture containing 25% N_2 and 75% H_2; raising the temperature to 350° C. during the period of ½ hr. and treating at this temperature for ½ hr.; treating ½ hr. at 400° C., and finally 2 hr. at 450° C. Original activity is stated to be restored by this procedure. Addition to German Patent Appl. R 97,394 (abs. **3175**).

3087. ———. [Process for Removing Alcohols and the Like Oxygenated Compounds From the Primary Synthesis Product.] German Patent Appl. R 110,690, R 582, filed July 30, 1941 (*Cl. IV d–23 b*). FIAT Reel K–20, frames 207–213; PB 70,211; TOM Reel 177, frames 1,629–1,635; TOM Reel 36, bag 3,454, item 36; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, ch. 39, 1948, p. 96.

Process as described consists in intimately mixing the primary synthesis product from the hydrogenation of CO at temperatures of 100° or <with a hydroscopic metal salt such as Zn, Ca, or Mg chloride and then separating the addition compound from the supernatant mixture of hydrocarbons (by distillation or decantation).

3088. ———. [Process for Removing Calcium From Cobalt Solutions.] German Patent 683,691, R 403, Sept. 19, 1938. TOM Reel 37, bag 3,451, item 35, 3 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 4, ch. 133, 1949, p. 19.

In removing Ca from Co solutions by precipitating the Ca as CaF_2, the solutions are treated with soluble fluorides in the presence of Mg salts. The Co-Mg solution is acidified, suitably up to a pH of 2–4, before the addition of a soluble fluoride. In removing the Ca from Co solutions, which also contain Fe and Al salts, the Fe and the Al are first precipitated by means of alkali carbonate solutions, whereupon, after addition of Mg salt, the Ca is precipitated by means of a soluble fluoride.

3089. ———. [Process for Removing Oxygenated Compounds From Hydrocarbon Mixtures.] German Patent Appl.—, R 690, filed Sept. 9, 1943. FIAT Reel K–30, frames 7,887–7,890; PB 73,587; TOM Reel 37, bag 3,451, item 36, 4 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 5, ch. 147, 1949, p. 9.

In removing oxygenated compounds from synthetic and natural hydrocarbon mixtures, the latter are passed over layers of highly porous silica gel and/or Al_2O_3 at normal, super- or sub-pressure and at room temperature. Before using, the adsorbent is dried for a short time at temperatures > 100°, preferably > 150°. The desorption of the adsorbed fraction is effected by displacement with H_2O, after which it is extracted with organic solvents such as acetone, ether, alcohol, paraffin, furfurol, and the like, and the adsorption agent, after becoming exhausted, is reactivated by acid treatment.

3090. ———. [Process for Repressing the Foaming of Gas-Washing Liquors.] German Patent Appl. —, R 664, filed Feb. 6, 1943. FIAT Reel K–30, frames 7,979–7,980; PB 73,587.

Foaming of gas-washing liquors, known as "alkazid," containing strong bases and weak acids such as solutions of the alkali-salts of amino-carboxylic acids, can be repressed by adding 0.2–0.5 gm. of high molecular aliphatic alcohols with > 12 C. atoms in the molecule to each l. of washing solution.

3091. ———. [Process for Separating Branched-Chain Fatty Acids From Mixtures of Their Isomers and Homologs.] German Patent Appl. —, R 614, filed May 14, 1942. FIAT Reel K–30, frames 7,686–7,689; PB 73,587; TOM Reel 36, bag 3,454, item 36, 4 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, ch. 9, 1948, p. 23.

In the separation of branched-chain fatty acids from mixtures of their isomers and homologs by the incomplete saponification and extraction of the unsaponified portion, the extent of incomplete saponification is so chosen that no noteworthy separation in accordance with molecular size occurs, whereupon the treatment is repeated many times. For example, the operation may be performed in such a way that at the beginning a 95% saponification takes place whereby the unsaponified residue is extracted with benzine and the 1st low-freezing fraction removed. The remaining soap mixture is converted with mineral acids into a mixture of free fatty acids, which are again so far incompletely saponified that still no separation by molecular size occurs. Thus the 2d low-freezing fraction is obtained. This method of treatment is continued as long as the freezing point of the extracted fraction remains low enough.

3092. ———. [Process for Separating Mixtures of Fatty Acids or Fatty Acid Salts and Neutral Oils.] German Patent Appl. —, R 648, filed Dec. 18, 1942. FIAT Reel K–30, frames 8,024–8,027; PB 73,587; TOM Reel 36, bag 3,454, item 36, 4 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, ch. 14, 1948, p. 37.

Mixtures consisting of fatty acids or fatty-acid salts and neutral oils are separated by dissolving the fatty acids or fatty-acid salts with H_2O or a mixture of H_2O and alcohol. Before, during, or after the H_2O treatment, alkaline or acid reacting materials are added to the reaction mixture until a pH concentration of 7 is attained, whereupon neutral oils insoluble under these conditions are separated. This may take place under normal or slightly increased temperature. Mineral acids or gaseous CO_2 or even fatty acids can be utilized at normal or increased pressure as the acid-reacting materials.

3093. ———. [Process for Separating Mixtures of Isomeric Fatty Acids.] German Patent Appl. —, R 609, filed May 1, 1942. FIAT Reel K–30, frames 7,702,706; PB 73,587; TOM Reel 36, bag 3,454, item 36, 5 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, ch. 8, 1948, p. 20.

It has been found that when mixtures of fatty acids are saponified, those having straight chains are 1st reduced, then those with slightly branched chains, and lastly those that are more strongly branched. By incomplete saponification, therefore, mixtures of isomeric fatty acids can be separated in accordance with their degree of branching, and separation of various fractions be made dependent on the extent of the saponification. The mixture of straight chain or slightly branched saponified fatty acids on the one hand and the more extensively branched unsaponified fatty acids on the other hand can be separated in different ways. For example, the aqueous soap solution can, after the addition of alcohol, be extracted in known manner with benzine. The fatty acid mixture can also contain unsaponifiable hydrocarbons, since these after saponification either separate directly, or insofar as they are dissolved in the soap solution, can be extracted by means of benzine. In case the fatty acid mixtures contain not only isomeric fatty acids of like molecular magnitude, but also acids of different molecular size, it is preferable to 1st separate them by fractional distillation or other suitable means, such as fractional solution or crystallization, into as many narrowly cut fractions of approximately the same size molecules as possible, in order that with incomplete saponification the separation according to isomers is not upset through separation according to molecular size. This process does not, however, permit of the smooth separation by homologs when isomers are simultaneously present. The present invention rests on the knowledge that the same mode of action applied under other conditions to mixtures of isomeric fatty acids makes possible a separation of the isomers. A good separation is, however, only obtainable when no homologs or, in any case, only such homologs are present that are approximately of the same molecular size. The process is applicable to acid mixtures from any source whatever. It is especially suitable for acid mixtures whose original C chain was produced during the catalytic hydrogenation of CO, whereby the acid-forming carboxyl group was produced either primarily or through direct oxidation or by the catalytic water gas reaction and subsequent oxidation. Gives detailed example of each described method.

3094. ———. [Process for Separating Mixtures of Sulfuric Acid Esters of High-Molecular Hydrocarbons and Paraffin Hydrocarbons.] German Patent Appl. —, R 688, filed Aug. 25, 1943. FIAT Reel K–30, frames 7,893–7,895; PB 73,587; TOM Reel 37, bag 3,451, item 36, 3 pp.

Method of the original German Patent Appl. R 116,698 (abs. **3096**) is improved by having the neutralization of the esters take place with an essentially H_2O-free, finely pulverized alkali hydroxide, which, if desired, is previously heated to 350°–450° and finally again cooled to room temperature, about 20°. A yield of 93% of theory is reported.

3095. ———. [Process for Separating Mixtures of Sulfuric Acid Esters of High-Molecular Hydrocarbons on the One Hand and Paraffin Hydrocarbons on the Other.] German Patent Appl. —, R 707, filed Mar. 10, 1944 (*Cl. IV d–12 o*). TOM Reel 37, bag 3,451, item 36, 3 pp.

In the further development of the process described in German Patent Appl. R 116,698 (abs. **3096**), after neutralizing the esters with alkali or earth alkali hydroxides, finely pulverized inorganic or organic substances, such as talc, soda, or starch together with H_2O, are added and the mixture is heated for a few hours at 30°–90°, preferably 30°–50°.

3096. ———. [Process for Separating Mixtures of Sulfuric Acid Esters of High-Molecular Hydrocarbons or of Paraffin Hydrocarbons.] German Patent Appl.

R 116,698, R 677, filed July 9, 1943 (*Cl. IV d–12 o*). FIAT Reel K–30, frames 7,936–7,940; PB 73,587; TOM Reel 37, bag 3,451, item 36, 5 pp.

In separating mixtures of sulfuric acid esters of high-molecular hydrocarbons, especially those of molecular size C_{12}–C_{20}, and of paraffin hydrocarbons, the mixtures, after neutralization of the esters with highly concentrated alkaline liquors, suitably 65–75%, or earth alkaline oxides or hydroxides, are continuously extracted at 20°–40° with small amounts of low-boiling organic solvents, chiefly pentane and/or hexane.

3097. ———. [Process for Separating Soda Soaps From Soap Mixtures Containing Hydrocarbons.] German Patent Appl. —, R 640, filed Nov. 4, 1942. FIAT Reel K–30, frames 7,596–7,599; PB 73,587; TOM Reel 36, bag 3,454, item 36, 4 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, chap. 11, 1948, p. 28.

In separating soda soaps from soap mixtures containing hydrocarbons but no free alkali hydroxides, an amount of H_2O or aqueous alcohol mixture is used which is 10–15 times > the weight of the soap mixture itself. To prevent foaming of the mixture or the formation of emulsions, 10–15% of ethyl alcohol is added. Example: A synthesized mixture of soda soaps and aliphatic hydrocarbons consisting of about 25 kg. of soda soaps and 30 kg. of paraffin hydrocarbons, C_{10}–C_{18}, are mixed with 200 l. of H_2O and 40 l. of 50% ethyl alcohol, and the mixture is stirred well for 10 min. The liquid is then heated to about 60°, whereupon 2 sharply defined layers separate, the upper consisting of neutral oil, which is separated, and the lower of an aqueous-alcohol soap solution, from which the alcohol is separated by distillation. The soap is then salted out from the alcohol-free aqueous soap solution. About 24 kg. of raw soap, containing only 1.2% of neutral oil, is obtained.

3098. ———. [Process for Separating Soda Soaps Produced by Aldehyde Oxidation From Hydrocarbon-Containing Reaction Mixtures.] German Patent Appl. R. 110,735, R 584; filed Aug. 4, 1941 (*Cl. IV a–23 e*). TOM Reel 36, bag 3,454, item 36, 4 pp; TOM Reel 39, bag 3,453, item 1 (revised Oct. 8, 1941); Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, ch. 3, 1948, p. 8.

Soda soaps produced by aldehyde oxidation can be separated from reactor mixtures of hydrocarbons produced in the catalytic hydrogenation of CO by H_2O or aqueous alcohol solutions when the reaction mixture does not contain free alkali hydroxide. The amount of H_2O or aqueous alcohol solution should be 10–15 times the weight of the soap. To prevent foaming the H_2O or solvent mixture used in extracting the soap contains an antifoam agent such as 10–15% of ethyl alcohol.

3099. ———. [Process for Separating the Alcohol From Hydrocarbon-Alcohol Mixtures.] German Patent Appl. —, R 673, filed June 29, 1943. FIAT Reel K–30, frames 7,951–7,954; PB 73,587; TOM Reel 37, bag 3,451, item 36, 4 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 5, ch. 144, 1949, p. 4.

To separate the hydrocarbon-alcohol mixture obtained by synthesis from CO and H_2, the mixtures are extracted with aqueous or aqueous-alcoholic solutions of surface active material, such as fatty acids or sulfonates, at normal temperature or up to about 100°. This method has the advantage of being less costly than the usual previous use of H_2SO_4 or of acid-reacting salt solutions as $ZnCl_2$ solutions.

3100. ———. [Process for the Activation of Catalysts Used in the Hydrogenation of Carbon Monoxide.] German Patent Appl. R 116,862, R 686, filed Aug. 4, 1943 (*Cl. IV d–12 o*). FIAT Reel K–30, frames 7,903–7,907; PB 73,587; TOM Reel 37, bag 3,451, item 36, 5 pp.; TOM Reel 177, frames 1493–1497; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, ch. 8, 1948, p. 20.

Catalysts of Co or Ni made by precipitation from their sulfate solutions by soda are subjected to an activating wash with a solution of alkali hydroxide or carbonate of a comparatively lower concentration than the precipitating solution, for example, 0.1 N or less. The activating wash may be preceded by a wash with H_2O.

3101. ———. [Process for the Aromatization of Hydrocarbons.] German Patent Appl. R 103,379, R 404, filed Sept. 19, 1938 (*Cl. IV d–12 o*). TOM Reel 41, bag 2,744, item 14, 3 pp.

In aromatizing aliphatic hydrocarbons in accordance with the method of German Patent 763,831 (abs. **3004**), the reaction is continued only uptil the H_2 content of the end gas freed from the liquid reaction products by condensation amounts to at least 80%, and then the catalyst is regenerated by burning with air until the CO_2 content of the combustion gas has decreased to 1–5%. If regeneration is carried too far the activity of the catalyst falls off sharply and recovers very slowly and if not far enough only a partial aromatization is obtained. After regeneration is completed the catalyst should be treated for a short time with H_2.

3102. ———. [Process for the Catalytic Addition of Water Gas to Olefins.] German Patent Appl. —, R 655, filed Jan. 9, 1943. FIAT Reel K–30, frames 8,007–8,010; PB 73,587; TOM Reel 36, bag 3,454, item 36, 4 pp.; Meyer Transl. PC–S–V, Oxo, vol. 1, ch. 6, p. 12.

In performing the catalytic addition of water gas to olefins under increased pressure at about 200°, the catalysts are dissolved in mediums, such as H_2O or aqueous solutions, that are virtually insoluble in the olefins to be reacted. The catalyst solution is prepared by treating metals, metal oxides and/or metal salts that are able to form metal carbonyl hydrides. Other materials such as metals, oxides, salts, metalloids, kieselguhr, with organic acids and/or hydrocarbons can be present. Whereupon, in the presence of mediums that are virtually insoluble in olefins, water gas is reacted therewith under elevated pressure and at temperatures of approximately 50°–250°. Example: 57 kg. of a hydrocarbon mixture b. 210°–220° is mixed with 2 kg. of a reduced, finely ground Co–ThO_2–MgO–kieselguhr catalyst, and 10 l. of H_2O is added. The mixture is then treated at 135° and 150 atm. for 45 minutes with water gas. Hereby 8.13 gm. Co are dissolved per l. of H_2O. 6 l. of this solution is mixed with 4.5 kg. of a hydrocarbon fraction b. 179°–200° containing 65% olefins. The reaction mixture is then treated for 15 hr. at 135° and 150 atm. with water gas in a pressure vessel. The reaction product separated from the catalyst solution contains 2.14 kg. of oxygenated compounds.

3103. ———. [Process for the Catalytic Conversion of Hydrocarbons Especially Their Aromatization.] German Patent Appl. R 110,308, R 578, filed July 12, 1941 (*Cl. IV d–23 b*). TOM Reel 36, bag 3,454, item 36, 4 pp; TOM Reel 177, frames 1,625–1,628; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, ch. 38, 1948, p. 94.

Presence of oxygenated compounds in the starting material interferes with the catalytic conversion of hydrocarbons (aromatization, polymerization, dehydrogenation). Such compounds are virtually eliminated by passing the vaporized hydrocarbon mixture over a metallic oxide, for example, Al, Mg, or alkaline earth oxide, at 150°–400° C. In time the catalyst loses its activity and is regenerated in a current of air. Aromatization and polymerization are then carried out as usual. Removal of oxygenated compounds raises

the aromatic content of the final product from 26–49% by volume.

3104. ———. [Process for the Catalytic Conversion of Hydrocarbons, Particularly Their Dehydrogenation or Aromatization.] German Patent Appl. —, filed Nov. 20, 1939. TOM Reel 41, bag 2,744, item 14, 5 pp.

Hydrocarbons are converted in the presence of known catalysts and with regenerative utilization of the heat developed by the combustion of the surface-deposited C by the aid of a converter packing consisting of catalyst substances and refractory heat-storage material, the latter being in granules of the same or nearly the same size as the catalyst and in intimate mixture with it. An especially suitable mixture is one consisting of 40 parts by volume of catalyst in granules of 2–3 mm. in size and of 60 parts of Fe–free refractory chamotte of 3–4 mm. size.

See German Patent Appl. R 104,998 (abs. **3010**).

3105. ———. [Process for the Catalytic Cracking, Dehydrogenating or Aromatizing of Hydrocarbon Oils.] German Patent Appl. R 108,779, R 544, filed Nov. 1940 (*Cl. IV d–23 b*). TOM Reel 39, bag 3,453, item 1.

Carbon deposits are removed from the catalyst by blowing air heated to about the reaction temperature from top to bottom of the catalyst chamber at the rate of 285–855 $m.^3$ of air per $m.^3$ of catalyst per hr. The reaction time is such that the removal of the C causes only a slight heating of the catalyst to not more than an average 60°–80°.

3106. ———. [Process for the Catalytic Cracking of Hydrocarbons.] German Patent Appl. R 105,624, R 464, filed July 8, 1939 (*Cl. IV d–23 b*). TOM Reel 177, frames 1,594–1,600; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 31, 1948, p. 77.

Procedure for maximum yields of high octane fuels from H-rich, heavy hydrocarbons is developed. Low partial pressures of hydrocarbons, about $\frac{1}{30}$ kg. per $cm.^2$, obtained by addition of inert gas or preferably steam, are essential. Acid activated earths, impregnated with a solution of phosphoric and boric acids or of phosphoric acid alone, were used. In certain instances, addition of Co or other metal salts was useful. Temperatures 480°–600° were used, depending on the starting materials. Cu, Cu alloys, alloyed steels, tin plated tubes, and ceramics may be used for the converters. Fe alloyed with Cr or Al is also suitable. 2-stage operation gave about 90% liquid hydrocarbons. The yield of 90–95 octane gasoline was about 50%.

3107. ———. [Process for the Catalytic Cracking of Hydrocarbons.] German Patent Appl. R 108,555, R 540, filed Oct. 17, 1940 (*Cl. IV d–23 b*). TOM Reel 39, bag 3,453, items 1 and 2.

In the catalytic cracking of hydrocarbons, such as those b. 200°–360° obtained from the hydrogenation of CO, to olefinic low-boiling hydrocarbons, which are easily polymerized to antiknock gasoline, the operation is performed at normal or increased pressure and in the presence of catalysts consisting chiefly of acid-activated bleaching earths impregnated with small amounts, 1–3%, of a mixture of H_3BO_3–H_3PO_4 or with H_3PO_4 alone an dif desired activated with Co or a similar salt.

3108. ———. [Process for the Catalytic Cracking of the Hydrogenation Products of Carbon Monoxide to Olefinic, Low-Boiling Hydrocarbons.] German Patent Appl. —, R 720, filed July 20, 1944. FIAT Reel K–30, frames 7,782–7,790; PB 73,587; TOM Reel 37, bag 3,451, item 36, 7 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 5, ch. 149, 1949, p. 13.

In the catalytic cracking of synthetic hydrocarbons to olefins, especially those which are capable of being polymerized to high antiknock gasolines, the cracking takes place at 500°–520° at catalyst loads up to 20 cc. of added product per 100 cc. of catalyst per hr. (preferably 10 cc.) in presence of such quantities of steam that the partial pressure of the added hydrocarbons amounts to about 10–20% of the total pressure. The catalysts used have been precipitated with NH_3 at about 50° from a mixture of silicic acid solution and an Al salt solution, washed under maintenance of an alkali reaction until the alkali salts have been thoroughly removed, dried, and heated to about 500°. The SiO_2 content lies 30–50%, preferably 33–40%. Example: 690 cc. of water glass solution are diluted with 12 l. of H_2O and 390 cc. HNO_3 (1:1) added with stirring. A clear silicic acid solution is formed. 3,000 gm. $(Al(NO_3)_3)$. 9 H_2O are dissolved in 4 l. of H_2O, and the clear solution is mixed with the silicic acid solution. The mixture is warmed to about 50°. 2,000 cc. of a concentrated solution of NH_3 is added to this mixture with stirring. The precipitation temperature rises to about 55°. The resulting precipitate is removed and washed several times with H_2O, while maintaining an alkaline medium, until the salt is thoroughly removed, dried, shaped, and heated to 500°. The finished catalyst has an alkali content $<0.2\%$. 12 cc. per hr. of a diesel oil fraction from the Fischer-Tropsch synthesis b. 200°–350° and 12 cc. of H_2O are passed over 100 cc. of this catalyst at 500°. The yield is 11% by weight of a gasoline b. 50°–200° and 31% by weight of C_3–C_5 olefins from which by polymerization 27.9% by weight of polymer gasoline can be obtained. Together with the 2.1% by weight of C_5 paraffins obtained from cracking and the 0.6% by weight of C_5 olefins not touched by the polymerization, there are obtained altogether 41.6% by weight of gasoline b. up to 200° and having an octane number of 81.

3109. ———. [Process for the Catalytic Polymerization of a Mixture of Olefins.] German Patent Appl. R 104,047, R 426, filed Dec. 14, 1938 (*Cl. 12 o–1.06*). TOM Reel 177, frames 1,574–1,577; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, ch. 26, 1948, p. 66.

Mixture of ethylene, propylene, and butylene or ethylene alone is polymerized to gasoline by passing it over a Ag-activated H_3PO_4 catalyst at about 250° and 100 atm. while drenching the catalyst with polymer gasoline or with a Fischer-Tropsch gasoline condensate b. 140°–200°. The propylene and butylene polymerize readily, but the ethylene requires recycling.

3110. ———. [Process for the Catalytic Production of Hydrocarbon-Nitrocompounds.] German Patent Appl. —, R 637, filed Oct. 3, 1942. TOM Reel 36, bag 3,454, item 36, 5 pp.

In preparing nitrocompounds from concentrated HNO_3 and olefins, the wholly or partly vaporized reactants are collectively or individually preheated and then passed over catalysts at temperatures $>60°$, preferably $>150°$, and under pressure of about 5 atm. The amount of charge is as high as possible, at least >1 part by volume, preferably >10 parts by volume, of liquid raw materials to each part by volume of catalyst per hr. The conversion catalyst consists of silica gel, activated bleaching earth or other Al–Mg silicates, calcined Al_2O_3, bauxite or other Al silicate singly or mutually admixed, if desired with addition of acid-insoluble heavy metal oxides. Under the described conditions, theoretical yields of 85–90% are obtained.

3111. ———. [Process for Dehydrogenating Hydrocarbons, Particularly of Propane and Butane.] German Patent Appl. —, R 460, filed June 30, 1939. TOM Reel 41, bag 2,744, item 14, 4 pp.

Catalyst is used consisting of Al_2O_3 and Cr_2O_3 activated with Co and ThO_2. A suitable catalyst consists of 66% by weight Al_2O_3, 30% Cr_2O_3, 3.5% Co, and 0.5% ThO_2. The most favorable operating conditions are a

pressure of 1 atm. and 580°. A 20–30% higher yield of olefins can be obtained than by previous methods.

3112. ———. [Process for Deliming Burned Magnesia.] German Patent Appl. R 115,221, R 660, filed Jan. 25, 1943 (*Cl. IV b–12 m.*). FIAT Reel K–30, frames 7,889–7,991; PB 73,587; TOM Reel 177, frames 1,478–1,480; TOM Reel 36, bag 3,454, item 36, 3 pp; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, ch. 4, 1948, p. 11.

Lime-containing magnesia is suspended in cold H_2O (preferably condensed H_2O) and then treated at <70° (preferably <40°) with a solution of Mg nitrate in the proportions of 0.7–1 kg. MgO in form of $Mg(NO_3)_2$ to 1 kg. of CaO. The mixture is vigorously stirred for 48 hr. at about 20°, washed with cold condensed H_2O, filtered and the MgO precipitate further washed. The product contains <1% of CaO and is a very suitable material for catalyst preparation.

3113. ———. [Process for the Improved Production of Esterlike High-Molecular Compounds of Waxy Nature.] German Patent Appl. R 111,074, R 593, filed Sept. 22, 1941 (*Cl. IV d–12 o*). TOM Reel 36, bag 3,454, item 36, 5 pp.; Meyer Transl. PC–S–IV, vol. 1, ch. 5, 1948, p. 12.

High-boiling hydrocarbon mixtures from such sources as petroleum paraffin, lignite paraffin, montan wax, or synthetic paraffin from CO hydrogenation are oxidized with N_2-containing gases with addition of nitrosyl H_2SO_4, and toward the end of the reaction polyvalent alcohols are slowly added to the reaction mass without any change in the temperature. The alcohols may be partly or wholly substituted by Alkyl-, aryl-, chlorine-, sulfate, phosphate-, or amine-groups. After the alcohols are added, the reactants are treated for 1–2 hr. with nitrous gases. During or after the reaction, waxy, oily, or fatty substances containing carboxyl groups are added, especially those that occur as residues in the catalytic conversion of water gas to olefinic hydrocarbon mixtures. Example: 2,500 gm. of hard paraffin obtained from the hydrogenation of CO and having a solidifying point of 91° are mixed with 500 cc of nitrosyl H_2SO_4 and then exposed at a temperature of 122° for 14 hr. to an hourly flow of 3,000 *N* l. of ammonia combustion gases, which contain 8.5% NO and 5% O_2. After 14 hr. the gas flow is reduced to 100 *N* l. per hr. During the period of 110 minutes, 1,600 gm. of a synthetic C_{13} alcohol, obtained by the catalytic conversion of water gas to C_{12} olefins, are introduced dropwise. After the reaction is completed, the reactants are washed with H_2O. There are obtained 3,480 gm. of an ivory-colored, waxlike product having a saponification number of 115, a neutralization number of 4.5, and a hydroxyl number of 12. An almost pure ester is obtained, containing only about 20% of unsaponifiable compounds.

3114. ———. [Process for Improving Lubricating Oils.] German Patent Appl. —, R 405, filed Sept. 19, 1938. TOM Reel 37, bag 3, 451, item 35, 4 pp.

Lubricants, which have been prepared by the polymerization of unsaturated hydrocarbons obtained by the careful cracking of a synthetic gasoline fraction b. 200°–300°, are improved by treating the finished polymerizate with elementary S at a raised temperature. Before the S treatment, the oil is subjected to a treatment with activated bleaching earth followed by vacuum disillation to the desired flame point. Then about 0.1–1% of S and 20–100% of the S of a vulcanization accelerator such as diphenylthiourea are added to the oil with heating to 160° for 5 hr. After sulfurization is completed, the oil is steam distilled at 180° for 30 min. under an absolute pressure of 3 mm. Hg. In this manner the saponification number, as well as the Cu test to active S, is brought to the desired point. The oil thus obtained shows a high aging stability. No H_2S is split off by heating and no attack by S on metal is seen.

3115. ———. [Process for the Oxidation of Synthetic Paraffin.] German Patent Appl. R 110,978, R 587, filed Sept. 8, 1941. TOM Reel 36, bag 3,454, item 20, 5 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, ch. 1, 1948, p. 1, and chap. 6, p. 15.

Synthetic paraffins with more than 16 C atoms, particularly those high-melting hard paraffins from the hydrogenation of CO, are treated in the presence of H_2SO_4 or nitrosyl sulfuric acid with nitrous gases. Before the oxidation, superoxides that easily evolve O_2, such as leadsuperoxide, are added. By such treatment yields of 94–94.5% of oxidation products are obtained.

3116. ———. [Process for Polymerizing Olefins by Means of Metal Halogenides.] German Patent Appl. —, R 682, filed July 19, 1943. FIAT Reel K–30, frames 7,921–7,924; PB 73,587; TOM Reel 37, bag 3,451, item 36, 4 pp.

In carrying out the polymerization of olefinic hydrocarbons with metal halogenides, the olefins are gradually, that is, in the course of 1 or more hours, introduced into a previously prepared, heated catalyst oil whose activity is maintained by the addition of metal halogenides such as $AlCl_3$. After the hydrocarbons are added the heating is continued. Suitable olefinic hydrocarbons are those produced in the hydrogenation of CO under conditions favoring their maximum production. Catalyst oil is defined as the double compound formed during previous reactions between metal halogenides and hydrocarbons, so much being drawn off after each reaction that the amount calculated on the respective addition remains constant. To produce very low viscosity oils at high reaction temperatures, small amounts of $AlCl_3$ and proportionally larger amounts of catalyst oil are used.

3117. ———. [Process for Polymerizing the Oxygenated Products From the Hydrogenation of Carbon Monoxide.] German Patent Appl. R 117,891, R 697, filed Jan. 12, 1944 (*Cl. IV d–23 b*). FIAT Reel K–30, frames 7,859–7,860; PB 73,587; TOM Reel 177, frames 1,502–1,503; TOM Reel 37, bag 3,451, item 36, 2 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, ch. 10, 1948, p. 26.

In working up the liquid products of CO hydrogenation, the presence of oxygenated products has been found troublesome in the process of polymerization. It has been found possible to remove this difficulty by passing the products in vapor state at 150°–400° over a catalyst of Al_2O_3. MgO or alkaline earth oxides and by this means reducing the O content to negigible proportions without affecting in any way the hydrocarbon content. Poymerization can then be carried out in the usual manner. Addition to German Patent Appl. R 110,308 (abs. **3103**).

3118. ———. [Process for Polymerizing Unsaturated Hydrocarbons.] German Patent Appl. —, R 424, filed Dec. 13, 1938. TOM Reel 37, bag 3,451, item 35, 2 pp.

In polymerizing unsaturated gaseous hydrocarbons under the application of pressure and raised temperatures, using phosphoric acid catalysts, the latter are constantly washed with suitable gasolines or heavy gasolines, which remain liquid under the given conditions of pressure and temperature. Such liquids as hydrogenated polymer gasoline or the saturated condensed gasoline b. in the range 140°–200° obtained in the catalytic conversion of CO with H_2 are suitable. The purpose of the washing treatment is to remove the high-molecular substances that deposit on the catalyst. The life of the catalyst is thus considerably lengthened, and the yield of polymer gasoline increased.

3119. ———. [Process for the Post Treatment of Soaps Made of Free Fatty Acids.] German Patent Appl. R 110,734, R 583, filed July 31, 1941 (*Cl. IV d–23 d*). TOM Reel 36, bag 3,454, item 36, 5 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, ch. 2, 1948, p. 5.

Soap is extracted with acetone, the Ph of which is regulated, by the addition of alkaline reacting compounds, to the Ph value of the soap to be treated. A pH value of 8.8–9.1 is suitable and can be set without difficulty by the aid of NH_3. The unpleasant smell usually associated with synthetic soap can be virtually eliminated by adding about 1% of pyridine to the acetone.

3120. ———. [Process for Preparing Cobalt-Magnesium Catalysts for the Conversion of Carbon Monoxide–Hydrogen Mixtures.] German Patent 764,643, Sept. 27, 1937; appl. R 100,366, R 360 (*Cl. 12 o–1.03*). TOM Reel 37, bag 3,451, item 35, 3 pp.; Auszüge deut. Patent-Anmeldungen, vol. 6, p. 295; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 4, ch. 128, 1949, p. 9.

In preparing Co-Mg catalysts for the catayltic conversion of CO–H_2 mixtures by the simultaneous or consecutive precipitation of the Mg and Co from the solution of their nitrates or chlorides, use is made of a Mg solution showing a larger content of Mg than corresponds to the stoichiometric ratio of Mg: Co in the catalyst under preparation. Example: A solution containing 24.91 gm. Co in the form of the nitrate and 3.97 gm. MgO likewise in the form of the nitrate (thus 16 parts MgO : 100 parts of Co) is precipitated at the boiling temperature with a 10% Na_2CO_3 solution, 1–2 min. being required altogether. The necessary amount of carrier substance is introduced and immediately filtered. A precipitate is obtained that contains in addition to the total amount of Co, 2.42 gm. of MgO, that is, 9.75 parts MgO : 100 parts of Co.

3121. ———. [Process for Preparing of High-Octane Hydrocarbons.] German Patent Appl. R 109,970, R 569, filed May 2, 1941 (*Cl. 23 b–1.04*). TOM Reel 36, bag 3,454, item 20, 5 pp.; TOM Reel 39, bag 3,453, item 1; TOM Reel 177, frames 1,620–1,624; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 37, 1948, p. 91; vol. 2, chap. 77, 1948, p. 5.

Large yields of high-octane gasolines (motor octane=97) are obtained by catalytic cracking of hydrocarbons mixed with steam and isomerization of the cracking products. The hydrocarbon mixture is composed of paraffinic hydrocarbons b. >150° C. and low-boiling olefins (C_4, C_5, C_6) that are readily isomerized together with the cracking products in the presence of phosphoric acid catalysts. The ratio of the partial pressure of hydrocarbons to that of steam should be <0.2. Cracking is carried out in the presence of activated Al silicates at about 500° C. 3 examples.

3122. ———. [Process for Preparing Lubricants Highly Resistant to Oxidation.] German Patent Appl. —, R 431, filed Feb. 9, 1939. TOM Reel 37, bag 3,451, item 35, 4 pp.

According to a previous German Patent Appl. R 94,-081 (abs. **3152**), high molecular hydrocarbon oils are produced by cracking the liquid hydrocarbons b. >150°, obtained by the catalytic hydrogenation of CO and by polymerizing the cracked gasoline thus obtained with known condensation agents. It has also been stated in German Patent Appl. R 97,688 (abs. **2917**) that it is of advantage in producing synthetic lubricants to use only such cracked gasolines whose various fractions show quite definite densities. It has now been found that lubricants with special oxidation-resistant properties can be prepared by separating the cracked gasoline into a higher and a lower boiling fraction and then polymerizing only the former fraction to lubricating oil. The most suitable fraction is that above about 75° as this contains chiefly olefins with double end bonds and polymerizes most satisfactorily. The lubricant thus obtained, after separation of the condensation medium, is treated at about 170°–180° with a small amount of Al chloride or at 230°–250° with bleaching earth to improve the quality of the oil.

3123. ———. [Process for Producing Benzinelike Hydrocarbons by the Catalytic Polymerization of Olefins.] German Patent Appl. R 102,113, R 387, filed Apr. 16, 1938 (*Cl. IV d–12 o*). TOM Reel 37, bag 3,451, item 35, 2 pp.; TOM Reel 177, frames 1,549–1,551; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 20, 1948, p. 52.

In the polymerization of olefins to gasoline under the use of pressure and catalysts, undesirable increases in temperature and the resulting formation of heavy polymers are avoided by diminishing the flow velocity of the hydrocarbons under conversion and promoting the progressive polymerization of the olefins from bottom to top of the reaction space by progressively enlarging the cross section of the stream flow in the same direction. Diagram.

3124. ———. [Process for Producing Benzinelike Isomeric Hydrocarbons From an Olefinic Raw Material.] German Patent Appl. R. 102,114, R 385, filed Apr. 16, 1938 (*Cl. IV d–12 o*). TOM Reel 37, bag 3,451, item 35, 3 pp.; TOM Reel 177, frames 1,542–1,544; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 18, 1948, p. 48.

Low-boiling (<80°) monoolefins can be polymerized into gasoline b. 100°–200° by operating at pressures of about 100 atm. and at temperatures of 150°–200° in presence of a polymerizing catalyst such as H_3PO_4 on kieselguhr. At the above pressures and temperatures and a velocity of 1.5–4 l. per l. of catalyst per hr. a conversion of 40–55% can be attained.

3125. ———. [Process for Producing Condensation Products.] German Patent Appl. —, R 693, filed Sept. 15, 1943. FIAT Reel K–30, frames 7,878–7,881; PB 73,587.

Condensation products are produced by reacting formaldehyde and urea in the presence of the conversion products of aliphatic hydrocarbons with concentrated HNO_3. Example: A mixture of 36 gm. paraformaldehyde, 20 gm. urea, 5 gm. KOH, 35 cc. H_2O and 35 cc. of nitrocompounds, obtained by the reaction of concentrated HNO_3 with the C_6 fraction of the gasoline arising from the hydrogenation of CO, was intensively stirred for 48 hr. at 60°. (German Patent Appl. R 114,103 (abs. **3127**) and R 114,246 are cited in connection therewith.) After cooling the unreacted nitrocompounds were separated and the semisolid condensation product dried. There results a solid, somewhat brittle, dark mass melting >220°. It is insoluble in cold H_2O, alcohol, acetone, and the usual organic solvents and slightly soluble in boiling H_2O.

3126. ———. [Process for Producing Gasol by the Catalytic Conversion of Gas Mixtures Containing Carbon Monoxide and Hydrogen.] German Patent Appl. R 108,661, R 543, filed Nov. 4, 1940 (*Cl. IV d–12 o*). TOM Reel 39, bag 3,453, item 1.

Gas such as water gas is passed into a mixture of liquid hydrocarbons containing a CO–hydrogenation catalyst. The synthesis gas is recycled in proportion of 1 vol. of fresh gas to 2–3 of residual gas.

3127. ———. [Process for Producing Hydrocarbon-Nitrocompounds.] German Patent Appl. R 114,103, R 634, filed Sept. 18, 1942. TOM Reel 36, bag 3,454, item 36, 6 pp.

Hydrocarbon-nitrocompounds are produced from HNO_3 and olefin hydrocarbons, such as those prepared through the hydrogenation of CO, by reacting concentrated HNO_3 (1.48 sp. gr.) with the olefinic hydrocarbons at temperatures 20°–250° for periods of 5 min. or less and at any pressure. A small amount of dehydrating agent such as H_2SO_4, P_2O_5, or Na_2SO_3 may be added. The resulting nitrocompounds, after separation of the HNO_3 and the paraffinic fractions, are fractionated under reduced pressure and then separated from the unreacted paraffin layer by direct vacuum distillation or by extraction with selective solvents (MeOH) and subsequent vacuum distallation. Theoretical yields of 85–90% may be obtained.

3128. ———. [Process for Producing Hydrocarbons by the Catalytic Hydrogenation of Carbon Monoxide.] German Patent Appl. R 115,338, R 662, filed Feb. 1, 1943 (*Cl. IV b–26 d*). FIAT Reel K–30, frames 7,981–7,984; PB 73,587; TOM Reel 177, frames 1,481–1,484; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 5, 1948, p. 13.

Fischer-Tropsch catalysts that have become exhausted are cleaned and sieved, oxidized with air, and subjected to treatment with S-containing gases, such as coke-oven gas, until thoroughly impregnated and are then used to remove organic S compounds from synthesis gas. For example, a coke-oven gas containing 10–15 gm. of organic S after removal of the H_2S and passed through the catalyst at 400°–450° contained not more than 0.1–0.5 gm of S per 100 $m.^3$ after 1,000 hr. of use.

3129. ———. [Process for Producing Methane From Mixtures of Oxides of Carbon With Hydrogen.] German Patent Appl. R 112,110, R 604, filed Feb. 4, 1942 (*Cl. IV d–12 o*). FIAT Reel K–30, frames 7,715–7,716; PB 73,587; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, chap. 82, 1948, p. 18.

In producing CH_4 from mixtures of oxides of C with H_2, catalysts of Ni are used containing 5–50 parts MgO to 100 parts of Ni deposited on carrier substances, such as kieselguhr, in amounts preferably of about 50 parts to 100 of Ni. The gases are passed over the catalyst at a rate of about 25–100 l. per 4 gm. Ni per hr.

3130. ———. [Process for Producing Oxygenated Carbon Compounds by the Catalytic Addition of Water Gas to Olefins.] German Patent Appl. —, R 654, filed Jan. 8, 1943. FIAT Reel K–30, frames 8,011–8,013; PB 73,587; TOM Reel 36, bag 3,454, item 36, 3 pp.; Meyer Transl. PC–S–V, Oxo, vol. 1, chap. 5, p. 10.

In producing oxygenated hydrocarbons by the catalytic addition of water gas to olefins or olefin-containing hydrocarbon mixtures, the conversion is carried out $< 200°$, if desired far $< 200°$, in presence of steam, whereby super-atmospheric reaction pressures are used. The amount of H_2O added amounts to 0.1–100% by volume of the amount of hydrocarbon to be treated. Example: 710 gm. of a hydrocarbon mixture b. 41°–74° and containing 73% of olefins were mixed with 45 gm. of a reduced Co : ThO_2 : MgO : kieselguhr catalyst and treated for 17 hr. with water gas in a pressure stirring apparatus. A reaction pressure of 150 atm. and a temperature of 135° were maintained under energetic stirring. From the resulting product, 180 gm. of oxygenated compounds were isolated, which formed oximes with hydroxylamine hydrochloride. By operating with the addition of 35 cc. of H_2O, the water gas treatment could be completed in 14 hr. with production of 495 gm. of oxime-forming products.

3131. ———. [Process for Producing Solid and Liquid Hydrocarbons by the Stepwise Catalytic Conversion of Carbon Monoxide and Hydrogen.] German Patent Appl. R 100,570, R 366, filed Apr. 11, 1944 (*Cl. IV d–12 o*). FIAT Reel K–22, frames 1,222–1,225.

In operating on Co catalysts the 1st step is under atmospheric pressure and the further steps under increased pressure of 7–10 atm. The CO : H_2 ratio in the synthesis gas mixture is regulated in each step by the addition of H_2 or of a CO–H_2 mixture, so that in the 1st step the gas undergoing conversion contains more CO than corresponds to a radio of CO : H_2=1 : 2, whereas, in the succeeding steps, the synthesis gas is regulated to a ratio of CO : H_2=1 : 2 by the addition of water gas. The yield of liquid products is considerably increased by this method.

3132. ———. [Process for Producing Unsaturated Hydrocarbons by the Catalytic Hydrogenation of Carbon Monoxide.] German Patent Appl. R 114,-182, R 636, filed Sept. 26, 1942 (*Cl. IV d–12 o*). FIAT Reel K–30, frames 7,606–7,609; PB 73,587; TOM Reel 177, frames 1,513–1,515A; TOM Reel 36, bag 3,454, item 36, 4 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 13, 1948, p. 33.

In the production of unsaturated hydrocarbons by means of CO hydrogenation and the use of water gas or other CO-rich gas mixtures with gas recycle or addition of inert gas, the operation is performed with a constant gas composition and with a decreased amount of charge. A gas-recycle or inert-gas ratio is used that lies between 1 space volume of fresh gas to 2 of recycle (or inert) gas and 1 space vol. of fresh gas to 4 of recycle (or inert) gas. By decreasing the charge by 20%, and using a ratio of water gas to recycle gas of 1 : 3 instead of a single passage, there was an increase of olefins in the product up to 200° from 39–68.5% and 200°–300° from 23–48.5%.

3133. ———. [Process for Recovering Thorium.] German Patent 745,557, Nov. 30, 1944; appl. R 103,507, R 408, filed Oct. 7, 1938 (*Cl. IV b–12 m*). TOM Reel 37, bag 3,451, item 35, 3 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 4, chap. 135, 1949, p. 22.

This application is a further development of the process, German Patent 729,059 (abs. **274**), for recovering Th from Fe–Th sludges resulting from precipitation. These sludges are dissolved in H_2SO_4, and the Th is precipitated from the resulting solution as $K_2Th(SO_4)_3$ by addition of K_2SO_4. It has now been found that in the decomposition of the $K_2Th(SO_4)_3$ double salt to Th bicarbonate by heating with alkali carbonate solution, a K_2SO_4 : Na_2SO_4 ratio of 1 : 1 must not be exceeded in the reaction mixture. A part of the soda solution used for precipitating the Th may be replaced by potash. By maintaining the above ratio, a virtually Fe-free Th precipitates.

3134. ———. [Process for Recovering Thorium.] German Patent 745,859, Dec. 6, 1944; appl. R 103,605, R 413, filed Oct. 22, 1938 (*Cl. IV b–12 m*). TOM Reel 37, bag 3,451, item 35, 6 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 4, chap. 136, 1949, p. 24.

The bircarbonate obtained by the method of German Patent 745,557 (abs. **3133**) still contains 0.3–0.5 parts of Fe_2O_3 per 100 parts ThO_2. It has now been found that if the $K_4Th(SO_4)_3$ still containing a little Fe is treated with an excess of alkali carbonate solution until the Th bircarbonate first precipitated is redissolved, the alkali Th double carbonate solution is freed of the last traces of Fe by heating and subsequent filtration. The Th double carbonate solution, which has been freed of Fe, is decomposed with H_2SO_4 and the sulfate solution separated from the precipitated Th bicarbonate is again used for treating fresh Fe–Th sludge. By decomposing the above double carbonate solution with HCl and cooling the solution from which the precipitated Th bircarbonate has been filtered, the resulting alkali sulfate crystallizing out is used for treating fresh Th–Fe sludge. Flowsheets are shown.

3135. ———. [Process for Recovering Thorium for Catalyst Manufacture from Iron-Thorium Slurries Occurring in Working-up Spent Catalysts for the Hydrogenation of Carbon Monoxide.] German Patent Appl. —, R 725, filed Sept. 15, 1944. FIAT Reel K–30, frames 7,745–7,748; PB 73,587; TOM Reel 37, bag 3,451, item 36, 4 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 4, chap. 129, 1949, p. 11.

Slurries are treated with alkali bicarbonates or substances forming these or with mixtures of the same with alkali carbonates. The thoria is separated from the solution by neutralization with acids, or use may be made of solid or gaseous CO_2 at normal or elevated pressure and whatever temperature desired. The CO_2 is set free by expanding the solution freed of thoria, whereupon the CO_2 and the soda solution resulting thereby are returned to the process. The solution obtained from the Fe–Th slurry, if desired after cutting back with suitable amounts of soda solution of proper conceneration, is employed directly for the preparation of catalysts.

3136. ———. [Process for Refining High-Molecular Wax Acids.] German Patent Appl. —, R 665, filed Feb. 24, 1943. TOM Reel 36, bag 3,454, item 36, 4 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, chap. 4, 1948, p. 10.

In refining high-molecular wax acids, which were prepared by the oxidation of high-melting paraffins with alkali bichromate H_2SO_4 or with nitrous gases in presence of nitrosylsulfuric acid, by the saponification of the oxidation products with caustic potash, by their subsequent extraction with the hydrogenation products of CO, and by the acidifying, washing, and drying of the extraction residues, these are subjected at 100°–125° to a careful oxidative treatment with alkali bichromate H_2SO_4 or with nitrous gases in presence of nitrosylsulfuric acid. The product, after washing and drying, is of clear ivory color and is suitable as a substitute for montan wax and similar products.

3137. ———. [Process for Regenerating Catalysts for the Gasoline Synthesis.] German Patent Appl. R 101,215, R 373, filed Jan. 6, 1938 (*Cl. IV d–12 o*). PB Report 412, May 15, 1945; TOM Reel 37, bag 3,451, item 35, 2 pp.; Meyer Transl. PC–S–II, Fischer-Tropsch Process, vol. 4, chap. 130, 1949, p. 13.

Catalysts that have been used for the synthesis of gasoline from CO–H_2 are regenerated by dissolving in acids and by precipitating effective metals at $> 300°$ with flowing inert gases, particularly steam. As a further development of the process of the previous German Patent Appl. R 97,521 (abs. **3176**), the steam is passed at a rate of at least 1 m. per sec. through thick layers of relatively small transverse diameter.

3138. ———. [Process for Regenerating Catalysts for the Hydrogenation of Carbon Monoxide.] German Patent Appl. —, filed Nov. 5, 1938. TOM Reel 37, bag 3,451, item 35, 1 p.

In the further development of the process of German Patent Appl. R 97,394, (abs. **3175**), for the regeneration of catalysts that have been used for the catalytic conversion of CO–H_2 mixtures, the H_2 treatment is continued beyond the duration of paraffin removal and with a gradual increase in temperature. Example: A catalyst prepared in the usual manner by precipitation consisting of 100 Co : 5 ThO : 8 MgO : 200 kieselguhr, and which had been used for 3,500 hr. at temperatures of about 185°–192°, was 1st treated for 2½ hr. at 200° with a N_2–H_2 mixture (25 : 75). The temperature was then raised to 350° within ½ hr. Further H_2 treatment was then carried out by 1st heating for ½ hr. at 350°, another ½ hr. at 400°, and a final 2 hr. at 450°. The catalyst was again put into operation at 185°, at which temperature it showed its original activity.

3139. ———. [Process for Sulfonation of the Olefinic Products of Carbon Monoxide Hydrogenation.] German Patent Appl. R 108,369, R 538, filed Mar. 16, 1943 (*Cl. 12 o–23.01*). FIAT Reel B–196, frames 267–269; TOM Reel 39, bag 3,453, item 1.

Raw materials for the sulfonation are those hydrogenation products that were obtained by the simultaneous addition of gases, which did not take part in the hydrogenating reaction or gases that were still rich in CO owing to very brief contact with the catalyst. Products produced from synthesis gases having very nearly equal parts by volume of H_2 and CO, or from the recycled gases that contained about 2.5–4.0 parts of recycle gas to 1 part of fresh gas also may be used.

3140. ———. [Process for Sulfurization of Lubricating Oils.] German Patent Appl. —, R 406, filed Sept. 19, 1938. TOM Reel 37, bag 3,451, item 35, 2 pp.

Sulfurization of lubricants, by treating the oils with S at increased temperatures, is performed in the presence of substances having vulcanization accelerating properties such as diphenylguanidine, diphenylthiourea, or hexamethylenetetramine. Suitable amounts of each are $<1\%$ of S and $<0.5\%$ of the accelerator. After the reaction is completed, the sulfurized oil is steam distilled in a vacuum to free the oil of unpleasant smelling, volatile S compounds as well as any remaining unreacted vulcanization accelerator still present. The oils thus obtained have a high degree of stability.

3141. ———. [Process for Treating the Products of Carbon Monoxide Hydrogenation With Recovery of Fatty Acids.] German Patent Appl. R 110,168, R 572, filed May 23, 1941 (*Cl. IV d–12 o*). TOM Reel 36, bag 3,454, item 36, 3 pp.; Meyer Transl. PC–S–IV, Wax Oxidation, vol. 1, ch. 19, 1948, p. 46.

In treating the products of CO hydrogenation performed at usual or increased pressure and increased temperature with recovery of fatty acids, the reaction products containing olefins are subjected, after possible fractionation, to the action of CO and H_2 at increased temperature, 100° and above, and at strongly increased pressure of at least 100 atm. in the presence of catalysts under such conditions that the olefin hydrocarbons have absorbed about 1 mol. of CO and H_2. The mixture obtained is subjected to a mild oxidation, and the fatty acids obtained thereby are removed. The olefin-containing raw material is treated with water gas at about 130° and 150 atm. for 6 hr. or more.

3142. ———. Process for Treatment of Spent Cobalt Catalysts. British Patent Appl. 26,275, filed Sept. 6, 1938.

Process for the treatment of Co catalysts that are produced by the precipitation of the catalytically active metals in the presence of kieselguhr and that are employed for benzine synthesis from CO and H_2 by dissolving in HNO_3 and reprecipitating the catalytically active constituents in which the spent catalysts are treated with HNO_3 that contains no more than 20%, and preferably no more than 3–5%, of free HNO_3.

3143. ———. [Process for Working-Up the Residual Catalyst Oils Which Arise in the Polymerization of Olefins to Lubricating Oils by Means of Aluminum Chloride.] German Patent Appl. —, R 683, filed July 21, 1943. FIAT Reel K–30, frames 7,918–7,920; PB 73,587; TOM Reel 37, bag 3,451, item 36, 3 pp.

In working up the residual catalyst oil occurring in the polymerization of olefins to lubricating oils by heating in the presence of such oils, if necessary after the addition of $AlCl_3$, the mixture is heated with porous material to temperatures $>200°$, preferably up to

220°–240°. A separate heating of lubricating and catalyst oil may be to somewhat lower temperatures, for example, up to 190°, and then to higher temperatures of 220°–240° after addition of the porous material. The proportional amounts of each substance are suitably 100 parts lubricating oil : 2–3 catalyst oil : 5 porous material. The addition of 1% $CaCO_3$ improves the process, as do the higher temperatures as stated. By this method the catalyst oil occurs in an easily filterable, granular, sandy form easily removable from the apparatus. An essential improvement in the working of the polymerization process is noted.

See also German Co. Office No. R 682 (abs. **3116**).

3144. ———. [Production of Alcohols.] German Patent Appl. R 112,068, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 309.

Pure alcohols are obtained by the catalytic addition of water gas to olefinic mixtures. Before the addition occurs, the mixture is divided into 2 or more fractions, the highest boiling fraction of which boils at a lower point than the lowest-boiling reaction product. Addition to German Patent Appl. R 106,852 (abs. **3158**).

3145. ———. [Production of Ethers.] German Patent Appl. R 112,048, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 309.

Ethers are obtained by etherification of alcohols that have been obtained by the catalytic reaction of CO and H_2 on olefins or by reduction of the Oxo products formed in the catalytic addition of water gas to olefins.

3146. ———. [Production of High-Molecular Alcohols.] German Patent Appl. —, R 527, filed Aug. 19, 1940. FIAT Reel K–20, frames 246–249; PB 70,211.

High molecular alcohols with at least 6 C atoms in the molecule are produced by adding water gas to olefinic primary products of the CO hydrogenation. Between the addition of water gas and the hydrogenation, a treatment with condensing agents takes place.

3147. ———. [Production of High-Molecular Fatty Acids.] German Patent Appl. R 108,639, PA 755,183, filed Oct. 31, 1940 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 267–269; PB 83,253.

In the production of fatty acids by oxidation of paraffins obtained by synthesis from CO and H_2 in accordance with the process of German Patent Appl. R 107,858 (abs. **2909**), the oxidizing agent is an acidified alkali-bichromate solution and repeated oxidation treatments with loss of material are necessary. It has now been found that better results are obtained if a paraffin is used that has been produced from a synthesis gas the CO : H_2 ratio of which is $<1:2$, particularly water gas, and which has been recycled. The resulting hydrocarbons have a higher olefin content and require only a double oxidation to obtain a product with 34% of fatty acids. By the shortened oxidation time a yield of 85–90% is obtained instead of 70–75% by the longer method. In 1 example a hard paraffin produced over an Fe catalyst at 235° and 20 atm. pressure has an I value of 6.6, a solidifying point of 96°, a penetration value of 1.5, a neutral value of 0, and a saponification value of 1.08. 1,000 gm. of this paraffin were treated 2 times for 4 hr. at 60°–120° with a mixture of 1,250 gm. of Na bichromate and 7,000 gm. of 55% H_2SO_4. A yield of 8,681 (sic) gm. of a fatty acid material was obtained having a neutral value of 34.1, a saponification value of 34.1, a penetration value of 0.5, an I value of 1.0, and a solidifying point of 96°. The equal neutral and saponification values reveal the absence of fatty acid esters.

3148. ———. [Production of High-Molecular Hydrocarbon Oils.] German Patent Appl. R 95,050, PA 199,203, filed Mar. 11, 1939 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 974–978; PB 83,253.

After the separation of the high molecular hydrocarbon oils produced by cracking and condensation in accordance with the process of German Patent Appl. R 94,081 (abs. **3152**), the used condensation agent is employed as distributing medium for additional small amounts of fresh condensation agent.

3149. ———. [Production of Hydrocarbons by Catalytic Hydrogenation of Carbon Monoxide.] French Patent 836,273, Jan. 13, 1939. Chem. Abs., vol. 33, 1939, p. 5633.

Synthesis is effected in apparatus comprising cooling tubes and plates of good heat conductivity. The pressure in the reaction chamber is maintained substantially the same as that of the cooling fluid passing through the cooling tubes. A mixture of 1 part of CO to 2 parts of H_2 is passed up through a reaction chamber containing a catalyst. Hot H_2O at 186° under a pressure of 11 atm. is passed through the cooling tubes so that the reaction temperature does not exceed 187°. The pressure of the gases in the reaction chamber is maintained at 11 atm. On leaving the chamber the gas is cooled and H_2O, spirits, and oils are condensed. The residual gas is then treated with active C to remove hydrocarbons similar to gasoline and low-boiling spirits. A Co-Th catalyst may be used.

See also British Patent 502,771 (abs. **3199**), Australian Patent 106,931 (abs. **3202**), and Indian Patent 25,177 (abs. **3203**).

3150. ———. [Production of Kieselguhr Suitable for Carrier for Hydrogenation Catalyst.] German Patent Appl. R 103,980, PA 967,306, filed Dec. 6, 1938 (*Cl. 12 o–1.03*). FIAT Reel B–196, frames 411–414; PB 83,253; PB Report 412, May 15, 1945.

Kieselguhr to be used as a synthesis catalyst support is treated with a relatively volatile acid such as HCl or HNO_3 to remove inorganic impurities and is then oxidized below the sintering temperature to remove organic matter and the remaining traces of acids. Alternatively the metals may be removed as bicarbonates by blowing CO_2 through a suspension of kieselguhr, after which the kieselguhr is washed, dried, and calcined 1 hr. at 550° C.

3151. ———. [Production of Lubricants.] Belgian Patent 416,717, Dec. 1, 1936; appl. filed July 28, 1936; in Germany Aug. 24, 1935. Chem. Zentralb., 1937, II, p. 3417.

Hydrocarbon oils obtained from water gas and b. $>$ 150° are cracked and the resulting olefins condensed to lubricants.

3152. ———. [Production of Lubricants.] German Patent Appl. R 94,081, PA 568,242, filed Aug. 24, 1935 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 902–908; PB 83,253.

Liquid product produced by the CO–H_2 reaction at 180° and normal pressure over a Co catalyst is separated and the fraction b. $>$ 150° is cracked under 8 atm. pressure and at 493°. A fraction distilling up to 200° with a specific gravity at 20° of 0.702 is reacted for 48 hr. at —20° with 5% $AlCl_3$. The reaction product is H_2O washed free of catalyst, dried, treated with bleaching earth, and vacuum distilled. There are obtained per 100 parts of cracked product 53 parts of oil, which after separation of refrigeration oil, gives 43 parts of a highly valuable lubricating oil (pole height 1.75–1.9, absolute viscosity 12–22 E at 50° and flow point of —32° to —20°).

3153. ———. [Production of Lubricants.] Indian Patent 23,278, Feb. 13, 1937; appl, filed Oct. 5, 1936. Chem. Zentralb., 1937, II, p. 2465.

The products obtained by the hydrogenation of CO are separated and the hydrocarbons b. $>$ 150° are wholly or partly cracked at temperatures of 450°–

550° and at a pressure of 8–15 atm. They are then wholly or partly condensed in known manner by the aid of condensation agents such as $AlCl_3$.

3154. ———. [Production of Oxo Compounds.] German Patent Appl. —, R 487, filed Jan. 26, 1940. FIAT Reel K–20, frames 309–311; PB 70,211.

Olefinic hydrocarbons are conducted, together with CO and H_2, over condensing or polymerizing catalysts or the products obtained by the reaction of olefins with CO and H_2 are subjected to a condensing or polymerizing treatment. Addition to German Patent Appl. R 103,362 (abs. **2800**).

3155. ———. [Production of Oxygenated Derivatives of Aliphatic Hydrocarbons.] French Patent 869,163, Jan. 26, 1942; appl. filed Jan. 10, 1941. Chem. Zentralb., 1942, I, p. 3039.

Fatty acids and alcohols are formed by the catalytic reaction of CO and H_2 on olefins, which have first been fractionated. Example: A mixture of olefins b. 150°–350° is broken down into 4 fractions. (1) 165°–220° =olefins C_{10}–C_{12}; (2) 220°–255°=olefins C_{13}–C_{14}; (3) 255°–295°=olefins C_{15}–C_{16}; (4) 295°–330°=olefins C_{17}–C_{19}. The aldehydes and alcohols thus obtained are easily oxidized to fatty acids. The products possess a high degree of purity.

See also United States Patent 2,415,102 (abs. **1991**).

3156. ———. [Production of Plastics and the Like.] Italian Patent 389,594, Dec. 17, 1940. Chem. Zentralb., 1943, I, p. 218.

Aldehydes from the oxo synthesis can be used in the production of phenol- and alkyd-resins.

3157. ———. [Production of Pure Aliphatic Oxygenated Compounds, Particularly Alcohols and Fatty Acids.] Belgian Patent 440,397, Oct. 15, 1941; appl. filed Jan. 28, 1941. Chem. Zentralb, 1942, I, p. 1054.

Before the catalytic conversion of CO and H_2 the hydrocarbons to be treated are fractionated.

3158. ———. [Production of Pure Oxygenated Derivatives of Aliphatic Hydrocarbons, Particularly Fatty Acids or Alcohols.] German Patent Appl. R 106,852, PA 61,045, filed Jan. 27, 1940 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 883–886; PB 83,253.

In producing fatty acids or alcohols by reacting CO and H_2 with olefins at raised temperature and pressure with eventual oxidation or reduction, the working-up of the olefin-containing mixtures, particularly such as have an average boiling range of 150°–350°, is performed in such a way that the heavy oil is divided into 2 or more fractions of such characteristics that in each fraction the highest boiling constitutent boils at a lower degree than the lowest boiling reaction product. The process offers particular advantage for the thorough working-up of olefinic synthetic or natural hydrocarbon mixtures to pure oxygenated derivatives such as fatty acids or fatty alcohols. For example, the heavy oil fraction of such a hydrocarbon mixture of b. p. 165°–330° is separated into 4 fractions of boiling ranges 165°–220°, 220°–255°, 255°–295°, and 295°–330°, which closely correspond to the olefins C_{10}–C_{12}, C_{13}–C_{14}, C_{15}–C_{16}, and C_{17}–C_{19}. These fractions, which fulfill the supposition that the highest boiling constituent boils at a lower degree than the lowest boiling reaction product, are subjected to the water-gas conversion, whereby the reaction product is separated through fractional vacuum distillation into nonconverted diesel oil, an aldehyde fraction, and a portion consisting of various oxygenated conversion products. The aldehydes are then oxidized into fatty acids or reduced into alcohols of molecular weights C_{11}–C_{20}.

3159. ———. [Production of Solvents and Softeners.] German Patent Appl. R 106,771, no date (*Cl 12 o–11*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 300.

Solvent and softening agents, which contain oxygenated derivatives of aliphatic hydrocarbons, such as alcohols, ketones, esters, and ethers, are obtained by treating olefins with CO and H_2 in the presence of catalysts at elevated temperatures and pressures.

3160. ———. [Production of Synthetic Soap.] German Patent Appl. R 118,114, no date (*Cl. IV a–23 d*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 837.

To produce synthetic soaps from the liquid products of CO hydrogenation, the heavy oil fraction is separated, alkalized, and the resulting wash liquor, after neutralization with fatty acids in the same wash liquor, evaporated to dryness.

3161. ———. [Production of Waxes, Synthetic Resins, Plastics, Solvents and Softeners.] Belgian Patent 440,341, Jan. 17, 1941, Oct. 15, 1941; in Germany Jan. 17, 1940. Chem. Zentralb., 1942, I, p. 2605.

See French Patent 868,102 (abs. **3162**).

3162. ———. [Production of Waxes, Synthetic Resins, Plastics, Solvents, and Softeners.] French Patent 868,102, Dec. 18, 1941; appl. filed Dec. 14, 1940. Chem. Zentralb., 1942, I, p. 2605.

Alcohols, aldehydes, ketones, or carboxylic acids, obtained by the conversion of olefins with CO and H_2 and, if desired, by reduction and oxidation, are esterified or condensed. Thus by esterifying a carboxylic acid of 16 C atoms with an alcohol of 14 C atoms a good wax for impregnating and textile finishing is obtained.

3163. ———. [Protection of Catalysts From Air.] French Patent 845,301, Aug. 18, 1939. Chem. Abs., vol. 35, 1941, p. 1196.

Catalysts used in organic reactions, especially those for the synthesis of hydrocarbons from CO and H_2, are protected against the action of air by impregnating them with CO_2 at a temperature below 30°.

3164. ———. [Purifying Aldehydes and Ketones.] German Patent Appl. —, R 512, filed May 10, 1940. FIAT Reel K–20, frames 295–298; PB 70,211.

Aldehydes and ketones, obtained by the catalytic reaction of water gas with unsaturated C compounds, are treated with aqueous solutions of inorganic or organic acids and salts under any pressure and at temperatures below the boiling point. In doing so, concentration, temperature, and duration must be chosen so that the refractive index of the liquid remains virtually constant.

3165. ———. [Purifying Aldehydes and Ketones From the Oxo Process.] German Patent Appl. R 107,598, no date (*Cl. IV d–12 o.*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 301.

Aldehydes and ketones, which were obtained by the catayltic action of water gas on unsaturated hydrocarbons, are purified by treating them below their boiling points with aqueous solutions of acids and salts or mixtures of both.

3166. ———. [Recovery of Carboxylic Acids.] German Patent Appl. R 116,742, no date (*Cl. IV a–23 d*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 837.

Carboxylic acids or their derivatives are recovered from the alkali liquor concentrates by melting the mixture, distilling, and finally treating in a finely divided form. Distillation is stopped when, by slow cooling, 5–20% of the melted mass separates out in the form of an oily upper layer. Addition to German Patent Appl. R 115,996 (abs. **3083**).

3167. ———. [Recovery of Carboxylic Acids.] German Patent Appl. R 116,743, no date (*Cl IV a–23 d*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 837.

Carboxylic acids are recovered from the concentrates obtained by treating the primary products of CO hydrogenation with alkalies after their decomposition with crude carboxylic acids, driving off the unsaponifiable constituents, and distilling off the H_2O, while maintaining a H_2O to oil ratio of 5:2 to 2:1. Addition to German Patent Appl. R 115,996 (abs. **3083**).

3168. ———. [Refining Low-Boiling Hydrocarbon Oils.] Italian Patent 374,759, June 28, 1939. Chem. Zentralb., 1940, II, p. 1536.

Low-boiling hydrocarbon oils are treated at about 150°–400° with acid activated bleaching earth to which has been added $AlCl_3$, $ZnCl_2$, BCl_3, $FeCl_3$, or H_3PO_4. There is attained both a removal of the resinous constituents and an increase in the octane number. The method is very suitable for treating the cracked gasoline obtained as a product of hydrocarbon synthesis from water gas.

3169. ———. [Regenerating Benzine Synthesis Catalysts.] Indian Patent 25,835, Feb. 18, 1939; appl. filed Oct. 31, 1938. Chem. Zentralb., 1940, I, p. 325.

See French Patent 842,278 (abs. **2969**).

3170. ———. Regenerating Catalysts. British Patent 484,962, June 9, 1938; appl. filed Sept. 22, 1937. Chem. Abs., vol. 32, 1938, p. 8088.

In regenerating catalysts used in benzine synthesis by dissolving the metals in acid and again precipitating and reducing them, the catalyst is first treated at 300° or more with H_2, steam, or inert gases or with 2 or more of these simultaneously or successively to remove deposited organic substances. When steam is used the pyrophoric properties of the catalyst are destroyed. If desired, an extraction with solvents may precede the treatment with gases. In an example a catalyst consisting of Co, ThO_2, and kieselguhr is specified.

3171. ———. [Regenerating Catalysts.] French Patent 826,820, Apr. 11, 1938. Chem. Abs., vol. 32, 1938, p. 8088.

See British Patent 484,962 (abs. **3170**).

3172. ———. [Regenerating Cobalt Catalysts.] Belgian Patent 429,795, Aug. 19, 1938. Chem. Zentralb., 1939, II, p. 3160.

Used Co catalysts are treated with HNO_3, which contains not more than 20% free acid.

3173. ———. Regenerating Cobalt Catalysts. British Patent 504,700, Apr. 28, 1939. Chem. Abs., vol. 33, 1939, p. 7974.

Co catalysts that are precipitated on kieselguhr and have been used for the synthesis of benzines from CO and H_2 are regenerated by solution in HNO_3 and reprecipitation of the catalytically active material, the acid containing not more than 20% and preferably no more than 3–5% of free HNO_3. The catalysts are treated above the melting point of the solid paraffins contained in the catalyst, such as, at 70°–90°, the kieselguhr being readily separated by filtration, and the paraffins separating as an oily layer.

3174. ———. [Regenerating Catalysts.] Austrian Patent 160,722, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 157.

See British Patent 484,962 (abs. **3170**) and French Patent 826,820 (abs. **3171**).

3175. ———. [Regenerating Catalysts.] German Patent Appl. R 97,394, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 294.

Catalysts for the benzine synthesis from mixtures of CO and H_2 are regenerated by treating the exhausted catalysts with H_2 at temperatures >300° followed by solution in acids and precipitation.

3176. ———. [Regenerating Catalysts.] German Patent Appl. R 97,521, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 294.

Catalysts for the benzine synthesis from water gas are regenerated by heating to 300° with a stream of inert gases, dissolving in acids and precipitating the catalytically active metals. Addition to German Patent Appl. R 97,394 (abs. **3175**).

3177. ———. [Regenerating Catalysts.] German Patent Appl. R 101,354, filed Jan. 21, 1938 (*Cl. IV d–12 o*). PB Report 412, May 15, 1945.

Spent catalyst, after being freed from paraffin, is discharged and reworked by initial solution of active components in ammonium carbonate solution instead of acid. This is stated to facilitate elimination of impurities, but details are not given.

3178. ———. [Regenerating Catalysts.] German Patent Appl. R 103,371, filed Sept. 20, 1938 (*Cl. IV b–12 n*). PB Report 412, May 15, 1945.

Calcium impurity in Co nitrate solution prepared in reworking catalysts is precipitated by a soluble fluoride in the presence of added Mg (nitrate). Any excess of soluble fluoride over that required to precipitate Ca will precipitate as MgF_2, thus leaving no fluoride in solution to precipitate inactive Co fluoride when Na_2CO_3 is added.

3179. ———. [Regenerating Catalysts.] German Patent Appl. R 103,712, filed Nov. 7, 1938 (*Cl. IV d–12 o*). PB Report 412, May 15, 1945.

Used synthesis catalyst is subjected to oxidation under unspecified conditions except elevated temperature before regeneration with H_2 whereby the regeneration is said to proceed more rapidly and effectively.

3180. ———. [Regulating Gas Flow Through Catalyst.] German Patent Appl. R 105,508, filed June 24, 1939 (*Cl. IV d–12 o*). PB Report 412, May 15, 1945.

Process and apparatus whereby more uniform flow is maintained through a bed of synthesis catalyst by supplying the synthesis gas through a valve or orifice causing a considerably greater pressure drop than the catalyst bed itself.

3181. ———. [Removing Reaction Heat in the Carbon Monoxide Hydrogenation.] German Patent App. —, R 479, no date. FIAT Reel K–20, Jan. 5, 1940, frames 312–316; PB 70, 211.

Fraction of the hydrogenation product resembling diesel oil and b. 200°–320° can be used as conductor in removal of reaction heat. Rough draft of a patent application.

3182. ———. [Removing Chlorine From Hydrocarbons.] French Patent 837,002, Feb. 1, 1939. Chem. Abs., vol. 33, 1939, p. 5865.

Hydrocarbons are subjected to a heat treatment, preferably under pressure, in the presence of MgO or ZnO and fuller's earth. The temperature of the treatment may be 130°–180°. The treatment is applied to hydrocarbons obtained by polymerization of olefins or mixtures of hydrocarbons containing unsaturated hydrocarbons in the presence of condensation agents containing Cl, for example, $AlCl_3$.

3183. ———. [Removing Heat of Reaction.] Austrian Patent 158,770, no date. Schmidt, J. Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 163.

See French Patent 822,636 (abs. **3200**), Indian Patents 24,210 (abs. **2905**) and 351,470 (abs. **2906**), and United States Patent 2,148,545 (abs. **505**).

3184. ———. [Removing Heat of Reaction.] German Patent Appl. R 106,704, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 300.

Heat of reaction arising in the hydrogenation of CO is removed by using a part of the higher hydrocarbons from the synthesis itself as the circulating cooling liquid.

3185. ———. Revivification of Catalyst. British Patent Appl. 17,027, filed 1937.

Yield is increased by removing more high-boiling products from the catalysts with solvents than is necessary for revivification.

3186. ———. Revivification of Catalyst. British Patent (Provisional) 33,814, filed 1936.

High-boiling hydrocarbons deposited on the catalyst are removed with H_2, steam, or solvent. The revivification is carried out in situ and at temperatures not higher than the normal reaction temperature. The use of the fraction of the product boiling 130°–140° is recommended as the solvent, the extraction being carried out at 110°. By these means the catalyst life may be extended greatly beyond the usual 1 or 2 mo.

3187. ———. Selective Extraction of Oxygen-Containing Organic Compounds from Their Mixtures with Aliphatic Hydrocarbons. British Patent 668,866, 1952. Fuel Abs., 1952, abs. 4968.

Mixtures of the primary products obtained by the hydrogenation of CO in the presence of Fe catalysts are treated with a polyhydric alcohol, an aromatic nitro-compound, an aromatic amino-compound, or an O compound of the furan group under such extraction conditions that the extractive mediums are liquid.

3188. ———. [Separating Fatty Acids.] German Patent Appl. R 113,007, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 310.

Branched fatty acids are separated from mixtures of isomeric and homologous fatty acids by incomplete saponification so that no decrease worth mentioning occurs in the molecular weight and then extracting the unsaponified fractions.

3189. ———. [Separating Mixtures of Esters and Paraffins.] German Patent Appl. R 118,283, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 319.

Mixtures of sulfuric acid esters of high-molecular hydrocarbons and paraffin hydrocarbons are first neutralized with alkali and then continuously extracted with low-boiling hydrocarbons. Addition to German Patent Appl. R 116,698 (abs. **3096**).

3190. ———. [Separating Mixtures of Sulfuric Acid Esters and Paraffin Hydrocarbons.] German Patent Appl. R 116,974, no date (*Cl. 12 o–23*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 316.

Mixtures of sulfuric acid esters of high-molecular hydrocarbons (C_{12}–C_{20}) and paraffin hydrocarbons are separated by neutralization of the esters at high temperatures with very finely pulverized alkali hydroxides and again cooled, followed by extraction with low-boiling organic solvents. Addition to German Patent Appl. R 116,698 (abs. **3096**).

3191. ———. [Separation of Fatty Acids.] German Patent Appl. R 112,882, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 310.

Isomeric fatty acid mixtures (in branched or slightly branched fractions) are separated by partial saponification followed by removal of the unsaponified, branched fractions.

3192. ———. [Sulfonation of Alcohols.] German Patent Appl. R 106,644, no date (*Cl. IV d–21 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 299.

Production of sulfonates of higher aliphatic alcohols, which were obtained by the reaction of CO and H_2 on olefins.

3193. ———. [Sulfonation Products.] German Patent Appl. R 107,966, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 302.

Production of sulfonation products from those compounds obtained by the catalytic treatment of unsaturated hydrocarbons with 4 or more C atoms with CO and H_2.

3194. ———. [Sulfonation Products of Unsaturated Hydrocarbons.] German Patent Appl. —, R 519, filed July 12, 1940. FIAT Reel K–20, frames 258–263; PB 70,211.

Oxo compounds obtained from unsaturated hydrovarbons with 4 or more C atoms by catlytic reaction with CO and H_2 are hydrogenated to alcohols and then sulfonated.

3195. ———. [Sulfuric Acid Esters From High-Molecular Olefins.] German Patent Appl. R 107,549, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 301.

H_2SO_4 esters are obtained from high-molecular olefinic hydrocarbons by treating them with a cooled mixture of H_2SO_4 and paraffin hydrocarbons.

3196. ———. [Synthesis Gas.] German Patent Appl. R 96,610, no date (*Cl. 12 i–1.01*). Auszüge deut. Patent-Anmeldungen, vol. 7, p. 309.

C deposition can be avoided in the conversion of gaseous hydrocarbons into CO and H_2 by means of CO and steam by adding to the conversion gas enough steam that the dew point of the reaction mixture lies at about 50°–65°.

3197. ———. [Synthesis Gas.] German Patent Appl. R 97,949, no date (*Cl. 12 i–1*). Auszüge deut. Patent-Anmeldungen, vol. 7, p. 310.

Water gas without special purification is partly converted with steam and catalysts. The gas mixture containing CO and H_2 in ratio 1 : 2 is freed from H_2S by thorough purification.

3198. ———. [Synthesis of Gasoline.] French Patent 819,701, Oct. 26, 1937. Chem. Zentralb., 1938, I, p. 3736; Chem. Abs., vol. 32, 1938, p. 3141.

In the catalytic transformation of mixtures of CO and H_2, the support for the catalyst used contains no soluble constituents, or the soluble constituents are extracted by solution or rendered insoluble. Suitable supports difficultly soluble in acids include $BaSO_4$, carborundum, Cr_2O_3, Al_2O_3, and silicates such as steatite and refractory earth. Mg carbonates may be used as a support insoluble in alkalies.

3199. ———. Synthesis of Hydrocarbons. British Patent 502,771, Mar. 24, 1939; appl. filed Apr. 5, 1938. Chem. Abs., vol. 33, 1939, p. 6872.

Catalytic conversion of CO and H_2 into mainly liquid or solid hydrocarbons in apparatus comprising cooling tubes and heat-conducting metal sheets disposed thereon is effected at an elevated pressure corresponding approximately to the vapor pressure of the cooling agent flowing through the tubes. The walls of the tubes need not be resistant to pressure, and cost is therefore reduced. Thus, a gas consisting of CO and H_2 in the ratio 1 : 2 is passed under 11 atm. pressure through a furnace comprising rows of cooling tubes on which sheets of heat-conducting metal, traversed by the tubes, are disposed perpendicularly at about 10 mm. intervals, a Co catalyst activated with Th filling the interspaces; H_2O at 186° and 11 atm. flows through the cooling tubes so that the reaction temperature need not exceed 187°, the exit gases are cooled to condense H_2O, benzine, and oils, and are treated with active C to remove lower boiling hydrocarbons.

See also French Patent 822,636 (abs. **3200**).

3200. ———. [Synthesis of Hydrocarbons.] French Patent 822,636, Jan. 5, 1938. Chem. Abs., vol. 32, 1938, p. 4324.

In the synthesis of hydrocarbons, such as gasoline from CO and H_2, with a solid catalyst, a tubular heat-exchange system placed in a hermetically closed casing and traversed by a cooling agent is used. The tubes are all connected to a common tank of cooling H_2O, which rises in the tubes to replace the heated H_2O which passes to a steam generator.

3201. ———. [Synthesis of Hydrocarbons.] French Patent 836,701, Jan. 25, 1939. Chem. Abs., vol. 33, 1939, p. 5410.

In the synthesis of hydrocarbons by catalytic reduction of CO, the gaseous hydrocarbons that are eliminated after condensation of the oils are adsorbed by active charcoal or other agent. At the commencement of the treatment of the adsorption agent to remove the adsorbed gases, the gas given off contains about 97% of CO_2, and this fraction is collected separately as a source of CO_2.

3202. ———. Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. Australian Patent 106,931, Apr. 20, 1939; appl. filed Apr. 9, 1938.

See British Patent 502,771 (abs. **3199**), and French Patent 836,273 (abs. **3149**).

3203. ———. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Indian Patent 25,177, Apr. 1, 1939; appl. filed Apr. 26, 1938.

See British Patent 502,771 (abs. **3199**) and French Patent 836,273 (abs. **3149**).

3204. ———. [Synthesis of Lubricating Oils.] French Patent 809,226, Feb. 26, 1937; appl. filed July 27, 1936. Chem. Zentralb., 1937, II, p. 3849; Chem. Abs., vol. 31, 1937, p. 6866.

S-free carbon monoxide + H_2 (1:2) is passed at 100° and atmospheric pressure over Co catalyst. The liquid portion from the reaction product is separated by cooling, the remainder by adsorption on active C, the part b. above 150° is cracked at 450°–550° and 8–15 atm. The fraction boiling up to 200° is separated from the cracked product and treated with 5% $AlCl_3$ for 48 hrs. at 20° with stirring. After the reaction product is washed with H_2O and treated with bleaching earth, it is distilled in vacuum. 43 parts of lubricating oil are obtained from 100 parts of cracked product.

3205. ———. [Synthesis Reaction.] French Patent 869,162, no date. Kainer, p. 209.

Synthesis reaction can be directed toward the production mainly of hydrocarbons b. $< 200°$ by using a concentrated catalyst and recycling the synthesis gas.

3206. ———. [Synthesis Resins.] German Patent Appl. R 106,772, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 300.

Resins are obtained from oxo compounds produced by the catalytic reaction of CO and H_2 on olefins.

3207. ———. [Synthetic Gasoline.] French Patent 899,045, no date. Kainer, p. 264.

Cracking of synthetic oils to antiknock gasoline is performed in presence of hydrocarbons with 4–6 C atoms, especially unbranched olefins, and of steam in presence of catalysts consisting of Al hydroxide. The partial pressure of the steam is at least 3–4 times that of all the hydrocarbons. The yield of gasoline with an octane number of 97 usable as aviation fuel after addition of tetraethyl Pb is essentially better than when the cracking is done in the presence of the olefins alone or steam alone. The unbranched gaseous olefins are likewise converted up to 50% into branched olefins.

3208. ———. [Synthetic Hydrocarbons.] French Patent 48,512, Mar. 8, 1938; appl. filed June 3, 1937. Chem. Abs., vol. 33, 1939, p. 172.

Larger amounts of paraffin are obtained in the synthetic production of hydrocarbons from CO and H_2 by extracting the paraffin from the catalysts more frequently than is necessary for the regeneration of the catalysts. A mixture of gasoline and hydrocarbons of high boiling point are used as solvent.

See also French Patent 812,883 (abs. **2920**).

3209. ———. [Synthetic Production of Hydrocarbons.] German Patent Appl. R 109,774, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 306.

Hydrocarbon mixtures with high olefin contents are produced synthetically by hydrogenation of CO. There are added to the initial synthesis gas, in addition to hydrocarbons with a 3-fold C bond, hydrocarbons with a double C bond, particularly C_2H_4. Addition to German Patent 764,165 (abs. **2987**).

3210. ———. [Temperature Regulation in the Condensation and Polymerization of Unsaturated Hydrocarbon Oils.] German Patent 684,016, Nov. 20, 1939 (*Cl. 12 o–1.01*). Schmidt, J.; Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 185; Chem. Abs., vol. 34, 1940, p. 3488.

Inert vaporizable cooling material, such as liquefied propane, butane, pentane, or mixtures of these hydrocarbon materials, is employed.

3211. ———. [Treatment of Residues From Paraffin Oxidation.] German Patent Appl. R 115,082, no date (*Cl. 12 o–11*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 313.

Distillation residues from paraffin oxidation (oxide pitch) are worked up by repeated treatment at elevated temperature with sulfuric acid solutions of alkali bichromate.

3212. ———. [Washing Agents.] German Patent Appl. —, R 530, filed Aug. 20, 1940. FIAT Reel K–20, frames 250–253; PB 70,211.

Valuable washing, wetting and dispersing agents can be produced by sulfonation of aldehydes and aldehyde mixtures formed by the action of water gas on olefinic hydrocarbon mixtures of the CO hydrogenation. The aldehydes or their mixtures must be subjected beforehand to a condensation by means of alkaline or other condensing agents accompanied by complete or partial splitting off of H_2O.

3213. ———. [Waxes From Synthetic Paraffin.] German Patent Appl. R 114,807, no date (*Cl. 12 o–11*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 313.

Valuable wax acids are obtained by the oxidation of synthetic hard paraffin with chromic acid or nitrous gases in the presence of nitrosyl H_2SO_4; neutralization with concentrated KOH; extraction with a hydrocarbon fraction boiling below the softening point of the reactants, suitably a heptane fraction; and splitting by treatment with mineral acids.

———. *See* abs. **11, 13, 184, 274, 276, 373, 454, 706, 713, 756, 757, 830, 914, 915, 916, 917, 918, 952, 1883, 1914, 2111, 2112, 2113, 2114, 2137, 2139, 2142, 2145, 2792, 2794, 2796, 2797, 2800, 2805, 2807, 2809, 2810, 2813, 2816, 2817, 2818, 2821, 2831, 2832, 2833, 2834, 2835, 3300, 3752, 3753, 3838, 3888.**

RUHROEL G. m. b. H. *See* abs. **1124a.**

RUMPF, W. *See* abs. **1996, 2672, 2678, 2679, 2689.**

RUPING, H. *See* abs. **1029.**

3214. RUPP, W. H. (Standard Oil Development Co.). Gases Rich in Hydrogen. United States Patent 2,514,340, July 4, 1950; appl. filed Dec. 22, 1948, Serial No. 66,613; 10 claims (*Cl. 260–450*). Chem. Abs., vol. 44, 1950, p. 8625.

Tail gases from hydrocarbon synthesis with CO and H_2, amounting to 5,000–10,000 cu. ft. per bbl. of liquid products, after condensation of liquid hydrocarbons,

are relatively low in H_2 and CO content and high in CO_2, N_2, and unsaturated hydrocarbons, so that this gas is unsuitable for recycling. CO_2 and hydrocarbons of 3 or more C atoms are scrubbed from 1 part of this gas (10–30%) at a pressure of 100–500 p. s. i. and at 50°–150° F. with an absorbent oil (which may be a 150°–500° F. or narrower cut from petroleum or synthesis oil). The quantity of oil used is 40–200 gal. per 1,000 cu. ft. of total tail gas scrubbed and all of it is used in each stage. The gas from this 1st step has a H_2 content of about 50%, about 2 times that of the tail gas, and can be used for many hydrogenation purposes or as a makeup gas in the hydrocarbon synthesis. The rich oil is then used to remove hydrocarbons from the larger part of the tail gas, preferably by using the same temperature and pressure conditions as in the 1st stage. The rich oil from the 2d stage is then stripped to remove CO_2 and hydrocarbons. The gas from the 2d step may be used as a fuel or, in certain cases, used as a makeup gas after removing CO_2 by conventional means.

RUSCHENBURG, E. *See* abs. **1911.**

RUSCHIN, K. *See* abs. **886.**

RUSSELL, F. R. *See* abs. **3724.**

RÜTGERSWERKE A.-G. *See* abs. **1788.**

3215. RUTHRUFF, R. F. Catalytic Conversion of Fischer Synthesis Product. United States Patent 2,467,407, Apr. 19, 1949; appl. filed Nov. 8, 1944, Serial No. 562,567; 8 claims (*Cl. 196–50*).

When the fraction of Fischer synthesis product b. 410°–650° F. is catalytically cracked with a synthetic silica-magnesia complex catalyst, gasoline of 75 octane number is produced with comparatively little gas loss. The gasoline to gas ratio is 3. Gives 19 examples of catalyst preparation. Example: To 25 l. of a solution containing a total of 800 gm. $MgSO_4 \cdot 7\ H_2O$ there were added over a period of 4 hr., with stirring, 1.93 l. of a solution containing 376 gm. Na_2SiO_3. The resulting precipitate was separated from the mother liquor by settling and decanting. It was washed by making a slurry with H_2O, settling, and decanting. This washing operation was repeated several times, and the precipitate was finally separated by filtration. The product contained 38.5% magnesia and 61.5% silica on the H_2O free basis. The catalyst may contain from a trace up to 1% zeolitic Na oxide. 15 United States patents cited.

3216. ———. Hydrocarbon Synthesis With Fluidized Catalyst. United States Patent 2,557,842, June 19, 1951; appl. filed Jan. 8, 1945, Serial No. 571,914; 3 claims (*Cl. 260–449.6*).

Synthesis reaction takes place in a reactor in which there is a single elongated bed of fluidized synthesis catalyst, which moves between 2 zones, an upper reaction zone located above an intermediate point at which the CO–H_2 mixture is introduced and a lower catalyst reactivating zone where H_2 is entered for reactivation purposes. In conducting the reaction, the synthesis gas is divided into 2 portions. The larger part is introduced into the reaction zone at the intermediate point, where as the smaller part is mixed with steam and subjected to reaction conditions such that it is converted to H_2 and CO_2. The CO_2 is removed and the residual H_2 is then entered in part to the reaction zone and in part to the reactivating zone. Deactivated catalyst that has moved down to the reactivation zone is reactivated by the H_2 stream, which also moves the reactivated catalyst back up into the reaction zone. 12 United States patents are cited.

3217. RUTLEDGE, T. F., AND SEGER, F. M. (Socony-Vacuum Oil Co., Inc.). Method of Purifying a Lubricating Oil Feedstock With Zinc Halides. United States Patent 2,622,094, Dec. 16, 1952; appl. filed Mar. 11, 1949, Serial No. 81,013; 3 claims (*Cl. 260–450*).

Synthetic lubricants of good color, high viscosity index and low C residues can be obtained by treating complex olefinic charge stock from Fischer-Tropsch reaction with Zn chloride. The treated charge is distilled to remove any reaction products that may dissolve in the excess hydrocarbon present. The distillate contains purified and concentrated olefins, particularly normal, alpha monoolefins. The fraction b. 100°–600° F., predominantly 150°–500° F. is taken overhead. Filtration of the charge before distillation will remove any occluded solid particles. The distillate is converted to lubricant by heating to 625° F. for 10 hr. 11 United States patents cited.

3218. RUTLEDGE, T. F., SEGER, F. M., SACHANEN, A. N., AND GARWOOD, W. E. (Socony-Vacuum Oil Co.). Synthetic Lubricants. United States Patent 2,569,429, Sept. 25, 1951; appl. filed Sept. 28, 1950, Serial No. 187,368; 19 claims (*Cl. 260–450*).

Complex olefin mixture obtained by a Fischer-Tropsch reaction and boiling substantially within the range 150°–600° F. is treated with a saturated solution of an alkali metal salt of a monohydroxy aromatic compound such as *m*-cresol (an aqueous solution of K *m*-cresylate is preferred). An extract layer and a raffinate layer are formed; the 2 layers are separated, and the raffinate layer is converted into the synthetic lubricant.

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3219. SABATIER, P. [Manufacture of Methane or Mixtures of Methane and Hydrogen.] French Patent 400,656, June 15, 1908. Chem. Abs., vol. 5, 1911, p. 988.

Water gas is passed over hot reduced Ni. The composition of the water gas is maintained constant by employing a constant temperature in the furnace, and the gas is subjected, after passing through a solution of Na_2CO_3, to a 2d decarbonator in a NaOH or KOH lye. Having sufficient moisture after this treatment, the gas is passed over the Ni without addition of H_2O vapor.

3220. ———. Methane or Mixtures of Methane and Hydrogen. United States Patent 956,734, May 3, 1910; appl. filed Aug. 11, 1908, serial No. 448,058. Chem. Abs., vol. 4, 1910, p. 2366.

Making CH_4 or mixtures of CH_4 and H_2 by passing steam over C in retorts maintained at a temperature of 970°, freeing the resulting gas from CO_2 by passing successively through alkali carbonate and hydroxide solutions and from S by passing over heated Cu, and finally passing the purified gases over heated Ni at 300°–450°, preferably 350°.

3221. ———. [Process of Manufacturing a Mixture of Gases Containing Hydrogen and Methane.] French Patent 355,900, July 5, 1905. Chem. Abs., vol. 1, 1907, p. 1645.

Gas containing H_2 and CO or a mixture of CO_2, CH_4, and H_2 is passed over reduced Ni, Fe or Co heated to 300°–500°. Some C deposits on the metal, and steam is passed over it while heated to 400°–500°, CO_2, CH_4 and H_2 being produced with regeneration of the metals.

See also Sabatier and Reid, Catalysis in Organic Chemistry, 1922, pp. 145–148.

3222. SABEL, F. (I. G. Farbenindustrie A. G.). [Water Gas From Coke and Gaseous Hydrocarbons.] German Patent 728,547, Oct. 29, 1942; appl. filed Oct. 4,

1940 (*Cl. 24 e–1.07*). Chem. Abs., vol. 38, 1944, p. 1096.

Hydrocarbon gas or gases containing hydrocarbons is mixed at least with 25% by volume of steam. The mixture is preheated by the hot gases from the slagging generator to approximately 700°, mixed with O_2, and blown into the generator. At least 20% of the slag from the generator is mixed with fresh coke and fed into the generator.

———. *See* abs. **3954, 3955.**

3223. SABEL, F., AND KEILIG, F. (I. G. Farbenindustrie A. G.). [Gas Mixtures.] German Patent 679,601, Aug. 9, 1939 (*Cl. 26 a–12*). Chem. Abs., vol. 33, 1939, p. 9600.

A mixture of CO and H_2 is obtained by heating gaseous or vaporized hydrocarbons with steam in chambers in which the O_2 from oxidizing heating gases is removed. Thus, CH_4, C_2H_6, propane, butane, or mixtures of these are treated with steam in a chamber of sillimanite stone or bauxite with oxidizing heating gas.

3224. SABEL, F., LAUDENKLOS, H., WENZEL, W., AND KEILEG, F. (Standard Catalytic Co.). Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,251,554, Aug. 5, 1941; appl. filed Apr. 29, 1939, Serial No. 270,920; in Germany, May 7, 1938; 5 claims (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 7156.

Hydrocarbons are produced in the presence of a conversion catalyst, such as a Co-Th oxide catalyst, from a mixture containing not more than about 2 parts of H_2 to 1 part of CO, with reactivation of the catalyst at intervals by increasing the proportion of H_2 to at least 2.5 : 1.

SACHANEN, A. N. *See* abs. **3218, 3314.**

3225. SACHSSE, E., AND BARTHOLOMÉ, E. (I. G. Farbenindustrie A. G.). [Hydrogen–Carbon Monoxide Mixtures.] German Patent 739,445, Aug. 12, 1943 (*Cl. 26 a–11*). TOM Reel 26, item 11, frames 592–595; Chem. Abs., vol. 39, 1945, p. 5440.

Gaseous hydrocarbons are preheated to approximately 1,000° or higher and are commingled with vapors of the Fe-group metals. The mixture is passed over stationary catalysts and incompletely burned with O_2 in the presence of steam.

3226. SAFFORD, R. V. (Stanolind Oil & Gas Co.). Conditioning Iron Catalyst. United States Patent 2,533,694, Dec. 12, 1950; appl. filed Feb. 1, 1947, Serial No. 725,974; 4 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 2182.

New or regenerated alkali-activated Fe catalyst can be reduced in a fluidized state by treating the catalyst with a H_2-rich gas 50°–300° F. above the synthesis temperature at 200–300 p. s. i. and a linear gas velocity of 1–3 ft. per sec. The reducing gas is passed upwardly through the catalyst in a dense, turbulent, suspended phase. The temperature is increased above 700° F., until there is a tendency for the catalyst to settle. Then the temperature is decreased until the catalyst is freely suspended. The temperature is increased or decreased to maintain the dense, turbulent, suspended phase. 5 United States patents cited.

———. *See* abs. **2760.**

3227. SATO, T. (Nippon Fats & Oils Co.). [Fatty Acid From the Oxidation of Paraffin Hydrocarbon.] Japanese Patent 4,375 (1951), Aug. 8, 1952. Chem. Abs. vol. 47, 1953, p. 2473.

In the oxidation of paraffin hydrocarbons, Mn soap is used as a main catalyst, with either SiO_2 or Al_2O_3 gel, SiO_2–Al_2O_3 gel, or other silicate gels, 1 or more, as a catalyst promoter.

SATTLER, J. *See* abs. **946.**

3228. SAUTER, E. (Braunkohle Benzin A. G.) [Alkalizing Molded Catalysts.] German Patent 738,368, July 8, 1943; appl. B 196,298, filed Nov. 28, 1941 (*Cl. 12 o–1.03*). FIAT Reel AA–90, frames 1,496–1,497; PB 70,275; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 6, chap. 175, 1949, p. 34; Chem. Abs., vol. 38, 1944, p. 4106.

Contact catalysts used for synthesizing hydrocarbons from CO and H_2 are treated in their reduced state with solutions of alkalies in an organic solvent. The solvent is anhydrous or H_2O-poor, preferably an alcohol. The saturation of the catalyst with alkalies is carried out in the contact furnace, whereupon the solvent is distilled off.

3229. ———. [Catalyst Tube for Reaction Furnaces.] German Patent 748,373, Nov. 1, 1944; appl. filed Apr. 12, 1942 (*Cl. 12 g–4.02*). FIAT Reel J–5, frames 542–544; PB 70,145.

Catalyst tube for catalytic furnaces, in which the reagents are admitted into the catalyst mass through a perforated tube, particularly in hydrocarbon synthesis from CO and H_2, is made to extend only part way, probably 1/10 to 1/2, through the catalyst bed. The flow resistance through the entrance tube is regulated by the size and gradation of the cross section of the tube or by packing with granular material of different sizes. Diagram.

3230. ———. (Braunkohle-Benzin A. G.). [Starting Contact Catalysts.] German Patent 728,766, Dec. 3, 1942; appl. B 182,388 filed Mar. 16, 1938 (*Cl. 12 o–1.03*). FIAT Reel AA–90, frames 1,460–1,461; PB 70,275; Chem. Zentralb., 1943, I, p. 1742; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 5, chap. 159, 1949, p. 44; Chem. Abs., vol. 38, 1944, p. 470.

Contact catalysts for synthesizing hydrocarbons out of CO and H_2 are treated with CO_2 to render them immune to air. The contacts are then arranged within the reaction oven. To lower the initial activity of the catalyst, the layers that first come in contact with the reacting gases are treated with the solid or liquid synthesized product within the reaction oven.

3231. SAUTER, E., AND DENKER, H. (Braunkohle-Benzin A. G.). [Regeneration of Catalysts.] German Patent 738,813, July 29, 1943 (*Cl. 12 g–4.01*). Chem. Abs., vol. 39, 1945, p. 5461.

C- and tar-poisoned catalysts are generated by treatment with hot oxidizing gases.

SAWADA, Y. *See* abs. **1876.**

SCHACHT, W. *See* abs. **1124a.**

SCHAEFER, H. *See* abs. **212.**

3232. SCHAEFER, H., AND LORENZ, W. (Braunkohle-Benzin A. G.). [Raising the Efficiency of Cobalt Catalysts.] German Patent 732,684, Feb. 11, 1943; Appl. B–182,409, filed Mar. 17, 1938 (*Cl. 12 o–1.03*). FIAT Reel AA–88, frames 3,479–3,480, PB 70,273; Chem. Zentralb., 1943, II, p. 96; Chem. Abs., vol. 38, 1944, p. 842.

The Co catalysts are treated in a mixture containing CO and H_2 in an approximate ratio of 1 : 2. First, the catalysts are treated in the gaseous mixture to which is added a considerable volume of steam. Then they are treated in the gas without steam.

3233. SCHAFFGOTSCH-BENZIN G. m. b. H. [Diesel Fuel.] German Patent 756,066, no date; appl. Sch. 124,004 (*Cl. 12 d–1.04*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 528.

Mixed diesel fuel consisting of tar oils and hydrocarbon oils from the hydrogenation of CO is purified by heating with addition of metal halogenides and finally separating the precipitated resinous and asphaltic material. ZnCl is used as the metal halogenide.

3234. ———. [Drying Oil.] German Patent Appl. Sch 126,583, no date (*Cl. 22 h–2*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 692.

Raw material for the olefins to be used are the paraffin hydrocarbons from CO hydrogenation with about 14–35 C atoms, and a Cl content of >20–30% by weight. Addition to German Patent Appl. Sch 126,218.

3235 ———. [Lubricants.] German Patent Appl. Sch 127,057, no date (*Cl. 12 o–1.01*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 352.

Lubricants are made from the hydrocarbons from the Fischer-Tropsch synthesis b. >150°. These hydrocarbons are treated above their higher chlorination stage with 25% Cl or more by utilizing bleaching earth, bauxite, silica gel, kieselguhr at higher temperatures.

3236. ———. [Lubricants and Resins.] German Patent Appl. Sch 124,495, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 346.

Lubricants and resins are obtained from C_2H_2 and olefins, particularly those olefins from the Fischer-Tropsch synthesis or from the cracked products thereof. The C_2H_2 is passed with or without pressure into the olefin mixture or with it over catalysts, which may consist of the halogenides of metals of groups 1–5 or active metals.

3237. ———. [Sulfonic Acids.] French Patent 53,488, no date. Kainer, p. 291.

Alcohols occurring in the Fischer-Tropsch synthesis process are converted into sulfonic acids by treatment with SO_2 and air in the presence of small amounts of halogens, (2 parts SO_2, 1 of air, and 0.1 of Cl).

See also French Patent 901,555.

3238. ———. [Waxes.] German Patent Appl. Sch 124,795, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 346.

Waxlike materials are obtained from the hydrocarbons b. >450° from CO hydrogenation by oxidation with O_2 under pressure in presence of substances yielding H ions as inorganic acids and their acid salts.

3239. SCHALCH, J. (Van Schaack Bros. Chemical Works). Reaction of Olefins With Carbon Monoxide. United States Patent 1,973,662, Sept. 11, 1934. Chem. Abs., vol. 28, 1934, p. 6723.

In forming O-containing derivatives, an aliphatic hydrocarbon containing a double bond, such as olefinic material from oil cracking, is caused to react at an elevated temperature, suitably about 130°, and under sufficient pressure to maintain a liquid phase, with CO, in contact with finely divided Ni.

SCHALL, A. *See* abs. **1031.**

SCHALLER, P. *See* abs. **756, 757, 817, 2145, 2818.**

3240. SCHALLER, P., FROELECKE, E., MEYER, K., ROELEN, O., AND LÜBEN, R. (Hydrocarbon Synthesis Corp.). Thorium Recovery From Precipitates Also Containing Iron. United States Patent 2,330,750, Sept. 28, 1943. Chem. Abs., vol. 38, 1944, p. 1331.

Precipitates such as those from a spent catalyst treatment, which contain Th and a substantial amount of Fe, as obtained by the action of an alkaline precipitating agent on salt solutions containing Th and Fe, are treated by a method that involves a first stage including the steps of dissolving the precipitates in an acid, such as NHO_3, adding to the solution thus obtained more alkali carbonate, such as Na_2CO_3, than required to convert all the Th in the solution into Th carbonate, thereby precipitating all of the Fe while leaving most of the Th in solution as Th alkali metal double carbonate, and separating the precipitate from the solution; at least one subsequent stage including the steps of dissolving the last-mentioned precipitate containing the Fe and some of the Th in an acid, such as HNO_3, and adding to the solution thus obtained approximately the same quantity of alkali carbonate as used in the first stage, so that all Fe present is again precipitated while substantially all the Th that was associated with the Fe remains in solution, a moderately elevated temperature, suitably about 40°–50°, being employed in the precipitation of the Fe in the first stage and a higher temperature, suitably about 75°–90°, in the precipitation of the Fe in any subsequent stage.

3241. SCHAPPEI, H. (Mannesmannröhren-Werke). [Contact Ovens for Synthesizing Hydrocarbons by the Fischer and Tropsch Process.] German Patent 720,685, May 13, 1942; appl. M 140,068, filed Dec. 4, 1937 (*Cl. 12o–1.03*). Chem. Zentralb., 1942, II, p. 1087; Chem. Abs., vol. 37, 1943, p. 2546.

Describes rectangular device that supports the catalyst and efficiently cools the catalytic reaction of the Fischer-Tropsch process. The pipes carrying the cooling liquid are connected with each other and with the walls of the vessel by a number of metal fins. The metal fins have a dual purpose—to assist in the efficient heat exchange and to strengthen the apparatus.

SCHAPPERT, H. *See* abs. **2678.**

3242. SCHARMANN, W. G. (Standard Oil Development Co.). [Catalytic Conversion of Carbon Monoxide and Hydrogen Into Hydrocarbon.] French Patent 963,693, July 18, 1950; appl. filed Dec. 1, 1947; in United States, Dec. 12, 1946. Chem. Zentralb., 1950, II, p. 2271.

Fe catalyst of usual type is passed in suspended form with the unconverted synthesis gas residues into the reaction chamber. The converters consist at least of 2 chambers connected in series. A stream of fresh CO and H_2 is injected at suitable locations into the upwardly directed gas stream. The catalyst is suspended in a flowing and turbulent medium.

3243. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,451,879, Oct. 19, 1948; appl. filed Apr. 25, 1945, Serial No. 590,219; 6 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 1171.

In the synthesis of hydrocarbons from CO and H_2 the catalyst is continuously, or at relatively short intervals, withdrawn from the reaction zone and stripped of liquid or waxy material until it is substantially dry. In this state the catalyst is better adapted to fluidization and is returned to the reactor. The cleansing is accomplished by volatilization. 4 United States patents cited.

See also British Patent 606,863 (abs. **3244**).

3244. ——— (Standard Oil Development Co.). Hydrocarbons From Carbon Monoxide. British Patent 606,863, Aug. 20, 1948. Chem. Abs., vol. 43, 1949, p. 1171.

Appears to correspond to United States Patent 2,451,879 (abs. **3243**).

3245. ——— (Standard Oil Development Co.). Production of Fuel Gases. United States Patent 2,527,154, Oct. 24, 1950; appl. filed Oct. 18, 1946, Serial No. 703,989; 9 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 335.

Process is given for producing a marketable pipe line fuel gas from Fischer-Tropsch tail gas. The tail gas is subjected to catalytic gasphase hydrogenation, temperature 650°–850° F. with Fe or Ni catalyst, 500°–750°F. with Co catalyst pressure 100–1,000 p. s. i. The heating value may be still further increased by removal of H_2O and unconverted CO_2. 6 United States patents cited.

3246. ——— (Standard Oil Development Co.). Production of Hydrogen-Containing Gas Under Pressure. United States 2,537,708, Jan. 9, 1951; appl. filed Aug.

11, 1945, Serial No. 610,342; 2 claims (*Cl. 23–212*). Chem. Abs., vol. 45, 1951, p. 2653.

Gives 2-stage process for preparation of synthesis gas. In the 1st stage steam, hydrocarbon-containing process gas and CO_2, if desired, are reformed in presence of a suitable catalyst and superatmospheric pressure. The product, containing CO, H_2, CO_2, H_2O, and some hydrocarbon gas, is passed through an oxidizing zone where part of remaining hydrocarbon gas is converted to CO and H_2 at temperatures higher than those used in the 1st stage and superatmospheric pressure equal or lower (due to pressure drop) than those in the 1st stage. The hydrocarbon-process gas feed stream may be split with 1 part forced through the reforming stage and the other forced directly to the oxidizing zone. 4 United States patents cited.

3247. ——— (Standard Oil Development Co.). Recovery of Hydrocarbons From Gaseous Streams. United States Patent 2,577,634, Dec. 4, 1951; appl. filed Oct. 23, 1948, Serial No. 56,218; 7 claims (*Cl. 260–450*).

Effluent or tail gases from a hydrocarbon synthesis plant are cooled, the condensed material removed in a high-pressure separator, and the gases contacted with a finely divided adsorption medium, such as active charcoal, employing the fluidized solids technique. The adsorbed material is then stripped from the adsorbent in a fluidized solids stripping zone, and the resulting vapors are cooled and condensed hydrocarbons separated out. The uncondensed gases are now very rich in hydrocarbons and are passed to a small oil absorption system of conventional design. The scrubbed gas from the fluid solids adsorption unit, which is at a pressure only slightly<than in the hydrocarbon synthesis reactor, is advantageously passed through expansion machines to obtain power and refrigeration. This refrigeration may be used to cool the absorbing oil and the overhead from the fluid stripper, as well as the overhead stream from the reaction chamber before it enters the scrubbing system. Thus, a large amount of liquid is condensed out of the overhead gas, and the scrubbing requirements are correspondingly less.

3248. ——— (Standard Oil Development Co.). [Synthesis of Hydrocarbons.] French Patent 925,684, Sept. 10, 1947; appl. filed Apr. 16, 1946.

See United States Patent 2,451,879 (abs. **3243**).

3249. ——— (Standard Oil Development Co.). Synthesis of Hydrocarbons. United States Patent 2,463,912, Mar. 8, 1949; appl. filed Dec. 12, 1946, Serial No. 715,798; 15 claims (*Cl. 260–449*). Chem. Abs., vol. 43, 1949, p. 4447.

Reacting gases are passed upwardly in series through 2 or more reactors with conventional means for heat control. The gas velocities are adapted to establish dilute catalyst phases at the prevaling particle size and to carry the catalyst upward through the successive reactors into the final dense phase reactor from which the catalyst is recycled. Product gas may be recycled to any or all of the various stages to control the desired flow velocities and/or partial pressures of the constituents of the gas phases. Gas velocities of 1–20 ft. per sec. at particle size 5–150 μ are suitable to establish dilute phase densities of 0.5–10 lb. per cu. ft. at space velocities of 2,000–20,000 vol. per vol. per hr. of fresh CO and H_2. The dense phase reactor is preferably operated at low gas velocities of 0.1–3 ft. per sec. to obtain bed densities of 20–150 lb. per cu. ft. at reduced space velocities of 5,000 vol. per vol. per hr. of fresh CO and H_2. The desired differences in the superficial gas velocities within the individual reactors may be established by proper choice of reactor diameters in combination with proper gas recycle ratio. The deposition of C on the Fe catalyst is thus substantially reduced. 2 United States patents cited.

3250. ——— (Standard Oil Development Co.). Synthesis of Hydrocarbons. United States Patent 2,467,861, Apr. 19, 1949; appl. filed Apr. 15, 1947, Serial No. 741,694; 17 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 5928.

Preferred catalyst mixture is made up of 75–95 parts by weight of reduced Fe pyrites ashes or sintered synthetic FeO promoted with about 0.3–1% Na_2CO_3 as the low-activity, low-selectivity, low-carbonizing component and about 5–25 parts by weight of NH_3 synthesis catalyst as the high-activity, high-selectivity strongly carbonizing component. Optimum conditions depend on the composition of the specific catalyst mixture used. Good results are obtained when fresh synthesis gas with or without recycle gas is passed upward through a fluidized mixture of catalyst particles, 50- to 400-mesh, at a gas velocity, 0.1–3 ft. per sec. to establish a bed density of 50–150 lb. per cu. ft. and a gas throughput of 5–25 cu. ft. of fresh $CO:H_2$ in ratio of 0.5–1:1 per lb. of catalyst per hr. Temperatures of 550°–850° F. and pressures 150–1,000 p. s. i. are suitable for most catalyst mixtures, particularly Fe-base catalyst mixtures. 9 United States patents cited.

3251. ——— (Standard Oil Development Co.). Synthesis of Hydrocarbons. United States Patent 2,530,998, Nov. 21, 1950; appl. filed Dec. 28, 1945, Serial No. 637,693; 3 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 1751.

Fe catalysts from Fischer-Tropsch synthesis may be reactivated by treatment with an oxidizing gas, such as air and/or O_2, followed by reduction with H_2 or synthesis tail gas. Oxidation at 900°–1,500° F. may be carried to the point at which oxidation of the metal component of the catalyst takes place. Reducing temperature is 800°–1,400° F. Enough oxidizing gas is added to the reduction zone to generate by limited combustion of reducing gas sufficient heat to maintain the reduction temperature. 1 foreign patent and 10 United States patents cited.

———. *See* abs. **146, 147, 3722.**

3252. Scharmann, W. G., and Barr, F. T. (Standard Oil Development Co.). Method of Producing Motor Fuel. United States Patent 2,436,938, Mar. 2, 1948; appl. filed Feb. 22, 1945, Serial No. 579,300; 13 claims (*Cl. 196–56*).

Gives process for producing motor fuel from solid carbonaceous materials by distillation-extraction treatment without the use of extraneous sources for the extracting oil. An acyclic hydrocarbon oil, predominantly paraffinic, having an end boiling point similar to that of the volatile constituents of the carbonaceous material is used. The synthetic hydrocarbon oil may be obtained by subjecting the distillation residue to a water-gas reaction with steam, obtaining a $CO:H_2$ synthesis-gas mixture from the water gas and synthesizing liquid hydrocarbons from this gas. Because of the absence of aromatics and naphthenes in the synthetic oil, an amount not much greater than the volatile oils in the solid material may be used. The total oil may be made up in part of oil obtained in the extraction process or from any conversion thereof. When the synthetic oils, free of pitches and tars, are used, the pitch and tar of the solid material are either retained by the distillation residue or converted into low-boiling, noncoking oils so that the process yields a substantially pitch and tar-free distillate of considerably reduced coking tendency. 14 United States patents cited.

3253. ———. (Standard Oil Development Co.). Producing Motor Fuel. Canadian Patent 449,868, July 13, 1948; appl. filed Sept. 6, 1945, Serial No. 531,246. Chem. Abs., vol. 42, 1948, p. 7006.

Liquid motor fuel is continuously produced by suspending powdered coal in an acyclic hydrocarbon oil of end b. p. 700°–800°, subjecting it to a distillation-extraction operation at temperatures of 700°–800°, separating the distillate and coked residue, reacting the latter with steam to produce water gas and recovering therefrom a synthesis gas suitable for the catalytic synthesis of liquid hydrocarbons, then separating the gasoline from the heavier oil, and utilizing the latter in producing the coal suspensions. Corresponds to United States Patent 2,436,938 (abs. **3252**).

3254. SCHARMANN, W. I. (Standard Oil Development Co.). [Synthesis of Hydrocarbons.] French Patent 919,065, Feb. 26, 1947; appl. filed Dec. 17, 1945; in United States, Dec. 20, 1944. Chem. Zentralb., 1947, II, p. 741.

MeOH and other alcohols and liquid hydrocarbons with >1 C atom in the molecule are produced by the interaction of H_2 on CO in presence of catalysts, which contain 15–25% by weight of wax and oil.

3255. SCHEELINE, H. W., ETHERINGTON, L. D., AND MORGAN, J. P. (Standard Oil Development Co.). Recovery of Fatty Acids From Dilute Aqueous Solutions. United States Patent 2,526,508, Oct. 17, 1950; appl. filed Aug. 19, 1948, Serial No. 45,036; 5 claims (*Cl. 260–540*).

This invention deals with a solvent extraction process for concentration of a lower fatty acid or a mixture of lower fatty acids present in the dilute aqueous solution. A high-boling polar organic solvent is used as extractant. Such solvents are methyl cyclohexanone, b. p. 165° C; furfural, b. p. 162° C; isophorone, b. p. 215° C; the cresols and C_5–C_{12} carboxylic acids. 1 literature ref. and 10 United States patents cited.

SCHENK, K. *See* abs. **2835.**

3256. SCHERING, A. G. [Production of Aliphatic Aldehydes.] German Patent Appl. Sch 127,363, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen,, vol. 6, p. 353.

Aliphatic aldehydes or their compounds are produced from CO, H_2, and olefins by passing the latter with up to 6 C atoms at temperatures <about 200° and under pressures of 50 atm. and upward (100–150 atm.) over catalysts, with metals of the Fe group (Co) as the main constituents.

3257. SCHEUBLE, R. (I. G. Farbenindustrie A. G.). Methanol Synthesis. United States Patent 2,083,125, June 8, 1937. Chem. Abs., vol. 31, 1937, p. 5384.

In the purification of crude MeOH produced synthetically, it is diluted with H_2O to about 10–35% by volume, and the resulting aqueous solution is washed with a solvent (such as CS_2 or benzine b. 50°–60°), which is scarcely miscible with H_2O and with the aqueous MeOH and which has a selective solvent action on the impurities present and a lower boiling point than that of MeOH.

SCHEUERMANN, A. *See* abs. **1944, 2211.**

3258. SCHEUERMANN, A., AND MARECEK, E. (I. G. Farbenindustrie A. G.). [Iron Catalyst.] German Patent Appl. —, OZ 11,450, filed Mar. 25, 1939. Bureau of Mines transl. T–433, January 1948.

Fe or Ni catalysts are produced by dropping a solution of Fe or Ni salts into an alkaline precipitating solution for a period of over 3 hr. Appears to correspond to United States Patent 2,296,405 (abs. **3259**).

3259. ——— (Alien Property Custodian). Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,296,405, Sept. 22, 1942; appl. filed Mar. 7, 1940, Serial No. 322,768; in Germany, Mar. 25, 1939; 6 claims (*Cl. 260–449*). Chem. Abs., vol. 37, 1943, p. 1246.

Use is made of a catalyst containing Fe and Ni, prepared by slowly precipitating reducible Fe and Ni compounds, as by use of a K_2CO_3 solution, from a solution of salts of the metals, at a temperature <40° and in a solution, the *p*H of which is maintained at not less than 8 during the precipitation. Ag and Al_2O_3 may be conjointly used.

3260. SCHEUERMANN, A., MEISENHEIMER, K., AND KOTZSCHMAR, A. (Standard Catalytic Co.). Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,274,639, Mar. 3, 1942; appl. filed Mar. 1, 1940, Serial No. 321,692; in Germany, Feb. 11, 1939; 8 claims (*Cl. 260–449*). Chem. Abs., vol. 36, 1942, p. 4320.

Hydrocarbons containing more than 1 C atom are produced with use of Co-containing catalysts, in the preparation of which a reducible Co compound, such as the carbonate, is gradually precipitated from a solution of a Co salt, such as $Co(NO_3)_2$, during a period at least of 3 hr., suitably by use of K_2CO_3 and in the presence of diatomaceous earth.

3261. SCHEUERMANN, E. (I. G. Farbenindustrie A. G.). [Iron Catalysts.] German Patent Appl. I 68,608, OZ 12,534, filed Jan. 8, 1941 (*Cl. IV d–12 o*). FIAT Reel 164, frames 3,197–3,202; PB 25,608; PB 75,191; Bureau of Mines Transl. T–433, Jan. 1948; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 7, ch. 184, 1950, p. 6.

Catalyst composed of Fe, with alkaline compounds, kieselguhr, and MgO in amounts of 10% or more, is used for the production of paraffin at about 5 atm. Details for making the catalyst are presented. The proportions of the constituents are about as follows, calculated on the Fe in weight %: Cu 10–50, alkali 4–20, MgO 20–60, kieselguhr 25–100. The conversion of the CO is carried out at temperatures of 220°–250° and pressures of 10–25 atm. The yield of products b. >320° is about 50–60% of the total. They are snow-white paraffins with <10% of olefins.

3262. SCHEXNAILDER, R. E. (Standard Oil Development Co.). Preparation of an Oxo Synthesis Catalyst. United States Patent 2,500,210, Mar. 14, 1950; appl. filed Oct. 31, 1946, Serial No. 707,033; 3 claims (*Cl. 252–451*). Chem. Abs., vol. 44, 1950, p. 4607.

Silica hydrogel is impregnated with salts of Co, Th, and Cu. These salts are then decomposed on the silica. Thus, a $Na_20.3.25SiO_3$ solution of 1.2 sp. gr. is mixed with H_2SO_4 of 1.12 sp. gr., and the washed hydrogel is mixed with $Co(NO_3)_2$, $Th(NO_3)_4$, and $Cu(NO_3)_2$ by milling. The plasticized mass is heated to 550° F. to decompose the nitrates to oxides. The catalyst is activated at about 850° F. and consists of Si 65, Co 32, Th 5, and Cu 1%.

3263. ——— (Standard Oil Development Co.). [Synthetic Alcohols.] French Patent 953,180, Dec. 1, 1949; appl. filed Sept. 16, 1947; in United States, Oct. 31, 1946. Chem. Zentralb., 1950, II, p. 340.

Synthetic alcohols are produced from a mixture of olefins, CO, and H_2 in presence of a catalyst consisting of SiO_2-gel impregnated with salts decomposable in the warm Co, Th, and Cu, for example, with the nitrates of the metals. A mixture of 60% SiO_2, 32 Co, 5 Th, and 1 Cu may be used. A mixture of diisobutylene, H_2, and CO is treated with this catalyst. The Oxo synthesis reaction is 1st applied for 5 hr. at 135° and 210 atm., followed by hydrogenation for 12 hr. at 177° and 175 atm. The conversion product has the following constants: Hydroxyl No. 286, carbonyl No. 9, saponification No. 7, acid No. 1.3.

See also United States Patent 2,500,913 (abs. **3264**).

3264. SCHEXNAILDER, R. E., JR. (Standard Oil Development Co.). Oxo Synthesis Followed by Hydrogena-

tion to Alcohols. United States Patent 2,500,913, Mar. 14, 1950; original appl. Oct. 31, 1946, Serial No. 707,033; divided and this appl. Jan. 23, 1948, Serial No. 4,059; 6 claims (*Cl. 260–632*).

Preparation is given for a catalyst especially good for the Oxo synthesis. Silica hydrogel is impregnated with salts of Co, Th, and Cu, and the salts are decomposed at 400°–600° F. for 1–6 hr. The composition is silica 15–70%, preferably 60%, Co 20–40%, preferably 30%, Th 3–8%, Cu below 5%, preferably 1–3%. The catalyst is activated at 800°–1,200° F. 1 literature ref., 1 foreign patent, and 4 United States patents are cited.

———. *See* abs. **1852.**

SCHILLER, G. *See* abs. **1889.**

3265. SCHILLER, G., AND WIETZEL, G. (I. G. Farbenindustrie A.-G.). Hydrogen from Hydrocarbons. United States Patent 2,056,911, Oct. 6, 1936; appl. filed Jan. 11, 1932. Chem. Abs., vol. 30, 1936, p. 8541.

Gas comprising a vaporized hydrocarbon, such as a mixture of CH_4 with higher hydrocarbons, is brought into contact at a temperature of 400°–1,000° and in the presence of steam, successively with 2 layers of different catalysts, the 1st of which contains a metal of the Fe group, such as Ni, distributed in a set hydraulic binding agent, and the 2d of which has a higher catalytic activity than the 1st and contains an Fe-group metal with an activating addition of a nonreducible oxide of a metal from groups 2–6 of the periodic system, such as oxides of Al and Mg, and is at a higher temperature than that of the 1st catalyst.

See also United States Patent 2,038,566 (abs. **1110**).

3266. SCHILLER, J. C. (Standard Oil Development Co.). Alkali Metal-Trioxalate Ferriate Catalyst and Method for Its Preparation. United States Patent 2,465,282, Mar. 22, 1949; appl. filed Dec. 26, 1946, Serial No. 717,578; 10 claims (*Cl. 252–231.5*). Chem. Abs., vol. 43, 1949, p. 4448.

Preparation of this catalyst appears to correspond to that given in United States Patent 2,465,279 (abs. **3269**).

3267. ——— (Standard Oil Development Co.). Alpha Iron-Oxide-Alkali Metal Trioxalate Ferriate Catalyst and Process of Preparation. United States Patent 2,465,280, Mar. 20, 1949; original patent appl. filed Dec. 20, 1946, Serial No. 717,578; divided and this appl. filed June 1, 1948, Serial No. 30,498; 10 claims (*Cl. 252–474*). Chem. Abs. vol. 43, 1949, p. 4448.

Preparation of this catalyst appears to correspond to that given in United States Patent 2,465,279 (abs. **3269**).

3268. ——— (Standard Oil Development Co.). [Catalysts for the Synthesis of Hydrocarbons or Oxygenated Compounds From Carbon Monoxide and Hydrogen.] French Patent 960,312, Apr. 17, 1950; appl. filed Oct. 15, 1947. Chem. Zentralb., 1951, I, p. 2109.

Catalyst materials consist of a major amount of Fe oxide in the form of either α- or γ-oxide, ferrosoferric oxide or magnetite, a smaller amount of Fe-trioxalate, and an alkali metal, such as K. The mixture in the form of small balls is 1st heated with air for about 4.5 hr. at 537° and then reduced with steam at 471°–871°. A mixture is used for the catalyst that consists of 0.2–20% alkali metal and trioxalate and 80–99.8% of Fe oxide.

3269. ——— (Standard Oil Development Co.). Ferro-Ferric Oxide-Alkali Metal Trioxalate Ferriate Catalyst and Process of Preparation. United States Patent 2,465,279, Mar. 22, 1949; original appl. filed Dec. 20, 1946, Serial No. 717,578; divided and this appl. filed June 1, 1948, Serial No. 30,497; 10 claims (*Cl. 252–474*). Chem. Abs., vol. 43, 1949, p. 4448.

Catalysts contain 80–99.8% Fe oxide and 0.2–20% alkali metal trioxalatoferrate (III) and are suitable for the synthesis of hydrocarbons from CO and H_2. For example, $Fe_2(SO_4)_3$ 25 parts and $BaC_2O_4H_2O$ 50 parts in H_2O 600 parts are warmed several hr., filtered, and the filtrate evaporated to yield $K_3Fe(C_2O_4)_3 3H_2O$ (I). A thoroughly mixed slurry of (I) 5% and Fe_3O_4 95% is dried at 100°, pulverized, pelleted, heated 4.5 hr. at 1,000° F. in an O_2-containing atm., and reduced 24 hr. at 700° F. in a current of 1,000 vol. H_2 per vol. catalyst per hr. (I) may also be prepared by mixing aqueous solutions containing $Fe_2(SO_4)_3$ 20 parts and $K_2C_2O_4$ 100 parts, respectively.

3270. ——— (Standard Oil Development Co.). Gamma-Iron Oxide-Alkali Metal Trioxalate Ferriate Catalyst and Process of Preparation. United States Patent 2,465,281, Mar. 22, 1949; original appl. filed Dec. 20, 1946, Serial No. 717,578; divided and this appl. filed June 1, 1948, Serial No. 30,449; 10 claims (*Cl. 252–474*). Chem. Abs., vol. 43, 1949, p. 4448.

Preparation of this catalyst appears to correspond to that in United States Patent 2,465,279 (abs. **3269**).

3271. ——— (Standard Oil Development Co.). Method for Synthesis of Hydrocarbons and Oxygenated Organic Compounds. United States Patent 2,525,080, Oct. 10, 1950; appl. filed Dec. 20, 1946, Serial No. 717,579; 9 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 1326.

Fe catalyst for use in Fischer-Tropsch synthesis is prepared by mixing Fe oxide and 2–5% by weight of an alkali metal trioxalate ferriate, such as $K_3Fe(C_2O_4)_3 3H_2O$ in H_2O to form a thin slurry. The mixture is dried at 100° C., pulverized, and pelleted. The pills are calcined for 4.5 hr. at 1,000° F. and reduced with H_2 at 700°–1,600° F. Reaction temperature is 450°–675° F., pressure 100–500 p. s. i., H_2: CO ratio 2 : 1–1 : 1 and feed rates 100–1,500 vol. of feed per vol. catalyst per hr. 4 literature refs., 1 foreign patent, and 3 United States patents cited.

See abs. **2064, 2344, 2345, 2346.**

3272. SCHILLER, J. C. AND EKHOLM, E. L. (Standard Oil Development Co.). [Active Iron Catalysts for the Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen.] French Patent 970,001, Dec. 28, 1950; appl. filed Aug. 4, 1948. Chem. Zentralb., 1951, I, p. 2109 .

Ferrosoferric oxide containing K_2CO_3 as promoter is 1st treated with CO at temperatures below 400°, for example, 260°–400°, at most for 30 min. After interrupting the CO stream, the temperature is reduced to 205°–371°, and a mixture of CO and H_2 is passed over the catalyst.

3273. SCHILLER, J. C., BETHEA, S. R., AND MOSESMAN, M. A. (Standard Oil Development Co.). Process for Hydrogenation of Carbon Monoxide. United States Patent 2,546,017, Mar. 20, 1951; appl. filed Dec. 11, 1948, Serial No. 64,744; 8 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 4430.

Catalytic material including a support highly resistant to disintegration is suspended in a mixture of H_2 and CO. As the suspension is carried into the reaction zone, a small quantity of catalytic material such as salts and oxides of Group VIII elements such as Fe, Co, Ni is added. It may be added as an aqueous or alcoholic solution or as a suspension of the catalytic compound or as a finely divided powder suspended in a gas. If it is added as a solution, it is pumped into the reactor at a number of points. If it is added as a solid, it is blown into the reactor at a pressure higher than that within the reaction zone. When it is added as a solution, the particles of inert support already within

the reactor become coated with the catalytic compound. When it is blown in, it is added to the support either as a mechanical mixture or as a deposit. The amount of catalytic compound added may vary 0.1–10% of the supported material circulating in the system. Usually 1–5% by weight will give good results. 9 United States patents cited.

SCHLECHT, L. *See* abs. **783, 2373, 2430, 2431.**

3274. SCHLECHT, L., AND KEUNECKE, E. (I. G. Farbenindustrie A. G.). Metal Carbonyls. United States Patent 1,996,833, Apr. 9, 1935; appl. filed Nov. 14, 1932, Serial No. 642,601; in Germany, Sept. 17, 1928; 8 claims (*Cl. 23–203*). Chem. Abs., vol. 29, 1935, p. 3472.

CO is caused to react on a sulfidic compound of at least 1 metal, such as Ni or Fe, capable of forming a metal carbonyl, under conditions of temperature and pressure that are suitable for producing the metal carbonyl from the free metal and that serve for converting the sulfide into carbonyl.

SCHLICKUM, J., & Co. *See* abs. **2077.**

3275. SCHLIEMANN'S, E., EXPORT-CERESIN-FABRIK, [High-Molecular Acids.] German Patent Appl. Sch 127,682, no date (*Cl. 12 o–11*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 354.

High-molecular acids are obtained from hard paraffin of the Fischer-Tropsch process by oxidation, first with air and then with CrO_3 or CrO_3 mixtures.

3276. ——— [Obtaining Lustrous Hard Paraffin From the Paraffins of Carbon Monoxide Hydrogenation.] French Patent 888,604, Dec. 17, 1943; appl. filed November 26, 1942. Chem. Zentralb., 1945, I, p. 1328.

Hard paraffin from CO hydrogenation is heated just above the melting point, separated from still solid particles, and cooled with formation of large-scale plates, which are extracted at room temperature with light benzine. The undissolved remaining hard paraffin can be used in shoe polish or furniture polish.

3277. ———. [Powdery Surface Protective Agent.] German Patent Appl. Sch 127,212, no date (*Cl. 22 g–10–01*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 641.

Addition of 2–10% of a mineral oil b.>250° to the hard, if desired, colored fractions, of the hard paraffin occurring in the hydrogenation of CO by the Fischer-Tropsch method.

3278. SCHMALFELDT, H. [Apparatus for Generating Water Gas, Synthetic Gas, and for Cracking Hydrocarbon Gases.] German Patent 713,913, Oct. 23, 1941; Appl. Sch. 114,556 filed Dec. 1937 (*Cl. 24 e–13.02*). Chem. Abs., vol. 38, 1944, p. 1865.

3279. SCHMALFELDT, H., AND WINTERSHALL A. G. Apparatus and Methods for Gasifying Powdered Fuel. British Patent 453,546, Sept. 14, 1936. Chem. Abs., vol. 31, 1937, p. 1590.

In the production of water gas or gas for the synthesis of benzine by the gasification of pulverulent fuel injected through inlets into a gasifier by means of circulating gases containing steam heated in regenerators and supplied to the gasifier through inlets below the aforesaid inlets, a superpressure is created between the regenerators and the gasifier by a reduction in the cross section of the gas inlets, so as to prevent or reduce the flow of gas between the reaction chamber and the heated regenerator.

3280. ———. Apparatus and Methods for Gasifying Powdered Fuel. British Patent 453,547, Sept. 14, 1936. Chem. Abs., vol. 31, 1937, p. 1590.

Circulating gas is produced in the process and heated in a heater wherein the discharged gas is utilized to predry the original fuel fed into the gas stream from a hopper, the drying gas being charged with the completely or partly gasified dust.

3281. ———. [Gas for Benzine Synthesis by the Pressureless Method.] German Patent 693,370, June 13, 1940; (*Cl. 24 e–1.05*). Chem. Abs., vol. 35, 1941, p. 4941.

Water gas required is generated chiefly from brown coal or its derivatives. Part of the gases is not converted into benzine. This residue is freed of CO_2 and part of it returned to the converter. The amount returned depends on the N_2 content, and care should be taken not to allow too much N_2 to get into the converter.

3282. ———. [Water Gas or Synthesis Gas From Lignite Dust.] Italian Patent 351,674, Mar. 31, 1937. Chem. Zentralb., 1938, I, p. 2664.

Lignite dust is gasified by means of a circulating stream of rinse gas into which the dust remaining in suspension is introduced. The reaction space per $m.^3$ of water gas or synthesis gas produced is not less than 0.03 $m.^3$ The dust must be finer than 60% of the residue on the 4,900-mesh sieve.

3283. ———. [Water Gas or Synthesis Gas From Powdered Lignite.] Italian Patent 351,291, Mar. 31, 1937. Chem. Zentralb., 1938, I, p. 2663.

Lignite is gasified in a circulating gas stream that enters the gasification zone at >1,300°. In order to obtain a low CH_4 content in the gas, the dust concentration of the added lignite per $m.^3$ of circulating gas at 0° and 760 mm. Hg is chosen at >500 gm. A part of the already gasified char dust is returned to the highly heated stream of circulating gas and to the freshly added dust as soon as the latter is degassed.

3284. SCHMIDT, F. L. [Treating Solid Paraffins.] German Patent Appl. Sch 120,816, no date (*Cl. 23 b–2.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 782.

Solid paraffins occurring in the production of hydrocarbons from CO and H_2 are first melted, then placed in an excess of cold solvent, and the flocculent high-melting paraffin separated.

3285. ———. [Treating Solid Paraffins.] German Patent Appl. Sch 122,072, no date (*Cl. IV d–23 b*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 783.

Solid paraffins from the production of hydrocarbons by the hydrogenation of CO are melted and then mixed with cold solvent. Addition to German Patent Appl. Sch 120,816 (abs. **3284**).

SCHMIDT, O. *See* abs. **3765.**

3286. SCHMIDT, O., AND SEYDEL, K. (I. G. Farbenindustrie A. G.). [Oxygenated Organic Compounds.] German Patent 492,245, June 19, 1925. Chem. Abs., vol. 24, 1930, p. 2468.

Crude mixture of oxygenated organic compounds obtained by the catalytic reduction of oxides of C is purified by catalytic hydrogenation in the vapor phase at atmospheric pressure. The crude mixture may be preliminarily distilled or otherwise purified. Gives examples.

3287. SCHMIDT, O., AND UFER, H. (I. G. Farbenindustrie A. G.). [Methanol.] German Patent 608,361, Jan. 22, 1935 (*Cl. 12 o–5.01*). Chem. Abs., vol. 29, 1935, p. 6251.

In making MeOH by the catalytic reduction of CO by means of H_2, the catalyst consists of compounds of Ti or metals of the 4th group of the periodic table, with optional addition of other activators. Thus, the catalysts may be made by soaking asbestos fiber with $Th(NO_3)_4$ and $Cu(NO_3)_2$ solution, treating KOH and heating to 200° in a current of H_2. Addition to German Patent 565,880 (abs. **3765**).

3288. ——— (I. G. Farbenindustrie A. G.). [Methyl Alcohol.] German Patent 600,677, July 28, 1934 (*Cl. 12 o–5.01*). Chem. Abs., vol. 28, 1934, p. 7267.

In preparing MeOH by the catalytic reduction of CO by H_2 under high temperature and pressure, the mixture of CO and H_2 in suitable proportions is passed over the catalyst at 200°–250°. The catalyst contains 1 or more catalytic elements, together with V or Mn or both. Cr or neighboring elements of the 6th group are not used with Mn. Thus, the catalyst may be prepared by dissolving $CdCO_3$ in HNO_3, adding $Zn(NO_3)_2$ and $Mn(NO_3)_3$ and precipitating by adding K_2CO_3. The precipitate is washed and mixed with a carrier, such as pumice, and dried to form the catalyst. The reaction temperature is 250°–300° for this catalyst.

See also French Patent 571,355 (abs. **3291**) and German Patent 565,880 (abs. **3765**).

3289. Schmidt, O. and Ufer, J. (Badische Anilin-u. Soda-Fabrik). Methanol. British Patent 229,715, Mar. 26, 1925; appl. filed Aug. 23, 1923. Ind. Eng. Chem., vol. 17, 1925, pp. 981–982; Chem. Zentralb., 1926, I, p. 2508; Chem. Abs., vol. 19, 1925, p. 3093.

Oxides of C are caused to react with H_2 under the action of heat and pressure in the presence of a catalyst comprising at least one of the "hydrogenating" elements Cu, Ag, Au, Zn, Cd, and Pb, associated with one or more of the elements Ti, V, Cr, Mn, Zr, Ce, Th, Cb, Ta, Mo, W, U, or B or their compounds. The catalysts should be free from alkali metals and from Fe, Ni, and Co. In using mixtures of Zn with oxides of Cr, Mn, Mo, Ti, or Ce, the gaseous mixture must contain a greater volume of H_2 than of C oxides, and this condition is also desirable when other catalysts are used. The catalyst may be prepared by treating a carrier, such as asbestos, with salts of the catalytic metals, such as a boiling solution of Cu nitrate and Cr acetate and then with Na_2CO_3, filtering, washing, drying, and reducing with H_2. Several other examples of catalysts are also given. In making MeOH, temperatures of 220°–260°, pressures of 35–150 atm., and gas velocities of 1–250 $m.^3$ (calculated on atmospheric pressure per hour for each kgm. of catalyst) are used.

See also British Patents 229,714 (abs. **91**) and 228,959 (abs. **90**).

3290. ——— (Badische Anilin-u. Soda-Fabrik). Methanol. Canadian Patent 251,486, July 7, 1925; appl. filed July 11, 1923. Chem. Zentralb., 1926, I, p. 2148; Chem. Abs., vol. 19, 1925, p. 3272.

CO or CO_2 mixed with a greater volume of H_2 is brought into contact with a catalyst at 200° and a pressure at least of 30 atm. The catalyst contains Cu and 1 or more of the elements Ti, V, Cr, Mn, or B but is free from Fe or Ni.

See also abs. **1602, 3289, 3291, 3292, 3294.**

3291. ——— (Badische Anilin-u. Soda-Fabrik). [Methanol.] French Patent 571,355, May 16, 1924; appl. filed Oct. 1, 1923. Chem. Zentralb., 1926, I, p. 2148.

See British Patent 229,715 (abs. **3289**).

3292. ——— (Badische Anilin-u. Soda-Fabrik). [Methanol.] Swiss Patent 107,853, Nov. 17, 1924; appl. filed Sept. 26, 1923. Chem. Zentralb., 1926, I, p. 2148.

See British Patent 229,715 (abs. **3289**).

3293. ——— (I. G. Farbenindustrie A. G.). Methanol and Other Organic Compounds From Carbon Oxides. United States Patent 1,818,165, Aug. 11, 1931; appl. filed Apr. 29, 1924. Chem. Abs., vol. 25, 1931, p. 5436.

An oxide of C, at elevated temperature and pressure, together with H_2, is passed over a catalyst containing Cu 10 parts and Zn 1 part.

3294. ——— (Badische Anilin-u. Soda-Fabrik). [Production of Methanol.] Hungarian Patent 88,531, no date.

See abs. **1602, 3289, 3290, 3291, 3292.**

3295. Schmidt, O., Seydel, K., and Feller, A. (I. G. Farbenindustrie A. G.). Purifying Catalytic Products or Other Oxygen-Containing Organic Compounds. United States Patent 1,684,640, Sept. 18, 1928; appl. filed June 9, 1926. Chem. Abs., vol. 22, 1928, p. 4536.

Mixtures of alcohols, aldehydes, ketones, and esters or other O-containing compounds of a higher order than MeOH, such as may be obtained by the catalytic hydrogenation of oxides of C, are treated in the vapor phase with H_2 at a temperature at least of 50° (but<the temperature at which decomposition of the organic compounds would begin) in the presence of a hydrogenating catalyst, such as a Ni-Cu or Ni-Al catalyst. This treatment serves to improve the color and odor of the material.

3296. Schmidt, W. (C. Otto & Co. G. m. b. H.). [Apparatus for Treating Products of Benzine Synthesis.] German Patent 709,843, July 17, 1941 (*Cl. 26 d–9.01*). Chem. Abs., vol. 37, 1943, p. 3590.

Arrangement for neutralizing the acid components resulting from the catalytic treatment of gases in the synthesis of benzine.

See also French Patent 846,605 (abs. **2559**).

3297. Schmitt, F. (Böhme Fettchemie G. m. b. H.). [Leather Dressing.] German Patent 748,312, no date. Kainer, p. 283.

Oxidation products of synthetic paraffin are used to make dressings for leather.

3298. ——— (Böhme Fettchemie G. m. b. H.). [Stuffing Leather.] German Patent 743,089, Oct. 28, 1943 (*Cl. 28 a–9*). Chem. Abs., vol. 40, 1946, p. 758.

Fatty substance, particularly train oil, for leather stuffing is replaced partly or entirely by the fraction from so-called condenser oil (the condensate from the oxidation of paraffin) obtained by the action of NH_3 on the oil and separating the upper layer. This fraction constitutes the main part of the saponifiable constituents.

See abs. **180, 2094.**

Schneider, C. *See* abs. **2357, 2358, 2359, 2360.**

3299. Schneider, W. (I. G. Farbenindustrie A. G.). [Cracking and Hydrogenation Catalysts.] German Patent 712,505, Sept. 25, 1941 (*Cl. 23 b–1.04*). Chem. Abs., vol. 38, 1944, p. 1102.

$CaSiO_3$ is intimately mixed with a solution of an Al or Mg salt at an elevated temperature. The product is filtered, washed, dried, and then reheated. This product is used as catalyst or as carrier for catalysts in cracking and hydrogenation processes.

See abs. **2336, 2337.**

3300. Schnur, F. (Ruhrchemie A. G.) [Catalytic Hydrogenation of Carbon Monoxide.] German Patent 817,596, Oct. 18, 1951; appl. filed July 30, 1949 (*Cl. 12 o*). Chem. Zentralb., 1952, I, p. 951.

Catalytic hydrogenation of CO takes place in the liquid phase with fixed or granular catalyst, the liquid medium and the synthesis gas flowing in the same direction through the catalyst packing. The liquid medium is carried off from the catalyst packing below the uppermost catalyst level and to the cooling apparatus. Diagram.

3301. Schoenmakers, P. J., and van de Putte, W. L. (N. V. de Bataafsche Petroleum Maatschappij). [Mixing and Bringing Into Reaction a Gaseous Hydrocarbon and an Oxygen-Containing Gas.] Netherlands Patent 71,499, Dec. 15, 1952. Chem. Abs., vol. 47, 1953, p. 7198.

Hydrocarbon gas and an O_2-containing gas are mixed in such proportion, that by their reaction a mixture can be formed consisting for the greater part of CO and H_2, in a mixing chamber with annular section, to which the gases are supplied in tangentially directed, alternate turbulent streams, while the mixture leaves the chamber through a narrowed annulus and forms eddies in the combustion space that maintain the flame at the end of the annulus.

3302. SCHOFL, K. (Didier-Werke A. G.). Externally Heated Vertical Oven, Operating Continuously, for Synthesizing Gas From Fuels.] German Patent 711,-719, Sept. 4, 1941; appl. D 79,688, filed Jan. 1939 (*Cl. 26 a–8.01.*). Chem. Abs., vol. 37, 1943, p. 4231.

SCHRADER, H. *See* abs. **694.**

3303. SCHRADER, H., AND HAVESTADT, L. (Goldschmidt A. G.). [Lubricant for Dry-Drawing Iron and Steel Wire.] German Patent 744,022, Jan. 7, 1944; appl. G 103,792, filed July 9, 1941 (*Cl. 23 c–1.04*). TOM Reel 36, bag 3,454, item 22, 2 pp.

Residue from the evaporation of the alkaline wash liquors, occurring in the purification of the hydrocarbon mixtures from the Fischer-Tropsch process, has been found suitable as a lubricant in wire-drawing process.

3304. SCHREYER, R. C. (E. I. Dupont de Nemours Co.). One-Step Butyl Alcohol Process. United States Patent 2,564,130, Aug. 14, 1951; appl. filed July 24, 1948, Serial No. 40,622; 7 claims (*Cl. 260–632*).

Butanols are prepared by reacting propylene, butyl formate, H_2O, CO, and H_2 under pressure 350–1,500 atm. and temperature 225°–300° in the presence of a Co-containing catalyst, such as Co acetate. The reaction product contains *n*-butanol and isobutanol, which are separated from the product mixture. The formation of additional amounts of butyl formate from propylene, CO, and H_2 is suppressed by the butyl formate introduced initially. The presence of H_2O in the initial mixture has been found necessary for high conversion and high yield of butanols.

SCHREYER, R. C. *See* abs. **256.**

SCHUBARDT, W. *See* abs. **2373, 2430, 2431.**

SCHUFF, W. *See* abs. **648.**

SCHULER, E. T. *See* abs. **3885.**

3305. SCHULZ, E. H., AND EISENSTECKEN, F. (Vereinigte Stahlwerke A. G.). Catalytic Production of Hydrogen. British Patent 314,870, July 3, 1928. Chem. Abs., vol. 24, 1930, p. 1475.

Gas mixture rich in H_2 is obtained by passing distillation gases, hydrocarbons, or gaseous mixtures containing hydrocarbons over catalysts, such as Fe, Co, Ni, Cr, Al, Mn, Si, C, Cu, V, W, and compounds or mixed crystals of these elements, in admixture with superheated steam at temperatures of 1,000° or higher. An example is given of the passage of coke-oven gas, together with superheated steam, at 1,100° over a catalyst comprising Cr and Al to obtain a product composed almost entirely of H_2, N_2, and CO. A passage of carborundum may be used for the reaction, and when so used it also has the effect of a catalyst. Gases thus produced are suitable for use in NH_3 or MeOH synthesis or in reducing metal oxides.

SCHUNCK, W. *See* abs. **1064, 1946, 1947.**

3306. SCHUNCK, W., AND TAEGER, K. (I. G. Farbenindustrie A. G.). [Removing Water From Synthetically Produced Oil.] German Patent 522,559, Apr. 13, 1931; appl. filed Nov. 2, 1923 (*Cl. 12 o–1*). FIAT Reel AA89, frames 370–371; PB 70,274; Chem. Abs., vol. 25, 1931, p. 3669.

Oily products containing MeOH, obtained by the catalytic hydrogenation of CO, are dehydrated by mixing with benzine and others and separating the hydrocarbon layer from the oil layer. Examples state that the H_2O content of the crude oil is reduced from 18% to 2.5% and from 20% to 6%.

SCHUSTER, C. *See* abs. 271.

3307. SCHUSTER, C., AND EILBRACHT, H. (Badische Anilin-u Soda-Fabrik). [Production of Oxygen-Containing Organic Compounds, Particularly Aldehydes and Ketones.] German Patent 809,807, Aug. 2, 1951; appl. filed Oct. 2, 1948 (*Cl. 12 o*). Chem. Zentralb., 1952, I, p. 599.

In the treatment of olefins with CO and H_2 at elevated temperatures and pressures and in the presence of catalysts, solutions of the organic compounds of the catalyst metals in organic solvents are treated previous to the reaction with CO or gases containing it.

SCHWARTE, G. *See* abs. **1761, 1762.**

3308. SCHWARTE, G., AND JAHRSTORFER, M. (I. G. Farbenindustrie A. G.). [Waxy or Petrolatumlike Substances.] German Patent 713,627, Oct. 16, 1941 (*Cl. 12 o–5.02*). Chem. Abs., vol. 38, 1944, p. 1658.

Residues from fatty-acid distillation are heated with catalysts promoting splitting off of CO_2. The product is then reduced.

See also German Patent 733,401 (abs. **1611**).

SCHWARZ, H. *See* abs. **276.**

3309. SCHWARZKOPF, P., AND DEUTSCHE GLÜHFADEN-FABRIK. [Methane From Hydrogen and Carbon Oxides.] German Patent 362,462, Oct. 28, 1922; appl. filed Jan. 15, 1921. Chem. Zentralb., 1923, II, p. 250.

CH_4 is obtained by passing a gas mixture of H_2 and C oxides over catalysts of Mo or W or other heavy, fusible metals of the same group. The reaction velocity is high, and the gas can be passed at a speed of 600 m. per hr. over the glowing Mo.

SCHWEITZER, C. E. *See* abs. **874.**

SCOTT, J. W., JR. *See* abs. **435.**

3310. SCOTT, N. D. (E. I. du Pont de Nemours Co.). Methyl Formate and Methanol by Hydrogenation of Carbon Monoxide. United States Patent 1,946,918, Feb. 13, 1934; appl. filed May 13, 1932, Serial No. 611,237 (*Cl. 260–106*). Chem. Abs., vol. 28, 1934, p. 2371.

CO and H_2 are absorbed in a solution of an alcohol containing a plurality of alcoholates, such as those of Na and Cd.

3311. SCOTT, N. D., AND WESTON, P. E. (Canadian Industries, Ltd.). Hydrogenation of Organic Compounds. Canadian Patent 329,226, Jan. 10, 1933. Chem. Abs., vol. 27, 1933, p. 1359.

Organic compounds are hydrogenated by agitating in contact with an aqueous solution containing I and/or HI at 150°–250° and supplying H_2 at 600–800 lb. per in.^{2} Typical reductions obtained are: (1) Aldehyde or ketone to a hydrocarbon; (2) unsaturated linkage to saturated; (3) alcohols to hydrocarbons.

3312. SCOTT, S. L. (E. I. du Pont de Nemours Co.). Hydrogenation of Carbon Monoxide-Olefin Polymers. United States Patent 2,495,292, Jan. 24, 1950. Chem. Abs., vol. 44, 1950, p. 3294.

Copolymers of CO with monoolefins are hydrogenated over Ni, Zn chromite, or Cu chromite catalysts to yield polyhydroxy-containing polymers, which are generally pliable and rubbery. Solvents used for hydrogenation include dioxane and hydrocarbons.

SEELEY, C. H. *See* abs. **208.**

3313. SEELIG, H. S., AND ZISSON, J. (Standard Oil Co. of Indiana). Catalyst for Carbon Monoxide-Hydrogen Synthesis. United States Patent 2,480,341, Aug. 30, 1949; appl. filed Dec. 26, 1947, Serial No. 794,120; 4 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 309.

$CO–H_2$ mixture is contacted under synthesis conditions at a temperature 500°–600° F., with an Fe catalyst promoted by FeF_3. The preferred amount of FeF_3 is 0.9–9 mol. %, based on the total mols. of FeF_3 and Fe_3O_4. 7 United States patents cited.

SEEMANN, W. *See* abs. **3888.**

SEGER, F. M. *See* abs. **3217, 3218.**

3314. SEGER, F. M., AND SACHANEN, A. N. (Socony-Vacuum Oil Co., Inc.). Synthetic Lubricants. United States Patent 2,500,160, Mar. 14, 1950; appl. filed Feb. 7, 1948, Serial No. 6,993; 8 claims (*Cl. 260–669*). Chem. Abs., vol. 44, 1950, p. 4669.

Oil of at least 100 viscosity index and low pour point is prepared by heating noncatalytically straight chain normal, α mono-olefin (5–12 C atoms) and styrene to 500°–700° F. from about 10 hr. to about 1 hr., respectively. The molar proportion of the olefin in the charge is greater than the styrene. Wax from Fischer-Tropsch synthesis may be used as charge. 2 United States patents cited.

SEGESSER, J. R. *See* abs. **2015.**

3315. SEGURA, M. A. (Standard Oil Development Co.). Catalyst for Reduction of Oxides of Carbon With Hydrogen. United States Patent 2,476,920, July 19, 1949; appl. filed Dec. 22, 1945, Serial No. 637,062; 14 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 8076.

Pyritic ores, such as pyrite, marcosite, and pyrrhotite, are roasted at 1,800°–2,200° F. to produce Fe_2O_3 which is then gently sintered. A typical analysis of such roasted material is: Fe_2O_3 96.2%, reducible O_2 combined with Fe 27.0%, silica 1.5%, and S<0.05. The material is ground to preferred size for fixed bed or fluid-type reactor. The catalyst is impregnated with 0.5–10% promoter, such as Na_2CO_3 K_2CO_3, KCl, K_2HPO_3, or alkali metal aluminates. Cu, Ag, Ni, and Th oxide may be used. The promoters may be mixed with the roasted ore and fused. The catalyst is reduced with H_2 at 550°–1,100° F. 1 foreign patent and 7 United States patents cited.

3316. ——— (Standard Oil Development Co.). Catalyst for the Synthesis of Hydrocarbons. United States Patent 2,540,599, Feb. 6, 1951; appl. filed Nov. 9, 1946, Serial No. 708,940; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 4024.

Catalysts that are resistant to disintegration as a result of carbonization and other causes are composed of Fe particles bonded together by an organic thermosetting resinous material. 8 United States patents cited.

3317. ——— (Standard Oil Development Co.). Catalyst Recovery in Hydrocarbon Synthesis Processes. United States Patent 2,479,420, Aug. 16, 1949; appl. filed Sept. 26, 1946, Serial No. 699,561; 10 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 9420.

If proper particle-size distribution does not exist in a fluidized bed of Fe catalyst, the heat transfer coefficient will be poor, which causes poor fluidization, large losses of catalyst fines, poor heat transfer, and large temperature gradients. In this invention the catalyst is withdrawn from the reactor, resintered, and returned to the reactor in a particle size greater than the powdered Fe removed from the reactor. The method is especially recommended for handling powdered catalyst in synthesis of hydrocarbons in a delayed settler, bottom drawoff reactor. 3 United States patents cited.

3318. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,552,347, May 8, 1951; appl. filed May 20, 1947, Serial No. 749,335; 5 claims (*Cl. 260–449.6*).

$CO–H_2$ reaction is carried out using a fluidized catalyst consisting essentially of a major proportion of Fe, about 2–8% by weight of V, and a minor proportion of an alkali metal compound selected from the group consisting of the oxides, carbonates, chlorides, and fluorides of Na and K. The presence of the V is found to have a C-inhibiting action, which allows a longer life for the catalyst. 10 United States patents, 1 foreign patent, and 1 literature ref. cited.

———. *See* abs. **2185, 2186, 3856, 3857.**

3319. SEGURA, M. A., AND MCADAMS, D. R. (Standard Oil Development Co.). Process of Reclaiming a Contaminated Iron Catalyst. United States Patent 2,483,850, Oct. 4, 1949; appl. filed July 23, 1947, Serial No. 763,106; 4 claims (*Cl. 252–417*). Chem. Abs., vol. 44, 1950, p. 2206.

Carbonaceous contaminant is burned from the Fe catalyst at 1,000°–1,150° F., until the catalyst does not contain more than 30 nor less than 5 wt. % carbonaceous material. The treated catalyst is cooled to a temperature below the b. p. of H_2O. It is mixed with enough H_2O to form a moist, loosely compacted mass. The mass is sintered at 2,000°–2,200° F. for 0.5–2.0 min. quenched, and reground. 2 United States patents cited.

3320. SEGURA, M. A., MCADAMS, D. R., AND SPICER, W. E. (Standard Oil Development Co.). Preparation of a Fluid Catalyst for Hydrocarbon Synthesis. United States Patent 2,541,671, Feb. 13, 1951; appl. filed Sept. 5, 1946, Serial No. 695,042; 4 claims (*Cl. 252–474*). Chem., Abs., vol. 45, 1951, p. 4430.

Fluidizable Fe catalysts are obtained by subjecting reduced, precipitated Fe oxides to a sintering treatment 1,300° F. in an oxidizing atmosphere and grinding the sintered material to 30–250 μ or 60–400-mesh. A reducing treatment 800°–1,500° F. may precede or follow the grinding. It is important that the sintering be after any treatment with liquids or solids, which affects the chemical composition and/or physical structure of the catalyst. Best results are obtained with Fe oxide powders, with uniform particle size less than 30 μ. Fluidizability is combined with high attrition and high activity. 10 United States patents cited.

3321. SEGUY, J. D. (Universal Oil Products Co.). Cracking Hydrocarbon Oils. United States Patent 2,039,459, May 5, 1936; appl. filed Dec. 14, 1932. Chem. Abs., vol. 30, 1936, p. 4309.

Oil, such as a residual petroleum oil, is cracked in a cracking zone, and residue separated from vapors is treated with air and steam at temperatures sufficiently high to form a gaseous mixture containing CO and H_2; this mixture is introduced into an independent zone maintained under synthesizing conditions of temperature, pressure, and catalysis in which the CO and H_2 are synthesized into condensable products (suitably in the presence of a catalyst), and the vapors from this synthesis are combined with vapors from the cracking operation; the commingled vapors are fractionated, and resultant reflux condensate is passed to the cracking zone, the fractionated vapors being finally condensed. Describes apparatus.

SEIFERT, W. *See* abs. **2109.**

3322. SELDEN CO. [Synthesis of Ammonia.] French Patent 670,396, Feb. 27, 1929. Chem. Abs., vol. 24, 1930, p. 1941.

Catalysts for the synthesis of NH_3 are composed of 2-component or multi-component zeolites or nonsiliceous base-exchanging compounds associated with catalytically active components, either chemically combined or mixed. Carriers may be used for the base-exchange compounds. Stabilizers and stabilization promoters may be used. Fe compounds are a preferred ingredient of the contact masses. The catalyst is preferably pretreated with NH_3, H_2, or N_2. Gives examples.

———. *See* abs. **1743, 1744, 1745, 1746, 1747, 1748, 1749, 1750, 1751, 1752, 1753, 1754, 1755, 1756, 1757, 1758.**

3323. SELLERS, F. B. (Texaco Development Corp.). Catalytic Synthesis of Hydrocarbons. United States Patent 2,464,532, Mar. 15, 1949; appl. filed Sept. 10, 1948, Serial No. 48,740; 10 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 4448.

This patent is related to United States Patent 2,464,501 (abs. **836**), which uses the typically high temperature thermal energy of a synthesis gas generator effluent to convert hydrocarbon synthesis products. The present invention goes a step further in that it concurrently effects removal of C deposits laid down during the conversion or cracking step in such a manner as to supplement the synthesis gas with substantial additional quantities of H_2 and CO. The thermophore is raised in the heating zone to a temperature materially above the conversion range and, after withdrawal from contact with the hot effluent gas stream, the C-coated particles are subjected to H_2O vapor and CO_2. At temperature >1,200° F. and within the maximum upper limit of temperature to which the thermophore may be raised by the high temperature generator effluent (2,000°–3,000°), the H_2O vapor and/or CO_2 decomposes and removes the C deposits with substantial formation of synthesis gas. 6 United States patents cited.

3324. ———. (Texaco Development Corp.). Process for the Hydrogenation of Coal. United States Patent 2,572,061, Oct. 23, 1951; appl. filed Sept. 16, 1948, Serial No. 49,583; 3 claims (*Cl. 196–53*).

Heavy oil produced by liquid-phase hydrogenation of coal is admixed with particles of low-ash bituminous coal in size range of 3/32 in. to 200-mesh. About 5 bbl. of oil are admixed with each ton of crushed coal to form a readily pumpable slurry. $FeSO_4$ is admixed with oil and added to the slurry at the rate of 4 lb. per ton of coal as catalyst for the hydrogenation reaction. The slurry is pumped at about 1 ft. per sec. into a heating coil at a pressure of 500 p. s. i. H_2 is supplied to the heating coil at the rate of 18,000 standard cu. ft. per ton of coal. The suspension of coal and oil is heated in the heating zone to 650°–1,200° F. The temperature at the outlet of the heating coil is about 1,000° F. and the pressure 350 p. s. i. About 95% of the oil is vaporized on passing through the heating coil. The temperature of the mixture discharged from the heating coil is reduced to about 650° F. at 350 p. s. i. The condensed liquid, powdered coal, and uncondensed vapors are admixed with an additional 18,000 standard cu. ft. of H_2 and passed at 10,000 p. s. i. pressure into a hydrogenation zone. The effluent of the hydrogenation step is separated without reduction in pressure into a gaseous fraction, predominantly H_2, which is recycled, a heavy-oil fraction or crude product of the hydrogenation step and residual solid or pitch. A portion of the heavy oil is returned to the mixing zone for admixture with fresh coal. The heavy oil product amounts to about 1,700 lb. per ton of coal fed to the process.

3325. SELYAKOV & MELIK-BOGDASSOROWA. [Methanol Synthesis.] Russian Patent 48,259, no date. SCHMIDT, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 218.

Synthesis without catalysts, but with activation of the gases by supersonic waves.

3326. SENSEL, E. E. (The Texas Co.). Method and Apparatus for Catalytic Conversion. United States Patent 2,411,760, Nov. 26, 1946; appl. filed Apr. 13, 1944, Serial No. 530,844; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 41, 1947, p. 1507.

Reaction tower has a number of separate beds of solid granular catalyst spaced apart, one above the other, with an intervening screen or porous bed of noncatalytic material in the spaces between. Liquid is collected between the noncatalytic material and the catalyst bed immediately below and discharged directly from the tower. CO and H_2 are passed continuously through the reactor. Conversion conditions are maintained in the catalyst beds. A cooling liquid is introduced in zones between catalyst beds and mixes with the gas stream as it goes through the noncatalytic bed. Then it is withdrawn with the liquid products, and the gaseous stream of reactants continues to flow toward the next catalytic bed.

———. *See* abs. **159, 160, 161, 162, 2632, 3640.**

3327. SENSEL, E. E., AND BECK, R. A. (The Texas Co.). Apparatus for Effecting Catalytic Reactions. United States Patent 2,562,993, Aug. 7, 1951; appl. filed Oct. 1, 1946, Serial No. 700,507; 2 claims (*Cl. 23–288*).

The reactor contains a central rotating helical screw for elevating the fluidized solid catalyst mass through the reaction zone. The operation is applied to the Fischer-Tropsch synthesis reaction.

3328. ——— (The Texas Co.). Catalysts for Hydrocarbon Synthesis. United States Patent 2,517,035, Aug. 1, 1950; appl. filed Mar. 28, 1947, Serial No. 737,996; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 9658.

Lanthanum oxide is a highly active promoter in catalyst for CO conversion, particularly precipitated supported Co catalyst. It may be used with or without conventional promoters such as thoria or magnesia. A suggested composition in wt. % is 32 Co : 64 calcined diatomaceous earth : 3 magnesia and 1 lanthanum oxide. Fused Fe catalyst may also be promoted with lanthanum oxide. An example shows the lanthanum promoted Co catalyst to be 23% more effective for CO conversion to liquid hydrocarbon compounds than the thoria promoted catalyst. 6 United States patents cited.

3329. ——— (The Texas Co.). Catalytic Conversion Process. United States Patent 2,414,276, Jan. 14, 1947; appl. filed Aug. 28, 1943, Serial No. 500,380; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 41, 1947, p. 2559.

CO and H_2 are contacted with a powdered hydrogenation catalyst. A stream of hydrocarbon reaction products is continuously withdrawn from the reaction zone and fractionated after the catalyst particles and the H_2O produced in the reaction have been removed. Normally gaseous naphtha is separated from the higher boiling hydrocarbon fractions. Used catalyst powder containing adsorbed hydrocarbons in the kerosine and gas-oil range and wax is withdrawn from the reaction zone and passed through a separate reactivating zone from which it is recycled all or in part to the reaction zone. The heavy hydrocarbons or fractions of predominantly paraffinic character may be passed to the reactivation zone, wherein they are converted in the presence of the used catalyst undergoing reactivation. H_2 is continuously passed through the reactivation zone. This zone is held at a temperature high enough to cause cracking of the hydrocarbons passing through the reactivation zone or deposited on the used catalyst. Normally gaseous or liquid hydrocarbons such as gasoline are produced.

3330. ———. Hydrogenation of Carbon Monoxide. United States Patent 2,437,051, Mar. 2, 1948; appl. filed Mar. 24, 1944, Serial No. 528,004; 2 claims (*Cl. 260–449.6*). Chem. Abs. vol. 42, 1948, p. 3933.

When reacting CO and H_2 in contact with a catalyst, the yield of relatively unsaturated liquid hydrocarbons can be increased by carrying out the process at a temperature range 392°–450° F. and at pressures of atmosphere and above, the catalyst consisting of a major proportion of metallic Co in admixture with ThO_2 and with an amount of Na_2CO_3 corresponding to about 0.55–2.85% of Na based on the weight of the Co and deposited on a siliceous support. The method may be varied within wide limits, including the proportions of CO and H_2, reaction pressure, space velocity, etc., since

the effect of the addition of the alkaline metal compound apparently is independent of variables other than temperature. Increasing the amount of Na_2CO_3 above the lower limit raises the optimum reaction temperature and above the range specified reduces the yields of liquid hydrocarbons at all temperatures.

3331. ——— (The Texas Co.). Method for Catalytically Synthesizing Hydrocarbons. United States Patent 2,501,695, Mar. 28, 1950; appl. filed Oct. 1, 1946, Serial No. 700,508; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 5082.

$CO–H_2$ mixture is converted directly to hydrocarbons of higher molecular weight by passage in contact with a hydrogenation catalyst at a velocity not great enough to fluidize the catalyst mass, but with the catalyst itself aerated by mechanical agitation. The powder is aerated to an apparent density less than its normal settled density. Any means of agitation may be used. 1 foreign patent and 7 United States patents cited.

3332. Sensel, E. E., and Stewart, M. M. (The Texas Co.). Supported Catalysts for the Conversion of Carbon Monoxide Containing Reactants. United States Patent 2,517,036, Aug. 1, 1950; appl. filed June 11, 1947, Serial No. 754,026; 3 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 9658.

Effective catalyst for CO conversion is one in which a metal of the Fe group is supported on a material made up of equal proportions by weight of silica-stabilized alumina and uncalcined diatomaceous earth. The alumina contains 5 wt. % silica and 0.8% alkali, expressed as % by weight of Na oxide. Conventional promoters may be used. A composition is given in weight % as 32 Co : 3 magnesia : 1 thoria : 32 uncalcined diatomaceous earth : 32 alumina, stabilized with 5 silica. 5 United States patents cited.

3333. Sensel, E. E., Millendorf, A. J., and Beck, R. A. (The Texas Co.). Method of Synthesizing Hydrocarbons and the Like. United States Patent 2,503,356, Apr. 11, 1950; appl. filed July 1, 1946, Serial No. 680,830; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 7516.

In the Fischer-Tropsch synthesis CO and H_2 at 390° F. are passed into contact with a catalyst, the major part of which is Co and the minor part Th, essentially free from alkali metal compounds. The unreacted CO and H_2 are passed at 430° F. into contact with a catalyst mainly metallic Co with minor proportion Th containing 5.5 wt. % Na carbonate based on the weight of metallic Co. The heat liberated by the reaction with the alkali metal-free Co catalyst is used to raise the temperature for the reaction with the Co–Na carbonate catalyst. 1 literature ref. and 8 United States patents cited.

3334. Sépulchre, F. [Synthesis Gas.] French Patent 915,433, Nov. 6, 1946; appl. filed May 23, 1945. Chem. Zentralb., 1949, No. 2, p. E 145.

To simplify the production of synthesis gas for catalytic gas synthesis through the gasification of fuel, the conversion of CO, and decomposition of hydrocarbons, the conversion of the undesirable gas constituents is carried out directly in the gas producer at very high temperatures of about 1,500°–1,800°. By this method the conversion of the undesirable constituents is carried out, not by H_2O vapor, but by hydrocarbons or their oxygenated compounds, since the cracking of the H_2 in these requires less energy than does the cracking of steam. To avoid cooling the gas between the injection of the hydrocarbon and the gas-collection points, a special arrangement for directly combining both steps and mutually regulating them is described.

3335. Seraphim, J., and Deschamps, P. E. L. J. [Fluid Catalytic Reactions.] French Patent 874,063, July 28, 1942. Chem. Abs., vol. 47, 1953, p. 5186.

An apparatus for carrying out fluid, gas or liquid, catalytic reactions, consisting of a series of catalyst chambers, each equipped with cooling and heating devices to maintain the optimum temperature, is applicable to the formation of CH_4 from water gas, the hydrogenation or pyrolysis of C_2H_2, the decomposition of low-molecular hydrocarbons, and the condensation of phenols to phenyl ethers.

Seydel, K. *See* abs. **3286, 3295.**

3336. Shabaker, H. A. (Houdry Process Corp.). Forming Gaseous Sulfides and Sulfidation Therewith. United States Patent 2,494,587, Jan. 17, 1950; appl. filed Dec. 4, 1947, Serial No. 789,611; 17 claims (*Cl. 252–450*). Chem. Abs., vol. 44, 1950, p. 4211.

Application of the invention is shown in the following example: Propane is burned in air to give, after drying, a composition of 1.3 mol. % H_2, 1.6 mol. % CO, 12.7 mol. % CO_2, and 84.4 mol. % N_2 by vol. The gas is heated to 1,350° F. and 5 mol. % free S is added to the gas stream in finely powdered form or as atomized liquid. The hot mixture is brought in contact with a clay such as acid-activated montmorillonite in pelleted form for 2 hr. The total volume of gas is sufficient to provide H_2S and CS_2 in 4 times the equivalent theoretically required to convert the Fe present in the clay (2% as Fe_2O_5) to Fe sulfide. The Fe sulfide is removed from the clay by leaching. 3 United States patents cited.

Shalders, E. W. *See* abs. **793, 794, 795.**

3337. Shankland, R. V., Shields, S. E., and Thiele, E. W. (Standard Oil Co. of Indiana). Refining of Synthetic Hydrocarbon Mixtures. United States Patents 2,581,560, Jan. 8, 1952; appl. filed Nov. 8, 1947, Serial No. 784,880; 5 claims (*Cl. 260–450*).

Hydrocarbon mixture obtained by synthesis from CO and H_2 consists essentially of hydrocarbons having about 5–20 C atoms per molecule with 0.5–5.0% of combined O. The mixture is characterized by a bad odor and extreme instability toward O_2 with a marked tendency toward discoloration and gum formation. The mixture can be refined and purified by treatment with a silica-alumina catalyst of gel structure, containing about 10–25 wt % of Al_2O_3, at 625°–775° F. and with a severity factor

$$\left[\frac{\text{C : O}}{(W_o \text{ per hr. per } W_c)} = 1.5\right]$$

within the range 0.02–2.0. A catalyst–oil-weight ratio of about 2 : 1 to 5 : 1 is employed, and a weight space velocity of about 2–10 lb. of oil per hr. per lb. of catalyst.

3338. Shapleigh, J. H. (Hercules Powder Co.). Gas Mixture for Ammonia Synthesis. United States Patent 2,578,490, Dec. 11, 1951. Chem. Abs., vol. 46, 1952, p. 2271.

Corrosion difficulties are encountered in handling NH_3 synthesis gas mixtures containing more than 2 p. p. m. N oxides. While it is convenient to use flue gases for the N_2 source or to prepare it by the combustion of natural gas, the combustion products may contain as much as 250 p. p. m. N_2 oxides. A gas mixture for NH_3 synthesis is prepared by mixing flue products from the combustion of hydrocarbon or natural gas with a mixture of H_2 and CO obtained by cracking hydrocarbon or natural gas over a supported Ni catalyst. An excess of steam is added to this mixture, and it is passed over a CO conversion catalyst (Cr oxide–Fe oxide, Fe oxide, or promoted Fe oxide) at 300°–400°; this substantially reduces the CO content of the gas and the N oxides to <2 p. p. m.

3339. Sharp, L. G., and Carmody, D. R. (Stanolind Oil & Gas Co.). Extraction of Organic Oxygenated Compounds From Hydrocarbon Mixtures. United States Patent 2,568,517, Sept. 18, 1951; appl. filed June 4,

1949, Serial No. 97,288; 16 claims (*Cl. 260–450*). Chem. Abs., vol. 46, 1952, p. 2566.

Oxygenated organic compounds, such as aldehydes, ketones, alcohols, etc., obtained in the Fischer-Tropsch hydrocarbon synthesis process and existing in hydrocarbon solution, are extracted therefrom by treatment 1st with a bisulfite-fatty acid soap mixture in which the latter may be derived by neutralizing the crude fatty acids obtained in the hydrocarbon synthesis process, steam distilling the resulting aqueous extract, and then further extracting the resultant fraction of oxygenated organic compounds with a 2d bisulfite-fatty acid soap solution derived from acids having 5–7 C atoms. The following operating conditions are preferred: Temperature of extraction 37°–43°, fatty acid soap concentration in the solution 20–25%, bisulfite concentration 5–7.5%, pH of extractant solution 6.8–7.3, ratio of extractant solution to crude hydrocarbon mixture 4 : 1 to 10 : 1. The method thus described will yield a product containing less than 5% of contaminant hydrocarbons.

SHARPLES CHEMICALS, INC. *See* abs. **2556. 2557.**

SHELL DEVELOPMENT CO. *See* abs. **394, 465, 472, 475, 476, 623, 650, 651, 652, 656, 772, 773, 936, 937, 1086, 1100, 1841, 1984, 2048, 2164, 2731, 2732, 3341, 3355, 3796, 3798, 3799, 3833.**

3340. SHENDEROVICH, F. S. [Molybdenum Catalyst for the Hydrogenation of Hydrocarbons.] Russian Patent 46,889, May 31, 1936. Chem. Abs., vol. 33, 1939, p. 3548.

Activated C impregnated with Mo salts is heated in H_2 atm. to 350°–450° at atm. pressure.

SHERRED, J. A. *See* abs. **3799.**

SHESHIN, A. I. *See* abs. **1795.**

SHIELDS, S. E. *See* abs. **3337.**

3341. SHIRAS, R. N. (Shell Development Co.). Addition of Carbon Monoxide-Hydrogen to Unsaturated Compounds. United States Patent 2,490,283, Dec. 6, 1949; appl. filed Feb. 3, 1947, Serial No. 726,085; 9 claims (*Cl. 260–632*). Chem. Abs., vol. 44, 1950, p. 2541.

Oxygenated compounds are produced by catalyzed addition of synthesis gas to unsaturated hydrocarbons in 2 steps. The synthesis gas for the 1st step is rich in CO. The ratio H_2 : CO is below 1.5 : 1. The synthesis gas for the 2d step is lean in CO, with ratio H_2 : CO greater than the 1.5. The reaction takes place under adsorption conditions in an adsorption zone. The liquid containing dissolved H_2 and CO is passed from the adsorption zone to the 1st synthesis step. Liquid intermediate synthesis product is produced and passed to the 2d synthesis step. Lean gas is passed from the adsorption zone to the 2d step. 2 United States patents cited.

SHOEMAKER, B. H. *See* abs. **282.**

SHOWA ELECTRO-INDUSTRIES CO. *See* abs. **3715.**

SHULTZ, J. F. *See* abs. **21.**

3342. SIEMENS-SCHUCKERTWERKE A. G. [Catalyst Chamber.] Netherlands Patent 49,169, no date. J. Schmidt., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 163.

See British Patent 483,418 (abs. **3344**).

3343. ———. [Catalytic Preparation of Gasoline.] French Patent 819,808, Oct. 27, 1937. Chem. Abs., vol. 32, 1938, p. 3141.

In the preparation of gasoline by the Fischer-Tropsch process the heat liberated in the contact furnace is removed continuously by a cooling fluid, the temperature of which is controlled by an automatic regulator, which has an indirect action and maintains, whatever the position of the regulated organ, a virtually constant temperature. Describes apparatus.

3344. ———. Temperature-Control System for Use in the Manufacture of Synthesis Products by Means of a Catalyst. British Patent 483,418, Apr. 20, 1938. Chem. Abs., vol. 32, 1938, p. 7316.

Temperature of a cooling medium is controlled by an indirect regulator so that a desired temperature is maintained irrespective of the position of the regulated member such as a valve controlling the exit of steam from a cooling jacket. A member, subject to the steam pressure in an outlet pipe from a chamber to which cooling H_2O is supplied, selectively connects with contacts adjustable in accordance with a desired temperature or pressure and permitted range of variation. The apparatus described is for producing gasoline from C or coke-oven gas and steam. The catalyst is in a chamber, and the product is mixed with water gas and passes to apparatus for further treatment.

3345. ———. [Temperature Regulation in Benzine Synthesis.] Austrian Patent 153,232, no date. Schmidt, J. Das Kohlenoxyd, Akad. Verlagsgesell. Leipzig, 1950, p. 163.

See British Patent 483,418 (abs. **3344**) and French Patent 819,808 (abs. **3343**).

3346. SILICA GEL CORP. Catalytic Reactions With Suspended Catalysts. British Patent 304,269, July 12, 1927. Chem. Abs., vol. 23, 1929, p. 4756.

In reactions such as SO_3 or NH_3 production, or hydrogenation of oils, a pulverized catalyst such as silica gel, which may carry Pt, Fe, and Cu, or Ni according to the reaction to be effected, is mixed with the gas and carried through the reaction space, then separated, revivified, and reused. The gas need not be freed from contact poisons as these will be taken up by the catalyst and removed from it in the revivification. Describes an apparatus and numerous details.

———. *See* abs. **2343.**

3347. SIMA, G. [Apparatus for High-Pressure Synthesis From Carbon Monoxide.] Japanese Patent 98,954, Jan. 9, 1933. Chem. Abs., vol. 27, 1933, p. 5591.

Inner surface of the apparatus is lined with a material that has a catalytic effect in the reaction.

See also Japanese patent 94,998 (abs. **3348**).

3348. ———. [Catalysts.] Japanese Patent 94,998, Mar. 15, 1932. Chem. Abs., vol. 27, 1933, p. 2771.

Catalysts are prepared by treating fine pieces of granules of Cu, Fe, Zn, or Ni or their alloys with a volatile acid (NHO_3 HCl) or a solution of metallic salts (nitrate or chloride of Cu) and then heating the products at <300°.

SIMON, W. *See* abs. **1804, 1805, 2673, 2680, 2681.**

3349. SIMPSON, T. P. (Socony-Vacuum Oil Co.). Method for Controlling Space Velocity. United States Patent 2,446,986, Aug. 10, 1948; appl. filed Apr. 8, 1944, Serial No. 530,221; 2 claims (*Cl. 23–288*). Chem. Abs., vol. 42, 1948, p. 8458.

Space velocity in a catalytic reaction vessel of the moving-bed type can be controlled by a mechanical arrangement that provides for varying the height of the catalyst bed by using feed pipes that can be set at various lengths. Because space velocity is an important variable and because such vessels operate most satisfactorily at relatively uniform loading, the oil throughout rate is held constant and the control means are confined to varying the volume of catalyst. For example, in a reactor of a given cross section, space velocity may be doubled by cutting the height of the bed in ½. 1 foreign patent and 5 United States patents cited.

SINCLAIR REFINING CO. *See* abs. **3736, 3737, 3738, 3739.**

SKAPERDAS, G. T. *See* abs. **2065.**

3350. SLATER, W. L. (The Texas Co.). Addition of a Desiccant to a Fluidized-Iron Reduction Process. United States Patent 2,550,609, Apr. 24, 1951; appl. filed Dec. 24, 1947, Serial No. 793,765; 4 claims (*Cl. 252–472*). Chem. Abs., vol. 45, 1951, p. 7337.

In preparing catalysts for the synthesis of hydrocarbons from CO and H_2 the Fe catalyst comprising Fe oxides is reduced by passing H_2 therethrough at about 700° F. and 200–400 p. s. i. until reduction is about 80% complete and the reaction slows considerably in the presence of H_2O vapor. Then a powdered desiccant material is added, such as the carbide of Ca or Al, which absorbs the H_2O and forms a dry solid product capable of being separated from the catalyst particles. The passage of H_2 may be then continued until reduction is substantially complete. The method is applicable to fixed bed, moving bed, or suspended type of operation.

3351. SLATINEANU, E. (Gewerkschaft Auguste). Hydrocarbon Mixtures. United States Patent 2,213,415, Sept. 3, 1940; appl. filed Dec. 15, 1936, Serial No. 115,949 (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 461.

Process of producing mixtures of hydrocarbons comprises subjecting a composition consisting of CH_4, at least 1 member of the group constituted by CO and CO_2, and at least 1 member of the group constituted by H_2 and H_2O at a temperature, that ranges approximately 225°–380° and is too low to cause a substantial proportion of the CH_4 to be cracked to a pressure of >500 atm. that suffices to cause a polarization of the CH_4 present, the molecular proportions of the components of the composition being so chosen that the molecular quantity of the CH_4 present in the starting gas mixture amounts to at least ¼ of the molecular quantity of the C oxides present and the free energy of the resulting reaction has a value that does not exceed +5,000 kcal. per mol. of the product to be produced, calculated according to the notation adopted by Lewis and Randall.

SLOSS-SHEFFIELD STEEL & IRON CO. *See* abs. **204.**

3352. SMEYKAL, K. (I. G. Farbenindustrie A. G.). Catalytic Purification of Oxygen-Containing Hydrogenation Products of Oxides of Carbon. United States Patent 2,059,495, Nov. 3, 1936; appl. filed Nov. 29, 1932. Chem. Abs., vol. 31, 1937, p. 512.

Product is treated with H_2 at 100°–300° under a pressure of 50 atm. or more in the presence of Ni and W sulfides or other catalytic sulfide of a heavy metal of group 1, 2, 4, 5, 6, or 8 of the periodic system or O compounds of such heavy metals, such as Ni thiovanadate, which on heating leave behind oxides not easily reduced under the reaction conditions or oxides or hydroxides of such heavy metals combined with acids in a complex form.

3353. ——— (I. G. Farbenindustrie A. G.). [Oxygenated Organic Compounds From Hydrogen and Oxides of Carbon.] German Patent 631,382, June 23, 1936 (*Cl. 12 o–5.01*). Chem. Abs., vol. 30, 1936, p. 6005.

Oxygenated organic compounds prepared from H_2 and oxides of C are refined by catalytic treatment with H_2 at 100°–300° and a pressure of more than 50 atm. The catalysts used are prepared by subjecting salts of metallic acids of the 5th or 6th periodic group to complete or partial reduction with H_2S. Gives examples.

See abs. **453, 1040, 1041, 1042, 3834.**

3354. SMEYKAL, K., AND ASINGER, F. (I. G. Farbenindustrie A. G.). [Breaking Emulsions of Mineral Oils.] German Patent 727,289, Sept. 24, 1942 (*Cl. 23 b–1.05*). Chem. Abs., vol. 37, 1943, p. 6871.

Sulfonic acids or sulfonates obtained by the action of a halogen and SO_2 on aliphatic hydrocarbons followed by saponification are used to break oil emulsions. The hydrocarbons, b. 190°–240°, are obtained by catalytic hydrogenation of C oxides.

3355. SMITH, A. E., AND BEECK, O. A. (Shell Development Co.). Lithium-Aluminum Catalyst. United States Patent 2,474,440, June 28, 1949. Chem. Abs., vol. 43, 1949, p. 6762.

Gives directions for producing an improved catalyst of the type in which a catalytically active promoter is supported on the surface of an adsorptive support. The improved Al_2O_3 support itself may be employed as a catalyst for reforming Fischer-Tropsch gasolines.

3356. SMITH, E. F., AND VOORHEES, V. (Standard Oil Co. of Indiana). Recovery of Organic Acids With an Amine Solution. United States Patent 2,568,095, Sept. 18, 1951; appl. filed Apr. 29, 1949, Serial No. 90288; 10 claims (*Cl. 260–450*).

Organic acids dissolved in the hydrocarbon solution obtained by hydrogenating CO in the presence of an alkali-promoted Fe catalyst are recovered by treating the solution at a temperature 10°–60° with an aqueous extractant solution containing 5–25 wt. % of a H_2O-miscible amine such as triethanolamine. The resulting extract is backwashed with a liquid hydrocarbon to remove any organic oxygenated compounds other than organic acids. The resulting purified aqueous extract is then extracted countercurrently at elevated temperature above about 75° with a H_2O-immiscible organic acid fraction, whereby the greater portion of the acids are liberated from the amine and are selectively extracted by the H_2O-immiscible organic acid. The organic extract is fractionally distilled to separate a H_2O-miscible organic acid fraction and a H_2O-immiscible organic acid fraction. The depleted amine solution is stripped of residual acids by steam distillation and recycled to step 1 of the process.

3357. SMITH, H. G., AND SYNTHETIC AMMONIA & NITRATES, LTD. Methanol Synthesis. British Patent 275,345, May 12, 1926. Chem. Abs., vol. 22, 1928, p. 2171.

Catalyst for production of MeOH, higher alcohols, and other O-containing organic compounds from C oxides and H_2 at elevated temperatures and pressures comprises a basic Zn chromate of the formula $4ZnO \cdot CrO_3$. This catalyst enables a temperature of 300°–400° to be employed for the synthesis and is not poisoned by S. Volatile compounds of Fe, Ni, and Co should be excluded.

3358. SMITH, H. G., FRANKLIN, R. G., AND IMPERIAL CHEMICAL INDUSTRIES, LTD. Catalysts for Methanol Snythesis. British Patent 316,113, Apr. 20, 1928. British Chem. Abs., 1929, B, p. 814. Chem. Abs., vol. 24, 1930, p. 1650.

Catalysts for the synthetic production of MeOH and higher alcohols are prepared by igniting a starting material comprising a decomposable carbonate of a known MeOH catalyst and then forming the product into pellets. Precipitated basic Zn carbonate or Zn and Cr carbonates may be used, and a catalyst containing Cr and Mn also is mentioned.

3359. SMITH, L. B. (Standard Oil Development Co.). [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen by the Fluidized Process.] French Patent 944,450, Apr. 5, 1949; appl. filed Apr. 1, 1947; in United States July 24, 1946. Chem. Zentralb., 1950, I, p. 1174.

Gas mixture is passed under the reaction conditions through a fluidized layer of catalyst, and finely divided clay (acid treated bentonite or the like) is mixed with the catalyst (Fe, Co) in the reaction zone to improve its flowability and to cut down the loss of solids therefrom.

See abs. **464, 3723.**

3360. SMITH, L. B., AND KREBS, R. W. (Standard Oil Development Co.). Hydrocarbon Synthesis Reaction. United States Patent 2,498,845, Feb. 28, 1950; appl. filed May 7, 1946, Serial No. 667,786; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 4656.

Spent fluidized Fe catalyst is treated with H_2 at temperatures 600°–700° F. CH_4 is introduced to purge the catalyst of the H_2 used in the regeneration. Synthesis gas is added in gradually increasing amounts together with CH_2 under synthesizing conditions until the synthesis gas represents 100% of the fresh feed. In this way temperature is controlled during the start up of the reaction cycle and does not vary to any appreciable extent. 2 foreign and 3 United States patents cited.

SMITH, P. V. *See* abs. **315, 2339, 2407, 2408, 2409, 2410, 2412.**

3361. SMITH, W. M. (Standard Oil Development Co.). Catalytic Reaction of Olefins With Carbon Monoxide and Hydrogen. United States Patent 2,557,701, June 19, 1951; appl. filed Mar. 19, 1948, Serial No. 15,802; 4 claims (*Cl. 260–604*).

Oxo process, whereby olefinic compounds, CO, and H_2 are reacted to produce oxgenated organic compounds, is improved by controlling the temperature level in the adiabatic reaction zone without the disadvantages inherent in recirculating large volumes of cooling gases and by maintaining a high concentration of Co carbonyl catalyst throughout the carbonylation reaction zone. The reactants are contacted under carbonylation conditions, comprising temperatures 250°–375° F. and pressures 2,500–3,500 p. s. i., with a Co carbonylation catalyst in the form of an oil-soluble soap such as Co naphthenate. Liquid reaction products comprising aldehydes and containing Co carbonyl are withdrawn from the reaction zone and passed through a cooling zone into a separation zone maintained under the same pressure as the reaction zone. The liquid products are separated from uncondensed gases, and a portion of the cooled liquid products containing Co carbonyl is recycled to the reaction zone. The presence of dissolved Co carbonyl in the fresh feed at the reactor inlet is a distinct advantage.

3362. ———. (Standard Oil Development Co.). Hydrogenation Process. United States Patent 2,574,355, Nov. 6, 1951; appl. filed Aug. 13, 1948, Serial No. 44,219; 3 claims (*Cl. 260–450*).

Oxygenated compounds contained in a hydrocarbon synthesis product formed by the hydrogenation of an oxide of C are reduced, without substantial hydrogenation of olefins and aromatics contained therein, by treating the synthesis product with H_2 at elevated temperatures and pressures (700° F. and 100 p. s. i.) in the presence of a catalyst consisting essentially of 1 of the class consisting of Co and Ni chemically combined with a metal oxide of group VI on active Al_2O_3. A suitable catalyst comprises a mixture of Co molybdate ($CoMoO_4$) and Mo trioxide on Al_2O_3. Gives directions for preparing the catalyst. The object of the process is to improve the quality of the synthetic oil and thereby the gasoline made therefrom.

3363. ———. (Standard Oil Development Co.). Production of Synthesis Gas. United States Patent 2,522,468, Sept. 12, 1950; appl. filed Dec. 28, 1945, Serial No. 637,614; 3 claims (*Cl 252–373*). Chem. Abs., vol. 44, 1950, p. 11,068.

Synthesis gas $H_2 : CO = 1 : 1$ can be made by reforming CH_4 with steam in presence of CO_2, using a Ni catalyst, superatmospheric pressure, and 1,500° F. temperature.

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
$$H_2 + CO_2 \rightleftharpoons CO + H_2O$$
$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$

1 literature ref. and 4 United States patents cited.

3364. SMITH, W. M., LUENING, W. D., AND LANE, S. C. (Standard Oil Development Co.). Synthesis of Oxygenated Organic Compounds. United States Patent 2,596,920, May 13, 1952; appl. filed July 30, 1948, Serial No. 41,668; 20 claims (*Cl. 260–604*). Chem. Abs., vol. 47, 1953, p. 1728.

In a continuous carbonylation process, oxygenated organic compounds are formed in the presence of Co catalyst and Co carbonyls become dissolved in these reaction products. These dissolved Co compounds are recovered by passing the reaction products containing them to a decomposition zone maintained under conditions of temperature and pressure just sufficient to prevent decomposition of the liquid reaction products but enough to maintain a substantially rapid rate of Co carbonyl decomposition and its separation as metallic Co. Temperatures of 200°–400° F. and pressures of 50–150 p. s. i. g. are generally suitable for an oxygenated product having an average of 6 or more C atoms per molecule. A liquid product is obtained comprising aldehydes substantially free of dissolved catalyst.

3365. SNOEK, J. L., WENT, J. J., AND HAAYMAN, P. W. (Hartford National Bank & Trust Co.). Magnetic Cores. United States Patent 2,636,860, Apr. 28, 1953. Chem. Abs., vol. 47, 1953, p. 7138.

By mixed-crystal formation of ferrites with positive and negative magnetostriction it is possible to obtain a ferrite with a Curie temperature >50° and ratio of magnetization intensity at saturation to magnetostriction constant $>2\times10^{10}$. These materials are suitable for use in magnetic cores for low values of magnetic induction, as in radio, telegraphy, and telephony. For example, mixtures of MnO_2, ZnO_2, and Fe_2O_3 in molecular ratios of 21–25 : 25 : 50–54 are ground for 3 hr. in a ball mill. From the mixture, with H_2O as a plasticization agent, a rod is formed and sintered in pure N_2 for 2 hr. at 1,300°, then cooled in N_2 to room temperature in 0.5 hr. Likewise mixtures of NiO, ZnO and Fe_2O_3 in molecular ratios 12.6–15 : 29.4–35 : 50–58 were formed into ferrite rods. Magnetic properties were determined.

SOCIETÀ ANON. CARBURANTI ITALIANI SINTETICI. *See* abs. **2706.**

3366. SOCIETÁ ANON, FORNI ED IMPIANTI INDUSTRIALI. Gas Suitable for Chemical Synthesis. British Patent 633,718, Dec. 19, 1949; appl. filed Feb. 18, 1947. Gas World, vol. 133, 1951, pp. 240–241; Chem. Abs., vol. 44, 1950, p. 4229.

CO–H_2 mixture suitable for chemical synthesis is secured by gasification of high-volatile coal in 1 producer, using a mixture of O_2 and steam, and by cracking the hydrocarbons in this gas and reducing the CO_2 to CO by passing the gas from the 1st producer down through the fuel bed in a 2d producer. The cracked gases are cooled by the ash bed in the 2d producer. The bed then serves for superheating steam and O_2 when the flow through the producers is reversed. Coal is fed to the top of the producer that is on the gas-making cycle.

3367. SOCIETÀ ANON. PRODOTTI ITALIANI SINTETICI. Methanol From Carbon Monoxide and Hydrogen. British Patent 493,531, no date. Chem. Zentralb., 1939, I, p. 5127.

See Belgian Patent 418,643 (abs. **3370**), and French Patent 814,434 (abs. **3369**).

3368. ———. [Methanol Synthesis.] Italian Patent 345,674, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 218.

See French Patent 814,434 (abs. **3369**).

3369. ———. [Methyl Alcohol.] French Patent 814,434, June 23, 1937. Chem. Abs., vol. 32, 1938, p. 957.

H_2SO_4 is caused to act on marble, the CO_2 is reduced to CO in the presence of wood charcoal and Fe turnings, and the CO is hydrogenated under pressure and

at high temperature to form MeOH. An example of a fuel contains MeOH, 94.53%; synthetic camphor, 0.01%; acetone, 0.165%; Et_2O, 1%; turpentine oil, 0.01%; and C_6H_6 4.285%.

3370. ———. [Methyl Alcohol From Carbon Monoxide and Hydrogen.] Belgian Patent 418,643, Apr. 30, 1937; appl. filed Nov. 28, 1936. Chem. Zentralb. 1937, II p. 3528.

See French Patent 814,434 (abs. **3369**).

3371. SOCIETÀ ITALIANA RICERCHE INDUSTRIALI. [Carbon Monoxide and Hydrogen Mixture.] Swiss Patent 162,458, Sept. 1, 1933. Chem. Abs., vol. 28, 1934, p. 588.

Mixture of CO and H_2 free from O_2 is produced by leading H_2 containing O_2 as an impurity into a solid fuel distillation retort at a zone where the temperature is high enough to ensure that the O_2 reacts with the fuel. The CO–H_2 mixture is suitable for the synthesis of MeOH by passage over suitable catalysts.

3372. ———. [Catalyst.] Swiss Patent 162,460, Sept. 1, 1933. Chem. Abs., vol. 28, 1934, p. 590.

Catalyst suitable for use in the synthesis of NH_3 is prepared by fusing natural or synthetic magnetite and reducing so that the product does not contain an excess of FeO over Fe_2O_3.

3373. ———. [Gas Producer.] French Patent 680,849, Aug. 27, 1929. Chem. Abs., vol. 24, 1930, p. 3932.

Describes a gas producer for the production of mixtures of CO and H_2 by gasification of solid fuel with O_2 or O_2 and steam or O_2 and CO_2.

See also British Patent 306,959.

3374. ———. [Methyl Alcohol.] Italian Patent 272,064, Aug. 31, 1928. Chem. Zentralb., 1935, I, p. 3476.

Catalytic reduction of CO by H_2 is performed in presence of 10–20 vol. % of CH_4.

3375. ———. [Mixtures of Carbon Monoxide and Hydrogen.] German Patent 612,046, Apr. 12, 1935 (*Cl. 12i–1*). Chem. Abs., vol. 29, 1935, p. 4924.

See Swiss Patent 162,458 (abs. **3371**).

3376. ———. [Oxygen-Free Mixture of Carbon Monoxide and Hydrogen.] French Patent 755,493, Nov. 25, 1933; appl. filed May 11, 1933. Chem. Zentralb., 1934, I, p. 2072; Chem. Abs., vol. 28, 1934, p. 1481.

The O_2 content of a gas mixture containing hydrocarbon gases and H_2O_2 is caused to disappear by burning with a part of the gas mixture. The end gas is suitable for the catalytic synthesis of MeOH.

See also Swiss Patent 162,458 (abs. **3371**).

3377. ———. [Synthesis of Organic Compounds.] French Patent 660,108, Sept. 8, 1928. Chem. Abs., vol. 24, 1930, p. 127.

In the production of organic liquids by catalysts at high temperature and pressure, such as in the production of MeOH from H_2 and CO, the heat of the reaction mixture coming from the catalysis chamber is used for the distillation and rectification of the crude liquid product obtained by the process.

3378. ———. [Synthetic Higher Alcohols.] French Patent 801,771, Aug. 17, 1936. Chem. Abs., vol. 31, 1937, p. 1426.

Mixture of gases and vapors from the catalytic apparatus is subjected to a fractional condensation by passing it through 2 or more condensers, each of which is provided with a separator collector for the condensed liquid.

3379. ———. [Utilization of the Heat in Catalytic Reactions.] Italian Patent 268,367, Apr. 14, 1928. Chem. Zentralb., 1935, II, p. 122.

Heat in the reaction gases from the synthesis of MeOH from CO and H_2 is utilized for the distillation and fractionation of the products obtained in the catalytic process.

3380. SOCIÉTÉ ANON. AMMONIAQUE SYNTHÉTIQUE ET DÉRIVÉS. [Catalyst Favoring the Reaction of Water Gas.] Belgian Patent 446,167, July 31, 1942. Chem. Abs., vol. 39, 1945, p. 799.

Pieces of wood are impregnated with a solution of a Mg salt and then with ammoniacal water. The impregnated wood is carbonized, and the product is impregnated with a solution of a K salt.

SOCIÉTÉ ANON. DE GAS COMPRIMÉ. *See* abs. **626.**

3381. SOCIÉTÉ ANON. DES CHARBONS ACTIFS ET PROCÉDÉS E. URBAIN. [Methanol.] French Patent 641,195, Mar. 2, 1927. Chem. Abs., vol. 23, 1929, p. 1141.

Mixture of CO and H_2 for the production of MeOH is obtained by passing over known catalysts a mixture of a hydrocarbon such as CH_4, CO_2, and steam at temperatures 600°–1,200°.

SOCIÉTÉ ANON. LE PÉTROLE SYNTHÉTIQUE. *See* abs. **22, 23, 24.**

3382. SOCIÉTÉ CHIMIQUE DE LA GRANDE PAROISSE, AZOTE ET PRODUITS CHIMIQUES. [Alcohols and Ammonia.] French Patent 649,711, July 15, 1927. Chem. Abs., vol. 23, 1929, p. 2989.

A mixture of CO, N_2, and H_2 is passed to a plant for producing alcohol (for example, MeOH), then to an NH_3 plant, and the residual gases are returned to the stream of gas to the alcoholic plant.

3383. ———. [Aliphatic Oxygen Componds.] French Patent 705,590, Jan. 28, 1930. Chem. Abs., vol. 25, 1931, p. 5175.

Aliphatic O compounds are prepared by the action of CO and H_2O in the presence of catalysts composed of a mixture of rare earths associated with at least 1 element of each of the 2 following series: (a) K, Na, Li, Be, Mg, Ca, Ba, Sr, (b) Cu, Mg, Zn, Cd, Pb, V, Cr, Mo, Sb, Bi, B, Al, W, Si, Ti, Zr, Th. Gives an example of the preparation of a mixture of lower fatty acids and their esters.

3384. ———. Artificial Zeolitic Catalysts. Britsh Patent 343,807, Feb. 7, 1930. Chem. Abs., vol. 25, 1931, p. 4672.

Catalysts suitable for the production of O-containing aliphatic compounds from CO and H_2O or steam are prepared by the union of salts of strongly alkaline nature with metallates (salts of amphoteric metals) with or without addition of neutral or substantially neutral salts. The catalysts contain at least 1 element of the 2 groups: (a) K, Na, Li, V, Cr, Mo, Mn, Fe, Co, Ni, Ag, Cu, Zn, Cd, Pb, Sb, Bi, Ca, Sr, Ba; and (b) Be, Mg, Al, Ce, rare earths, B, Si, Ti, Zr, Th, U and W; and the precipitation of the zeolite is carried out in a medium of pH between 8 and 6.8. Describes various details and examples of procedure.

3385. ———. Catalytic Production of Alcohols, Aldehydes, Ketones, Acids, Ethers, and Esters. British Patent 296,049, Aug. 24, 1927. Chem. Abs., vol. 23, 1929, p. 2186.

Various O-containing organic compounds are obtained by the reaction of CO (or a suitable gas containing CO) on H_2O in the presence of a mixed catalyst containing at least 1 element of the series K, Na, Mg, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Hg, Pb, As, Sb, Bi, in association with at least 1 element of the series Be, Mg, Al, Ce, Si, Ti, Zr, Th, U, Li, Ca, Sr, Ba, and W. Temperatures up to 550° and pressures up to 600 atm. may be used, and the walls of the reaction vessels may be made of chrome, silicon or Mn steels or of Cu or Ag. Gives examples of the production of: (1) Alcohols with a catalyst formed of Mn carbonate, MgO and Al_2O_3; (2) formic acid with a catalyst of Th oxide and

K_2CO_3; (3) ethers with a catalyst of Cu, Th, and Bi compounds precipitated on pumice; (4) alcohols with a catalyst formed of Mn oxide, MgO, and Al_2O_3; (5) alcohols and other organic compounds with use of a catalyst comprising a precipitate obtained by treating a solution formed from HCl, antimonious oxide, and Th nitrate with $(NH_4)_2CO_3$; (6) alcohols with a catalyst formed by treating a solution of Pb nitrate and Sr nitrate with $(NH_4)_2CO_3$; and (7) production of lower aliphatic alcohols and acids with a catalyst containing Th and Co and prepared similarly to the catalyst of "6."

See also French Patent 651,167 (abs. **3392**).

3386. ———. [Catalytic Reactions.] French Patent 644,266, Apr. 30, 1927. Chem. Abs., vol. 23, 1929, p. 1701.

In exothermic catalytic reactions in which the gases are heated indirectly before reaction by the catalyst, the gases are made to pass along 2 or more distinct heating surfaces, and the heat transmitted may be be controlled by varying the path of the gases.

3387. ———. [Catalytic Reactions.] French Patent 652,574, Apr. 11, 1928. Chem. Abs., vol. 23, 1929, p. 3523.

In exothermic catalytic reactions carried out under pressure, the fresh gas is caused to arrive between the wall supporting the pressure and an inner tube containing the catalytic material, to protect the wall against the temperature. The gas is mixed with the residual gas from the reaction chamber from which the product of the reaction has been removed, and the mixture enters a heat exchanger before passing to the reaction chamber.

See also French Patent 644,266 (abs. **3386**).

3388. ———. [Formaldehyde.] French Patent 630,483, 1926.

See German Patent 557,650 (abs. **3389**).

3389. ———. [Formaldehyde.] German Patent 557,650, May 28, 1927. Chem. Abs., vol. 27, 1933, p. 515.

Co virtually free from H_2, is passed over a catalyst with H_2O or steam at temperatures >200° and preferably at 320°–360°, to yield CH_2O. The catalyst consists of oxides or salts of Mg, Zn, Mn, Sn, or Sb or other metals of the same groups. Apparatus is indicated.

3390. ———. [Methanol and Ammonia.] French Patent 35,096, Feb. 22, 1928. Chem. Abs., vol. 24, 1930, p. 1942.

Mixtures of water gas and gases partly or wholly burnt or gases of like composition and containing hydrocarbons previously transformed into CO, CO_2, H_2O, and H_2 are used for the production of MeOH and NH_3. Addition to French Patent 649,711 (abs. **3382**).

3391. ———. [Methanol Synthesis.] Italian Patent 278,927, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 218.

Combining MeOH synthesis with NH_3 synthesis.

3392. ———. [Organic Oxygen Compounds.] French Patent 651,167, Aug. 24, 1927. Chem. Abs., vol. 23, 1929, p. 3231.

Alcohols, aldehydes, ketones, acids, esters, and other organic O compounds are produced by the action of CO, or gases containing it, on H_2O in the liquid or gaseous state in the presence of mixed catalysts containing at least 1 of the series: K, Na, Mg, V, Cr, Mo, Fe, Co, Ni, Cu, Ag, Zn, Cd, Hg, As, Sb, Bi, associated with at least 1 of the series: Be, Mg, Al, Ce, Si, Ti, Zr, Th, U, Li, Ca, Sr, Ba, W. In examples, mixed carbonates of Mn, Mg, and Al are reduced at 300° with CO, and a mixture of CO and H_2O is passed through at 450°, the excess of H_2O contains 5–6% of various alcohols. A solution of ThO_2 and K_2CO_3 in HCOOH is dried on pumic stone, a current of CO at 250° and 500 atm. is passed over it, and finally a mixture of CO and H_2O, a solution of HCOOH is obtained. Soluble and insoluble esters are obtained when $CuCO_3$, ThO_2, and Bi_2O_3 are used, a solution of alcohol when MnO_2, Al, and Mg or $Pb(NO_3)_2$ and $Sr(NO_3)_2$ are used; alcohols and other compounds when Sb_2O_3 and $Th(NO_3)_4$ are used; fatty acids and alcohols when $Th(NO_3)_4$ and $Co(NO_3)_2$ are used.

3393. ———. [Organic Oxygen Compounds.] French Patent 705,683, Feb. 7, 1930. Chem. Abs., vol. 26, 1932, p. 151.

Aliphatic compounds containing O are made by the action of CO on H_2O or steam in the presence of catalysts composed of artificial zeolites prepared by the union of salts of a strongly alkaline nature with metallates (salts of amphoteric metals), with or without the addition of neutral or practically neutral salts. The catalysts contain at least 1 element from each of the series: (1) K, Na, Li, V, Cr, Mo, Mn, Fe, Co, Ni, Ag, Cu, Zn, Cd, Pb, Sb, Bi, Ca, Sr, Ba; (2) Be, Mg, Al, Ce, rare earths, B, Si, Ti, Zr, Th, U, W. The catalysts are prepared in a medium with a pH value between 8 and 6.8 and when they contain reducible metallates, may be reduced in 2 stages, first at about 200° with dilute reducing gas and then at 300°–500° under pressure with concentrated reducing gas. Gives examples.

3394. ———. [Synthesis of Formaldehyde.] Belgian Patent 342,025, no date. Das Kohlenoxyd, by J. Schmidt. Akad. Verlagsgesell., Leipzig, 1950, p. 230.

From CO and steam at 200°–600° and raised pressure in presence of Mg, Mn, Sn, Sb, or their oxides or salts.

See French Patent 630,483 (abs. **3388**).

3395. ———. [Zinc Catalyst.] French Patent 924,109, no date. Schmidt, J., das Kohlenoxyd. Akad. Verlagsgesell., Leipzig, 1950, p. 209.

Catalyst of Cr_2O_3–ZnO with 1–20% Zn or Pb and 0.1–0.2% coconut charcoal.

3396. Société d'électrochimie, d'électrométallurgie et des aciéries électriques d'usine. [Catalyst Tube.] French Patent 643,923, Apr. 16, 1927. Chem. Abs., vol. 23, 1929, p. 1534.

Catalyst tube for synthesis under high pressure comprises 2 chambers inside a hollow cylinder that are capable of being traversed successively by the gas, both serving as catalyst chambers or 1 as a preliminary purification chamber. The chambers may be concentric and may be separated by a heating element such as an electric spiral.

3397. ———. [Methanol.] French Patent 764,836, May 29, 1934. Chem. Abs., vol. 28, 1934, p. 5834.

MeOH is purified by treating it with Cl, Br, or I, which forms esters with the impurities, and these are separated by distillation.

Société de produits chimiques et engrais d'Auby. *See* abs. **2697**, **2698**.

3398. Société des mines de Dourges. Ammonia and Methanol From Coke-Oven or City Gas. British Patent 366,268, Jan. 21, 1931. British Chem. Abs., 1932, B, p. 329; Chem. Abs., vol. 27, 1933, p. 591.

See French Patent 706,506 (abs. **3399**).

3399. ———. [Methanol Synthesis.] French Patent 706,506, Feb. 28, 1930. Chem. Abs., vol. 26, 1932, p. 266.

Mixture of CO, H_2, and N_2 produced in French Patent 706,504 (abs. **3400**) is converted into MeOH and NH_3. The CO and part of the H_2 are converted into MeOH by synthesis, the MeOH is removed, and the remaining H_2 and N_2 are converted to NH_3.

3400. ———. [Residual Gases From the Manufacture of Hydrogen.] French Patent 706,504, Feb. 28, 1930. Chem. Abs., vol. 26, 1932, p. 266.

Residual gases from the manufacture of H_2 by Fe-steam processes are converted into a mixture of CO, H_2, and N_2 by bringing the gases into contact with coke heated externally to about 1,200°.

3401. ———. [Residual Gases From the Manufacture of Hydrogen.] French Patent 706,505, Feb. 28, 1930. Chem. Abs., vol. 26, 1932, p. 266.

The mixture of CO, H_2, and N_2 is desulfurized by passing it over a catalyst of CuO. The mixture is then washed in alkaline solution or passed over FeO and then washed.

———. *See* abs. **198.**

3402. SOCIÉTÉ D'ÉTUDES ET DE CONSTRUCTION MÉTALLURGIQUES. [Blast-Furnace Gases.] French Patent 683,615, Jan. 28, 1929. Chem. Abs., vol. 24, 1930, p. 4502.

The excess of gases from blast furnaces is enriched in H_2 by converting the CO therein to CO_2, treated with steam, and used for the synthesis of NH_3 or MeOH.

3403. SOCIÉTÉ D'ÉTUDES MINIÈRES ET INDUSTRIELLES. Nitrides and Ammonia. British Patent 245,762, Jan. 8, 1925. Chem. Abs., vol. 21, 1927, p. 304.

Nitrides of metals such as Fe, Co, Ni, W, and Mo are prepared by heating the metal in a N_2-containing gas at ordinary or low pressure in the presence of N compounds of Li. NH_3 is synthesized by passing a mixture of N_2 and H_2 at atmospheric or other pressure and at 550°–600° over a mixture of a metal of the Fe group, a N compound of Li, and an oxide of a metal of the Al group.

3404. ———. [Production of Methane.] French Patent 590,744, June 22, 1925; appl. filed Feb. 15, 1924. Chem. Zentralb., 1926, I, p. 2837.

Mixtures of CO and H_2 are heated and passed over catalyst of Rh black precipitated on asbestos or pumice.

3405. SOCIÉTÉ D'ÉTUDES SCIENTIFIQUES ET D'ENTREPRISES INDUSTRIELLES. [Hydrocarbons.] French Patent 692,395, June 12, 1929. Chem. Abs., vol. 25, 1931, p. 1259.

Unsaturated hydrocarbons, particularly C_2H_2 and gaseous mixtures for the synthesis of oxygenated organic products and NH_3, are made by separating coke-oven gas into its constituents by liquefaction, mixing the H_2 or gas rich in H_2 thus obtained by separation of air into its constituents, using the O_2 from this air for the regulated combustion of air or a part of the CH_4 or gas rich in CH_4 from the coke oven gas, separating the unsaturated hydrocarbons from the combustion, and joining the residual gases of this separation composed of H_2, CO, and some N_2 with the H_2 from the coke oven gas to form a mixture suitable for the synthesis of compounds such as MeOH and NH_3.

3406. SOCIÉTÉ FRANÇAISE DE CATALYSE GÉNÉRALISÉE. [Acetic Acid]. French Patent 36,719, Jan. 26, 1929. Chem. Abs., vol. 25, 1931, p. 970.

AcOH is prepared by passing CO and H_2 over catalysts consisting of different forms of phosphates, silicates, and borates of Ni, Co, Cr, Fe, and Cu. These may be mixed with metals, oxides, or carbonates.

See also French Patent 681,958 (abs. **3408**).

3407. ———. [Acetic Acid.] French Patent 37,720, July 10, 1929. Chem. Abs., vol. 25, 1931, p. 4558.

AcOH is made catalytically from CO and H_2. The catalysts are BeO with or without Cu, Co, or Ni, or the chromates of Ru, Ni, Co, Cu, Fe, Mo, Mn, Ti, Al, or Mg. Any number of the above may be used together.

See also French Patent 681,958 (abs. **3408**).

3408. ———. [Acetic Acid.] French Patent 681,958, Jan. 11, 1929. Chem. Abs., vol. 24, 1930, p. 4306.

AcOH is made catalytically from CO and H_2; as catalysts may be used; (1) Ni, Cr, or Co taken separately or mixed, either as metal, oxide, or carbonate. If they are used as metals they may be in the form of alloys. (2) Any of the above may be mixed with $MnCO_3$.

3409. ———. Acetic Acid From Carbon Monoxide and Hydrogen. British Patent 342,283, Jan. 11, 1929. Chem. Abs., vol. 25, 1931, p. 5435.

Production of HOAc from CO and H_2 is affected by use of catalysts comprising 1 or more of the materials: Ni, Co, Cr, their oxides and carbonates, and Mn carbonate. The catalyst may be placed in a Cu-lined tube through which the gases are passed heated by electrical resistances.

3410. ———. [Catalyst for Methanol Synthesis.] Swiss Patent 125,266, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 209.

Sr-metal+PbO, Zn-metal+Bi_2O_3, metal predominating.

See also British Patent 265,948 (abs. **3412**) and French Patent 651,194 (abs. **1002**).

3411. ———. [Catalytic Apparatus.] French Patent 787,896, Sept. 30, 1935. Chem. Abs., vol. 30, 1936, p. 1268.

Space in which the gaseous reaction mixture circulates is divided into a number of narrow rectilinear conduits, for example, the gas passes through a number of long tubes and returns along the spaces between these tubes and outer surrounding tubes, the catalyst being in these spaces.

3412. ———. Methanol Synthesis. British Patent 265,948, Feb. 9, 1926. British Chem. Abs., B, 1928, p. 473. Chem. Age, 1927, p. 382. Chem. Abs., vol. 22, 1928, p. 433.

For catalytic synthesis of MeOH from CO and H_2 at elevated temperature and pressure, a catalyst is used comprising either a mixture of Sr and PbO, preferably in the proportion of 3 or 4 atoms of Sr for each molecule of PbO, or a mixture of 3 atom proportions of Zn with 1 mol. proportion of Bi_2O_3. Describes apparatus and gives details of the operation.

SOCIÉTÉ INDUSTRIELLE DES CARBURANTS ET SOLVANTS. *See* abs. **726.**

3413. SOCIÉTÉ INTERNATIONALE DES CARBURANTS ET DES INDUSTRIES CHIMIQUES "BREVETS CONSALVO". [Mixture of Hydrogen and Carbon Monoxide.] Belgian Patent 426,221, Mar. 31, 1938. Chem. Abs., vol. 34, 1940, p. 2543.

ZnO, CO_2, and H_2O are treated with excess of CaC_2. The CaC_2 is subsequently regenerated in the same chamber.

3414. ———. [Synthesizing Hydrocarbon Fuels.] Belgian Patent 438,756, Apr. 20, 1940. Chem. Abs., vol. 36, 1942, p. 3345.

Incoming coal is heated in 1 chamber to 450°–600°. It is then heated in a 2d chamber at 1,000°–1,100°. The CO produced is purified with the aid of Al_2O_3, charcoal, and Fe. The required H_2 is produced by the action of ZnO on a part of the liquid hydrocarbon obtained from heating the coal then by the action of H_2O on Zn obtained in the preceding step.

———. *See* abs. **431.**

3415. SOCIÉTÉ L'AIR LIQUIDE. [Acetylene, Hydrogen, and Carbon Monoxide.] French Patent 712,092, Feb. 25, 1931. Chem. Abs., vol. 26, 1932, p. 1866.

A mixture of C_2H_2, H_2, and CO is prepared by submitting gaseous hydrocarbons such as CH_4 to the action of an electric arc with the addition of a compound yielding O such as CO_2 or steam. The proportions may be chosen so that the H_2 and CO are in the right proportions for the synthesis of MeOH.

3416. ———. Ammonia Synthesis. British Patent 305,534, Feb. 6, 1928. Chem. Abs., vol. 23, 1929, p. 4781.

A catalytic system, as described in British Patent 268,721 (abs. **3428**), is modified by heating the gas after passage through the jacket of the apparatus and before entry to the reaction chamber.

3417. ———. Ammonia Synthesis. British Patent 307,039, Mar. 2, 1928. Chem. Abs., vol. 23, 1929, p. 5280.

In NH_3 synthesis or other exothermic catalytic gas reactions, preliminary purification of the gases is effected in a container surrounded by the catalyst for the main reaction so that indirect heat exchange occurs and the temperature of the purifying reactions is thus controlled; for example, in removing O_2 and CO by catalytic hydrogenation from gases for NH_3 synthesis. Describes an apparatus.

See also British Patent 305,534 (abs. **3416**).

3418. ———. Apparatus for Ammonia Synthesis or Similar Catalytic Reactions. British Patent 282,658, Dec. 24, 1926. Chem. Abs., vol. 22, 1928, p. 3744.

In apparatus of the type described in British Patent 268,721 (abs. **3428**), reacting gases are circulated through the inner catalyst-containing receptacle in indirect contact with the catalyst in excess of the quantity that will pass into direct contact with the catalyst, and the excess is discharged to the outside of the apparatus after heating. Describes various structural details.

3419. ———. [Apparatus for Carrying out Exothermic Catalytic Reactions.] German Patent 574,000, Apr. 11, 1933; appl. filed Mar. 9, 1929. Chem. Zentralb., 1934, I, p. 740; Chem. Abs., vol. 27, 1933, p. 4136.

System for preheating the gases used for the synthesis of NH_3 or for the production of alcohols from CO and H_2.

3420. ———. [Apparatus for Effecting Exothermic Catalytic Gas Reactions.] German Patent 585,278, Nov. 14, 1933 (*Cl. 12g–4.02*). Chem. Abs., vol. 28, 1934, p. 1226.

See British Patents 268,722 and 275,592 (abs. **3429** and **3426**).

3421. ———. [Apparatus for Effecting Exothermic Catalytic Gas Reactions.] German Patent 593,369, Mar. 2, 1934 (*Cl. 12g–4.02*). Chem. Abs., vol. 28, 1934, p. 2953.

See British Patent 307,039 (abs. **3417**).

3422. ———. [Apparatus for Effecting Exothermic Catalytic Gas Reactions.] German Patent 633,389, July 25, 1936 (*Cl. 12g–4.02*). Chem. Abs., vol. 30, 1936, p. 7395.

See British Patent 289,759 (abs. **3424**).

3423. ———. Catalytic Apparatus for Ammonia Synthesis. British Patent 289,823, Aug. 9, 1926. Chem. Abs., vol. 23, 1929, p. 937.

In an apparatus in which the gases are circulated through a space so as to have indirect heat exchange with the catalytic material, part of the catalytic material is placed within this space (suitably in concentric tubes). Describes various structural details.

See also British Patent 282,658 (abs. **3418**).

3424. ———. Catalytic Apparatus Suitable for Treating Gases for Ammonia Synthesis. British Patent 289,759, Apr. 30, 1927. Chem. Abs., vol. 23, 1929, p. 937.

Reacting gases are circulated over 2 or more distinct groups of surfaces enclosing the catalytic material, and the transfer of heat is regulated by varying the proportions of the gases that circulate over the different surfaces. The apparatus may be used with H_2 and N_2 containing varying quantities of CO for NH_3 synthesis.

3425. ———. Catalytic Production of Alcohols. British Patent 306,512, Feb. 22, 1928. Chem. Abs., vol. 23, 1929, p. 4949.

In the catalytic production of oxygenated organic compounds such as alcohols, an inert gas such as N_2 or an excess of H_2 is introduced into the gas mixture before reaction, and, with a gas mixture of suitable composition, the production of NH_3 may be combined with that of oxygenated organic compounds. Gives an example of the production of MeOH and NH_3 from a mixture of CO, N_2 and H_2. Describes an arrangement of apparatus.

3426. ———. Heat-Exchange System for Catalytic Processes. British Patent 275,592, Aug. 9, 1926. Chem. Abs., vol. 22, 1928, p. 2248.

Processes such as the NH_3 synthesis described in British Patent 268,722 (abs. **3429**) may be modified by passing the reaction products through the reaction chamber in such a way that they absorb heat from the hottest zone of the catalyst. Describes an apparatus and other modifications.

3427. ———. [Methanol Synthesis.] Swiss Patent 137,206, no date. Schmidt, J., Das Kohlenoxyd. Akad. Verlagsgesell., Leipzig, 1950, p. 217.

Gas recycle with excess of H_2 or N_2 combined with NH_3 synthesis.

See British Patent 306,512 (abs. **3425**).

3428. ———. Synthetic Ammonia. British Patent 268,721, Mar. 31, 1926. Chem. Abs., vol. 22, 1928, p. 1444.

An apparatus for NH_3 synthesis or other catalytic reactions at high temperature and pressure, arranged for absorption of heat of reaction by fresh reaction gases, is constructed for circulation, between the container for the catalyst and the outer pressure-resisting wall, of a gas which maintains the temperature of the wall within safe limits and is discharged to the outside of the pressure tube.

3429. ———. Synthetic Ammonia. British Patent 268,722, Mar. 31, 1926. Chem. Abs., vol. 22, 1928, p. 1444.

Specifies an apparatus in which heat is conveyed from hotter to cooler parts of the catalytic mass by reaction gases before they come into contact with the catalyst.

3430. Société nationale de recherches sur le traitement des combustibles. Apparatus for Effecting Exothermic Gaseous Reactions With a Solid Catalyst. British Patent 367,772, Oct. 18, 1930. Chem. Abs., vol. 27, 1933, p. 876.

See United States Patent 1,870,665 (abs. **63**).

3431. ———. [Apparatus for Exothermic Gas Reactions.] French Patent 699,438, Oct. 21, 1929. Chem. Abs., vol. 25, 1931, p. 3205.

Describes an apparatus for carrying out chemical reactions between gases in contact with a catalyst, such as, the production of NH_3 from N_2 and H_2 and of MeOH from CO and H_2.

3432. ———. [Manufacture of Methyl Alcohol.] French Patent 613,896, July 31, 1925. British Chem. Abs., 1928, B, p. 596.

CO and H are passed at 160°–180° and 150 atm. pressure over a catalyst consisting of precipitated Cu hydroxide reduced in H_2 at ordinary pressure; reduction begins at 140°, and the temperature must not exceed 450°–500°.

3433. ———. [Preparation of a Catalyst for Synthesis of Methyl Alcohol.] French Patent 610,649, Feb. 5, 1926. British Chem. Abs., 1928, B, p. 844.

Intimate mixture of Cu oxide (4 parts) and Zn oxide (96 parts) is prepared by precipitation of the mixed salts with boiling alkali; the precipitate is dried and reduced at lowest possible temperature with H_2 or CO. 200–250 gm. of methyl alcohol per hr. per dm^3 of this catalyst is produced from H_2 and CO at 150 atm.

3434. ———. [Preparation of a Copper Catalyst for Synthesis of Methyl Alcohol and Formaldehyde From Carbon Monoxide and Hydrogen.] French Patent 606,596, Feb. 27, 1925. British Chem. Abs., B, 1928, p. 857.

Boiling solution of Cu sulfate or nitrate, free from impurities, especially Fe, is treated with caustic alkali and the black hydrated oxide, washed free from alkali and dried in a vacuum at 50°, is mixed with 10–20% of the violet modification of metallic Cu and reduced at the ordinary pressure by H_2 or CO in a slow stream or diluted with N_2 or CH_4 not 130°–140°. The resulting porous, fine-grained, pyrophoric catalyst converts H_2 and CO at 275°–300° and 100–200 atm. into methyl alcohol and formaldehyde.

3435. ———. [Purifying Synthesis Gas.] French Patent 34,348, May 4, 1929; appl. filed Sept. 21, 1927. Chem. Zentralb., 1929, II, p. 1250.

Gas mixtures containing CO and H_2 are purified from carbonyl sulfide, Fe, and Ni-carbonyls by washing with a solution of NaOH in MeOH or H_2O at ordinary or raised pressure.

———. *See* abs. **63, 64.**

SOCIÉTÉ POUR L'INDUSTRIE CHIMIQUE Á BÀLE. *See* abs. **371.**

SOCONY-VACUUM OIL CO., INC. *See* abs. **1, 825, 826, 2116, 2538, 2762, 3217, 3218, 3314, 3349.**

SOENKSEN, H. *See* abs. **2087.**

3436. SOENKSEN, H., AND GRASSHOF, H. (I. G. Farbenindustrie A. G.). [Higher Alcohols From Carbon Monoxide Hydrogenation.] French Patent 870,896, no date. Chem. Zentralb., 1942, I, p. 3288.

See Norwegian Patent 63,409 (abs. **3438**).

3437. ——— (W. E. Currie). Recovery of Higher Oxygen-Containing Organic Compounds From Crude Oils Produced by the Catalytic Hydrogenation of Carbon Oxides. United States Patent 2,274,750, Mar. 3, 1942; appl. filed Aug. 16, 1939, Serial No. 290,518; in Germany Aug. 30, 1938; 7 claims (*Cl. 260–450*). Chem. Abs., vol. 36, 1942, p. 4320.

Process is employed for treating a crude oil such as that produced by the catalytic hydrogenation of CO, which involves subjecting such crude oil to an intense extraction with an organic solvent, such as isopentane, having a preferential solvent action on the higher boiling O-containing substances, while adding a highly soluble alkali metal compound such as K_2CO_3 which reduces the solubility of such higher boiling products in the portion miscible with H_2O in such a quantity that the resulting mixture contains a concentrated solution thereof, and separating the higher boiling products with the solvent in which they have dissolved.

3438. ——— (I. G. Farbenindustrie A. G.). [Separating Synthesis Products.] Norwegian Patent 63,409, no date. Kainer, p. 236.

Higher alcohols occurring in the hydrogenation of CO at high pressure are recovered from the crude oil mixture by extraction. Bases such as NaOH or K_2CO_3 or salts such as NaCl or Na acetate are added to lower the solubility of alcohols in H_2O. Pentane, isopentane, hexane, or propane can be used as solvents.

SÖLL, J. *See* abs. **1882.**

3439. SOLOMON, E. (M. W. Kellogg Co.). Dehydration of Organic Acids. United States Patent 2,581,452, Jan. 8, 1952; appl. filed Mar. 29, 1947, Serial No. 738,176; 14 claims (*Cl. 260–419*).

H_2O-soluble, fatty organic acids obtained in the catalytic hydrogenation of CO at elevated temperatures are removed from their aqueous solutions by selective solvent extraction by means of high molecular weight alkyl amines, such as tributylamine or triamylamine, or aromatic amines, such as quinoline and dimethylaniline. Two phases are produced, an extract phase and a raffinate phase. These are separated, and the solvent is recovered and returned to the process.

3440. ——— (M. W. Kellogg Co.). Separation of Organic Compounds. United States Patent 2,540,143, Feb. 6, 1951; appl. filed Nov. 14, 1946, Serial No. 709 881; 15 claims (*Cl. 260–450*). Chem. Abs. vol. 45, 1951, p. 5710.

Using normal pentane as a typical hydrocarbon solvent treating agent for removal of hydrocarbon impurities from aqueous alcohol solutions, the latter being representative of a group of aqueous solutions of oxygenated compounds that form azeotropes with hydrocarbons the invention, includes the following steps: (A) Separation of the aqueous alcohol stream in a hydrocarbon extraction column by countercurrent extraction with normal pentane, (B) stripping of pentane from heavy hydrocarbons in a pentane distillation column, (C) removal of pentane from the aqueous alcohol stream by distillation in a dependentanizing column, (D) combining the distillate (pentane-alcohol azeotrope) from the dependentanizing column with the distillate from the pentane distillation column and H_2O-washing the mixture thus obtained to recover hydrocarbon-free alcohols, and (E) recycling of pentane obtained from the H_2O-washing step for further use as a solvent treating agent. 2 United States patents cited.

See abs. **289, 290.**

SOLVAY PROCESS CO. *See* abs. **258, 259.**

3441. SPEAR, E. B. (Thermatomic Carbon Co.). Hydrocarbon Compound. Canadian Patent 264,324, Sept. 14, 1926; appl. filed Nov. 28, 1925. British Chem. Abs., B, 1927, p. 961; Chem. Abs., vol. 20, 1926, p. 3697.

CH_4 is passed through a heated retort to yield H_2 and C; a part of the C is deposited in the retort, and steam is thereafter passed through the retort while heated to combine with the C and yield a mixture containing CO and H_2.

SPEER, W. *See* abs. **3926, 3927, 3928.**

3442. SPENCE, J. A. (California Research Corp.). Recovery of Carbonylation Catalyst. United States Patent 2,547,178, Apr. 3, 1951. Chem. Abs., vol. 45, 1951, p. 5844.

Carbonyl-forming metal catalysts are separated from the organic products of a catalytic conversion process in which the carbonyl-forming metal has been used as the active catalyst component by causing the organic products to react with a gas containing O_2 at a temperature generally 100° below the effective oxidation temperature of the organic products until the entrained metal compounds are oxidized to a recoverable form. They are then separated from the organic products. The process is suitable for use with catalysts of Ni, Co, and Fe.

SPICER, W. E. *See* abs. **2377, 3320, 3882.**

3443. SPICER, W. E., AND MCADAMS, D. R. (Standard Oil Development Co.). [Iron Catalyst for Production of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 969,523, Dec. 21, 1950; appl. filed July 24, 1948. Chem. Zentralb., 1951, I, p. 2675.

Roasted pyrite material, such as pyrite, marcasite, or pyrrhotite, is pulverized, mixed with an alkaline

activating agent, and reduced at 370°–538° in a H_2 atm. with H_2. The temperature is then raised to 870°, and the material treated several hours at this temperature. About 3% of K_2CO_3 is added as the activating agent.

SPICER, W. L. *See* abs. **3857.**

3444. SPILLANE, P. X. Apparatus for Synthesis of Hydrocarbons, Alcohols and Formaldehyde. Australian Patent 111,151, July 29, 1940. Chem. Abs., vol. 36, 1942, p. 2481.

H_2 and CO at 250°–450° and 18–250 atm. are passed through an electric field of 60,000–100,000 v. and 6–37 x 10^6 cycles per second. Gives structural and operational details.

3445. ——— (Williams, K., Ping, P., and Lawrie, T. A.). Electrosynthesis of Carbon-Hydrogen Compounds. United States Patent 2,349,915, May 30, 1944; appl. filed Apr. 22, 1940, Serial No. 331,067, in Australia, Apr. 29, 1939; 5 claims (*Cl. 204–168*). Chem. Abs., vol. 39, 1945, p. 1360.

Mixture of H_2 and CO is passed through an alternating electrical field of which the potential difference is maintained at 60,000–100,000 v. and having a frequency synchronized to the molecular oscillation of H_2 and CO, for example, 6.0 x 10^6–37 x 10^6 cycles per sec. The catalysts used are prepared by precipitation of the respective hydroxide from mixed nitrate solutions with a boiling solution of NaOH, and include, for example, $ZnCrO_4$, reduced CuO, ZnO, BeO, Cr_2O_3, or their mixture, with ratios of Be : Cu 2–5 : 100, Mn : Cu 2–5 : 100 and 40 : 100, Ce : Cu 2–30 : 100 or Cu : Zr 100 : 3–10. They may be used with activated charcoal. The working temperature of the catalyst chambers is 250°–450° and 450°–600° and the pressure is varied in accordance to the desired final product, for example, in MeOH synthesis the pressure is about 200 atm., for synthesis of light hydrocarbons (up to octane) approximately 18 atm. and for hydroxyl derivatives up to 150 atm. Gives details of construction and diagram of the apparatus.

3446. SPINDLER, H. Hydrocarbon Fuel. British Patent 255,493, July 18, 1925. British Chem. Abs., 1927, B, p. 868. Chem. Abs., vol. 21, 1927, p. 2784.

Hydrocarbon mixture resembling crude petroleum is made by subjecting CH_4, alone or with added H—combining gases such as C_2H_2 and CO, to a decomposition temperature of 500°–950°, cooling the dehydrogenated products, and then passing them over a catalytic material to produce higher hydrocarbons. The successive stages of the process are carried out under pressure. Describes an apparatus. $ZnCl_2$, active C, Al powder, Mg powder, and Fe scale treated with alkali hydroxide may be used as catalyst substances.

3447. ———. [Production of Liquid Hydrocarbons.] French Patent 620,653, Nov. 26, 1925. Chem. Zentralb., 1927, II, p. 2790.

City gas is passed over glowing coke in an electric furnace whereby C_2H_2, H_2, and CO are obtained. These are passed at 200°–300° through Ni suspended in paraffin.

3448. SPUHLER, E. [Production of Hydrocarbons.] Swiss Patent 229,187, Jan. 3, 1944; appl. filed Aug. 4, 1941. Chem. Zentralb., 1944, II, p. 916.

Limestone is decomposed with HCl, and the CO_2 produced is reduced with H_2 to CO. The resulting mixture of CO and H_2 is converted by the Fischer-Tropsch process to hydrocarbons.

3449. STAALSYNDICAAT LEDEBOER. Reducing Iron Ores. British Patent 287,925, Mar. 30, 1927. Chem. Abs., vol. 23, 1929, p. 366.

In reducing Fe ore and melting the Fe formed by the combustion of a gaseous fuel, a combustion gas is used which contains virtually no O_2 and is produced by the complete or virtually complete combustion of the fuel by a surface combustion burner.

STAATSMIJNEN IN LIMBURG. *See* abs. **2694.**

STAENNINGS, C. *See* abs. **1622.**

STAIB, J. H. *See* abs. **314.**

STANDARD CATALYTIC CO. *See* abs. **45, 130, 131, 136, 572, 575, 973, 977, 1101, 1886, 2053, 2335, 2439. 2627, 2749, 3224, 3260, 3717, 3848.**

3450. STANDARD-I. G. Farbenindustrie A.-G. [Hydrocarbons.] French Patent 820,757, Nov. 18, 1937. Chem. Abs., vol. 32, 1938, p. 3586.

Hydrocarbons of the type of motor fuels or for mixing with motor fuels are made by hydrogenating C oxides in the presence of a catalyst, the reaction gases being diluted with enough inert gas so that the partial pressure of the C oxide and H_2 together is <5 atm. The reaction is regulated by regulating the proportion of reacting and inert gases.

———. *See* abs. **452, 2645, 2649, 2671, 2675, 3922.**

3451. STANDARD OIL CO. (I. G. Farbenindustrie A.-G.). Liquid Phase Process. German Patent Appl. —, OZ 10,479, filed Jan. 21, 1937. Bureau of Mines Transl. T–433, Jan. 1948.

Synthesis is carried out in a steadily maintained liquid phase with the medium principally or entirely consisting of oxygenated derivatives of hydrocarbons obtained in the liquid state under the conversion conditions (products of oxidation of paraffins).

———. *See* abs. **897, 898, 900, 902.**

STANDARD OIL CO. OF ILLINOIS. *See* abs. **901.**

STANDARD OIL CO. OF INDIANA. *See* abs. **2, 3, 41, 42, 43, 207, 208, 282, 329, 509, 628, 657, 899, 935, 990, 1108, 1768, 1769, 1770, 1771, 1772, 1773, 1774, 1775, 1776, 1777, 2093, 2134, 2135, 2587, 2628, 2709, 2739, 3313, 3337, 3356, 3725, 3762, 3840, 3910, 3911, 3912.**

STANDARD OIL CO. OF OHIO. *See* abs. **279.**

3452. STANDARD OIL DEVELOPMENT CO. Alcohol Synthesis. British Patent 651,250; appl. filed in United States May 20, 1948. Petroleum, vol. 14, 1951, p. 227.

Process proceeds in 2 stages: Formation mainly of aldehydes, and hydrogenation of the product to the corresponding primary alcohols. Carbonylation or the Oxo process may be used effectively with long- or short-chain olefinic compounds according to the alcohol required. The catalyst may be Fe or Co, preferably the latter. The hydrolysis products so formed may be at least partly recycled to the hydrogenation zone. Hydrolysis is performed in the presence of dilute mineral acid at 200°–250° F. or in a substantially neutral aqueous medium at 300°–400° F. The products are separated by steam or vacuum distillation.

3453. ———. Alcohols. British Patent 668,963, Mar. 26, 1952. Chem. Abs., vol. 46, 1952, p. 10,191.

Describes single-step process for the direct conversion of olefins containing 2–5 C atoms per molecule to alcohols containing 1 more C atom than the olefins employed. The method consists essentially of contacting the alcohols with CO gas and H_2 and 5–30% by weight of H_2O based on the olefin in the presence of a Co-containing catalyst at a pressure of 2,500–3,500 p. s. i. at a temperature of about 250°–450° F. According to British Patent 631,316 (abs. **577**) the reaction is carried out in a liquid medium (H_2O) and the catalyst used is H_2O soluble. According to this method the catalyst need not be H_2O soluble. Suitable catalysts are Co oleate or naphthenate, or Fe linoleate.

3454. ———. Alcohols. British Patent 672,349, May 21, 1952. Chem. Abs., vol. 47, 1953, p. 4356.

Yields of alcohols obtained from the reaction of olefins, CO, and H_2 with Co stearate are improved if the residue after removal of the alcohols is subjected to

repeated hydrogenation. Thus, an olefin C_7 cut b. 160°–170° F., CO and H_2 in 1.1 : 1 ratio, and Co naphthenate at 350° F. and 3,300 p. s. i. give an olefin conversion of 75–80%. Reduction of the oxygenated compounds thus obtained with 10% MoS_2 on charcoal at 450° F. and 2,900 p. s. i. gave a mixture containing 57.5 wt.–% alcohols b. 340°–370° and 17.4 wt.–% of bottoms. The alcohols were recovered, 1 l. of the residue was hydrogenated at 350° F. at 2,700 p. s. i. over Ni-kieselguhr catalyst, and the product saponified with 15% NaOH 5 hr. at 400° F.; a saturated ether amounting to about 30 vol. % of the original bottoms and C_{15}–C_{16} alcohols, also equivalent to about 30% of the bottoms, were recovered.

3455. ———. Alcohols From Olefins. British Patent 647,363, Dec. 13, 1950. Chem. Abs., vol. 45, 1951, p. 6654.

Describes an improved process for controlling the temperature and maintaining a high concentration of the catalyst in the conversion of olefins to oxygenated compounds by means of CO and H_2 with Fe and Co compounds as catalysts, by recirculating the product of the 1st stage of the reaction after cooling and removing the gases, thus providing a high concentration of catalyst at the reactor inlet so that the Oxo reaction proceeds throughout the length of the reactor. 3–7 vol. of the initial product are used per vol. of fresh olefin.

3456. ———. Catalyst. British Patent 671,552, May 7, 1952. Chem. Abs., vol. 46, 1952, p. 9288.

An active catalyst adapted to promotion of the water-gas-shift reaction is produced by extruding a mixture of Fe_2O_3, CrO_3, and H_2O and activating the extruded material by heating at a temperature in the range 538°–704°, preferably for approximately 8 hr., to convert the CrO_3 to Cr_2O_3. The final product will consist essentially of 93% Fe_2O_3 and 7% Cr_2O_3. Catalysts thus prepared may have a pellet-crushing strength of at least 80 lb. and an activity level corresponding to substantially equilibrium CO conversion in the temperature range 427°–482°. Describes an apparatus which the crushing strengths of cylindrical pellets $\frac{3}{16}$ in. in diameter by $\frac{3}{16}$ in. long are determined. In an example, 150 lb. Fe_2O_4 was mixed with 30 lb. CrO_3 and 5.5 gal. H_2O. Another 150 lb. Fe_2O_3 was added, and the mixture was extruded into pellets, which were heated for about 8 hr. at 593°. The effluent gas leaving a commercial CO conversion unit containing a catalyst prepared by the method described contained 1.3–1.4% CO. At 427°–482° the equilibrium value is about 1.2% unconverted CO. By eliminating the conventional wetting and drying steps in the preparation of the catalyst, losses amounting to 3.5–4.0% of the catalyst material are avoided.

See also United States Patent 2,631,086 (abs. **2377**).

3457. ———. [Catalyst.] French Patent 939,910, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 155.

Partly reduced Fe_2O_3.

3458. ———. [Catalyst Chamber.] French Patent 914,577, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 163.

Catalyst chamber with catalyst arranged in layers, the reaction gas being passed radially from the center outward.

3459. ———. Catalyst for Fischer-Tropsch Synthesis. British Patent 641,261, Aug. 9, 1950. Chem. Abs., vol. 44, 1950, p. 11067.

Catalyst is prepared by intimately combining Fe or an Fe oxide and 0.2–20% by weight of an alkali-metal ferrate (I), based on the weight of the Fe oxide; and subsequently bringing the mixture into contact with a reducing gas at a temperature of 371°–871°. Heating the catalyst mixture in an oxidizing atmosphere is a desirable operation before the heating in the reducing atmosphere. The Fe oxide constituent may be ferro-ferric oxide, or α– or γ–Fe_2O_3. K_2FeO_4 or Na_2FeO_4 are eminently suitable ferrates. The ferrate may be formed by adding an oxidizing agent such as Br to a mixture of $Fe(OH)_3$ and an alkali-metal hydroxide. This mixture is then added to the Fe oxide. The compounds are intimately mixed and the product dried before heating in air. An alternate method for preparation of the ferrate is ignition of finely divided Fe and an alkali-metal nitrate. The product is combined with the proper amount of Fe or Fe oxide and is treated in the usual way. While the (I) is preferably employed in purified form, the presence of minor proportions of relatively inactive contaminants is not detrimental. An analysis of a satisfactory ferrate is K_2FeO_4 75, KBr 20, $KBrO_3$ 5%. This ferrate was employed in a catalyst composition that consisted of ferrate 5 and ferro-ferric oxide 95 parts by weight. Desirable conditions for use of the catalyst in promoting reaction of a mixture of H_2 and CO are a temperature of 232°–357°, pressure 100–500 p. s. i. g., H_2 : CO present in a ratio of 2 : 1 to 1 : 1, and feed rate of 100–1,500 vol. feed per vol. catalyst per hr.

3460. ———. Catalyst for Fischer-Tropsch Synthesis. British Patent 641,266, Aug. 9, 1950. Chem. Abs., vol. 44, 1950, p. 11,067.

Hydrocarbon synthesis catalyst is prepared by mixing 5% $K_4Sb_2O_7$ with 95% Fe_3O_4 as follows: The mixture is slurried in EtOH, dried, ground, and calcined in air at 1,000° F. for 4.5 hr. The catalyst is reduced before use. High yields of hydrocarbons and oxygenated compounds are found when equimolar H_2+CO synthesis gas is passed over this catalyst at 550° F. and 150 p. s. i. with space velocity of 200. vol. per vol. catalyst per hr.

3461. ———. Catalyst for Producing Hydrocarbons From Carbon Monoxide and Hydrogen. British Patent 593,910, Oct. 29, 1947. Chem. Abs., vol. 42, 1948, p. 2088.

Hydrocarbons are produced in a process relatively insensitive to temperature change by hydrogenating CO at 300°–450° F. and at atmospheric or superatmospheric pressure over pelleted, supported, or fluidized Ni chromite catalyst. Such catalyst may be activated before or after use by controlled oxidation and reduction. If $NiSO_4$ is used in preparing the catalyst or S is present in feed gases, special purification is necessary. Thus $Ni(NO_3)_2$, 1,163 and H_2O, 3,200 were treated with $(NH_4)_2Cr_2O_7$,504 and H_20,2,400 gm. and concentrated NH_4OH, 550 cc. at about 165° F. The precipitate was filtered out, dried at 300° F., calcined for 1 hr. at 700° F., and reduced at about 760° F. with 2,000 vol. H_2 per hr. for 5 hr. The catalyst so prepared used at 360° F. with H_2 and CO in volume ratio 1.97 : 1 and at space velocity 118 vol. per hr. gave about 179 cc. liquid hydrocarbons wer $m.^3$ of reagents. Another batch of catalyst reduced with 2,200 vol. H_2 per hr. at 750° F. and used at space velocity 111–113 for 97 hr. gave (after the 1st 25 hr.) 132–168 cc. liquid hydrocarbons per $m.^3$ reagents.

3462. ———. [Catalyst Preparation.] French Patent 912,575, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950. p. 155.

Silica gel impregnated with metal salts, heated to oxide formation, and then reduced.

3460. ———. Catalyst Removal in Carbonylation Reaction. British Patent 660,737, Nov. 14, 1951. Chem. Abs., vol. 46, 1952, p. 4202.

Catalyst compounds are separated from the reaction products obtained in the carbonylation stage of an Oxo

synthesis reaction for the preparation of oxygenated organic compounds by reaction of CO and H_2 with olefinic compounds in the presence of a catalyst, by injecting steam at 0–200 p. s. i. g. and 100°–204° into the reaction products to decompose the catalyst compounds and by condensing the mixture of vapors to obtain a dispersion of the catalyst metal in H_2O. The dispersion is separated from the reaction products with subsequent recovery of the catalyst metal from the dispersion. In an example, steam at 171° was injected at 125 lb. pressure into a bomb containing 1 l. of H_2O and 500 cc. primary reaction product resulting from the carbonylation of a C_7 olefin in the presence of a Co catalyst. After the treatment the carbonylation product was found to contain 0.004% Co, as compared to 0.113% before steaming.

3464. ———. [Catalyst Support.] French Patent 914,125, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 155.

Clay activated with HCl and then with HF.
See also British Patent 593,940 (abs. **3513**).

3465. ———. Catalysts. British Patent 485,178, May 13, 1938. Chem. Abs., vol. 32, 1938, p. 8715.

Active catalysts of high mechanical strength are obtained by mixing with an effective catalyst substance, which is preferably in minor proportion at least 2 other substances, 1 as a major and the other as a minor ingredient capable of reacting with each other to the exclusion of the effective catalyst to form a compound or a solid solution having a melting point substantially higher than the reaction temperature and then heating the mixture at >1,600° F. for a time sufficient to effect an increase in mechanical strength but insufficient to cause substantial melting, the amount of compound or solid solution formed being <10% of the total catalyst. They are suitable for reactions occurring >900° F., for example, production of H_2 from steam and hydrocarbons, cracking of hydrocarbons to produce olefins, diolefins, and C_2H_2 destructive hydrogenation reactions, polymerization of unsaturated gaseous hydrocarbons to aromatic hydrocarbons, dehydrogenation of hydrocarbons, and the synthesis of MeOH. The effective catalyst may be Ni, Fe, or Cr oxide, and 1 of the reacting substances is preferably a difficultly reducible oxide. The mixture may be molded into shapes before the heating steps and may be subjected to reducing conditions afterward. H_3BO_3 22 and MgO 750 are added to $Ni(NO_3)_2 \cdot 6H_2O$ 1,455, dissolved in H_2O 500 parts and the paste dried and heated to 850°–900° F., the powder screened and compressed into tablets, heated to 1,700°–2,000° F. for about 36 hr. and the Ni oxide then reduced by H_2; the product may be used to obtain H_2 from CH_4 and steam at 1,525° F.

3466. ———. Catalysts for Use in Synthesis of Hydrocarbons. British Patent 623,815, May 24, 1949; appl. filed Aug. 23, 1946. Fuel Abs., vol. 6, 1949, abs. 4,120; Chem. Abs., vol. 44, 1950, p. 2205.

Describes improved process for the catalytic synthesis of liquid organic compounds by the reaction of CO and H_2 wherein the catalyst comprises a H_2-reduced Fe pyrite ash.

3467. ———. Catalytic Apparatus and Processes. British Patent 496, 159, Nov. 25, 1938; appl. filed Nov. 26, 1937. Chem. Abs., vol. 33, 1939, p. 2773.

Temperature of exothermic catalytic reactions is controlled by suspending the catalyst in a fluid capable of absorbing heat and passing this suspension through a reaction zone at a rate sufficient to remove excess heat. The invention is illustrated as applied to the synthesis of hydrocarbons from CO and steam.

3468. ———. Catalytic Conversion of Carbon Monoxide With Hydrogen. British Patent 659,315, 1951. Fuel Abs., vol. 11, No. 1, 1952, abs. 340.

Improved Fisher synthesis process comprises contacting a gas containing CO and H_2 in synthesis proportions under synthesis conditions with an Fe type catalyst comprising an Fe oxide reduced by an amount between 5–50% of complete reduction and containing between 0.5–5% of an alkali metal promoter.

3469. ———. Catalytic Conversion of Carbon Oxides With Hydrogen. British Patent 658,848, 1951. Fuel Abs., vol. 11, No. 1, 1952, abs. 336.

Improved catalysts for use in the catalytic conversion of CO and H_2 are prepared by mixing a minor proportion of C with a pure or commercial Fe oxide in finely divided form and then sintering the mixture with an oxidizing gas at 2,200°–2,500° F.

3470. ———. Catalytic Improvement of Hydrocarbon Synthesis Product. British Patent 641,121, Aug. 2, 1950; appl. filed Mar. 18, 1948. Chem. Abs., vol. 44, 1950, p. 11,067.

The gasoline prepared by Fischer-Tropsch-type synthesis is upgraded in the presence of severly deactivated cracking catalyst such as 87 : 13 wt. ratio silica-alumina, 65 : 35 wt. ratio silica-magnesia or bentonitic clay. Catalyst preferably contains up to 1% Fe contamination. The process is carried out in the vapor phase at 800°–1,000° F. with liquid hourly space velocity 2–5. Results are superior to bauxite treatment yielding more gasoline of higher octane number with less coke deposit. Octane number increase is due predominantly to isomerization of olefins. Includes examples of pilot-plant tests.

3471. ———. Catalytic Manufacture of Hydrocarbons and Oxygenated Hydrocarbons. British Patent 625,841, July 5, 1949; appl. filed Oct. 2, 1946. Fuel Abs., 1949, No. 5,011. Chem. Abs., vol. 44, 1950, p. 2205.

CO and H_2 are reacted in the presence of a powdered Fe catalyst, which is maintained in the reaction zone in the form of a dense fluid mass in the reactant gases. The reaction zone is kept at an elevated temperature under superatmospheric pressure. The contaminated catalyst is withdrawn and conveyed into a separate hydrogenation zone where it is kept under dense fluidized suspension at about 900° F. for enough time to effect removal of at least 80% of the contaminants, after which it is returned to the reaction zone.

3472. ———. Catalytic Re-Forming of Hydrocarbon Oil. British Patent 542,925, Feb. 3, 1942. Chem. Abs., vol. 36, 1942, p. 5006.

Catalyst in finely divided form is suspended in the oil vapors and recycled H_2 before their introduction into the reaction zone, the ratio of catalyst to oil being at least 2 : 1 by weight. This process can be applied to hydrocarbon oils derived from any source. For example, fractions b. 100°–500° F. obtained from the products of destructive distillation, destructive hydrogenation, carbonization, or hydrogenation of coals, tars, mineral oils, shales, peats, lignites, bitumens, and other carbonaceous materials, or hydrocarbon oils obtained by synthetic processes, such as the Fischer synthesis, may all be subjected to treatment by the process.

3473. ———. Catalytic Synthesis of Hydrocarbons British Patent 616,499, Jan. 21, 1949. Chem. Abs., vol. 43, 1949, p. 4448.

Liquid hydrocarbons can be synthesized in high yields by forcing a mixture of H_2 and CO in 0.7 to 1.3 molar ratio through a fluidized mass of catalyst (Co and ThO_2 on kieselguhr) in a single-stage reaction zone maintained under Fischer synthesis conditions of temperature and pressure, adding H_2 to the reaction zone at spaced points to maintain the H_2 to CO within 0.7 to 1.3 throughout the reaction zone.

3474. ———. Catalytic Synthesis of Hydrocarbons. British Patent 621,902, Apr. 22, 1949. Chem. Abs., vol. 43, 1949, p. 8121.

Liquid hydrocarbons can be produced from CO and H_2 by catalytic synthesis by employing a catalyst composed of an Fe compound with a minor proportion of a F compound of K as promoter. The Fe may be employed as an oxide, such as in the form of red or yellow Fe oxide and Fe ores such as hematite, limonite, and magnetite. The F compound of K (KF is the preferred promoter) may be present in amounts of 0.1–10%, preferably about 1% of the Fe oxide. A typical method of preparing the catalyst is as follows: Red Fe_2O_3 (99.9% Fe_2O_3) 340 is mixed with a solution of KF 3.4 gm. in 160 cc. of distilled H_2O to form a paste. This paste is dried at 350° F., blended with 4% of a pilling aid (stearates), pilled, and calcined 3 hr. at 850° F. The pills are reduced for 3 hr. with 1,000 vol. per vol. per hr. of H_2 at 900° F. and then sintered in H_2 for 4 hr. at 1,200° F. In carrying out the hydrocarbon synthesis, conventional synthesis conditions for Fe catalysts may be employed such as, temperatures of about 450°–850° F., preferably 500°–700° F., pressures of about 3–25 atm., H_2 : CO ratios in the range of about 0.6 : 1–3 : 1, and space velocities of about 100–2,500 vol. per vol. per hr. If the formation of large proportions of olefins is desired, it is preferred to employ reaction temperatures above 620° F. and preferably 630°–680° F.

3475. ———. Catalytic Synthesis of Hydrocarbons. British Patent 626,069, July 8, 1949. Fuel Abs., vol. 6, 1949, abs. 4,121; Chem. Abs., vol. 44, 1950, p. 2734.

Hydrocarbons are synthesized from a gas mixture containing CO and H_2 by passing the mixture upward through a reaction zone containing a fluidized, suspended, Fischer catalyst under suitable conditions of temperature and pressure for the synthesis reactions. The catalyst material is subsequently separated from the reaction products, wherein the finely divided solid catalyst material comprises particles ranging upward in size from 5 microns or less, the larger particles over 80 microns being predominantly smaller than 150 microns and containing no particles larger than 1,650 microns and having the following overall size distribution:

0–20 micron diameter less than 25%
20–80 micron diameter, less than 30–85%
Greater than 80 micron diameter, less than 45%.

3476. ———. Catalytic Synthesis of Hydrocarbons. British Patent 626,742, July 20, 1949; appl. filed Feb. 14, 1947. Fuel Abs., 1949, No. 5,012; Chem. Abs., vol. 44, 1950, p. 2205.

Mixture of gases containing CO and H_2 is forced into a reaction zone containing a bed of powdered fluidized Fe catalyst. Elevated temperature and pressure are maintained in the reaction zone, and the reactants remain there for enough time to effect the desired conversion. The Fe catalyst is withdrawn, quenched, and heated to a temperature of at least incipient fusion in the presence of an oxidizing gas, whereby agglomeration of the catalyst particles occurs, after which they are ground to a size > the Fe removed from the reaction zone and then returned to the process.

3477. ———. Catalytic Synthesis of Hydrocarbons. British Patent 631,322, Nov. 1, 1949. Chem. Abs., vol. 44, 1950, p. 3701.

In the production of a mixture consisting predominantly of hydrocarbons with a small amount of oxygenated hydrocarbons, H_2O, and CO_2 from a gaseous mixture of CO and H_2 by a Fischer-Tropsch reaction at a temperature 149°–371° and a pressure from atmospheric to 200 p. s. i. g. in contact with a catalyst consisting of a metal from Group VIII, the product is brought into contact with a dehydrating catalyst to dehydrate certain of the oxygenated hydrocarbons, such as alcohols, to H_2O and unsaturated hydrocarbons without altering substantially the structure of the hydrocarbons produced. The dehydrated product is cooled to recover liquid hydrocarbons, which are substantially free from the dehydratable oxygenated compounds. Specific examples of dehydrating catalysts are the oxides of Th, Al, W, and Cr. Temperatures in the range 149°–427° and pressures in the range of atmospheric to 500 p. s. i. g. may be used in the dehydration.

3478. ———. Catalytic Synthesis of Hydrocarbons. British Patent 631,457, 1949. Fuel Abs., vol. 7, 1950, abs. 2,130; Chem. Abs. vol. 44, 1950, p. 5082.

Process for the synthesis of hydrocarbons, which comprises contacting a gas mixture containing CO and H_2 in synthesis proportions under hydrocarbon synthesis conditions of temperature and pressure with a catalyst comprising a trivalent Fe oxide and at least an equimolecular proportion of 1 or more oxides of 1 or more bivalent metals other than Fe, which will form a spinel type compound with the Fe oxide or products obtained by reducing such mixtures.

3479. ———. Catalytic Synthesis of Hydrocarbons. British Patent 647,052, Dec. 6, 1950. Chem. Abs., vol. 45, 1951, p. 4430.

Describes apparatus for the synthesis of hydrocarbons and for regeneration of spent Fe catalyst. In the reactor a mixture of 31.5% CO and H_2 is passed upward through a layer with definite upper level of dense fluidized Fe catalyst, 100- to 400-mesh., d. 50 lb. per cu. ft. at a rate of 10,000 $ft.^3$ per hr., at about 600° F. and 15 atm. Used catalyst is withdrawn downward, 25 lb. per hr., from near the bottom of the layer in the reactor to a similar but smaller reactor where a stream of 220–230 cu. ft. per hr. of air or O_2-enriched air is passed upward through a layer of used catalyst to oxidize C and other contaminants. Regenerated catalyst is returned to the reactor.

3480. ———. Catalytic Synthesis of Hydrocarbons. British Patent 654,667; appl. filed in United States Nov. 8, 1946. Petroleum, vol. 14, 1951, p. 254.

Hydrocarbons, oxygenated or not, are synthesized from a gaseous mixture of CO–H_2 fed into a reaction zone over a bed of fluidized powdered Fe catalyst kept at high temperature and pressure. Powdered inert material such as sand or silica gel of particle size larger than that of the powdered catalyst is mixed therewith; the particle size of the next material being such that good fluidizing of the mixture is ensured, with substantially no movement of inert material as a whole relative to the body of the catalyst.

3481. ———. [Catalytic Synthesis of Hydrocarbons.] German Patent 811,347, Aug. 20, 1951; appl. filed Nov. 1, 1949 (*Cl. 12 o*). Chem. Zentralb., 1952, **I**, p. 951.

Hydrocarbons are synthesized from gas mixtures containing CO and H_2 with powdered Fischer-Tropsch catalyst and flowing upward through a reaction zone maintained under suitable temperature and pressure and at such a velocity that the powdered catalyst is in a dense turbulent state suspended in the flowing gas. The powdered catalyst is in particle sizes in microns as follows: 0–20μ<25%, 20–80μ 30–85%, larger than 80μ<45%. The gas velocity lies between 6 and 305 cm. per sec., the reaction temperature 176°–357°, and the pressure above normal. The reaction temperature and pressure depend upon the type of catalyst used (Fe or Co). The process yields both hydrocarbons and O-containing products.

3482. ———. [Catalytic Transformation.] French Patent 934,110, May 12, 1948; appl. filed Oct. 2, 1946. Chim. et ind., vol. 61, No. 3, 1949, p. 252.

Gas containing CO and H_2 in synthesis proportions is contacted with a catalyst containing 90–99.5% of an oxide of Fe and 0.1–10% of K fluoride and reduced at a high temperature before use. Example: Normally liquid hydrocarbons are obtained from a gaseous mixture containing 0.6–3 mol. of H_2 per mol. of CO at 260°–370° and 3–25 atm. pressure with a catalyst containing 99% of oxide of Fe and 1% of K fluoride.

3483. ———. Control of Carbon in Hydrocarbon Synthesis. British Patent 647,079, 1950. Fuel Abs., vol. 9, No. 3, 1951, abs. 1781.

Gaseous mixture containing CO, CO_2, and H_2 is contacted with a fluidized bed of powdered Fe catalyst in a reaction zone at synthesis temperatures and under superatmospheric pressure. The H_2 partial pressure is at least 100 p. s. i. in the reaction zone and that of the CO_2 at least 125 p. s. i. A hydrocarbon product and oxygenated hydrocarbons are recovered from the reaction zone.

3484. ———. Control of Catalyst Activity in the Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. British Patent 598,380, Feb. 17, 1948; appl. filed June 18, 1945. Chem. Abs., vol. 42, 1948, p. 5212.

In the hydrogenation of CO with a fluidized Fischer-Tropsch catalyst the activity of the catalyst gradually decreases. Means are provided to introduce the active components of the catalyst, such as Co activated with ThO_2 or MgO, either in pure form or in concentrated form on a carrier, through a hopper to the reaction zone. The activity of the catalyst is thus maintained at a constant level. The invention also provides for reducing the activity of the catalyst, if desired, by introducing the inert carrier to the reaction zone.

3485. ———. Cracking Oils; Catalytic Processes and Apparatus; Iron Carbonyl. British Patent 590,882, Oct. 30, 1942; appl. filed Sept. 12, 1941.

In fluid catalyst processes such as cracking, Fischer-Tropsch synthesis, hydrogenation, dehydrogenation, partial carbonization of coal, and production of Fe carbonyl from Fe oxide and CO, the velocities of the solids and fluids are controlled to maintain a dense phase of solids and gases in the reaction zone. The solids are introduced at the top of the reactor and the fluids at the bottom so that they flow in countercurrent. The reaction chamber is provided with perforated baffles, bubble trays, and packings similar to those used in a fractionating tower so that separate fluidized layers are formed.

3486. ———. Fatty Acid Production in Hydrocarbon Synthesis. British Patent 657,269, Sept. 12, 1951. Chem. Abs., vol. 46, 1952, p. 2783.

See United States Patent 2,521,436 (abs. **3986**).

3487. ———. Fischer-Tropsch Catalyst. British Patent 596,162, Dec. 30, 1947; appl. filed July 23, 1945. Chem. Abs., vol. 42, 1948, p. 3933.

Spherical particles of SiO_2 hydrogel are prepared by adding a small amount of emulsifying agent to the sol formed when separate solutions of Na silicate and H_2SO_4, HNO_3, or HCl are mixed by means of a jet. The mixture is subsequently emulsified by a 2d jet as the dispersed phase in 2–20 times its vol. of a wholly or partly immiscible substance, such as BuOH, ethers, naphtha, or light gas oil, at room temperature to 250° F. and atmospheric pressure to 50 p. s. i. H_2O is added after the sol is set to a hydrogel (1–60 min.), and the H_2O-gel mixture is separated. The gel is washed and impregnated with aqueous solutions of the nitrates of Co and Th in such proportions that the fluidized mass contains 15–40% Co and 2–10% Th. The impregnated gel is dried at 212° F. to reduce the H_2O content to 6–10% and then is heated 4 hr. at 420° F. to decompose the nitrates to the corroesponding oxides. The dried gel is formed into ⅛ in. pills and the Co oxide reduced to Co with H_2 for 4 hr. at 650°–700° F., with use of space velocities of 4,000–6,000 vol. per vol. of catalyst per hr. After reduction, apparent d. 56.1 lb. per cu. ft., the pills are ground to powder containing less than 25%, having particle size 0–20 micron diam. and having apparent density in the fluidized state of 10–35 lb. per cu. ft. Carbonates of Co and Th may be precipitated on the gel in place of nitrates. Mg, U, Mn, or Al nitrates, acetates or chlorides may replace Th. Catalysts thus prepared have improved resistance to attrition, contain less friable matter, and are retained better on the carrier. They are suitable in either fluidized or bed-type operations. Gives an example in which the Co–Th oxide catalyst is used to reduce CO at 390°–400° F. to liquid hydrocarbons.

3488. ———. Fischer-Tropsch Synthesis. British Patent 676,658, July 30, 1952. Chem. Abs., vol. 47, 1953, p. 7762.

Catalyst fines from Fischer-Tropsch synthesis are separated from the fluidized bed by entrainment in the product gases. The H_2–CO synthesis gas mixture is fed into a fluidized, finely divided Fe-catalyst bed maintained at 500°–750° F. and 250–750 p. s. i. at such a velocity that particles $<20\ \mu$ in size are entrained in the overhead gases. The fines are separated and may be agglomerated by sintering, then ground, classified, and reduced for recycling. By removing the fines continuously from the reaction mixture, wax formation is minimized. Since the fines contain more C than the larger particles, their removal from the catalyst bed leaves the latter with better heat-transfer and fluidization characteristics than if they are allowed to build up in the bed. The high C content of the fines also makes them readily susceptible to oxidative regeneration.

3489. ———. Fischer-Tropsch Synthesis by Fluidized Catalyst. British Patent 600,580, June 20, 1945, in United States Dec. 20, 1944. British Abs., B, II, 1948, p. 447.

In the synthesis of hydrocarbons by the Fischer-Tropsch process, accumulation of wax on the catalyst is kept <25% (preferably <15%) by withdrawing continuously a suitable proportion of the fluidized suspension as it gravitates down from the reaction vessel, solvent-extracting the wax from the catalyst so removed, and recycling the dewaxed catalyst.

3490. ———. [Fluidized Catalyst Bed.] French Patent 937,565, Aug. 20, 1948. Chem. Abs., vol. 44, 1950, p. 317.

To achieve a high fluidity of the bed and to have a maximum mass of particles per unit volume, the catalyst is made to contain at least 35% of 70–200 microns, 30–40% of 20–70 microns, and preferably none of 0–20 microns. The maximum value of 70–200 microns is 60–70%. Thus in catalytic cracking using Al_2O_3 on silica gel with 100% catalyst at 20–70 microns, the density of the bed will be 195 kg. per $m.^3$ for a speed of 60 cm. per sec. and 150 kg. per $m.^3$ for a speed of 42 cm. per sec. With 60% of 20–70 microns and 40% of 70–200 microns, the density is 240–300 kg. per $m.^3$ for equivalent speeds.

3491. ———. Fluidized Solid Systems. British Patent 646,557; in United States Sept. 19, 1947. Petroleum, vol. 14, 1951, p. 81.

Aim of this invention for use with pulverized coal is to classify the solids into 2 or more fractions of different particle size before feeding to the fluidized bed. The fraction containing the largest size particles is fed to the upper portion of the bed and that containing the

smallest size to the lower portion, and the intermediates are between the two. The method is explained by means of a diagram. The method and apparatus are applicable for carbonization or gasification of carbonaceous solids, or a catalytic reaction such as the synthesis of hydrocarbons from CO and H_2 in presence of an Fe-type fluidized catalyst.

3492. ———. Fuels. British Patent 631,319, Nov. 1, 1949. Chem. Abs., vol. 44, 1950, p. 3700.

In the production of liquid and gaseous fuels by the conversion of carbonaceous materials into a gaseous mixture containing CO and H_2 followed by the catalytic treatment of the mixture to produce normally liquid hydrocarbons and a fuel tail gas, the liquid-gas product distribution is controlled by recovering the fuel tail gas, and a portion of this gas, in excess of the desired requirement for fuel gas, is recycled to the reaction for production of the CO–H_2 mixture from carbonaceous material. The proportion of tail gas thus recycled may be altered from time to time in accordance with changing fuel requirements.

3493. ———. Gas Manufacture. British Patent 680,545, Oct. 8, 1952. Chem. Abs., vol. 47, 1953, p. 4065.

Carbonaceous materials are converted to H_2 and CO in this continuous 2-stage process. In the 1st stage, pulverized coke is heated to 2,000° F. in a fluidized bed by partial combustion with preheated air. The heated coke is transported through a reactor tube, where it is partly gasified with superheated steam, to a 2d fluidized bed where additional gasification reduces the temperature to about 1,700° F. Excess solids are discarded, and the rest are recirculated to the 1st reactor.

3494. ———. Gas Separation in Hydrocarbon Synthesis. British Patent 657,014, 1951. Fuel Abs., 1951, abs. 4034.

Continuous process for removing CO_2 from a hydrocarbon synthesis tail gas with absorptive solutions. The CO_2 is then removed from solution by a stripping gas, which is preferably synthesis gas or CH_4. The effluent is then passed as feed to the reactor.

3495. ———. Gaseous Fuels. British Patent 640,907; appl. filed Sept. 10, 1946. Petroleum (London), vol. 13, 1950, p. 328.

Heating value of gaseous product from gasification of solid carbonaceous material is improved by passing the mixture through a fluidized hydrogenation catalyst under suitable conditions of temperature and pressure. The feed gas is preheated to conversion temperature before entering the converter. Temperature is maintained uniform, 500°–575° F. by supply and removal of heat at any point of the catalyst zone. A wide range of catalyst may be used and a pressure up to 2,000 p. s. i. Cooled catalyst may be returned downward in a vertical column suspended in gas to form a catalyst suspension of relatively low density, which is returned to the conversion zone under the pseudo-hydrostatic pressure of vertical column. Preheating is effected with heat of reaction or by indirect heat exchange with the hot catalyst or reaction products. Claims include gasification of solid materials with steam to produce CO–H_2 mixture. Purified coal gas may be added to the gas mixture in the conversion zone. Part of the product may be continuously recycled.

3496. ———. Gases for the Synthesis of Hydrocarbons. British Patent 641,945, Aug. 23, 1950; appl. filed Mar. 17, 1947. Chem. Abs., vol. 44, 1950, p. 11,068.

Gases containing CO and H_2 are produced in a 3-stage process, which comprises: (1) Passing a hydrocarbon gas over a catalyst consisting of Fe, Co, Ni, or mixtures thereof, with or without Zn; (2) maintaining the greater portion of the catalyst in the reactor in the form of a metal but passing a relatively small amount to an oxidizing zone wherein it is oxidized; and (3) withdrawing oxidized catalyst from this zone and recycling it to the reactor in an amount substantially stoichiometrically equivalent to the hydrocarbon feed so as to provide in the reactor 1 atom of O_2 combined as reducible metal oxide per atom of C. Generally 90–95% of the catalyst in the reactor should be in the metallic form. A desirable catalyst consists of Ni 90–95% and Fe 10–5% by weight.

3497. ———. Gasification of Carbonaceous Solids. British Patent 668,941, 1952. Fuel Abs., 1952, abs. 4758.

Gas mixtures containing CO and H_2 are made by passing a gas mixture containing steam and O_2 through a mass of finely divided carbonaceaus material maintained in a gasification zone at an elevated temperature and in the form of a dense turbulent fluidized bed having a well-defined upper level. There is incorporated in the mass a halide-yielding elemental halogen and/or volatile halogen compounds under the prevailing reaction conditions in an amount sufficient to inhibit formation of CO_2 in favor of CO formation.

3498. ———. Hydrocarbon Synthesis. British Patent 634,882, 1950; appl. filed Sept. 3, 1947. Fuel Abs., vol. 7, 1950, abs. 4896; British Abs., B, II, 1950, p. 1022.

In the fluid catalyst process for synthesizing hydrocarbons and oxygenated hydrocarbons from a feed gas containing CO and H_2, where the latter are forced into contact in a reaction zone with a fluidized bed of powdered Fe catalyst maintained at elevated temperature and pressure, the bed of catalyst is maintained in fluidized condition, as evidenced by a high heat transfer coefficient, by adding more coarsely ground Fe powder to the fluidized bed than that contained therein responsive to the tendency of the powdered Fe in the fluidized bed to disintegrate physically into particles of smaller particle size.

3499. ———. Hydrocarbon Synthesis. British Patent 643,606, Sept. 20, 1950; appl. filed Apr. 1, 1948; in United States June 30, 1947. Petroleum (London), vol. 14, 1951, p. 24; Chem. Abs., vol. 45, 1951, p. 5391.

Improvements, particularly in cooling means for the fluidized catalyst bed for better temperature control, are claimed and described by means of a diagram.

3500. ———. Hydrocarbon Synthesis. British Patent 651,559; appl. filed in United States Nov. 28, 1947. Petroleum (London), vol. 14, 1951, p. 228.

Describes method for the use and reconditioning of finely divided catalysts having high activity and selectivity and used in well-known fluid-solids technique. C deposits are removed without appreciable oxidation of the spent catalyst by reacting it in the fluidized state with an oxidizing gas at about 1,000° F. and pressure of 1 atm. under conditions of quantitative composition of oxidizing gas to form atmosphere in the regeneration zone with virtually no free O_2, and CO and CO_2 in such amounts that the ratio of partial pressure of CO_2/CO equals or is less than value of the equation

$$r=10\left(-1.170+\frac{1730}{t+460}\right),$$

where r is ratio and t temperature in F.° and the sum of the partial pressures of CO_2 and CO is less than value of

$$S=(1+r)\times 10\left(-9.25+\frac{16170}{t+460}\right),$$

where S is the sum of the partial pressures. Such oxidizing gas may therefore be O_2, steam, or CO_2. Means are provided to remove heat of reaction or

increase it as may be required. Inert gas may be added to permit working at higher pressure. Flue gas from the top of the regenerator is recycled to the oxidizing gas inlet of the regeneration zone in amount 2–8 times that produced in the reaction. This gas may be contacted with oxidizing gas in a separate chamber so that all O_2 is converted to C oxides or H_2O vapor before passing into the regenerator; exothermic reaction is divided.

3501. ———. Hydrocarbon Synthesis. British Patent 654,492; appl. filed in United States Aug. 5, 1947. Petroleum (London), vol. 14, 1951, p. 254.

Hydrocarbons and oxygenated compounds are synthesized from CO–H_2 gas mixture by contacting it with a fluidized bed of powdered Fe catalyst at high temperature and pressure. The catalyst is first subjected to a preconditioning treatment substantially under synthesis conditions (pressure about 400 p. s. i.) and thus converted into a form resistant to fragmentation. Synthesis is then continued with a gas mixture having a lower ratio of H_2: CO, preferably 2 : 1.

3502. ———. Hydrocarbon Synthesis. British Patent 655,685, 1951. Fuel Abs., 1951, abs. 2906.

CO and H_2 are reacted in contact with a fluidized bed of powdered Fe catalyst and under a H_2 partial pressure in the synthesis reaction zone of 150–275 p. s. i., including the total H_2 content of the fresh and recycled gases. A total pressure is maintained >350 p. s. i. but <800 p. s. i., a temperature of 650°–725° F., and a total gas feed rate of fresh and recycled gases of substantially 10–200 standard ft.^{3} per lb. of catalyst per hr.

3503. ———. Hydrocarbon Synthesis. British Patent 655,827, 1951. Fuel Abs., 1951, abs. 2900.

Fischer synthesis process uses a dense fluidized Fe catalyst, which becomes contaminated with waxy material formed during the synthesis. A portion of the catalyst is continuously or intermittently withdrawn from the reaction zone and mixed with a liquid hydrocarbon fraction boiling in the gas oil range. The slurry thus formed is hydrogenated. The partly reduced and dewaxed catalyst and the hydrogenated slurry are separated, and the catalyst is recycled to the synthesis zone.

3504. ———. Hydrocarbon Synthesis. British Patent 657,528, 1951. Fuel Abs., vol. 11, No. 1, 1952, abs. 341.

Hydrocarbons and oxygenated organic compounds are catalytically synthesized from CO and H_2 by pretreating a powdered Fe catalyst in the form of a fluidized bed with a gaseous mixture containing H_2 and CO in a ratio of 2 : 40, preferably 2 : 35, molecules of H_2 per molecule of CO in a carbiding zone at 500°–800° F. and at substantially atmospheric pressure. The carbided Fe catalyst so formed is contacted as a fluidized mass in a synthesis zone with a mixture of gases containing CO and H_2.

3505. ———. [Hydrocarbon Synthesis.] French Patent 914,030, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 178.

Hydrocarbon synthesis with fluid catalyst in part at high pressure.

3506. ———. [Hydrocarbon Synthesis.] French Patent 938,437, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 178.

Hydrocarbon synthesis with fluid catalyst and with extensive circulation of the reaction gases and products.

3507. ———. Hydrocarbon Synthesis Process. British Patent 627,905, Aug. 18, 1949; appl. filed Nov. 22, 1946. Fuel Abs., 1949, abs. 5013; Chem. Abs., vol. 44, 1950, p. 4228.

Feed mixture comprising CO : H_2=1 : 3 is introduced into a synthesis reaction zone. The feed mixture is further characterized in that the concentration of the CO_2 is maintained at a relatively high level so that the molecular ratio of $\frac{H_2-CO_2}{CO+CO_2}$ is not over 2. The reaction zone is kept at a temperature and pressure adapted to produce the desired synthesis reaction.

3508. ———. Hydrocarbon Synthesis Process. British Patent 630,950, Nov. 9, 1946. British Coal Utilisation and Research Assoc., Monthly Bull., vol. 14, No. 1, p. 22; Chem. Abs., vol. 44, 1950, p. 5081.

Improved Fischer synthesis employing an Fe, Ni, or Co catalyst, wherein the feed gases are diluted with steam (1–20 mol. % of total feed) and a portion of the catalyst is led continuously from the synthesis zone to the hydrogenation zone. The temperature is 550°–1,100° F., pressure 100–750 p. s. i. The catalyst is reduced in the presence of H_2 and then returned to the synthesis zone.

3509. ———. Hydrocarbon Synthesis With Fluidized Catalyst. British Patent 591,981, no date. Schmidt, J, Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 163.

3510. ———. Hydrocarbons From Carbon Monoxide and Hydrogen. British Patent 615,381, Jan. 5, 1949. Chem. Abs., vol. 43, 1949, p. 4447.

Activity of a fluidized Fe or Co catalyst is maintained at a substantially constant level by the use of 2 or more hydrogenation zones in series. Fresh or regenerated catalyst of relatively high activity is fed to the last zone and passes successively by overflow devices through other hydrogenation zones to the 1st zone, in which it has relatively low activity, and is withdrawn. H_2 and CO are fed to the 1st zone and flow through the series of zones countercurrent to the flow of catalyst. In each zone some conversion takes place. The 1st zone is the largest and the zones become successively smaller so that the superficial and space velocities throughout the system remain approximately constant. Gives flow diagrams.

3511. ———. Hydrogenation Catalysts. British Patent 649,464, Oct. 1, 1947. Chem. Abs., vol. 45, 1951, p. 7337.

Metal carbonyl hydrogenation catalysts, of highest disintegration resistance, are used in the synthesis of hydrocarbons from CO and H_2 employing the fluid-catalyst technique. Best supports for the catalysts, such as $Fe(CO)_5$, were found among the synthetic spinels, such as $ZnO \cdot Al_2O_3$, $Cr_2O_3 \cdot Al_2O_3$, $CuO \cdot Al_2O_3$. The metal carbonyl is formed in the 1st zone and decomposed to deposit the metal on the carrier in a 2d zone whence the exit gases are recycled to the 1st zone. Other suitable supports are stable carbonates particularly those of Ba, Ca, or Zn, as well as active C, ordinary soft glass, and Si–Al_2O_3 composites.

3512. ———. Hydrogen-Containing Gases. British Patent 616,710, Jan. 26, 1949. Chem. Abs., vol. 43, 1949, p. 4836.

Mixture of CO and H_2 is manufactured in a 2-stage process, which comprises: (1) A mixture of steam, a hydrocarbon normally gaseous, and CO_2 is caused to react in the presence of a suitable catalyst at an elevated temperature and a pressure above atmospheric to form a product containing CO, H_2, CO_2, H_2O, and unchanged hydrocarbons; and (2) the product from stage 1 is passed into an oxidizing zone where it comes into contact with a gas containing free O_2, so that it is burned and the remainder of the hydrocarbon is largely converted to CO and H_2O. The 1st, or reformer, stage may be operated with gas throughputs in the range 500–4,000 vol. of theoretical H_2 plus CO per vol. catalyst per hr. Theoretical H_2 plus CO is

defined as the total molecules of H_2+CO obtained by complete conversion of the hydrocarbons with steam. Maximum re-former catalyst operating temperatures range 704°–816° to obtain hydrocarbon conversions of approximately 65–85%. At these temperature levels the operating pressure may be in the range 15–150 p. s. i. g. In the oxidizing stage the throughput may lie in the same volume range, with a minimum operating temperature 816°–982°, at pressures of 15–150 p. s. i., as set by the re-former operation. The addition in this stage of 0.25–0.45 mol. O_2 per C atom is preferable.

3513. ———. Improved Fischer-Tropsch Catalyst. British Patent 593,940, Oct. 29, 1947. Chem. Abs., vol. 42, 1948, p. 2088.

Catalysts suitable for use in fluid-flow processes, having improved attrition characteristics, are prepared using specially treated bentonite clay as the carrier. Filtrol that has been treated with a mineral acid, such as HCl, H_2SO_4, or HNO_3, is further treated with a 10% concentration of HF or H_2SiF_6 for ½ hr., after which it is separated and dried. Describes 2 methods of impregnating the carrier. In the 1st, H_2O soluble salts of Group VIII metals and H_2O-soluble salts of promoter metals, for example, Th, Mg, U, Mn, or Al, are mixed and taken up in suspended particles of treated clay, which is then dried and calcined at 400°–600° F. for 4–16 hr. The mass is then reduced by H_2 at 600°–900° F. in 2–6 hr., the H_2 having a space velocity of 3,000–8,000 vol. per vol. per hr. The final composition may contain 25–40% of free Group VIII metal and 3–10% of the promoter metal. The catalyst may be ground and pilled before reduction. In the 2d method the H_2O-containing impregnated clay is made alkaline by adding $(NH_4)_2CO_3$, K_2CO_3, or Na_2CO_3, which precipitates the metal salts as carbonates. The H_2O remaining is drained off and the impregnated clay calcined as before.

3514. ———. Improved Hydrocarbon Synthesis. Fluidized Bed. British Patent Appl. 4,538, 1948. Chem. Age, vol. 60, 1949, p. 389.

Catalyst is in finely powdered form arranged in beds through which an upward current of gas or vapor is passed to maintain a dense turbulent mass. The difficulty of deposition of C on the catalyst has been eliminated by using relatively high pressure in the reaction zone, ranging up to approximately 400 p. s. i., together with high H_2 partial pressure. Physical disintegration or other deterioration of the catalyst is also avoided. Operating conditions are controlled to give per $m.^3$ of $CO–H_2$ mixture, a minimum yield of 190 cc. butane and higher boiling constituents, or a minimum yield of propane and higher boiling constituents. The temperature of the reaction should be 650°–725° F. The catalyst may be any of the unsuitable Fischer type (Fe group), or Fe base, such as the synthetic NH_3 catalyst, pyrites ash catalyst, reduced red Fe oxide.

3515. ———. Improved Hydrocarbon Synthesis. British Patent 653,834, May 30, 1951. Chem. Abs., vol. 46, 1952, p. 1234.

Oxygenated hydrocarbons are separated from the vaporous products obtained by the hydrocarbon-synthesis reaction of H_2 with CO. The vaporous products are cooled to 40°–100° F., and an oil phase and an aqueous phase are obtained. The 2 phases are separated, and the aqueous phase is fractionally distilled to yield mainly EtOH,, PrOH, BuOH, and AmOH.

3516. ———. Improvements in or Relating to Hydrocarbon Synthesis. British Patent 652,477, Apr. 15, 1951. Chem. Abs., vol. 45, 1951, p. 9837.

The economics of the catalytic synthesis of hydrocarbons and oxygenated products from CO and H_2 are improved by better utilization of synthesis tail gas. This tail gas from a 1st synthesis stage, after suitable CO_2 removal, is converted by use of free O_2 in a secondary gas generator to produce a secondary synthesis gas, which is converted to synthesis products. Tail gas from the 2d synthesis stage is converted into synthesis gas and processed in a 3d synthesis stage.

3517. ———. Improvements in or Relating to the Production of Synthesis Gas Mixtures Containing Carbon Monoxide and Hydrogen. British Patent 635,913, Apr. 19, 1950; appl. filed May 20, 1947; in United States, Sept. 27, 1946; 6 claims. Chem. Abs., vol. 44, 1950, p. 7515.

Liquefied bituminous carbonaceous raw material is burned in a single reaction vessel containing a fluidized bed of refractory material. Pure O_2 with regulated quantities of added steam to supply H_2 is used. The temperature in the lower part of the retort is 1,500°–2,000° F., in the upper part 3,000°. In some instances, to produce a gas of certain composition, CO_2 is introduced into the bottom of the reactor with the O_2 and steam.

3518. ———. Improvements Relating to the Synthesis of Oxygenated Organic Compounds. British Patent 664,974, Aug. 3, 1949. British Abs., B II, 1952, p. 446.

Oxygenated compounds (especially those containing S), which are obtained from olefins (preferably $C_6–C_8$) by catalytic treatment with CO and H_2 at high temperature and pressures, are hydrogenated in the liquid phase to the corresponding alcohol more efficiently using a S-insensitive catalyst of good mechanical strength and selective activity to alcohol formation. The catalyst consists essentially of Mo sulfide (5–15 wt % of Mo calculated as MoO_3) on a C support. Hydrogenation is carried out at 400°–500° F. and 300–3,500 p. s. i. and at a feed rate of 0.2–1.0 vol. of oxygenated compounds per vol. of catalyst space per hr. and 5,000–15,000 $ft.^3$ of H_2 per bbl. of oxygenated compounds. The catalyst is prepared by impregnating C pellets with either $(NH_4)_2MoO_4$ and drying and heating in a stream of H_2S at 800°–900° F. or with a solution of MoO_3 in $(NH_4)_2$ S and drying to produce MoS_2.

3519. ——— (I. G. Farbenindustrie A. G.). [Improving the Antiknock Properties of Motor Fuels.] German Patent Appl. St 59,586, OZ 12,075, filed Mar. 27, 1940 (*Cl. 23 b.*). FIAT Reel 163, frames 1,486–1,495; PB 25,607.

Gasolines of aliphatic nature, such as those obtained by reduction of CO with H_2, may have their antiknock properties improved by a pressure hydrogenation in the vapor state under pressures of 5–30 atm., temperatures of 450°–550°, a H_2 partial pressure of 20–70% of the total pressure, but not to exceed 25 atm., and in presence of catalysts containing oxides of metals of group 6 on active silica gel or alumina. Suitable proportions of feed are 0.6 $m.^3$ H_2 per kg., of raw material and 1 kg. of raw material per l. of catalyst space per hr. A yield is obtained of 78% gasoline boiling up to 200°, containing 25% aromatic hydrocarbons, 33% of fractions boiling up to 100°, and an octane no. of 65.

3520. ———. [Iron Catalyst.] French Patent 934,-109, May 12, 1948; appl. filed Oct. 2, 1946. Chim. et Ind., vol. 62, No. 1, 1949, p. 49.

In the production of hydrocarbons from CO and H_2, the gas mixture is contacted with a catalyst consisting of sintered Fe pyrites reduced at 175°–345° under raised pressure. The catalyst may advantageously be impregnated with a solution of an activating substance, such as Na_2CO_3, K_2CO_3, KCl, and dried at 115° before being charged into the reactor.

3521. ———. Manufacture of Iron Catalysts and of Liquid Hydrocarbons and Oxygenated Compounds by the Aid of Such Catalysts. British Patent 620,775,

Mar. 30, 1949. Fuel Abs., vol. 7, 1950, abs. 3159; Chem. Abs., vol. 43, 1949, p. 6762.

FeO catalyst, suitable for catalytic synthesis of hydrocarbons or oxygenated compounds, is made by impregnating red FeO or other FeO powder with K_2CO_3 solution or other promoter, drying, sintering in a reducing atmosphere at 1,200°–1,600° F., and grinding. The resulting catalyst is easily fluidized and has a long effective life.

3522. ———. Metal Treatment of Oxo Alcohols. British Patent 678,997, Sept. 10, 1952. Chem. Abs., vol. 47, 1953, p. 2769.

See United States Patent 2,585,816 (abs. **2219**).

3523. ———. Mixtures of Carbon Monoxide and Hydrogen. British Patent 634,933, Mar. 29, 1950; appl. filed Apr. 21, 1947. Chem. Abs., vol. 44, 1950, p. 6605.

Reaction of gaseous hydrocarbons with Fe oxides to produce mixtures of CO and H_2 suitable for Fischer-Tropsch synthesis progresses more smoothly with high selectivity for H_2 and CO and minimum production of C in the presence of free Fe. Maximum atomic ratio of O to free Fe should be 6, and approximate atomic ratio of O to total Fe is specified to be 0.5–1.25. Describes process employing the technique of fluidized solids.

3524. ———. Mixtures of Carbon Monoxide and Hydrogen. British Patent 636,206, Apr. 26, 1950; appl. filed Mar. 31, 1947. Chem. Abs., vol. 44, 1950, p. 7515.

Example: For the preparation of 415,000,000 ft.^{3} of synthesis gas per day containing 175,000,000 ft.^{3} H_2, 175,000,000 ft.^{3} CO, and 65,000,000 ft.^{3} CO_2, from a coal containing 4.2 lb. H_2 per 100 lb. C with Fe oxide as the O_2 carrier, the suitable operating conditions are: Coal feed, 188 ton per hr.; process steam feed, 440,000 lb. per hr.; air feed to regenerator, 315,000 standard ft.^{3} per min.; solids circulated from regenerator to generator, 1,200 ton per min.; generator temperature, 1,800° F.; generator pressure, 100 p. s. i. g.; regenerator temperature, 1,900° F.; regenerator pressure, 1 p. s. i. g.; approximate height of standpipe from regenerator to generator, 100 ft.; preheating temperature of steam and air, 1,100° F.

3525. ———. Motor Fuel and Aromatic Hydrocarbons From Fischer Synthesized Hydrocarbons. British Patent 585,352, Feb. 5, 1947. Chem. Abs., vol. 41, 1947, p. 5710.

Hydrocarbons formed by Fischer synthesis are separated into a napththa fraction and a gas-oil fraction. The former is catalytically hydroformed and the latter catalytically cracked by conventional processes. The hydroformed products are fractionated into a light fraction, a heavy fraction, and an intermediate fraction rich in aromatics. The products of the cracking step are fractionated into gasoline, a light fraction, a heavy fraction, and a fraction rich in aromatic compounds. Aromatic hydrocarbons are separated from either or both of the fractions rich in aromatic compounds by solvent extraction, and the light and heavy fractions are blended to form a gasoline.

3526. ———. [Oxidation of Methane.] French Patent 934,111, May 12, 1948; appl. filed Oct. 2, 1946. Chim. et ind., vol. 61, No. 3, 1949, p. 252.

CH_4 is passed over a bed of oxide of Fe then over a reforming catalyst at elevated temperature. A mixture of CO and H_2 is obtained in the ratio of about 2 : 1. The reforming catalyst may be oxide of Ni deposited on magnesia.

3527. ———. Oxo Synthesis Process. British Patent 637,389, May 17, 1950. Fuel Abs., vol. 8, No. 2, 1950, abs. 1097; Chem. Abs., vol. 45, 1951, p. 173.

Continuous process is employed for the production of Oxo synthesis products that comprises the utilization of at least 2 reaction zones. Feed comprising olefins together with synthesis gas is introduced into an initial reaction zone containing a supported Co, Ni, or Fe catalyst along with H_2. Thus, the catalyst metal carbonyl, which is formed in the initial zone, is decomposed, and the metal itself collects in the secondary reaction zone. After the catalyst in the initial reaction zone is depleted to a predetermined critical minimum quantity, the flow of the stream is reversed with respect to the initial and secondary reaction zones.

3528. ———. Oxygenated Compounds. British Patent 629,915, Sept. 30, 1949; appl. filed Aug. 7, 1947. Chem. Abs., vol. 44, 1950, p. 4492.

Improved yields of alcohols are obtained by flushing the products of the synthesis, aldehydes from olefins, CO, and H_2, with H_2 before the hydrogenation of the aldehydes to alcohols. This flushing removes CO and metal carbonyl formed from the catalyst; the flush gases can be used for the synthesis.

3529. ———. Oxygenated Organic Compounds. British Patent 640,115, July 12, 1950. Chem. Abs., vol. 44, 1950, p. 10,302.

By washing a synthetic olefin with alkali to remove acidic components, the yields on subsequent oxygenation and hydrogenation to give alcohols are increased. Thus, a mixture of H_2 : CO=2 : 1 is passed over an Fe catalyst containing Al_2O_3, 1.5 and K_2O, 1.5% at 650° F. and 400 p. s. i. The product fraction, b. 250°–300° F., gravity 53.4° A. P. I., hydroxyl no. 9, carbonyl no. 274, saponification no. 42, acid no. 32.8, and Br no. 92, was washed with 5% NaOH at 70°–90° F. for 12 min. to give a hydrocarbon mixture of gravity 56.5° A. P. I. hydroxyl no. 23, carbonyl no. 33, saponification no. 11, acid no. 0.9, and Br no. 88. A sample of the untreated olefin was caused to react with H_2 : CO=1.2 : 1 in the presence of 11% catalyst, Co, 31.2, Cu, 0.9; ThO_2, 5.6; and SiO_2, 62.3% at 275° F. and 3,000 p. s. i. for 5 hr. to give a 16% oxygenated product. The treated olefin under similar conditions gave 86% conversion. The oxygenated product is hydrogenated in the presence of Ni on kieselguhr, or in the presence of the oxygenation catalyst, to yield alcohols.

3530. ———. Oxygenated Organic Compounds. British Patent 659,712, Oct. 24, 1951. Chem. Abs., vol. 47, 1953, p. 146.

In the reaction of olefins with CO and H_2 to form oxygenated organic compounds in the presence of a Co carbonyl catalyst, a continuous process is described for removal of the catalyst from the product as metallic Co and subsequent conversion of the Co to the carbonyl in the liquid phase, with either pentane or some of the olefinic reaction mixture as solvent. 2 decobalters connected to the reaction vessel are used alternately; while 1 carries out separation of the catalyst from the reaction product, the other is treated with CO–H_2 gas mixture used in the initial synthesis under conditions favorable to the formation of the carbonyl and in the presence of a solvent. If pentane is used in this step, it is partly removed by distillation before the catalyst is returned to the reaction vessel. Gives 2 diagrams of the apparatus.

3531. ———. Oxygenated Organic Compounds. British Patent 670,898, Apr. 30, 1952. Chem. Abs., vol. 47, 1953, p. 3335.

See United States Patent 2,530,989 (abs. **2584**).

3532. ———. Preparation of Catalysts. British Patent 657,224, Feb. 21, 1949. British Abs., B, I, 1952, p. 38.

Fluidizable sintered Fe catalyst, resistant to fouling and disintegration, and for use in the synthesis of hydrocarbons from CO and H_2, is prepared by impregnating red Fe oxide powder with alkali-metal salt promoter, for example, K_2CO_3 0.5–5 wt %, reducing in pill form at 485°–595° with H_2 (750–1,500 atm.) then breaking the pills into granules of <40-mesh, and sintering the latter at 680°–905° in nonoxidizing gas, for example, H_2 (100–200 vol. per vol. of catalyst per hr.).

3533. ———. Process and Catalyst for Synthesis of Hydrocarbons. British Patent 668,140, 1952. Fuel Abs., vol. 11, 1952, abs. 4028.

Recycling is eliminated, and a high yield of liquid olefins is obtained by a low-pressure process in which the catalyst is a physical mixture of an Fe catalyst promoted by an alkali metal salt and a finely divided support, which carries as active component a mixture of Co and Fe promoted with a minor amount of Th.

3534. ———. [Process for Carrying Out Exothermic Reactions.] French Patent 830,289, July 26, 1938. Chem. Abs., vol. 33, 1939, p. 1181.

In conducting exothermic gaseous reactions, the temperature of the reacting gases is maintained within the desired limits by passing the gases through the reaction zone in contact with, but countercurrent to, a solid catalyst maintained in suspension in a liquid, which is present in sufficient quantity to absorb the heat liberated during the reaction. When nongaseous reaction products are formed, they are removed from the reaction zone with the catalyst suspension and then separated from the catalyst. The process is applicable to the production of liquid hydrocarbons suitable for use as motor fuel by passing CO and H_2 in the ratio of 1:2 parts by volume over a catalyst such as Ni, activated by an oxide of Al, Mn, or Th, at a temperature of 190°–215°.

3535. ———. [Producing Fuels.] French Patent 933,719, Sept. 18, 1946, in United States Dec. 22, 1945. Chim. et ind., vol. 60, No. 4, Oct. 1948, p. 349.

Nonvolatile carbonaceous material is gasified by means of heat and steam to obtain CO and H_2, which are treated catalytically to produce normally liquid hydrocarbons and a combustible gas. The liquid hydrocarbons are withdrawn, and a part of the combustible gas is recycled in the thermal treatment of the carbonaceous material.

3536. ———. Production of Alcohols by the Catalytic Hydrogenation of Carbonyl Compounds. British Patent 666,066, May 19, 1948. British Abs., B, II, 1952, p. 580.

Improved yields of alcohols are obtained from the hydrogenation of C_{7-9} carbonyl compounds using NiS and WS_2 catalysts under the following conditions: Temperature 400°–450° F., liquid feed rate 0.5–1.0 vol. per vol. per hr. and a catalyst age of <1,500 hr. and then distilling off the alcohols. The carbonyl compounds used are produced by the Oxo synthesis from olefins, CO, and H_2 and are 95–100% converted by hydrogenation. For example, an oxygenated material produced by treating olefinic C_7-hydrocarbon feedstock of b. p. 180°–210° with H_2 and CO in the presence of Co oleate catalyst at 325°–375° F. and 2,800–3,200 p. s. i. is hydrogenated in fixed-bed batch operation using a catalyst of NiS 90 and WS_2 10 wt. %. In a run designed to give complete hydrogenation, under the following conditions: 410° F., 2,700 p. s. i., liquid feed rate, 1.01 vol. per vol. per hr.; and catalyst age, 760 hr., distillation of products gives unconverted olefin feed (<215°), 18.4; cracked products (215°–265°), 3.6; unhydrogenated carbonyl compounds (265°–340°), 2.0; alcohols (340°–370°), 60.6; and bottoms, 15.4%.

3537. ———. Production of Fuel Gas. British Patent 632,386, 1949. Fuel Abs., vol. 7, 1950, abs. 3165.

This as a process for increasing the heating value of tail gas obtained by reacting CO and H_2 in presence of Fischer synthesis conditions and removing normally liquid synthesis products from the total synthesis product, which comprises contacting the tail gas in a conversion zone with a hydrogenating catalyst under hydrogenating conditions adapted for the substantially exclusive formation of saturated normally gaseous hydrocarbons whereby a final hydrogenated tail gas is produced, which contains a normally gaseous mixture of high heating value having a H_2 content amounting to only a small fraction of that of the initial tail gas.

3538. ———. Production of Gases Containing Carbon Monoxide and Hydrogen From Hydrocarbons. British Patent 657,585, 1951. Fuel Abs., vol. 11, No. 1, 1952, abs. 335.

Hydrocarbon in gaseous form is passed upward through a reaction zone kept at an elevated temperature and containing a catalyst bed comprising metallic Cu on a finely divided support at such a velocity that the catalyst remains suspended in the gas in a dense, highly turbulent form. Meanwhile a quantity of CuO supported on a finely divided carrier equivalent to the amount of hydrocarbon fed to the reaction zone is fed thereto and the product gas continuously removed therefrom, along with deposited metallic Cu on a carrier material.

3539. ———. Production of Water Gas From Solid Carbonaceous Materials. British Patent 626,743, July 20, 1949; appl. filed Feb. 14, 1947. Fuel Abs. 1949, abs. 4812. British Abs., I, B, 1950, p. 260; Chem. Abs., vol. 44, 1950, p. 8093.

Gas mixtures containing CO and H_2 are produced from solid carbonaceous materials and steam by passing the latter into a gasification zone containing a mass of finely divided solid carbonaceous material having an oxidation reactivity of T_{15}=200°–250° and T_{75}=250°–300° under such conditions as to form a dense fluidized mass of finely divided solid. The residual solid is removed from the gasification zone, subjected to treatment in the form of a fluidized ebullient mass with an oxidizing gas mixture to burn off the residual carbonaceous material and thereby heat the residual solid to a high temperature, and the heated solid recycled to the gasification zone to use the sensible heat of the heated solid to supply at least part of the heat required in the gasification zone. T_{15} and T_{75} are the temperatures at which the rate of heat release by oxidation of a sized sample becomes great enough to raise its temperature at rates of 15° per min. and 75° per min., respectively. The preferred highly reactive carbonaceous starting material is low-temperature coke obtained by carbonizing coal at temperatures, preferably 316°–510°, to an oxidation reactivity of T_{15}=200–10°, and T_{75}=250–60°. When low-temperature coke of this type is charged to a fluid gas generator, the gasification temperature may be lowered as much as 90°–180° beneath the level required for conventional charging materials, such as coal or high-temperature coke, without affecting steam conversion under otherwise equal conditions. Steam conversions of 98–99% may be achieved at temperatures of about 1,038°, whereas at 927° the steam conversion still amounts to about 80%. Oother suitable carbonaceous materials include certain bituminous or subbituminous coal, lignites, and brown coals uncoked, or coked at temperatures preferably 316°–538°.

3540. ———. Purification of a Contaminated Catalyst. British Patent 615,647, Jan. 10, 1949. Chem. Abs., vol. 43, 1949, p. 3994.

Solid Fischer-Tropsch catalyst, which contains an active hydrogenating constituent and is contaminated

with waxy and oily deposits, is purified by first subjecting it to the action of a H_2-containing gas under conditions to cause destructive hydrogenation of at least a part of the deposits and thereafter extracting the catalyst with a solvent for these deposits. Desirable conditions for the destructive hydrogenation are: 182°–260° and 0–300 lb. per in.^{2} gage pressure when a Co-type catalyst is used and 232°–399° and 25–350 lb. with an Fe-type catalyst.

3541. ———. Purification of Methanol. British Patent 660,773, Nov. 14, 1951. Chem. Abs., vol. 46, 1952, p. 8143.

Mixtures of MeOH and oxygenated hydrocarbons were fed to an intermediate point of a fractional distillation column and H_2O was fed to the top of the column at such a rate as to keep the internal reflux >65 mole % H_2O. The overhead products contained the oxygenated hydrocarbons, whereas aqueous solutions of MeOH were drawn off at the bottom.

3542. ———. Purification of Water-Insoluble Oxo Alcohols. British Patent 681,296, Oct. 22, 1952. Chem. Abs., vol 47, 1953, p. 2965.

See United States Patent 2,595,763 (abs. **314**).

3543. ———. [Purifying Synthesis Gas.] French Patent 930,178, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 167.

Synthesis gas is purified by passing over Cu on Al_2O_3 at 160°–300°.

3544. ———. Recovery of Fatty Acids From Dilute Aqueous Solution. British Patent 658,458, Sept. 12, 1949. British Abs., B, II, 1952, p. 6.

Fatty acids found in low concentration in the aqueous layer resulting from hydrocarbon synthesis reactions can be recovered by treating the dilute acid solution with a Bi compound (Bi_2O_3) to form Bi salts of the fatty acids, separating the salts, and regenerating the fatty acids from the salts by treating the precipitate with steam, H_2SO_4 or SO_3. The process used for recovering AcOH consists of feeding the aqueous solution into the lower portion of a reactor containing Bi_2O_3 such that the point of entry is < the level of the oxide. A colloidal suspension of BiOAc is formed, which overflows from the reactor zone and is coagulated with an electrolyte and then treated with H_2SO_4 to regenerate the AcOH.

3545. ———. [Refining of Hydrocarbon Oils From the Fischer-Tropsch Synthesis.] French Patent 921,299, May 2, 1947; appl. filed Feb. 5, 1946. Chem. Zentralb., 1947, II, p. 764.

Oils are fractionated into gasoline b. up to 216° and gas oil b. 226°–343°. The gasoline is reformed over oxidizing catalysts in presence of H_2 496°–510° and at 10.5–28 atm. pressure. The reformed gasoline is then fractionated into 3 fractions b., respectively, 54°–99°, 99°–121°, and above 121°, which are mixed with the gasoline fraction from the cracked product of the gas oil 440°–496°.

3546. ———. Removal of Cobalt From Olefin-Carbon Monoxide-Hydrogen Reaction Mixtures. British Patent 682,177, Nov. 5, 1952. Chem. Abs., vol. 47, 1953, p. 6434.

See United States Patent 2,596,920 (abs. **3364**).

3547. ———. Removal of Wax Contaminants From Catalysts. British Patent 614,406, Dec. 15, 1948. Chem. Abs., vol. 43, 1949, p. 3994.

Soluble waxy and heavy hydrocarbon contaminants are removed from finely divided catalysts used in the production of hydrocarbons from CO and H_2 by passing the catalyst material continuously as a slurry countercurrent to a stream of solvent, which has also been used to make the slurry. The preferred operation involves the use of enough oil to form a slurry having 1–4 lb. catalyst per gal. The mixer preferably is operated at 93°–121° and retains the slurry 0.25–2 hr. The slurry flows from the bottom of the mixer into the top of a set of vertical-tube washer elements arranged in parallel, and the catalyst settles through the solvent to the bottom. For good washing conditions 0.01–1.0 gal. upward-flowing solvent is used per lb. of slurry, and the upward average liquid velocity ranges 0.1–1.5 in. per minute. The length of the tube elements provides a washing time, which may range 0.5–6 hr. Baffles in the tube elements are particularly effective in promoting contact between catalyst and solvent when the upward flowing solvent is introduced in surges.

3548. ———. Separation of Hydrocarbons and Oxygenated Compounds From Mixtures. British Patent 664,525, 1952. Fuel Abs., vol. 11, No. 4, abs. 3123; Chem. Abs., vol. 46, 1952, p. 5295.

Process for separation of olefins from the mixture of hydrocarbons and oxygenated organic compounds produced in the Fischer-Tropsch synthesis process comprising treating the mixture with a solvent that can remove the oxygenated organic compounds selectively to form an extract phase containing the oxygenated organic compounds and a raffinate phase, separating this raffinate phase, and treating it with a solvent or adsorbent that will remove selectively the aromatic hydrocarbons, condensed ring hydrocarbons, and conjugated hydrocarbons to leave a 2d raffinate phase from which olefins suitable for polymerization to produce lubricating oil stocks may be separated.

3549. ———. Separation of Oxygenated Organic Compounds by Distillation. British Patent 655,698, Sept. 15, 1948. British Abs., B, II, 1952, p. 4.

Mixture of oxygenated compounds obtained during the Fischer-Tropsch synthesis or by oxidation of hydrocarbons is separated into components by distillation in presence of a large volume % of H_2O. Thus, an aqueous layer containing alcohols 84.6, ketones and aldehydes 11.2, esters 0.2, and acids 4 mol.-% at 91° is passed at 485 cc. per hr. to the midpoint of a 1-in.-diameter perforated plate column of 60 plates, while adding H_2O at 94° to the top of the column at 945 cc. per hr. with overhead temperature 84° and reflux ratio 15 : 1; 6.2% of material (ketones, aldehydes, esters) is collected as overhead and the bottoms fraction, comprising acids and alcohols, is passed at 91° into a 2d distillation zone at 1,310 cc. per hr. (reflux ratio 5 : 1). Alcohols are removed at 79° as overhead, and a solution of acids in H_2O is withdrawn from the bottom and recycled to the 1st column. The feed may be initially distilled to separate it into 2 fractions, 1 within the range of C_{1-2}–C_{1-3} alcohols, and the other C_{3-5}; both fractions are then subjected to extractive distillation as above.

3550. ———. Synthesis of Alcohols. British Patent 671,608, May 9, 1950. British Abs., B, II, 1952, p. 796; Chem. Abs., vol. 47, 1953, p. 4356.

Olefins are passed with CO and H_2 over a carbonylation catalyst (Co compound) at an elevated pressure and temperature. The product (a liquid mixture of aldehydes, H_2O, dissolved catalyst, and catalyst carbonyl) is dehydrated to about 0.5% H_2O content, subjected to heat and an inert stripping gas to remove catalyst, and then hydrogenated in presence of 8 wt. % of H_2O at 400°–550° F., under pressure of 2,800–3,200 p. s. i., over a Mo sulfide catalyst on activated C. High yields of alcohols of 1 more C than the olefins used are obtained.

See also British Patent 672,349 (abs. **3454**).

3551. ———. Synthesis of Hydrocarbons. British Patent 598,041, Feb. 9, 1948; appl. filed Aug. 29, 1945. British Abs., I, B, 1948, p. 386; Chem. Abs., vol. 42, 1948, p. 5645.

Catalytic synthesis of hydrocarbons from CO and H_2 is effected in 2 stages, stage A employing a fluidized powdered catalyst under operating conditions that preclude the formation of liquid hydrocarbons and waxes and stage B, 1 or more stationary beds of hydrogenation catalyst in which liquid hydrocarbons are formed. A mixture containing about 2 mols. of H_2 per mol. of CO enters the 1st reactor at <350°, 15–125 p. s. i. through a powdered (100–400 mesh) Co catalyst activated with ThO_2, while the temperature is maintained 205°–260°. With Fe catalysts, a $CO:H_2$ mol. ratio of 1:1 and 40–250 p. s. i. pressure 260°–343° are preferred. After scrubbing and removing entrained catalyst, the tail gas passes to the 2d reactor containing granular or pelleted catalyst, in which the preferred conditions for Co catalysts are 191°–232° and 15–125 p. s. i. and for Fe catalysts 260°–343° and 40–250 p. s. i. on the 1st reactor. The temperature is rigidly controlled by charging relatively small amounts of catalyst with the reactants, adding more catalyst as the rate of reaction diminishes considerably, and by using internal cooling tubes. Gasoline and gas oil are recovered from stage B.

See also United States Patent 2,434,537 (abs. **147**).

3552. ———. Synthesis of Hydrocarbons. British Patent 618,068, 1949. British Abs., II, B, 1949, p. 846.

Describes continuous process for the production of hydrocarbons, including normally liquid hydrocarbons, by forming a synthesis gas mixture of H_2 and CO and subjecting this to a synthesis reaction in the presence of a finely divided Fischer synthesis catalyst material maintained in fluidized form by the passage of the gas mixture therethrough, wherein a higher weight ratio of catalyst to reactant gas than can be obtained with a reactant gas alone is maintained by supplementing the reactant gas with a sufficient quantity of steam and separating the steam from the product by condensation.

3553. ———. Synthesis of Hydrocarbons. British Patent 631,682, 1949. Fuel Abs., vol. 7, 1950, abs. 2131.

Method of synthesizing hydrocarbons and oxygenated hydrocarbons that comprises feeding a mixture containing CO and H_2 to a 1st reaction zone containing a bed of fluidized powdered Fe or Co catalyst, maintaining the 1st reaction zone at elevated temperature and pressure, permitting the reactants to remain in the 1st zone for enough time to effect a restricted H_2 conversion, withdrawing a crude product from the 1st zone, cooling the product to form a condensate and gaseous fraction, withdrawing the latter from the cooling zone, charging a feed mixture comprising the gaseous fraction and containing a ratio of $H_2:CO$ higher than that in the mixture fed to the 1st zone to a 2d reaction zone containing a bed of fluidized powdered Fe or Co catalyst at a higher temperature than that of the 1st zone, permitting the reactants to remain in the 2d zone for enough time to effect the desired conversion, withdrawing the product from the 2d zone and causing it to pass to a cooling zone, and recovering from the cooling zone the normally liquid products formed in the 2d zone.

3554. ———. Synthesis of Hydrocarbons. British Patent 634,534, 1950; appl. filed Sept. 11, 1947. Fuel Abs., vol. 7, 1950, abs. 4895.

CO and H_2 in synthesis proportions and conditions are contacted with a fluidized suspension of finely divided catalyst. The amount of catalyst in the suspension is controlled at a concentration low enough to permit conversion and resultant heat release at a substantially uniform rate over an extended path of contact between the reactant gases and the catalyst. The unreacted CO and H_2 are withdrawn from the reaction zone and contacted with a dense, turbulent, fluidized mass of finely divided synthesis catalyst under conditions such that substantial completion of the conversion takes place.

3555. ———. Synthesis of Hydrocarbons. British Patent 650,794, Aug. 14, 1947. Ind. Chemist, vol. 27, 1951, pp. 229–230.

Catalysts for the synthesis of hydrocarbons are made of Fe, Co, or Ni microspheres and promoters such as KF or Na_2CO_3. Example: Fe spheres made by the metallization process were found to contain 87% of spheres of 80–120μ in size. They were hollow and of a substantially crystalline structure of Fe_3O_4. They were impregnated with 5% KF and used for the synthesis of hydrocarbons by fluidization. Catalysts less subject to attrition were produced.

3556. ———. Synthesis of Hydrocarbons. British Patent 656,122, 1951. Fuel Abs., 1951, abs. 4033.

Gas-liquid distribution in the reaction products is adjusted by regulating the ratio of $H_2:H_2+C$ in the feed-gas mixture.

3557. ———. Synthesis of Hydrocarbons. British Patent 671,490, May 7, 1952. Fuel Abs., 1952, abs. 516; Chem. Abs., vol. 46, 1952, p. 9830.

Hydrocarbons and oxygenated organic compounds are produced by contacting carbonaceous solids with an oxidizing gas containing steam so as to generate a gas mixture containing CO and passing this mixture to a synthesis zone. Gas generation and synthesis steps are conducted at approximately the same temperature.

3558. ———. Synthesis of Hydrocarbons and Catalysts Therefor. British Patent 632,961, 1949. Fuel Abs., vol. 7, 1950, abs. 3160.

Fe-containing catalyst, suitable for use in promoting the synthesis of hydrocarbons from CO and H_2, is formed by incorporating a fluoborate into Fe oxide, Fe hydroxide, or an Fe oxide ore in amounts such that the catalyst contains approximately 0.2–10 wt %, based on the Fe present, of the fluoborate and reducing at least a part of the Fe oxide to the metallic stage before or after incorporation of the fluoborate.

3559. ———. Synthesis of Hydrocarbons and Oxygenated Derivatives. British Patent 653,915, May 19, 1948. British Abs., B, I, 1951, p. 864. Chem. Abs., vol. 46, 1952, p. 712.

1:1–2 mixture of H_2 and CO, containing 2–8 vol. % of moisture is passed over an Fe group catalyst such as Fe promoted by 1–8% of an alkali-metal compound (K_2O) at 175°–315° per 200–700 p. s. i. (space velocity 2–30, preferably 10 $ft.^3$ per lb. of catalyst per hr.) to give oxygenated hydrocarbons. After separation of the latter, unchanged gases are passed at 10–75 $ft.^3$ per lb. of catalyst over spent catalyst at 295°–400° per 200–500 p. s. i. to give hydrocarbons useful as motor fuel. Addition of steam to the synthesis gas minimizes deposition of C on the catalyst.

3560. ———. Synthesis of Motor-Fuel Hydrocarbons. British Patent 591,989, Sept. 4, 1947; appl. filed May 8, 1944. Fuel Abs., vol. 3, 1948, abs. 147; Chem. Abs., vol. 42, 1948, p. 740.

Powdered Fischer-Tropsch catalyst is charged to a vertical reaction zone. Upwardly through this catalyst is passed a stream of H_2 and CO at a velocity of 0.5–10 ft. per sec. The catalyst is thereby maintained in a highly agitated, turbulent, and ebullient state. An elevated temperature and pressure are maintained in the reaction zone, and the gaseous reaction products are passed from the catalyst into a disengagement chamber. The velocity of the gases is reduced, allowing the entrained catalyst to fall back to the reaction zone while the reaction products free of catalyst are recovered from the top of the reaction zone. The temperature of the reactants in the reaction zone is maintained 400°–410° F. by causing a cooling fluid to flow

continuously in heat exchange relationship with the catalyst. The pressure is 5–150 p. s. i.

3561. ———. Synthesis of Octyl Alcohols. British Patent 663,240, Mar. 28, 1949. British Abs., B, II, 1952, p. 316; Chem. Abs., vol. 47, 1953, p. 1181.

Octyl alcohols are produced from heptene by interaction with H_2 and CO in the presence of a Co catalyst, which is maintained in constant amount in the carbonylation zone, condensation of the products and recycling of the gaseous phase and at least part of the liquid phase, treatment of the remaining liquid phase to remove Co as the free metal, and hydrogenation and distillation to obtain octyl alcohol. Thus, Co naphthenate is added to the heptene feed to give 0.1–0.3% of Co based on the heptene, the ratio of H_2: CO in the gas feed being 1.0–1.2: 1, and the carbonylation zone being maintained at 300°–360° F. and 2,900–3,500 p. s. i. Heptenes are fed to the zone at a rate of 0.4–0.6 vol. per vol. of reaction space per hr., fresh synthesis gas being fed in the ratio of 2,000–3,000 ft.^{3} per bbl. of heptene; time of residence in the zone is 1–3 hr., and 4–5 vol. of liquid products are recycled per vol. of fresh feed of heptene. With careful control, especially of temperature, octanals are obtainable in 80% yield, and octyl alcohols in 70–80% yield.

3562. ———. Synthesis of Oxygenated Organic Compounds. British Patent 667,617, Feb. 23, 1950. British Abs., B, II, 1952, p. 580; Chem. Abs., vol. 47, 1953, p. 1725.

In the production of alcohols by interaction of olefins with CO and H_2, the oxygenated product from the 1st stage of the Oxo synthesis is hydrogenated in the liquid phase in presence of a hydrogenation catalyst consisting essentially of a major proportion of charcoal supporting a minor proportion of MoS_3. A minor proportion of a P oxide or oxy-acid is added during the preparation of the catalyst and before sulfidation. The catalyst contains 5–15 wt. % of Mo calculated as MoO_3 and 0.01–0.3 wt. % P calculated as P_2O_5. Hydrogenation is carried out at 400°–500° F. and 2,500–3,000 p. s. i., with an oxygenated feed rate of about 0.3–1.0 liquid vol. per vol. of catalyst space per hr. and H_2 feed rate of 5,000–15,000 standard cu. ft. per bbl. of liquid feed.

3563. ———. Synthetic Lubricating Oils. British Patent 664,127, 1952. Fuel Abs., vol. 11, No. 4, abs. 3120.

1 molecular proportion of P oxychloride is reacted with 3 molecular proportions of a branched chain alcohol having 8–20 C atoms in the molecule or a mixture of such alcohols obtained by reacting CO and H_2 in presence of a catalyst and an olefin or mixture of olefins containing 7–19 C atoms per molecule. The resulting aldehydes are hydrogenated.

3564. ———. Temperature Control in Chemical Reactions Employing Powdered Catalytic Material. British Patent 626,070, July 8, 1949. Chem. Abs., vol. 44, 1950, p. 2294.

Temperature in a fluidized bed of powdered catalyst in a reaction zone is controlled by introducing a 2d solid material, which is inert and in powdered form such that it is carried through the reactor by the gases under treatment. The inert material is recovered, cooled, and returned to the reactor.

———. *See* abs. **33, 34, 35, 122, 132, 133, 134, 135, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 185, 186, 189, 190, 191, 192, 193, 194, 196, 272, 273, 296, 297, 300, 301, 314, 315, 316, 317, 330, 346, 347, 372, 439, 440, 441, 442, 460, 461, 462, 463, 464, 495, 496, 506, 642, 714, 724, 747, 762, 810, 811, 812, 813, 814, 818, 828, 829, 880, 881, 882, 883, 884, 885, 923, 924, 925, 926, 962, 963, 964, 965, 968, 969, 970, 971, 972, 974, 975, 976, 978, 979, 980, 981, 982, 983, 984, 985, 986, 987, 1033, 1034, 1049, 1050, 1051, 1052, 1054, 1055, 1056, 1057, 1065, 1066, 1067, 1068, 1069, 1080, 1081, 1082, 1083, 1760, 1785, 1786, 1787, 1849, 1850, 1851, 1852, 1858, 1859, 1860, 1953, 1954, 1955, 1956, 1957, 1958, 1959, 2039, 2040, 2041, 2042, 2043, 2044, 2062, 2064, 2091, 2092, 2100, 2101, 2102, 2103, 2146, 2147, 2148, 2149, 2150, 2151, 2155, 2156, 2158, 2159, 2160, 2161, 2162, 2166, 2167, 2168, 2169, 2184, 2185, 2186, 2205, 2213, 2219, 2221, 2339, 2344, 2345, 2346, 2377, 2396, 2401, 2402, 2403, 2404, 2405, 2406, 2407, 2408, 2409, 2410, 2412, 2413, 2414, 2415, 2416, 2417, 2418, 2419, 2420, 2421, 2422, 2423, 2424, 2425, 2435, 2436, 2437, 2438, 2549, 2553, 2561, 2562, 2563, 2564, 2565, 2566, 2575, 2582, 2583, 2584, 2585, 2586, 2626, 2690, 2691, 2692, 2693, 2746, 2824, 2825, 2826, 3214, 3242, 3243, 3244, 3245, 3246, 3247, 3248, 3249, 3250, 3251, 3252, 3253, 3254, 3255, 3262, 3263, 3264, 3266, 3267, 3268, 3269, 3270, 3271, 3272, 3273, 3315, 3316, 3317, 3318, 3319, 3320, 3359, 3360, 3361, 3362, 3363, 3364, 3443, 3569, 3710, 3711, 3712, 3713, 3714, 3716, 3718, 3719, 3720, 3721, 3722, 3723, 3724, 3749, 3750, 3764, 3817, 3818, 3819, 3820, 3821, 3822, 3823, 3824, 3825, 3826, 3841, 3842, 3843, 3844, 3845, 3846, 3847, 3849, 3850, 3851, 3852, 3853, 3854, 3856, 3857, 3879, 3880, 3881, 3882, 3892, 3893, 3894, 3895, 3936, 3985, 3986.**

3565. Stanolind Oil & Gas Company. Extractive Distillation of Oxygenated Organic Compounds. British Patent 684,968, Dec. 31, 1952. Chem. Abs., vol. 47, 1953, p. 6437.

See United States Patent 2,607,719 (abs. **610**).

3566. ———. Synthesis of Hydrocarbons and Oxygenated Organic Compounds. British Patent 655,454, Jan. 7, 1948. British Abs., B, I, 1951, p. 1055.

In the synthesis of hydrocarbons and oxygenated compounds by interaction of H_2 with CO and CO_2 at not less than 295° and more than 150 p. s. i. in presence of a fluidized Fe catalyst (particle size 1–200 μ), defluidization of the latter is prevented by limiting the CO content to 8–15%.

3567. ———. Treating Mixture of Hydrocarbons and Oxygenated Compounds. British Patent 655,690, 1951. Fuel Abs., 1951, abs. 2907.

Describes process for separating a preferentially oil-soluble organic oxygenated compound selected from the group consisting of alcohols, aldehydes, and ketones from a solution thereof comprising predominantly hydrocarbons. The solution is contacted with an aqueous extractant solution containing a substantially nonsurface-active salt of a preferentially oil-soluble carboxylic acid and stratifying and separating an aqueous extract containing the oil-soluble organic oxygenated compound.

———. *See* abs. **610, 922, 1112, 2011, 2309, 2310, 2311, 2312, 2313, 2314, 2441, 2639, 2640, 2641, 2642, 2758, 2759, 2785, 3226, 3339, 3794, 3858, 3859, 3860, 3861.**

Starke, A. *See* abs. **3915, 3920.**

Starr, C. E.,[1] Jr. *See* abs. **926.**

3568. Stassen, M., and Wirth, — (I. G. Farbenindustrie A.-G.). [Conducting Chemical Conversions.] German Patent Appl. —, OZ 13,716, filed Oct. 13, 1942. TOM Reel 19, item 148, frames 1,711–1,721; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 3, ch. 118, 1948, p. 35.

Describes apparatus for carrying out exothermic or endothermic reactions, which require special measures for the removal or introduction of heat, with diagram. It is particularly applicable to the catalytic conversion of CO and H_2 to multibranched hydrocarbons with considerable amounts of liquid and solid oxygenated derivatives. The apparatus is characterized by the use of bundles of horizontal or slightly inclined tubes, closed at one end, and filled with cold or hot liquids for

carrying away or for introducing the heat of reaction. Dip pipes on both sides conduct the cooling or heating liquid into the cold- or hot-liquid tubes. A vaporizing cooling agent and pressures of 8 or more atmospheres may be used.

3569. STEIK, K. T. (Standard Oil Development Co.). Ketenes. United States Patent 2,086,582, July 13, 1937; appl. filed Aug. 29, 1930, Serial No. 478,618; 8 claims (Cl 260–123). Chem. Abs., vol. 31, 1937, p. 6260.

Alcohol or aldehyde suitable for ketene production, for example, PrOH for the production of acetic ketene by dehydrogenation and heating, is subjected to progressively higher temperatures in stages, without removing intermediate reaction products between stages. By this mode of operation good yields are obtained.

STEIN, G. *See* abs. **2679.**

3570. STEINKOHLEN-BERGWERK "RHEINPREUSSEN". Activating Iron Catalysts. German Patent Appl. St 59,253, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 359.

Fe catalysts for the conversion of CO with H_2 are activated by the addition of traces of Cu, Ag, or Au to the catalyst just after its precipitation, washing, or drying. Addition to German Patent Appl. St 57,988 (abs. **3587**).

3571. ———. [Alcohols.] German Patent Appl. St 63,460, no date (*Cl 12 o–5.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 368.

Polyvalent alcohols are obtained by condensing ketones with pH<10 with aldehydes and hydrogenating the products.

3572. ———. [Alcohols.] German Patent 765,515, no date; appl. St 63,627 (*Cl. 12 o–5.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 368.

Alcohols are obtained from high-molecular olefins by absorbing the unconverted olefins with H_2SO_4, diluting the reaction mixture with ice, driving off the saturated hydrocarbons, and saponifying the alkyl esters.

3573. ———. [Catalyst for Hydrocarbon Synthesis.] German Patent Appl. St 59,597, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 359.

Catalyst consists of the usual base and an addition of oxides, carbonates, and basic carbonates of metals of group 8 in an amount of 10–300% of the amount of metal in the base catalyst.

3574. ———. [Catalyst Pellets.] German Patent Appl. St 61,200, no date (*Cl. 12 g–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 7, p. 227.

Production of dried pellets of pasty material as catalysts for the hydrocarbon synthesis. The material to be shaped is inserted into forms made of corrosion resistant material, provided with holes, and dried therein until the pellets are easily removed.

3575. ———. [Emulsifier and Binding Agent.] German Patent Appl. St 60,647, no date (*Cl IV c–22 g*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 643.

Paraffins m.>80° from the synthesis of hydrocarbons from CO and H_2 are oxidized and wholly or partly neutralized with alkali, NH_3, or organic bases.

3576. ———. [Hydrocarbon Synthesis.] German Patent 749,972, no date; appl. St 60,730 (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 361.

Oxidic Fe catalysts, which have been reduced in the gas phase with gas mixtures containing CO and H_2, are used for the hydrogenation of CO in the presence of a liquid medium consisting of suitable synthetic oils.

3577. ———. [Hydrogenation of Carbon Monoxide.] German Patent Appl. St 63,269, no date *Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 366.

CO is hydrogenated on Fe catalysts by using synthesis gas with <1.4 parts by volume of CO to 1 part by volume of H_2, whereby the partial pressure of the H_2 with a CO consumption of 80% is adjusted at 0.4–0.6 atm.

3578. ———. [Hydrogenation of Carbon Monoxide.] German Patent Appl. St 63,388, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 367.

CO is hydrogenated on Fe catalysts with synthesis gases at regulated space velocity.

3579. ———. [Hydrogenation of Carbon Monoxide.] German Patent Appl. St 63,406, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 367.

In a process for hydrogenating CO on Fe catalysts with synthesis gases containing 0.8–2.5 parts H_2 to 1 part of CO, the contact time of the synthesis gas with the Fe catalyst is restricted, in fact to $\frac{1}{8}$–$\frac{1}{15}$ of the normal contact time.

3580. ———. [Hydrogenation With Suspended Iron Catalyst.] German Patent 764,166, no date; appl. St 61,199 (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 362.

CO is catalytically hydrogenated with the catalyst in liquid suspension with continuous separation of liquid fractions by filtration. Over the surface of the filter and at a distance of 1–20 mm. a scraper moves so fast that no particles of catalyst are deposited on the surface of the filter.

3581. ———. [Hydrogenation With Suspended Iron Catalyst.] German Patent 766,025 (no date); appl. St 61,156 (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 362.

CO is hydrogenated by using Fe catalysts suspended in fine division in a liquid medium, with a concentration of catalyst base metal of 100–300 gm. per l. of suspension, a catalyst load of 0.4–3 l. of synthesis gas per gm. of catalyst base metal per hr., and a catalyst grain size between 0.005 and 1 mm.

3582. ———. [Improvement of the Synthesis for the Fischer-Tropsch Synthesis.] German Patent 743,995, Jan. 6, 1944; appl. St 57,247, Mar. 17, 1938 (*Cl. 12 o–1.03*). FIAT Reel E–29, frames 167–168; PB 70,432; FIAT Reel AA 89, frames 130–130A; Chem. Zentralb., 1944, I, p. 1354.

Synthesis gas is first freed from organic S in the known way, and then the still hot gas from the S purification is freed from resin-forming products at a temperature of up to 300° over polymerizing mediums such as active C or Fuller's earth. In this way, the resin-forming substances newly produced in the S purification are removed and thus the durability of the synthesis catalysts is prolonged.

3583. ———. [Inducting Catalysts.] German Patent Appl. St 63,730, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 369.

Catalysts for the hydrogenation of CO are inducted by using them for 1–5 days in step 1 and then in steps 2 or 3. Addition to German Patent Appl. St 63,406 (abs. **3579**).

3584. ———. [Induction of Iron Catalysts.] German Patent Appl. St 62,993, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 366.

Fe catalysts are inducted by pretreatment with CO or gases containing it at 200°–500° and thereafter with H_2 at 250°–600°.

3585. ———. [Iron Catalysts.] German Patent Appl. St 57,727, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 358.

Fe catalysts for the hydrocarbon synthesis from CO and H_2 are made by dissolving wrought Fe, ingot steel, in acids and precipitating the Fe together with the impurities by alkali.

3586. ———. [Iron Catalysts.] German Patent Appl. St 57,987, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 358.

Fe catalysts are made by dissolving wrought Fe, ingot steel, or mineral Fe in HNO_3 and thermally decomposing the nitrate. Addition to German Patent Appl. St 57,727 (abs. **3585**).

3587. ———. [Iron Catalysts.] German Patent Appl. St 57,988, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent Anmeldungen, vol. 6, p. 358.

Fe catalysts are made by using Fe, Fe salts, or mineral Fe of any degree of purity with additions of small amounts (0.005–0.5%) of Cu, Ag, or Au by precipitating the solution or by thermal decomposition of the nitrate and subsequently impregnating with traces of alkali salts. Addition to German Patent Appl. St 57,727 (abs. **3585**).

3588. ———. [Iron Catalysts.] German Patent Appl. St 58,992, no date (*Cl. IV d–12 o*). Auszüge deut. Patent Anmeldungen, vol. 6, p. 359.

Fe catalysts for hydrocarbon synthesis from CO and H_2 under normal and elevated pressure are made from compounds of bivalent Fe, which show a content or addition of at least 20 atom % of the corresponding compounds of trivalent Fe.

3589. ———. [Iron Catalysts.] German Patent Appl. St 62,149, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 364.

Fe catalysts for the synthesis of hydrocarbons by reduction of CO with H_2 are made precipitating the Fe with solid oxides, hydroxides, or carbonates of Mg, Ca, Sr, and Ba and by subsequent precipitation of the earth alkali going into solution using Na_2CO_3 and activating with alkali.

3590. ———. [Iron Catalysts.] German Patent Appl. St 62,515, no date (*Cl. IV d–12 o*). Auszüge deut. Patent Anmeldungen, vol. 6, p. 365.

Fe catalysts for the hydrogenation of CO to hydrocarbons with more than 1 C atom in the molecule at 150°–350° contain 0.05–10% of Ni; if desired they may subsequently be impregnated with traces (0.2–0.6%) of alkali compounds.

3591. ———. [Iron Catalysts.] German Patent Appl. St 63,234, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 366.

Fe catalysts for the hydrogenation of CO are pretreated at 200°–400° with a CO, which contains >60%, preferably >85%, of inert constituents such as N_2.

3592. ———. [Iron Catalysts.] German Patent Appl. St 63,302, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 367.

Fe catalysts for CO hydrogenation are made by oxidizing Fe carbonyl at temperatures <350° and adding activators to the Fe oxide obtained.

3593. ———. [Iron Catalysts.] German Patent Appl. St 63,407, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 367.

Fe catalysts for CO hydrogenation consist of kieselguhr, Mg, Cu, and 0.2–5% K_2CO_3. The Mg : kieselguhr ratio is 1 : 2–1 : 10.

3594. ———. [Iron Catalysts.] German Patent Appl. St 63,818, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 369.

Fe catalysts for CO hydrogenation are composed of kieselguhr, Mg, and Cu. The Mg can be wholly or partly replaced by other earth alkali metals or Mn. Addition to German Patent Appl. St 63,407 (abs. **3593**).

3595. ———. [Iron-Copper Catalysts.] German Patent Appl. St 58,177, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 358.

Fe–Cu catalysts are made by using gaseous or aqueous NH_3 as precipitating agent for the Fe salt solution.

3596. ———. [Ketones.] German Patent Appl. St 63,341, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 367.

Zn oxide catalysts for the dehydrogenation of secondary alcohols to ketones are made by impregnating granulated pumice with a solution of Zn salts, then carefully drying, and heating to 600°–1,000°.

3597. ———. [Method of Carrying Out the Hydrogenation of Carbon Monoxide on Iron Catalysts in a Liquid Medium.] German Patent Appl. St 61,846, PA 230,288, filed Apr. 3, 1943 (*Cl. 12 o–1.03*). FIAT Reel B–196, frames 862–868; PB 83,253.

In carrying out the hydrogenation of CO on Fe catalysts in a liquid medium under atmospheric or increased pressure, the fresh catalyst before induction with synthesis gas is reduced by a gas mixture containing CO and H_2 in the ratio of 2 : 1–1 : 3 in a liquid medium above the synthesis temperature. The fresh catalyst is not brought into contact with the reducing gas until the reduction temperature is reached. Example: A precipitated oxide catalyst containing 12 gm. Fe, 20 gm. Cu, and 40 gm. K_2CO_3 is ground fine with some synthesis oil, then suspended in more of the same oil and stirred by a lively stream of N_2. After the reduction temperature of 250° is reached, the catalyst is reduced under 10 atm. pressure with 8 l. of synthesis gas containing $CO : H_2 = 54 : 35$ per 10 gm. Fe hourly. The reduction is completed in 3 hr. after which the synthesis temperature is gradually reduced to 235°. The CO conversion amounts to 91–94%. There are formed per N m.^{3} of pure gas introduced products consisting of 11 gm. CH_4 and C_2H_6 and about 165 gm. chiefly of hydrocarbons, 122 gm. of which are liquids b. 25°–310°. Of this 90 gm. are a benzine fraction b. 25°–170°, having an olefin content of 64% and an octane No. of 76.

3598. ———. [Oil Washing of Distillation Gases.] German Patent Appl. St 59,708, no date (*Cl 26 d–10.10*). Auszüge Deut. Patent-Anmeldungen, vol. 15, p. 382.

Light oils are recovered from gases by washing with essentially O-free hydrocarbon mixtures obtained by the hydrogenation of CO.

3599. ———. [Process for Activating Iron Catalysts.] German Patent Appl. St 63,636, PA 705,256, filed Nov. 22, 1943 (*Cl. 12 o–1.03*). FIAT Reel B–196, frames 613–616; PB 83,253.

In activating Fe catalysts with CO or with gases containing it, the gas used for this purpose is passed over the catalyst, with recycling of part of the tail gas, at normal or slightly raised pressure or at subpressure and at temperatures of 180°–350°, preferably 200°–260°. The proportion of fresh gas to that of the recycled tail gas stands at 1 : 3 up to 1 : 15. The CO_2 is removed from the recycled tail gas by absorption in soda lime. This method allows the synthesis operation to be performed at 205° and 10 atmospheres with water gas. The yield of hydrocarbons with more than 1 C atom in the molecule amounts to about 150–160 gm. per N m.^{3} of $CO+H_2$. A conversion of CO of as high as 95% can be obtained.

3600. ———. [Production of Antiknock Motor Fuel.] German Patent Appl. St 60,337, PA 899,335, filed Dec. 24, 1940 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 828–834; PB 83,253.

In a process for producing antiknock motor fuel by reduction of CO and H_2 to liquid hydrocarbons and with the final polymerization of the gaseous olefins

thus obtained, use is made of a straight Fe catalyst with at least 99.5% of Fe (calculated on the amount of metal used) without the addition of S and with simultaneous use of high temperatures, normal or increased pressures, high gas velocity, or recycling. By the reduction of CO, chiefly gaseous, unsaturated hydrocarbons are formed in the 1st stage of the process, and in the 2d stage these are polymerized to antiknock motor fuel and mixed with the liquid primary gasoline. By this method, not only is the quantity of gaseous hydrocarbons suitable for subsequent polymerization greatly increased but also the olefin content. Furthermore, the life of the catalyst is considerably prolonged.

3601. ———. [Production of Catalysts.] German Patent Appl. St 58,750, PA 408,888, filed May 26, 1939. FIAT Reel B–196, frames 841–847; PB 83,252.

In producing catalysts in accordance with German Patent Appl. St 57,727 (abs. **3585**), characterized by the use of unpurified solutions of Fe, Fe salts, or minerals for production of Fe catalysts, and with German Patent Appl. St 57,988 (abs. **3587**), characterized by the addition of small amounts (0.005–0.5%) of Cu, Ag, or Au, only so much alkaline or ammoniacal precipitating agent is used to precipitate the catalyst from the solution of its salts as will establish at the end of the precipitation a pH concentration of 6.8–7.3. Particularly suitable is a pH concentration indicated by the change of litmus to a pale violet. The method as described removes 2 serious disadvantages of the former method: The great expenditure of time and apparatus in completing the filtration and washing, and the difficulty in washing the precipitate to a relatively nonalkaline state. The freedom from alkali is a preliminary condition for obtaining high activity and long life for the catalyst.

3602. ———. [Production of Catalysts.] German Patent Appl. St 59,723, PA 336,742, filed May 24, 1940 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 970–973; PB 83,253.

This patent application relates to the production of Fe catalysts suitable for the synthesis of hydrocarbons by using compounds of alkaline earths, Mg, Ca, Sr, or Ba that may simultaneously serve as precipitating agents, activators, and carriers. It has been found that these compounds do not injure the catalyst but rather impart improved properties, increased activity, and extended life to it. Example: 2 mol. of dissolved Fe nitrate are decomposed with 0.25 mol. Ba carbonate and 0.1 mol. Cu nitrate and shaken until no more CO_2 is evolved. Then 3.1 mol. of soda in solution is added and the mixture boiled. After washing 0.125%, calculated on the Fe, of K carbonate is added and the mixture dried.

3603. ———. [Production of Hydrogen.] German Patent 753,433, Oct. 2, 1936; appl. St 55,331 (*Cl. 12 i–1.01*). Auszüge deut. Patent-Anmeldungen, vol. 7, p. 320.

In producing H_2 by the Fe-steam process, the residual gases from the synthesis of gasoline are used as reducing gases.

3604. ———. [Production of Lubricants.] German Patent Appl. St 60,284, PA 325,783, filed May 2, 1921 (*Cl. 12 o–1.01*). FIAT Reel B–196, frames 835–840; PB 83,253.

In preparing lubricants by the polymerization of condensation of unsaturated and/or chlorinated saturated hydrocarbons with or without aromatic hydrocarbons in the presence of HF as catalyst, use is made of aliphatic hydrocarbons with more than 6 C atoms or the hydrocarbons obtained by the hydrogenation of CO with or without the use of pressure. Examples are presented of the use of (1) the olefin-rich fraction b. 160°–195°, (2) the chlorinated kogasin fraction b. 280°–320°, and (3) the same fraction in mixture with naphthalene and the heavy benzine from the benzine synthesis. The product has a viscosity of 4.5–6.2 E at 50° in (1) and (3) and 33 E in (2).

3605. ———. [Production of Lubricants.] German Patent Appl. St 60,695, PA 337,431, filed May 7, 1941 (*Cl. 12 o–1.01*). FIAT Reel B–196, frames 896–901; PB 83,253.

In the process for making lubricating oil by condensing chlorinated, saturated, and/or unsaturated hydrocarbons with or without aromatic hydrocarbons, there is used as the catalyst an impure Al containing foreign metals such as duralumin or metals alloyed therewith, such as Cu, Mg, Si, Mn, or other metals of groups 1, 2, 3, 4, 7, and 8. Activating the catalyst with Hg is not necessary. It is enough to add the catalyst to the mixture to be condensed and stir thoroughly. The reaction is then complete in 2.5 hr. Treating the catalyst with HCl will shorten the reaction time still more to 1–1.25 hr., whereas addition of 15% of $AlCl_3$ reduces it to 50–60 min. The same effect is obtained by adding an Al compound, which is obtained by the conversion at 60°–100° of chlorinated paraffin hydrocarbons b. 150°–350° with Al. Gives an example of the process and presents data on the yields and properties of the product using various Al catalysts.

3606. ———. [Production of Oxygenated Organic Compounds.] German Patent Appl. St 62,945, no date (*Cl. 12 o–5.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 366.

Oxygenated compounds are obtained by the hydrogenation of CO by using catalysts composed of metals of group 8 of the periodic system and by adding activating substances after induction of the liquid catalyst.

3607. ———. [Purifying Gases Containing Carbon Monoxide and Hydrogen.] French Patent 849,158, Nov. 15, 1939. Chem. Abs., vol. 35, 1941, p. 6400.

Resin-forming substances are removed by treatment with adsorbents, such as active C, and S-containing organic compounds by treatment with mixtures of alkali carbonates and Fe oxide or hydroxide at 150°–300°.

3608. ———. [Recovering Light Oils.] French Patent 872,238, June 2, 1942; appl. filed May 16, 1941, in Germany May 17, 1940. Chem. Zentralb., 1943, I, p. 807.

For washing the gases an essentially O-free hydrocarbon mixture, such as occurs in the hydrogenation of CO at normal or increased temperature, is used. The resinous, pitch, and asphaltic substances can be separated from the washing agent after its removal from the washer.

3609. ———. [Recovering Olefins From Synthetic Mixtures.] German Patent Appl. St 63,077, no date (*Cl. IV d–23 b*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 784.

Olefinic hydrocarbons are obtained from the mixtures of hydrocarbons occurring in the hydrogenation of CO by treating them with liquid SO_2 and removing the olefins, which settle out in the lower SO_2 layer.

3610. ———. [Regeneration of Synthesis Catalysts.] German Patent Appl. St 62,944, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 365.

Catalysts for the hydrogenation of CO made by precipitation from Fe chloride solutions are purified by treating the precipitation product after washing with Ag salt solutions.

3611. ———. [Separation of Light Hydrocarbons From the Reaction Gases of Carbon Monoxide Hydrogenation.] French Patent 51,588, Feb. 5, 1943; appl. filed May 26, 1941, in Germany Aug. 7, 1940. Chem. Zentralb., 1943, II p. 1692.

Process of the main patent is improved by first washing with an oil boiling about 260°–290° to remove the resinous impurities and then at room temperature with pure paraffin hydrocarbons from the hydrogenation of CO to remove the hydrocarbons.

See also French Patent 872,238 (abs. **3608**).

3612. ———. [Softener for Lacquer.] German Patent Appl. St 59,607, no date (*Cl. 22 h–3*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 693.

Softener for lacquers in the form of chlorination products of the compounds b. >150° from CO hydrogenation.

3613. ———. [Synthesis Catalysts.] German Patent 765,189, no date. Kainer, p. 78.

Inactive Fe oxides are very suitable for use as supports for Fe catalysts.

3614. ———. [Synthetic Hydrocarbons.] German Patent Appl. St 63,387, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 367.

High-molecular hydrocarbons are synthesized in the presence of a liquid medium by using Fe catalysts with little support or none at all and with small amounts of Cu, which contain alkali compounds corresponding to 0.7–5% by weight of alkali oxide.

3615. ———. [Synthetic Paraffins and Waxes.] German Patent Appl. St 63,450, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 368.

Solid paraffin and waxlike hydrocarbons are obtained from liquid hydrocarbons by conversion with gases containing CO and H_2 in presence of strongly alkalized catalysts containing elements of group 8, the alkali content of which corresponds to 10% by weight of alkali oxide.

3616. ———. Treating Coal-Tar and Like Tar Oils; Diesel Fuels. British Patent 502,802, Mar. 24, 1939; appl. filed Sept. 24, 1937. No. 25,879, Convention date Sept. 24, 1936. British Chem. Abs., B, 1939, p. 574; Chem. Abs., vol. 33, 1939, p. 7082.

Coal or like tars are produced and diesel fuels are formed by mixing the tar oils with paraffinic hydrocarbons of b. p. 180°–250° C. obtained in a benzine synthesis process and treating at atmospheric temperature with acid of at most 40% concentration. Washing, drying, and bleaching may follow. For example, 35 kg. of coal tar oil b. p. 180°–350° C. is mixed with 17 kg. of oil of the same b. p. obtained in the Fischer-Tropsch benzine synthesis shaken with 15 l. of 20% H_2SO_4 and either centrifuged or allowed to settle, and the 3 layers are separated. The raffinate is washed, dried, and treated with bleaching earth; the acid is reused, and the sediment is worked up to obtain heating oil or extract phenols.

See also French Patent 827,049 (abs. **3618**).

3617. ———. [Treating Tar Oils.] Austrian Patent 160,848, no date.

See French Patent 827,049 (abs. **3618**) and German Patent 747,401 (abs. **1897**).

3618. ———. [Treatment of Coal-Tar Oils.] French Patent 827,049, Apr. 14, 1938. Chem. Abs., vol. 32, 1938, p. 6846.

Coal-tar oils are mixed with a paraffin hydrocarbon mixture b. 180°–350°, preferably a synthetic mixture prepared from CO and H_2, and the mixture is treated with a dilute acid, preferably dilute H_2SO_4, at atmospheric temperature for a short time. The mixture is then allowed to settle, and the uppermost layer, consisting of a mixture of tar oil and paraffin hydrocarbons, is separated, washed, and dried and may then be used as fuel for diesel motors. Gives example.

3619. ———. [Use and Production of Iron Oxides as Catalysts for the Hydrogenation of Carbon Monoxide.] German Patent Appl. St. 60,623, PA 250,501, filed Apr. 1, 1941 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 852–861; PB 83,253.

Use is specified of Fe oxides as catalysts prepared from ferric salts in states of crystallization that lie between the state of amorphicity to X-ray diffraction and the state where the half width of the Debye-Scherrer lines is at least 10% greater than the diameter of the specimen and where the ratio of the integrated intensities of the 113 and 226 lines is at least 2. In preparing the active Fe oxides, they are precipitated from the Fe salt solutions and are dried in the temperature range 0°–300° in such a manner that for each respective drying temperature a corresponding maximum drying time is not exceeded. For example, the drying time at 20° should not exceed 1,000 hr., at 50° not more than 80 hr., at 100° not more than 35 hr., at 200° not more than 8 hr., and at 300° not more than 2 hr. Futhermore, they may be formed by the thermal decomposition of ferric salts or hydroxides at temperatures at most 400° and in time less than 30 min., preferably at 250°–300° and in 20–100 sec.

———. *See abs.* **1897, 1899, 1901, 1902, 1903, 1904, 1905, 1906, 1907, 1908, 1909, 1910, 1911, 1912.**

3620. STEINSCHLAEGER, M. Gas Mixtures Containing Carbon Monoxide and Hydrogen. British Patent 573,923, Dec. 13, 1945; appl. filed May 10, 1940. Chem. Abs., vol. 43, 1949, p. 4835.

Gas mixture containing 1.8–2.0 vol. H_2 per vol. CO, suitable for use in the Fischer-Tropsch synthesis, is prepared by heating coke with at least 150%, preferably 200%, of the theoretical amount of steam required for the water-gas reaction, at 900°–1,100°, to produce a gas containing more H_2 and CO_2 than is normally present in blue water gas. CO_2 is then removed from the gas, and the residue is mixed with coke-oven gas in such proportion as to produce a gas containing CO and H_2 in a proportion suitable for use in the Fischer-Tropsch process.

3621. ———. Gas Mixtures Containing Carbon Monoxide and Hydrogen. British Patent 573,924, Dec. 13, 1945; appl. filed May 10, 1940. Chem. Abs., vol. 43, 1949, p. 4836.

Gas mixture similar to that described in British Patent 573,923 (abs. **3620**) is prepared by mixing normal blue water gas with coke-oven gas in such proportion as to produce a gas containing the above-mentioned proportion.

3622. ———. Gas Mixtures Containing Carbon Monoxide and Hydrogen. British Patent 573,925, Dec. 13, 1945; appl. filed May 10, 1940. Chem. Abs., vol. 43, 1949, p. 4836.

Gas mixture is prepared by heating a coke-oven gas with steam at 1,200°–1,500° without a catalyst, or at 800°–900° in the presence of a Ni or Fe catalyst, and mixing the gas thus produced with blue water gas in such proportion as to produce a gas mixture containing CO and H_2 in a proportion suitable for use in the Fischer-Tropsch process.

3623. ———. Gas Mixtures Containing Carbon Monoxide and Hydrogen. British Patent 574,048, Dec. 19, 1945. Chem. Abs., vol. 42, 1948, p. 6091.

Gas mixture suitable for use in the Fischer-Tropsch synthesis is prepared by 1st heating a mixture of blue water gas, H_2, and coke-oven gas in the presence of Co or Ni catalyst, 160°–250°, to produce an oil and a residual gas. This gas is then heated with steam, 1,200°–1,450°, and the product mixed with blue water gas and a gas, which has been obtained by heating blue water gas with steam at 400°–550°. CO_2 is then separated from the gas mixture and a gas containing 1.8–2.0 vol. of H_2 per vol. of CO is obtained.

3624. ——— (Koppers Co.). Hydrocarbons From Hydrogen and Carbon Monoxide. United States Patent 2,220,357, Nov. 5, 1940; appl. filed Nov. 24, 1936, Serial No. 112,549; in Germany Nov. 26, 1935; 4 claims (*Cl. 190–449*). Chem. Abs., vol. 35, 1941, p. 1980.

Describes arrangement of apparatus and a process for making liquid hydrocarbons by catalytically treating 2 H_2 and 1 CO by means of a known catalyst capable of forming liquid hydrocarbons from 2 H_2 and 1 CO, which comprises: Making alternate blows of air and runs of water gas making steam through a generator fuel bed of carbonaceous fuel to produce original water gas containing H_2 and CO in ratio 2 : 1 during the blows, storing the heat of the spent blow gases in a conversion chamber separated from the generator fuel bed; during the runs, purifying the original 2 : 1 gas and then catalytically treating it in the presence of a catalyst known to be capable of reacting 2 H_2 and 1 CO to liquefiable hydrocarbons in a primary catalytic reaction chamber to form the liquid hydrocarbons from the 2 : 1 ratio of H_2 to CO, removing the liquid and solid products from the reaction gas left over from the primary catalytic reaction, and then flowing the residual leftover reaction gas together with the steam by themselves through the aforesaid conversion chamber and converting the gaseous hydrocarbons in the leftover-gas reaction gas to H_2 and CO in ratio 2 : 1 by the heat stored in the conversion chamber from the blow gasse of the previous blow of the generator fuel bed, thereafter catalytically treating the so converted 2 H_2 : 1 CO in the leftover reaction gas in the presence of a catalyst as aforesaid in a secondary catalytic reaction chamber separate from the primary catalytic reaction chamber to form further liquid hydrocarbons from the leftover gas and recovering the further liquid hydrocarbons from the reaction gases of the secondary catalytic reaction chamber.

3625. ——— (London Testing Laboratory, Ltd.). Hydrocarbons High in Olefins From Carbon Monoxide and Hydrogen. British Patent 515,037, Nov. 24, 1939; appl. filed Feb. 18, 1938. Chem. Abs., vol. 35, 1941, p. 4940.

Gaseous mixture, water gas, is passed over a CO catalyst 180°–210° at atmospheric pressure to produce hydrocarbons, and the product is passed over an Fe catalyst 200°–240° and 0–10 atm., whereby further hydrocarbon yields are obtained.

3626. ———. Process for the Synthetic Manufacture of Hydrocarbon Oils. United States Patent 2,630,-447, Mar. 3, 1953; appl. filed July 15, 1947, Serial No. 761,022; 2 claims (*Cl. 260–449.6*).

Snythesis gas with CO : H_2 ratio of 1 : 1.5–2 : 1 by volume is produced by reacting fixed hydrocarbon gases with CO_2 of residue gas produced in the CO–H_2 reaction. The synthesis gas is reacted in presence of Co, Ni, or Fe catalysts at 150°–400° C. The liquefiable olefin-rich hydrocarbons are separated from the residual gas. A large part of the CO_2 is separated from the residual gas and recycled to the initial gas-forming stage. The remainder of the residual gas is mixed with the synthesis gas and catalytically reformed to give a second synthesis gas mixture of controlled CO : H_2 ratio that is further synthesized. Successive CO_2 recycling, synthesis gas reforming, and hydrocarbon synthesis steps are repeated until the inert content of the residual gases has built up to the point where the yield of olefin-rich liquid hydrocarbons is substantially lowered. 6 United States patents cited.

3627. ———. Production of Gas Mixtures Containing Carbon Monoxide and Hydrogen. British Patent 575,377, Feb. 15, 1946, appl. filed July 5, 1939. British Abs., I, B, 1946, p. 197; Chem. Abs., vol. 41, 1947, p. 5286.

Gas mixture containing H_2 and CO in the vol. ratio 2 : 1, suitable for the Fischer-Tropsch synthesis, is prepared from coal gas, blue water gas, and a gas containing H_2 and CH_4 produced by heating in a current of H_2 the waxy deposit formed on the Fischer-Tropsch catalyst, by passing the mixed gases over a ThO_2-activated Co catalyst at 160°–220°, separating the oily products (97 gm. per $m.^3$), converting the residual gas, CO, 18%, H_2, 25%, CH_4, 35%; CO_2+N_2, 20%; C_nH_m, 2%, with steam on a Ni-Mo sulfide catalyst at 800°–900° into 2.2 vol. of synthesis gas containing CO, 24%; H_2, 64%, CH_4, 1; and CO_2+N_2, 11%, and finally adjusting the H_2 : CO ratio by adding blue water gas. Coal consumption is low, 3.5 ton per ton of primary products, owing to the complete utilization of the coke and coal gas.

3628. ———. Production of Water Gas and Like Synthesis Gas. British Patent 577,015, Sept. 15, 1941. British Abs., I, B, 1946, p. 224.

Using a regenerator heated by producer gas, or by blow gas from the water gas generator, the mixture of water gas with steam and/or CO_2 fed to the generator is preheated so that the make period is extended and the blow with air or O_2 shortened.

3629. ———. Unsaturated Hydrocarbon Oils. British Patent 581,174, Oct. 3, 1946, appl. filed Mar. 9, 1942. Chem. Abs., vol. 41, 1947, p. 1830.

Water gas containing CO and H_2 in a ratio of 1 : 1.5–2.1 by vol. is passed over a Co, Ni, or Fe catalyst at 150°–250° to give unsaturated oils and a residual gas. The latter is mixed with natural gas of liquid hydrocarbons and then treated with CO_2 and/or steam at 800°–1,500° to give a new synthesis gas, which is treated like the original water gas.

3630. ———. Water Gas. United States Patent 2,525,318, Oct. 10, 1950; appl. filed June 21, 1945, Serial No. 600,694, in Great Britain Aug. 11, 1942; 1 claim (*Cl. 48–208*).

Water gas, synthesis gas, and the like are produced from coal, coke, and liquid and gaseous fuels in equipment of the type used in standard carbureted water gas practice, but with some modifications in operating cycle. A generator is used containing incandescent solid fuel for decomposing steam. For producing water gas from bituminous coal additional regenerators are required for decomposing volatilized-coal constituents. The principal advantages of the method are that the usual uprun is not required and that both blast and make gases are passed through a waste-heat boiler for steam generation.

3631. ———. Water Gas and Like Gases. British Patent 561,338, May 16, 1944; appl. filed Aug. 11, 1942. Chem. Abs., vol. 39, 1945, p. 5440.

Production of blue water gas and like gases is based on the use of preheated steam and air. Different systems of generators are used depending on the kind of gas produced. In the manufacture of synthesis gas a unit consisting of a generator and 2 regenerators is used. Describes operation.

3632. ———. Water Gas and Like Synthesis Gases. British Patent 578,332, June 25, 1946. Chem. Abs., vol. 41, 1947, p. 1831.

Discontinuous water-gas process for generating blue gas is improved by supplying the heat for gasification partly by heating a hydrocarbon mixture by passage through a regenerator, previously heated by blow gas or producer gas, and passing this heated gas down through the fuel bed to complete the reforming partly carried out in the regenerator, and partly by preheating the coke fuel bed by blowing with O_2 or O_2-containing gases. Further heat may also be secured by recycling a portion of the hot make gases. Heat is

stored in the generator ash bed for use in superheating the steam or preheating the gas used in the later uprun.

3633. STEINSCHLAEGER, M., AND LONDON TESTING LABORATORY, LTD. Carbon Monoxide-Hydrogen Mixtures. British Patent 513,778, Oct. 23, 1939; appl. filed Feb. 17, 1938. Chem. Abs., vol. 35, 1941, p. 2304.

Mixtures suitable for conversion into hydrocarbons are produced by mixing a gas mixture consisting principally of CO and H_2 with coal distillation gases and passing the resulting mixture over a catalyst to produce gases rich in CH_4, these gases being then converted at 1,400°–1,450° with steam in a decomposing plant lined with refractory bricks. The primary gas mixture may be formed by mixing water gas with coal-distillation gases.

3634. STEINSCHLAEGER, M., AND OVERSEAS FINANCE & COMMERCE, LTD. Synthetic Production of Hydrocarbon Oils. British Patent 575,378, Feb. 15, 1946; appl. filed July 5, 1939. British Abs., I, B, 1946, p. 197; Chem. Abs., vol. 41, 1947, p. 5285.

Motor fuel and lubricating oil, both of high olefin content, are synthesized by passing blue water gas over a catalyst of Co activated with ThO_2 160°–250°, separating the olefinic oils produced, washing the CO_2 from the residual gas (0.4 vol.), and mixing the washed gas with a gas containing H_2 and CH_4 produced by heating in a current of H_2 the waxy deposit formed on the Fischer-Tropsch catalyst and a H_2-rich gas mixture produced by treating coal gas with steam on a Ni-Mo sulfide catalyst or by treating blue water gas with steam on a Co-ThO_2 catalyst to yield a synthesis gas containing CO, 29%; H_2, 58%; CH_4, 5%; and CO_2+N_2, 8%. The synthesis gas when passed over a Co, a Ni, or an Fe catalyst, which may be activated by ThO_2 or Cu, 160°–250° yields olefinic liquid products 140 gm. per $m.^3$. Products of still higher olefin content are obtained by using a synthesis gas containing CO 34%+H_2 51% prepared by suitable adjustment of the constituents mentioned.

3635. STENGEL, L. A. (Commercial Solvents Corp.). Catalytic Apparatus Suitable for Synthesis of Liquid Organic Products Such as Alcohols From Carbon Oxides and Hydrogen. United States Patent 1,803,306, Apr. 28, 1931. Chem. Abs., vol. 25, 1931, p. 3665.

Describes various structural details of an apparatus having an outer pressure-resisting vessel, an inner catalyst chamber, and inlet and outlet gas ports.

See also Canadian Patent 300,963 (abs. **597**).

3636. ——— (Commercial Solvents Corp.). Methanol Synthesis. United States Patent 1,754,371, Apr. 15, 1930; appl. filed Nov. 17, 1926. Chem. Abs., vol. 24, 1930, p. 2760.

See Canadian Patent 286,288 (abs. **3637**).

3637. ——— (Commercial Solvents Corp.). Synthesis of Methanol. Canadian Patent 286,288, Jan. 8, 1929. Chem. Abs., vol. 23, 1929, p. 1420.

H_2 and C oxides are passed in contact with liquid MeOH under pressure, the gases are heated by thermal contact with the hot gases from the reaction and contacted with a heated catalyst to produce MeOH, the gases are cooled and the MeOH formed is removed, the residual gas is combined with fresh gas, and the cycle is repeated.

———. *See* abs. **602, 603.**

3638. STEPHENSON, H. P. Catalysts for Hydrogenation Processes, Ammonia and Methanol Synthesis. British Patent 449,603, June 30, 1936. Chem. Abs., vol. 30, 1936, p. 8538.

Catalytic substances are mixed with a coal-oil mixture, which is then carbonized to yield a coke or semicoke in which the catalyst is finely distributed. The catalytic substances may subsequently be reduced or otherwise converted. The product may be used as produced or ground and, if desired, pelleted with the aid of a binder. Examples of catalytic materials are (1) Fe oxide or oxalate, with or without admixed promoters, (2) Ni oxide, carbonate nitrate, or formate, (3) Cu oxide, hydroxide, carbonate, or nitrate.

STERN, G. *See* abs. **1996, 2689.**

STERN, N. R. *See* abs. **947.**

3639. STEWART, M. M. (The Texas Co.). Preparation of Nonsintered Iron Catalyst. United States Patent 2,438,584, Mar. 30, 1948; appl. filed Dec. 22, 1945, Serial No. 637,114; 4 claims (*Cl. 252–257*). Chem. Abs., vol. 42, 1948, p. 8430.

Fe catalyst for use in a fixed bed or fluid system is prepared by a simplified method, which dispenses with the high temperature fusion step usually used in forming magnetite. Fe ore, Fe salt, or spent catalyst is placed in the reactor. Air is passed through the mass at a temperature range 750°–875° F. to remove C and effect at least partial oxidation of metallic Fe to either the ferrous or ferric state. The treatment is continued until C oxides are no longer found in the effluent. Then a 50:50 mixture of air and steam 700°–800° F. is admitted to further oxidize the material to Fe_2O_3 or magnetite, Fe_3O_4. This treatment is continued until the composition of the gas entering the reactor is approximately the same as the composition of the gas leaving the reactor. Air is discontinued and treatment with steam alone, 700°–800° F., to purge the catalyst of molecular O_2 is continued until the effluent is free of molecular O_2. A 50:50 mixture of steam and H_2 is introduced to convert the ferric oxide to magnetite. This is the critical step in the treatment. Ferric oxide would be reduced completely to metallic Fe by the H_2 were it not for the oxidizing effect of the steam. When partial reduction is complete, as shown by similarity of composition of gases entering and leaving the reactor, the magnetite is reduced to the metallic state by H_2 alone, 700°–800° F. Promoters such as K oxide, alumina, or magnesia enhance the activity of the catalyst. A good composition is 2–3% alumina, 1–2% K oxide, and 95–97% metallic Fe. This preparation or regeneration may be carried out in the same reactor in which the hydrogenation of CO takes place. 7 United States patents are cited.

———. *See* abs. **32, 3332.**

3640. STEWART, M. M., GARRETT, R. C., AND SENSEL, E. E. (The Texas Co.). Method of Effecting Catalytic Reactions Between Carbon Monoxide and Hydrogen. United States Patent 2,433,072, Dec. 23, 1947; appl. filed Aug. 24, 1943, Serial No. 499,772; 7 claims (*Cl. 260–449*). Chem. Abs., vol. 42, 1948, p. 2088.

Carrier liquid is saturated with gaseous reactant material at a pressure substantially above that of the reaction zone. This saturated liquid mixture is introduced to the reaction zone where, owing to reduction in pressure, gas is released as bubbles from the liquid and the liquid foams. The catalyst may be separately introduced to the reaction zone and dispersed within the foam or may be suspended or dispersed in the carrier liquid before or after it enters the reactor. The carrier liquid may be any liquid that is stable and inert under reaction conditions or may be made up from the reaction products. The method is advantageous in the Fischer-Tropsch process owing to the extensive area of liquid-gas interface provided by the foam. 4 patents and 1 literature ref. are cited.

3641. STEWART, S. G. (Phillips Petroleum Co.). Hydrocarbon Synthesis Catalyst. United States Patent 2,490,488, Dec. 6, 1949; appl. filed Mar. 28, 1947, Serial No. 737,993; 7 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 3701.

Molybdenum disulfide is admixed with an alkaline promoter, which is an alkali metal compound having an alkaline reaction, or one which leaves as a residue the corresponding alkali metal oxide on decomposition of the compound. Such compounds are the hydroxides and carbonates of Na and K carbonate as well as the oxides. The promoter is used as 0.5–5 weight % of the disulfide. A carrier may be used. 5 United States patents cited.

3642. ———. (Phillips Petroleum Co.). Synthesis-Gas Manufacture. United States Patent 2,606,158, Aug. 5, 1952; appl. filed Jan. 4, 1949, Serial No. 69,177; 6 claims (*Cl. 252–373*).

Natural gas, containing 20–40 mol. % C_2–C_4 paraffin hydrocarbons, is partly oxidized by an exothermic reaction in the presence of an O_2-containing gas at 2,000°–2,500° F. and for 0.1–1.5 sec. The product is rapidly quenched by indirect heat exchange with a propane cracking stock and cooled 1,200°–1,600° F., thereby supplying heat for thermally cracking the paraffin. The quenched partial oxidation product is cooled to <900° F. to prevent formation of CO_2 by the water gas shift reaction, the product of thermal cracking separated and a H_2 and CH_4 fraction recovered, a part of this fraction being passed to the partial oxidation step to raise the H_2 content of the product synthesis gas so that an optimum ratio of H_2 : CO in the range of 1.7 : 1 to 2.3 : 1 is obtained.

———. *See* abs. **2182.**

STIEBLING, E. *See* abs. **3838.**

3643. STILL, C. Conversion of Paraffin Hydrocarbons. German Patent Appl. St 55,477, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 357.

Paraffin hydrocarbons are converted into olefins by splitting off H_2 in presence of a catalyst at short contact time and with sudden cooling after leaving the catalyst space.

3644.———. [Recovering Hydrocarbons.] German Patent Appl. St 63,783, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 369.

Hydrocarbons with 2, 3, and 4 C atoms are recovered by adsorption in steps by means of low-boiling hydrocarbons.

3645. STIMSON, E. E. Gas Manufacture. British Patent 554,869, July 22, 1943. Chem. Abs., vol. 39, 1945, p. 1040.

Describes process for producing industrial gas mixtures containing CO and H_2 by the reaction of a suspension of powdered carbonaceous material in steam.

3646. ———. Gas Manufacture. Canadian Patent 423,377, Oct. 24, 1944, appl. filed Jan. 6, 1943; in Great Britain Jan. 20, 1942.

Production of a gas mixture containing CO and H_2 is effected by injecting burning powdered coal with O_2 and steam. The apparatus consists of a furnace having gas inlets tangentially inclined and arranged at a number of levels adapted to form a plurality of vortices having a common axis and direction of rotation.

3647. STORCH, H. H. (E. I. du Pont de Nemours & Co.). Copper-containing Catalyst Suitable for Use in Methanol Synthesis From Hydrogen and Carbon Monoxide. United States Patent 1,937,728, Dec. 5, 1933; appl. filed May 16, 1927. Chem. Abs., vol. 28, 1934, p. 1058.

Cuprammonium salt such as the sulfate or nitrate is treated, as by heating with NaOH, to form a Cu–O compound, and the latter is reduced at a temperature below the melting point of Cu.

3648. ——— (Roessler & Hasslacher Chemical Co.). Methanol Synthesis. United States Patent 1,681,750, Aug. 21, 1928; appl. filed May 16, 1927. Chem. Abs., vol. 22, 1928, p. 3893.

Mixture of H_2 and CO is passed over a heated catalyst comprising Cu obtained from a cuprammonium compound, for example by boiling the latter with NaOH and reducing with H_2.

3649. ——— (Roessler & Hasslacher Chemical Co.). Methanol Synthesis. United States Patent 1,681,751, Aug. 21, 1928; appl. filed May 16, 1927. Chem. Abs., vol. 22, 1928, p. 3893.

MeOH synthesis from H_2 and CO by use of a catalyst comprising Cu and fluoride of Ca, Ba, Sr, or Mg is specified.

3650. ——— (Roessler & Hasslacher Chemical Co.). Methanol Synthesis. United States Patent 1,681,752, Aug. 21, 1928; appl. filed May 16, 1927. Chem. Abs., vol. 22, 1928, p. 3893.

The catalyst comprises Cu formed by the reduction of CuO precipitated from a cuprammonium salt solution in intimate mixture with $Mg(OH)_2$.

3651. ——— (Roessler & Hasslacher Chemical Co.). Methanol Synthesis. United States Patent 1,681,753, Aug. 21, 1928; appl. filed May 16, 1927. Chem. Abs., vol. 22, 1928, p. 3893.

The catalyst comprises Pd and Cr_2O_3, AnO, or Ce_2O_3.

3652. ——— (Roessler & Hasslacher Chemical Co.). Methanol Synthesis. United States Patent 1,707,331, Apr. 2, 1929; appl. filed Aug. 2, 1927. Chem. Abs., vol. 23, 1929, p. 2449.

Catalyst comprising Cu and Ce fluoride or other rare earth fluoride is used in the synthesis of MeOH from H_2 and CO.

See United States Patent 1,681,750 (abs. **3648**).

3653. ——— (Roessler & Hasslacher Chemical Co.). Methanol Synthesis. United States Patent 1,738,971, Dec. 10, 1929; appl. filed Aug. 2, 1927. Chem. Abs., vol. 24, 1930, p. 865.

A gaseous mixture of H_2 and CO is passed in contact with a hot catalyst mass comprising Cu, magnesia, and silica.

3654. ——— (Roessler & Hasslacher Chemical Co.). Methanol Synthesis. United States Patent 1,875,273, Aug. 30, 1932; appl. filed Aug. 2, 1927. Chem. Abs., vol. 26, 1932, p. 5971.

Mixture of H_2 and CO is passed in contact with a hot catalyst comprising Cu and CaO.

STORCH, H. H. *See* abs. **611.**

3655. STÖWENER, F. (I. G. Farbenindustrie A. G.). [Catalytic Mass.] German Patent 664,817, Sept. 12, 1938 (*Cl. 12 g–4.01*). Chem. Abs., vol. 33, 1939, p. 332.

A hard, porous adsorptive or catalytic mass is prepared by mixing jellylike or granular precipitates or their dried products, which are virtually free from SiO_2, with just enough liquid to form a paste, drying the paste, and working up as an irreversible colloid or mixing with a peptization agent. Thus, an aqueous solution of $Ni_2(SO_4)_3$ and $MgSO_4$ is treated with a soda solution and the precipitated Ni and Mg compound separated, ground, and made into a paste with H_2O. The paste is dried and is used as a contact agent for making CH_4 from CO and H_2. Gives other examples.

3656. ——— (I. G. Farbenindustrie A. G.). [Deposition of Insoluble Metal Compounds on Carriers.] German Patent 740,634, Sept. 2, 1943 (*Cl. 12 g–1.01*). Chem. Abs., vol. 40, 1946, p. 182.

Compounds of the desired metal are made to react with nitrogenous derivatives of CO_2 in which at least 1 of the N atoms is bound to C. Particularly suitable for this process is urea or its derivatives. The metal organic product formed in the course of this reaction should be insoluble. The reaction is carried out in the presence of the material that is to act as carrier. The

whole is heated until an insoluble product is formed and then the metal urea is transformed to metal or metal oxide.

3657. Stöwener, F., Keunecke, E., and Becke, F. [Catalytic Reactions With Carbonaceous Materials.] German Patent Appl. —, filed Apr. 17, 1941; APC 389,039.

Silica gel, obtained by allowing a homogeneous sol (pH 3–4.5) to solidify, washing until a pH 3–5 is reached and drying at 200°–300° C. diameter, is saturated with H_2O vapor and impregnated with $Al(NO_3)_3$ solution, $Co(NO_3)_2$ solution and K_2CO_3 solution. A gas mixture consisting of CO and H_2 (1:2) is passed at 194° C. and at a velocity of 1.3 l. per gm. Co per hr. over the mass whereby liquid and solid hydrocarbons are obtained in a yield of 100 gm. per $m.^3$ of initial gas.

3658. Stratford, W. M. (Texaco Development Co.). Process for Synthesis of Hydrocarbons and the Like. United States Patent 2,486,505, Nov. 1, 1949; appl. filed June 20, 1945, Serial No. 600,471; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 1674.

Catalyst is disposed in a thin continuous layer on a moving surface, either cylindrical or flat, which travels through the reaction zone. A stream of CO and H_2 preheated 365°–400° F. diffuses through the catalyst layer, products are formed, and the temperature of the catalyst rises as a result of the exothermic heat of reaction. The catalyst layer moves out of the reaction zone and through a zone where it is cooled by spray of gas oil. The spray also reduces the accumulation of wax on the catalyst particles. The layer may be immersed rather than sprayed. Co promoted with magnesia or thoria and supported on Filter Cel and synthesis gas of $CO:H_2::1:2$ proportion are used in the example. 1 foreign and 10 United States patents are cited.

Stratford Engineering Corp. *See* abs. **2730.**

3659. Strevens, J. L., and National Coke & Oil Company, Ltd. Gaseous Mixtures. British Patent 480,820, Mar. 1, 1938. Chem. Abs., vol. 32, 1938, p. 6445.

In obtaining a gas mixture comprising H_2 and CO in the ratio of 2:1 for the catalytic conversion thereof to aliphatic hydrocarbons, water gas and coke-oven gas are blended with a permanent gas produced from the distillation of coal-oil mixtures. S compounds are removed from the mixture before its subjection to catalysis; other diluents, for example, CO_2, saturated and unsaturated hydrocarbons, or N_2 may remain therein.

Strong, J. S. *See* abs. **1854, 1855.**

Stuart, A. P. *See* abs. **1779.**

3660. Studien- und Verwertungs-G. m. b. H. Aliphatic Hydrocarbons. British Patent 454,948, Oct. 12, 1936. Chem. Abs., vol. 31, 1937, p. 1426.

See French Patent 788,286 (abs. **3661**).

3661. ———. [Aliphatic Hydrocarbons.] French Patent 788,286, Oct. 7, 1935. Chem. Abs., vol. 30, 1936, p. 1383.

Yield of aliphatic hydrocarbons containing more than 1 C atom in the mol. by catalytic synthesis from CO and H_2 is increased by transforming the CO and H_2 only incompletely at first, this being effected by using relatively low temperatures and/or insufficient H_2 and/or high speed of flow. The reaction products are condensed and the remaining gases returned for further treatment.

3662. ———. Catalytic Apparatus. British Patent 451,177, July 29, 1936; appl. filed Jan. 29, 1935. British Chem. Abs., 1936, B, p. 964; Chem. Abs., vol. 31, 1937, p. 294.

Cross tubes for temperature adjusting medium are made with such cross section and placed in such positions that the distance between any tube and the nearest point of its neighbor is approximately constant at all points, and free flow of the catalyst downwards is permitted for continuous renewal. In the reduction of CO to produce hydrocarbons above C_2, all the particles of catalyst are $<$ 10 mm. distant from the wall of an oil-containing tube and the tubes are oval (long axis vertical) with ends left round and expanded into tube sheets.

3663. ———. [Catalytic Gas Reactions.] French Patent 784,885, July 27, 1935. Chem. Abs., vol. 30, 1936, p. 584.

Catalytic mass is divided into thin layers of uniform thickness, and the reaction takes place in spaces formed by the exterior walls of chambers containing a circulating liquid used to control the temperature.

3664. ———. Catalytic Synthesis of Aliphatic Hydrocarbons. British Patent 518,614, Mar. 4, 1940; appl. filed July 30, 1938. Chem. Abs., vol. 35, 1941, p. 7413.

See French Patent 841,043 (abs. **3665**).

3665. ———. [Catalytic Synthesis of Aliphatic Hydrocarbons.] French Patent 841,043, May 9, 1939. Chem. Abs., vol. 34, 1940, p. 1685.

See United States Patent 2,149,515 (abs. **664**).

3666. ———. Cracking Oils. British Patent 453,973, Sept. 22, 1936. Chem. Abs., vol. 31, 1937, p. 1598.

Antidetonating benzines and lubricating oils are produced from the products formed in the synthesis of benzines from H_2 and oxides of C by removing the light benzines that boil up to 100°, and also the paraffin from the higher-boiling fractions, condensing the olefins in the higher-boiling fractions to form lubricating oils, removing the noncondensed fractions from the lubricating oils and cracking these fractions, if desired, together with the paraffins removed at an earlier stage. Thus 100 kg. of a raw product produced by treating water gas at 200° in presence of a catalyst comprising Co and ZnO is fractionally distilled up to 125°, whereby a light benzine having a 60% olefin content is obtained, and then up to 250° to give a heavy benzine, the residue comprising 21 kg. of crude paraffin. The heavy benzine distillate is polymerized with $AlCl_3$ for 2 hr. at 120° and allowed to settle for 6 hr. The upper layer is separated from the lower layer of $AlCl_3$ addition compounds and is distilled to 250° at normal pressure and then to 200° under vacuum. The residue of 10.5 kg. comprises a lubricating oil of viscosity under 1.9 and solidification point —36°. The distillate is cracked in admixture with the paraffin residue, 39 kg. of a cracked benzine having an octane number of 75 being obtained.

3667. ——— [Fuels and Lubricants.] Austrian Patent 147,493, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 186; Chem. Zentralb., 1937, I, p. 5149.

See French Patent 792,021 (abs. **3702**).

3668. ——— [Gas Purification.] Netherlands Patent 42,296, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 168.

See United States Patent 2,110,240 (abs. **2811**).

3669. ——— [Gas Purification.] Netherlands Patent 43,321, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 168.

See United States Patent 2,110,241 (abs. **2793**).

3670. ———. [Higher Hydrocarbons From Carbon Monoxide and Hydrogen.] Italian Patent 363,998, no date. Chem. Zentralb., 1940, I, p. 325.

See German Patent Appl. St. 56,470 and St. 56,856 (abs. **684, 680**) and United States Patent 2,149,515 (abs. **664**).

3671. ——— [Higher Hydrocarbons From Carbon Monoxide and Hydrogen.] Italian Patent 367,973, no date.

See German Patent appl. St. 56,470 (abs. **684**) and St. 56,856 (abs. **680**).

3672. ——— [Hydrocarbon Synthesis.] Italian Patent 363,973, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 179.

See British Patent 518,614 (abs. **3664**).

3673. ——— [Hydrocarbon Synthesis.] Netherlands Patent 41,919, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 179.

See United States Patent 2,149,515 (abs. **664**).

3674. ——— [Hydrocarbon Synthesis.] Netherlands Patent 48,189, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 179.

See United States Patent 2,206,500 (abs. **689**).

3675. ——— [Hydrocarbon Synthesis.] Netherlands Patent 49,595, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 179.

See United States Patent 2,243,918.

3676. ———. [Hydrocarbon Synthesis.] Norwegian Patent 62,024, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 179.

See British Patent 518,614 (abs. **3664**).

3677. ———. [Liquid Hydrocarbons by Reduction of Carbon Monoxide.] German Patent 708,889, July 31, 1941; appl. St. 52,782, filed Nov. 8, 1934 (*Cl. 12 o–1.03*). FIAT Reel AA 90, frames 1,478–1,482; PB 70,275; Chem. Abs., vol. 37, 1943, p. 3250.

In producing liquid hydrocarbons by the catalytic reduction of CO with regulation of the temperature by means of a system of horizontally and parellelly arranged tubes filled with a cooling liquid, each individual tube being provided with transverse fins standing vertically to the tube axis, the space between being packed with the catalyst, use is made to the best advantage of a known tube system, whose horizontal tubes or ducts are rectangular in shape and placed with their longer cross-sectional axes in the direction of the gas stream and are provided with rectangular fins touching each other.

3678. ———. [Long-Chain Hydrocarbons.] German Patent 676,919, June 19, 1939; appl. St 52,990 filed Jan. 3, 1935 (*Cl. 12 o–1.03*). FIAT Reel AA 88, frames 3,421–3,423; PB 70,273; Chem. Abs., vol. 33, 1939, p. 7310.

In the catalytic reduction of CO by the aid of superheated steam or salt solutions to form long-chain hydrocarbons, tubes of elliptical, rhomboidal or rectangular cross sections are used for the circulating system. Addition to German Patent 672,731 (abs. **693**).

3679. ———. [Multistage Hydrogenation of Carbon Monoxide.] Austrian Patent 160,916, Oct. 21, 1943; appl. filed Mar. 30, 1935. TOM Reel 36, bag 3451, item 8.

In the catalytic hydrogenation of CO, an increased yield is obtained by operation in several steps so arranged that the conversion of CO takes place incompletely in the separate steps with the exception of the last.

3680. ———. Paraffin. British Patent 500,950, Feb. 17, 1939; appl. filed July 17, 1937. Chem. Abs., vol. 33, 1939, p. 5869.

Corresponds to French Patent 824,893 (abs. **3681**).

3681. ———. [Paraffin.] French Patent 824,893, Feb. 17, 1938. Chem. Abs., vol. 32, 1938, p. 6256.

Paraffin, which is solid at ordinary temperature, is produced by passing a mixture of CO and H_2 at a pressure of 4–10 atm. and at <250° over a catalyst composed of Co impregnated with paraffin, which is solid at ordinary temperature, the cavities between the particles of catalyst not being filled, and the catalyst being placed so that the paraffin formed drops continuously.

3682. ———. [Paraffin.] French Patent 840,568, Apr. 27, 1939. Chem. Abs., vol. 33, 1939, p. 8984.

In the production of paraffin, solid at ordinary temperature, from gases containing CO and H_2, using catalysts containing Co and pressures of 2–50 atm., the length of time of the gas in the reaction chamber is increased almost proportionally to the increase of pressure.

See also French Patent 824,893 (abs. **3681**).

3683. ———. [Paraffin.] Italian Patent 352,611, July 9, 1937. Chem. Zentralb., 1938, I, p. 4264.

CO and H_2, 30:60%, are passed over a Co–Th catalyst at 4 atm. and 190°. The catalyst becomes coated with solid paraffin at the usual temperature in such a manner that the empty space does not become filled with it, and the catalysts are so arranged that the paraffin can continually drip from the bottom.

3684. ———. [Paraffins From Carbon Monoxide and Hydrogen.] German Patent 731,295, Feb. 5, 1943; German Patent Appl. St 55,126, filed Aug. 2, 1936 (*Cl. 12 o–1.03*). FIAT Reel AA–88, frames 3,475–3,478; PB 70,273; Ind. chim., vol. 32, 1945, p. 149; Chem. Abs., vol. 38, 1944, p. 633.

High yield of solid paraffin is obtained (100–123 gm. per $m.^3$ of gas) by passing a mixture of CO and H_2 (1 : 2) at a temperature <250° and a pressure 4–20 atm., over a fixed Co catalyst previously impregnated with paraffin and arranged in such a manner that the paraffin formed can be continuously evacuated.

3685. ———. [Procedure for the Catalytic Conversion of Carbon Monoxide and Hydrogen to Hydrocarbons.] German Patent Appl. St 61,125, filed Dec. 18, 1942 (*Cl. IV d–12 o*). Navy 5811 IV–1; TOM Reel 134, item IV–1, 6 pp.

It is possible by the isosynthesis process described to produce gasoline of high antiknock value. The process works with raised pressure and temperatures >350°, preferably >450°, but <600° and with a ThO_2 catalyst made from a diluted $Th(NO_3)_4$ solution precipitated with Na_2CO_3 and fixed on a carrier. At 40 atm. pressure with a synthesis gas $CO:H_2=50:40$, a throughput of 175 l. per hr. (referred to 1 atm.), a temperature of 500°, and a 1-stage operation, 33% of the gas was converted, producing 100 gm. gasoline and gasol (C_3+C_4) besides CH_4 and C_2 hydrocarbons per m^3. The gasoline, which contained predominantly branched-aliphatic hydrocarbons besides naphthenes and aromatics, had an olefin content of 15%, a refractive index n 20/D=1.40 and an octane no. (motor method) 80–90. Two-thirds of the C_4 fraction was iso-C_4H_{10}. The catalyst retained its efficiency for several mo. Under the same conditions, but with a pressure of 150 atm., the gas conversion was 66% and the hydrocarbon production 130 gm. per $m.^3$, and at 1,000 atm. and 450°, 85% of the gas was converted with, however, a content of 20% H_2O-soluble organic compounds in the liquid reaction products.

3686. ———. Process for Producing Solid Paraffin. British Patent Appl. 22,394, 1938.

Process for producing paraffin solid at room temperature from gases containing CO and H_2, using catalysts of Co or a mixed catalyst containing Co at temperatures lying <250° C. and under pressures of 2–50 atm. or greater, in which the optimum contact period of the gases, ascertained at atmospheric pressure, is increased approximately proportionately to the increase in the pressure, that is to say, when the pressure is raised the quantity of gas, determined as the optimum at

atmospheric pressure, is passed through the reaction chamber per hr.

3687. ———. [Process for the Catalytic Production of Branched Hydrocarbons.] German Patent Appl. St 62,439, filed Nov. 5, 1942 (*Cl. 12 o–1.03*). TOM Reel 100.

Production of branched hydrocarbons from a mixture of dimethylether and H_2 at temperatures >300° (preferably 400°–500°) and at increased pressure (preferably >100 atm.), using as catalyst oxides of the 3d and 4th groups of the periodic system (preferably ThO_2). Example: A mixture of dimethylether and H_2 (1 : 5) is conducted at 450° and 30 atm. over a Th catalyst produced by precipitation from a Th nitrate solution with soda resulting in a conversion of 12% of the dimethylether to iso-C_4 hydrocarbons and 15% to liquid hydrocarbons; at 150 atm. the conversion was 25 and 20%, respectively, and at 300 atm. 35 and 25%, respectively, the liquid products having an octane no. of 80.

3688. ———. [Production of Fuels From Carbon Monoxide and Hydrogen.] Belgian Patent 429,337, no date.

See German Patent applications St. 56,470 (abs. **684**) and St 56,856 (abs. **680**).

3689. ———. [Production of Paraffin.] Italian Patent 363,997, July 12, 1938. Chem. Zentralb., 1940, I, p. 326.

See French Patent 840,568 (abs. **3682**).

3690. ———. [Production of Paraffin Solid at Room Temperature by Catalytic Synthesis From Carbon Monoxide and Hydrogen.] Swedish Patent 91,811, Mar. 24, 1938; appl. filed July 27, 1937. Chem. Zentralb., 1938, II, p. 767.

See Norwegian Patent 56,163 (abs. **3701**).

3691. ———. [Purification of Gases in Two Steps.] Austrian Patent 155,035, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell. Leipzig, 1950, p. 168.

See French Patent 797,902 (abs. **3696**) and United States Patent 2,110,241 (abs. **2793**).

3692. ———. Purifying Gases. British Patent 452,417, Aug. 21, 1936. Chem. Abs., vol. 31, 1937, p. 1186.

Temperatures of 150°–300° are specified.

See also French Patent 784,337 (abs. **3693**).

3693. ———. [Purifying Gases.] French Patent 784,337, July 22, 1935. Chem. Abs., vol. 30, 1936, p. 272.

Compounds of S are removed from gases containing CO and H_2 by using alkaline carbonates in amount of at least 5% in intimate mixture with oxides or hydroxides of Fe capable of reacting at temperatures < that at which accessory reactions with CO would take place (230°).

3694. ———. [Purifying Synthesis Gas.] Austrian Patent 151,658, no date. Chem. Zentralb., 1938, I, p. 28.

See French Patent 784,337 (abs. **3693**), German Patent 651,462 (abs. **2812**), and United States Patent 2,110,240 (abs. **2811**).

3695. ———. Removing Sulfur From Gases. British Patent 469,933, July 30, 1937. Chem. Abs., vol. 32, 1938, p. 1079.

Gases containing CO and H_2 are desulfurized by bringing them into contact with a catalyst at >300°, whereby the bulk of the organic compounds are decomposed, treating them at a reduced temperature for the removal of H_2S, and finally bringing them into contact at an elevated temperature <300° with S-absorbing masses to remove the residual S. If desired, a preliminary elimination of H_2S can be effected before the first step of the above process is effected. Suitable catalysts for the first step are sulfurized metal turnings or steel wool, a mixture of Co sulfide and W oxide, Ni deposited on a ceramic carrier, or a spent sulferetted purifying mixture from the last step of the process. Suitable absorbents for the last step include finely divided metals, spent hydrogenation catalysts, for example, finely divided Co or mixtures of alkali metal carbonates and oxide or hydroxides of Fe. The 2d stage may be conducted by employing a mixture of Fe_2O_3 and Na_2CO_3 followed by a spent dehydrogenation catalyst.

See also French Patent 797,902 (abs. **3696**) and United States Patent 2,110,241 (abs. **2793**).

3696. ———. [Removing Sulfur From Gases.] French Patent 797,902, May 6, 1936. Chem. Abs., vol. 30, 1936, p. 7315.

In the catalytic removal of organic S from gases containing CO and H_2 in 2 steps with intermediate removal of H_2S resulting from the 1st step, the transformation is carried out at <300° by means of particularly efficaceous catalysts in the 2d step, while less efficaceous catalysts are used at a higher temperature in the 1st step. Thus, a mixture of an alkali metal carbonate and oxides or hydroxides of Fe are used in the 2d step, and the used catalyst from the 2d step may be then used in the 1st.

3697. ———. [Solid Paraffin by Synthesis From Carbon Monoxide and Hydrogen.] Austrian Patent 160,262, July 27, 1937. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 179.

See French Patent 824,893 (abs. **3681**), Swedish Patent 91,811 (abs. **3690**), and United States Patent 2,206,500 (abs. **689**).

3698. ———. [Solid Paraffin Products From Carbon Monoxide.] Indian Patent 24,384, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 179.

See United States Patent 2,206,500 (abs. **689**).

3699. ———. Solid Paraffins From Carbon Monoxide and Hydrogen. British Patent 517,002, Jan. 17, 1940; appl. filed July 27, 1938. Chem. Abs., vol. 35, 1941, p. 6597.

See French Patent 840,568 (abs. **3682**).

3700. ———. Synthesis of Higher Aliphatic Hydrocarbons. British Patent Appl. 22,734, 1938.

Process for producing higher aliphatic hydrocarbons that are solid, liquid, and readily liquefiable, from gases containing CO and H_2 with Fe contact masses or catalysts or mixed catalysts containing Fe, in which water gas or mixtures or CO and H_2 still richer in CO are passed, under pressures of 2–50 atm. or over and at temperatures <320°, over Fe contact masses or catalysts or mixed Fe catalysts that have been produced from Fe salt solutions of precipitation, or by the decomposition of Fe compounds.

3701. ———. [Synthetic Aliphatic Hydrocarbons From Carbon Monoxide and Hydrogen.] Norwegian Patent 56,163, Feb. 10, 1936; appl. filed April 24, 1935. Chem. Zentralb., 1937, I, p. 493.

The initial mixture of CO and H_2 is at first only incompletely converted through the use of suitable low temperature and/or through injection of H_2 and/or through use of increased flow velocity or in some other suitable way. The unconverted reaction mixture after complete or partial removal of the condensible constituents is subjected to a new complete or partial conversion. Co catalysts are used.

3702. ———. [Synthetic Antiknock Fuel.] French Patent 792,021, Dec. 21, 1935. Chem. Abs., vol. 30, 1936, p. 4314.

Aliphatic hydrocarbons produced catalytically under ordinary pressure from CO and H_2 are treated to separate constituents b. up to 100°. The monoolefins

in the constituents having a higher b. p. are polymerized, for example, with $AlCl_3$ to form lubricating oils, and the residue is subjected to cracking to obtain an antiknock fuel.

3703. ———. Synthetic Fuel Gas. British Patent 458,022, Jan. 7, 1937; appl. filed July 16, 1936. Chem. Abs., vol. 31, 1937, p. 4091.

Mixture of H_2 and CO in approximately the ratio 2:1 is obtained by alternately blowing the solid fuel in a gas producer with a mixture of steam and O_2 and a mixture of steam and a coal distillation gas, for example, coke-oven gas, and mixing the resulting gases in suitable proportion.

3704. ———. [Treatment of Gasoline From Carbon Monoxide and Hydrogen.] Indian Patent 22,982, Nov. 21, 1936; appl. filed June 29, 1936.

The gasoline obtained by synthesis from CO and H_2 and b. >100° is cracked to increase its antiknock property after it is subjected at 120° to polymerization with $AlCl_3$ for the purpose of obtaining the lubricating oils from the monoolefins contained therein. There are thus obtained 42% of primary gasoline with octane number of 65, 39% cracked gasoline with octane number of 75, and 10.5% lubricating oil with a viscosity pole height of 1.9.

———. *See* abs. **664, 671, 673, 674, 677, 678, 679, 680, 681, 682, 683, 684, 685, 686, 688, 691, 693, 709, 710, 711, 712, 2793, 2811, 2812.**

3705. Sueta, H., and Niwa, A. (Mitsubishi Chemical Industries Co.). [Catalyst for Isobutanol Preparation.] Japanese Patent 176,614, Aug. 30, 1948. Chem. Abs., vol. 45, 1951, p. 5392.

2:1:1 mol. mixture of $Zn(NO_3)_2$, $Cu(NO_3)_2$, and $Ca(NO_3)_2$ is precipitated with NaOH, filtered, dried, mixed with 1.5 mol. aqueous $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$, heated at 100°, and then slowly heated to 400°. The catalyst is used for synthesis of iso-BuOH from CO and H_2.

3706. Sugahara, S., Kodama, S., and Fujita, T. (Kyoto Imperial University). [Reaction Chamber for Oil Synthesis.] Japanese Patent 142,908, Apr. 7, 1941; appl. filed Sept. 23, 1938. United States Naval Tech. Mission to Japan, Index No. X-38(N)-7, Encl. (D), 1946, p. 247.

Gives arrangement of cooling pipe.

3707. Sugahara, S., Kodama, S., Tsuneoka, S., and Fujita, T. (Kyoto Imperial University). [Steam Generator Utilizing Heat of Chemical Reaction.] Japanese Patent 126,845, Oct. 6, 1938; appl. filed Dec. 17, 1937. United States Naval Tech. Mission to Japan, Index No. X-38(N)-7, Enclosure (D), 1946, p. 247.

Gives arrangement of cooling pipes in reaction chamber.

3708. Sullivan, F. W. (Hydrocarbon Research, Inc.). Method for the Synthesis of Hydrocarbons in the Presence of a Solid Adsorbent. United States Patent 2,583,611, Jan. 29, 1952; appl. filed July 13, 1946, Serial No. 683,324; 6 claims (*Cl. 260–449.6*).

The normally liquid reaction products, obtained from the hydrogenation of CO by contact of the synthesis gas with the relatively coarse, solid, particulate, fluidized catalyst suspended therein, are removed from the reaction zone by being adsorbed by relatively fine adsorbent particles also suspended in the gaseous medium. A suitable adsorptive agent is activated charcoal. When operating the process for the production of gasoline, the reactor contains as catalyst an Fe powder promoted with about 1–2% K_2O and 2–3% Al_2O_3, the particle size being about 60- to 200-mesh. The activated charcoal is of such particle size that all of the material passes through a 200-mesh screen. The synthesis gas comprising $CO:H_2=1:2$ and with about 14% CO_2 is passed into the reactor at about 550° F., the reaction zone being maintained at about 600° F. and 200 p. s. i. g. Before entering the reaction zone, the synthesis gas entrains about 0.1 lb. of powdered activated coconut charcoal per standard cu. ft. of feed gas. When operating in this manner, a substantial proportion of the reaction products is taken up by the adsorbent particles in the immediate vicinity of their formation within the reactor, withdrawn therefrom by these particles, and liberated in the reactivation chamber.

3709. ——— (Hydrocarbon Research, Inc.). Process for Catalytic Conversion of Carbon Monoxide and Hydrogen to Hydrocarbons or Oxygenated Hydrocarbons. United States Patent 2,626,275, Jan. 20, 1953; appl. filed Feb. 18, 1947, Serial No. 729,411; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 47, 1953, p. 6123.

Discrete particles of catalytically inert material with the same fluidizing characteristics as the catalyst particles is mixed with the catalyst. By thus increasing the area of cooling surfaces, the maximum unit charging rate of reactants per unit of catalyst is increased without impairing conversion. In an example, Fe catalyst of 200-mesh and finer, 60% passing through 325-mesh, pressure 250 p. s. i. g., space velocity 3,500 vol. per hr. per vol., and temperature of 625° F. are used. When the Fe catalyst is diluted in the ratio of 1 part by settled volume to 4 parts of finely powdered Cu, the space velocity of the synthesis gas may be increased to 12,000 vol. per hr. per vol., with the same pressure and temperature conditions as before. In some instances it may be possible to raise the reaction temperature as much as 100° F. above the optimum for the catalyst in question. 6 United States patents cited.

———. *See* abs. **1794.**

3710. Sumerford, S. D. (Standard Oil Development Co.). Synthesis of Hydrocarbons. United States Patent 2,497,964, Feb. 21, 1950; appl. filed July 20, 1946, Serial No. 685,012; 1 claim (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 4655.

CO and H_2 are reacted in presence of fluidized finely divided Fe-type catalyst at a temperature 500°–700° F. and a pressure 400–600 p. s. i. An O content of 5–30% by weight is maintained in the catalyst by injecting steam into the reactor. The amount is 0.05–0.8 part by volume of steam per part of H_2 in the total feed. 2 literature refs. and 7 United States patents cited.

3711. ——— (Standard Oil Development Co.). Treatment of Solid Diluent in Hydrocarbon Synthesis Process. United States Patent 2,471,913, May 31, 1949; appl. filed Feb. 27, 1947, Serial No. 731,406; 3 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 7214.

Catalyst fluidity in Fischer-Tropsch synthesis may be maintained by use of sand, pretreated with acid, as diluent. HCl is preferred, but H_2SO_4 or HNO_3 may be used for the pretreatment. 6 United States patents cited.

———. *See* abs. **2566.**

3712. Sumerford, S. D., and Buchmann, F. J. (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,541,677, Feb. 13, 1951; appl. filed Aug. 5, 1947, Serial No. 766,180; 11 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 4912.

Hydrocarbon synthesis process may be improved by preconditioning the catalyst with synthesis gas H_2: $CO=2.5–3:1$ CO for 40–200 hr. Low yields of desired products may be expected during this period. Following the preconditioning period, the $H_2:CO$ ratio may be 2:1 or lower, and the yield of C_{4+} hydrocarbons will

be increased. In fluidized operation good yields are obtained under severe conditions 600° F. and above, and H_2 : CO ratio 2 : 1 and serious disintegration of the powdered-Fe catalyst is prevented. 5 United States patents cited.

3713. ——— (Standard Oil Development Co.). [Synthesis of Hydrocarbons and Oxygenated Compounds From Carbon Monoxide and Hydrogen.] French Patent 968,691, Dec. 1, 1950; appl. filed July 2, 1948. Chem. Zentralb., 1951, I, p. 1825.

Synthesis is performed in the presence of a powdered, fluidized, Fe catalyst. It is first passed through a pretreatment zone before being worked up in the reaction zone. The reaction is carried out under a pressure of >24.5 atm. The partial pressure of H_2 in the pretreatment zone is 10.5–18.9 atm. and in the reaction zone 4.9–11.9 atm. A high ratio of H_2 : CO is first maintained and later set at most H_2 : CO=2 : 1. The hydrocarbon mixture obtained has an octane no. 60–90. In addition oxygenated compounds such as ethyl alcohol are obtained.

3714. SUMMERFORD, M. S. D. (Standard Oil Development Co.). [Synthesis of Hydrocarbons.] French Patent 953,667, Dec. 12, 1949; appl. filed Oct. 1, 1947; in United States, Feb. 2, 1947. Chem. Zentralb., 1950, II, p. 366.

Hydrocarbon synthesis from CO and H_2 is carried out on a fluidized catalyst consisting of a catalyst metal, such as Fe, mixed with an inert diluent material, such as sand, which has been pretreated with an acid, such as 3–12 *n*–HCl. Equal amounts by volume of catalyst metal and acid-treated sand are used. The sand serves as a heat carrier and avoids overheating of the catalyst, with reduction of C deposition and of decreasing efficiency of the catalyst.

SUN OIL CO. *See* abs. **1779, 2347.**

SUNEN-BENEDED, R. *See* abs. **2724.**

SURFACE COMBUSTION CORP. *See* abs. **428.**

3715. SUWA, T., AND HAMA, Y. (Showa Electro-Industries Co.). [Iron Catalyst for Ammonia Synthesis.] Japanese Patent 3,412, Sept. 1, 1952. Chem. Abs., vol. 47, 1953, p. 8975.

A mixture of powdered electrolytic Fe 210, Al powder 7, CaO 3, and KNO_3 9 gm. is molded with 250 kg. per cm.^{2} pressure, then oxidized as usual by a fusion method.

3716. SWEETSER, S. B. (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,453,874, Nov. 16, 1948; appl. filed Feb. 1, 1946, Serial No. 644.957; 9 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 1170.

The object of the invention is the reduction of the O content of the hydrocarbons produced synthetically from CO and H_2, using the Fe catalyst. The dehydrating constituent is mixed mechanically with the finished synthesis catalyst, so that both constituents retain complete identity and the one in no way affects the properties of the other. The Fe catalyst has a particle size, 50–300μ, the Al oxide 1–50μ. The concentration of Fe catalyst will be greater in the bottom of the reactor, and the concentration of Al oxide greater at the top. This results in a lower concentration of H_2O vapor in the lower part of the reactor and inhibits the water-gas shift reaction. Suitable dehydration catalysts are: Activated alumina, alumina gel, silica gel, Th oxide, Al phosphate, Mg phosphate, and Ca sulfate. The ratio of dehydrating catalyst to synthesis catalyst may be 0.1 : 2.0 on the vol. basis. The catalysts may be withdrawn separately from the reactor for reactivation. 6 United States patents and 1 foreign patent cited.

3717. ——— (Standard Catalytic Co.). Hydrogenation of Carbon Oxides. United States Patent 2,353,600, July 11, 1944; appl. filed Aug. 22, 1940, Serial No. 353,631; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 38, 1944, p. 6078.

Gas containing oxides of C and H_2 is passed downwardly through a reaction zone containing fresh catalyst in its upper part and relatively spent catalyst in its lower part. Fresh catalyst is continuously added above and spent catalyst withdrawn below. Temperature and pressure conditions are maintained in the reaction zone adapted to produce hydrocarbons containing more than 1 C atom per mol. The exothermic heat of reaction is removed by a boiling liquid cooling medium, such as H_2O, kept in heat-exchange relation with the catalyst. A reaction zone of such height is employed that the hydrostatic head of the cooling medium is sufficient to produce a pressure equivalent to that of a column of H_2O at least 30 ft. high, so that the boiling temperature of the cooling medium is appreciably higher at the lower part of the reaction zone than at the top.

3718. ——— (Standard Oil Development Co.). Hydrogenation of Oxides of Carbon to Produce High-Boiling Alcohols and Liquid Hydrocarbons. United States Patent 2,561,244, July 17, 1951; appl. filed Oct. 25, 1947, Serial No. 782,131; 2 claims. (*Cl. 260–449.6*).

Normally liquid hydrocarbons and higher boiling alcohols are produced by reacting a dried mixture of H_2 and CO in about equal molecular proportions in the presence of a fluidized Fe catalyst promoted with 3.5 wt. % of Al_2O_3 and 0.5 wt. % of K_2O. Careful reduction with a large volume of dry H_2 is necessary in the preparation of the catalyst. With such a fluidized catalyst, the pressure may vary 15–30 atm., the temperature 375°–435° F., and the space velocity 1,000–5,000 vol. of reactants per vol. of catalyst per hr. Under such reaction conditions, the conversion of CO and H_2 mixture varies from about 10–50 vol. % to maintain high selectivity to alcohols, mainly C_{10}–C_{17}. After the high-boiling alcohols are separated by condensation or adsorption on activated C or silica gel, the remainder of the crude product containing CO_2, H_2O, CO, and H_2 are contacted in a 2d reaction zone with a 2d fluidized Fe catalyst at temperature 550°–700°, pressure 15–30 atm., and space velocity 500–3,000 vol. per vol. per hr. The product from this reaction contains substantial amounts of normally liquid hydrocarbons. Diagram.

3719. ——— (Standard Oil Development Co.). Method of Catalyst Production and Utilization. United States Patent 2,619,449, Nov. 25, 1952; appl. filed Dec. 30, 1948, Serial No. 68,145; 16 claims (*Cl. 196–52*).

Water-gas generation system is operated in 2 or more stages. The coke is withdrawn from the 1st stage for use in catalytic or adsorption processes. The distribution of load between the 2 stages is such that the coke withdrawn from the 1st stage has a surface area of at least 500 m.^{2} per gm. The balance of the coke is then sent to a subsequent water-gas generation stage or stages and used for production of water gas or synthesis gas. In this combination process, the catalyst regeneration is entirely eliminated. 1 literature ref. and 6 United States patents cited.

3720. ——— (Standard Oil Development Co.). Process of Regenerating Synthesis Catalyst With Oxygen and Return of Oxidized Catalyst to the Synthesis Reactor. United States Patent 2,472,501, June 7, 1949; appl. filed Dec. 20, 1945, Serial No. 636,248; 3 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 6811.

Fluid Fe catalyst used in Fischer-Tropsch synthesis is regenerated with air or O_2-containing gas. A portion of the contaminated catalyst is withdrawn from the lower part of the reaction zone either intermittently or continuously at a slow rate and transferred to a 2d fluid-type reactor where it is regenerated with air. In

a continuous process the regenerator is much < the reactor. The ozidized catalyst is returned to the reactor at a very low rate, so that the ratio of oxidized to reduced catalyst will be low at all times and the oxidized material will gradually be converted to a reduced form. The rate of return of oxidized regenerated catalyst should be <2% of the total weight of catalyst in the reactor per hr. 2 foreign patents and 4 United States patents cited.

3721. ——— (Standard Oil Development Co.). Synthesizing Hydrocarbons. United States Patent 2,471,914, May 31, 1949; appl. filed Feb. 14, 1945, Serial No. 577,822; 7 claims (*Cl. 196–52*).

Product from the Fischer-Tropsch synthesis boiling in the gasoline range is aromatized, and the product boiling above the gasoline range is catalytically cracked or destructively hydrogenated. The gas-oil fraction is destructively hydrogenated. The H_2 formed during the aromatization is used in the destructive hydrogenation operation. 16 United States patents cited.

———. *See* abs. **2166.**

3722. SWEETSER, S. B., AND SCHARMANN, W. G. (Standard Oil Development Co.). Process for Water-Gas Generation. United States Patent 2,652,319, Sept. 15, 1953; appl. filed Jan. 3, 1949, Serial No. 68,946; 8 claims (*Cl. 48–206*).

Claim 1. The process of producing gas mixtures containing CO and H_2 comprises passing a stream of finely divided carbonaceous solid material into an initial water-gas reaction zone, forming a fluidized mass of solids therein, subjecting said mass to a gasification reaction with steam at temperatures of 1,500°–2,000° F. to produce a gas rich in H_2 and CO, withdrawing said gas from said water-gas reaction zone, withdrawing finely divided char of high surface area from said water-gas reaction zone, passing at least a portion of said char into a catalyst impregnation zone, impregnating in said zone said char with a catalyst promoting gasification of C, recycling said impregnated char of high surface area to said water-gas reaction zone, and recovering a gas rich in H_2 and CO from said last-named zone.

3723. SWEETSER, S. B., AND SMITH, L. B. (Standard Oil Development Co.). Heat Control in an Exothermic Reaction. United States Patent 2,468,521, Apr. 26, 1949; appl. filed Apr. 17, 1946, Serial No. 662,906; 8 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 4908.

Catalyst of particle size 150–250 μ is mixed with an inert material, such as alumina, fullers earth, or silica gel, of 1–50 μ particle size. The proportion of inert to catalyst is about 20–200% by weight of the catalyst. The proportion is lower in the case of nonsupported-type catalyst of relatively high density. The inert particles continuously pass out of the reaction zone with the product. They are separated and cooled with H_2O or a vaporizable hydrocarbon, such as a light naphtha fraction, separated from the vapor, and returned to the reactor. Indirect heat exchange may also be used, such as a fluid-type hydrocarbon synthesis reactor containing 100 cu. ft. of Fe catalyst, d. 150 lb. per cu. ft., utilize 45,000 cu. ft. per hr. of a synthesis gas containing 45% CO. With 95% conversion of the CO, the heat liberated amounts to 2,640,000 B. t. u. per hr. When clay with a specific heat of 0.25 is used as the diluent for the catalyst, it is necessary to circulate 34,000 lb. per hr. of clay between temperatures of 600° F. in the reactor and 250° F. in the cooler for the inert material to transfer all of the heat of reaction. If the Fe catalyst is mixed with 25% by weight of the clay, the desired cooling is obtained by circulation of the clay approximately 9 times per hr. in a complete cycle through the cooling system. 3 United States patents cited.

3724. SWEETSER, S. B., RUSSELL, F. R., AND BUCKER, E. R. (Standard Oil Development Co.). Fischer-Tropsch Catalyst. United States Patent 2,623, 021, Dec. 23, 1952. Chem. Abs., vol. 47, 1953, p. 2461.

An attrition-resistant Fischer-Tropsch catalyst is produced in a 4-stage process, which comprises: (1) Impregnating with an alkali-metal salt promoter a red Fe oxide powder, prepared by precipitating an Fe compound from an aqueous solution of an Fe compound and heating the precipitate to convert it to the oxide; (2) drying the impregnated material, pilling it, and granulating the pills to pass a 40-mesh screen; (3) reducing the Fe oxide in a stream of H_2 and continuing the passage of H_2 for 3–5 hr. after the temperature of the bed has been increased to 677°–871°, the rate of H_2 flow being 750–1,500 vol. per vol. catalyst per hr. during the initial part of the sintering period, wherein the Fe is reduced to <1% O and about 100–200 vol. per vol. catalyst per hr. during the remainder of the periods; and (4) finally cooling the catalyst to obtain a product requiring substantially no grinding. A catalyst prepared in the manner described with use for 451 hr. at 343°–368° and 400 p. s. i. g. pressure, with an H_2: CO feed-gas ratio of 1.1 and 12 standard cu. ft. per hr. of H_2+CO per lb. catalyst, showed a 65–95% conversion of H_2 +CO and a disintegration rate of 8 gm. of 0–20 μ material formed per 100 gm. of material present larger than 20 μ per 100 hr.

SWIFT, T. B. *See* abs. **2098.**

SYKES, H. J. *See* abs. **3824, 3826.**

3725. SYMONDS, F. L. (Standard Oil Co. of Indiana). Natural-Gas Conversion to Hydrogen and Carbon Monoxide. United States Patent 2,631,094, Mar. 10, 1953; appl. filed Aug. 31, 1945, Serial No. 613,792; 8 claims (*Cl. 48–196*). Chem. Abs., vol. 47, 1953, p. 5666.

Natural gas is injected into a fluidized bed of finely divided reducible metal oxide, such as Cu oxide, kept in turbulent suspension by the upflowing gas. At a temperature of 1,500°–3,000° F., the hydrocarbons are oxidized to CO_2 and H_2O vapor, and the metal oxide is reduced. The metal oxide is transferred to a 2d regeneration zone where it is reoxidized with air, then it is returned to the 1st zone. The hot gaseous products are passed from the 1st zone to the 2d with additional natural gas. The temperature in the 2d zone is kept at 1,200°–2,000° F. by the heat of the gaseous products. The CO_2 is reduced, and the natural gas is decomposed to form CO: H_2. 2 foreign patents and 11 United States patents cited.

SYNDICAT D'ÉTUDE ET D'EXPLOITATION DES CARBURANTS DE SYNTHÈSE. *See* abs. **606.**

SYNTHETIC AMMONIA & NITRATES, LTD. *See* abs. **209, 740, 741, 1115, 3357.**

SYNTHETIC OILS, LTD. *See* abs. **7, 2444, 2446, 2448, 2449, 2450, 2451, 2452, 2453, 2454, 2455, 2456, 2457.**

3726. SZIGETH, G. Production of a Water Gas Particularly Suitable for Synthetic Purposes. British Patent 533,877, Feb. 21, 1941; appl. filed Dec. 7, 1939. British Chem. Abs., 1941, B, p. 218; Chem. Abs., vol. 36, 1942, p. 1169.

Practically CH_4-free water gas low in CO_2 is obtained by gasification, with a relatively small excess of steam, of liquid oils and tars, in absence of a catalyst, at >1,100° and >10 atm., the temperature of reaction being maintained by the direct combustion with O_2 of a portion of the fuel charge. The steam is preferably supplied to the reaction vessel as water emulsified in the oil or tar.

See Hungarian Patent 127,066 (abs. **3729**).

3727. ———. [Water Gas for Technical Synthesis.] Italian Patent 378,638, Nov. 15, 1939; in Hungary, Dec. 10, 1938. Chem. Zentralb., 1942, I, p. 2736.

Water gas, which is practically free from CH_4 and poor in CO_2, is obtained by gasifying liquid fuels, such as mineral oils, their distillation residues, or bitumen, with an amount of steam only slightly exceeding that required for the water-gas reaction at pressures >10 atm., preferably at 15–20, and at temperatures >1,100°, preferably 1,200°–1,300°. The reaction temperature is attained by burning a part of the liquid fuel with O_2 in the reaction chamber.

3728. ———. [Water-Gas Production.] German Patent Appl. —, filed Nov. 10, 1939; APC 303,852.

Water gas suitable for use in the preparation of synthetic hydrocarbons can be formed by vaporizing light hydrocarbons, such as mineral oils, residual oils, and gas oils, with a small amount of excess steam at temperatures of 1,200°–1,300° C. and 15–20 atm. pressure, and admitting a small amount of O_2 to the reaction chamber. CH_4 formation is claimed to be at a minimum.

3729. ———. [Water Gas Suitable for Industrial Syntheses.] Hungarian Patent 127,066, June 16, 1941. Chem. Abs., vol. 35, 1941, p. 8263.

Liquid fuels, such as mineral oils, their distillation residues, gas oils, and tars, are gasified under a pressure of 15–20 atm. at 1,200°–1,300°, with a slight excess of steam. A part of the required moisture may be introduced as an aqueous emulsion of the fuel. The reaction temperature is maintained constant by igniting and oxidizing a part of the fuel by O_2 or air enriched with O_2. Gives structural details of the furnace.

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TABET, G. E. *See* abs. **875.**

TAEGER, K. *See* abs. **3306.**

TAHARA, H. *See* abs. **1892.**

TANABE, T. *See* abs. **2400.**

3730. TANKA, K. [Synthesis of Gasoline.] Japanese Patent 130,421, June 7, 1939. Chem. Abs., vol. 35, 1941, p. 1970.

In the reaction of CO with H_2 constant pressure is maintained by allowing part of the liquid to vaporize and controlling the amount of vaporization by heating or cooling.

3731. TAYLOR, A. W. C. (Imperial Chemical Industries, Ltd.). Production of Oxygen-Containing Compounds. British Patent 655,339, Oct. 22, 1948. British Abs., 1951, B, II, p. 1060.

Compounds, such as alcohols, are obtained by interaction of olefins of >2 C (C_3H_6 or C_4H_8) with H_2 and CO 100°–200° and 75 atm. in liquid phase (in an alcohol, or a paraffin of 12–16 C), in presence of a dissolved Co salt followed by treatment of the effluent with H_2 (under similar conditions) to precipitate metallic Co, which is recovered.

3732. TAYLOR, A. W. C., AND ACKROYD, N. (Imperial Chemical Industries, Ltd.). Separation of Aldehydes and Olefins From Cobalt. British Patent 655,976, Aug. 8, 1951. Chem. Abs., vol. 46, 1952, p. 7584.

Aldehydes obtained by reaction of olefins and CO with Co as catalyst and unreacted olefin are separated from Co by flash distillation. Thus, the reaction mixture of di-isobutylene, nonaldehyde, and Co at 92° was fed at the rate of 1.5 l. per hr. to a point ⅓ of the way down a steel column 38 x 2 in., packed with ¼ x ¼ in. stainless-steel gauze rings, heated to 150°–160° at the bottom and 125°–130° at the top; after 5 hr., 7.4 l. of aldehyde and olefin containing <10 p. p. m. Co were recovered. Similarly, propylene and mixed butyraldehydes were separated from Co and a paraffin oil solvent.

3733. TAYLOR, A. W. C., TURNER, G., AND IMPERIAL CHEMICAL INDUSTRIES, LTD. Aliphatic Aldehydes. British Patent 633,184, Dec. 12, 1949. Chem. Abs., vol. 44, 1950, p. 4924.

Heating a mixture of an olefin, CO, and H_2 under pressure to 90°–180° in the presence of a Co catalyst yields predominantly an aliphatic aldehyde. Thus, di-isobutene at a rate of 2 l. per hr. and a 3 : 1 mixture of H_2 and CO at a rate of 6 $m.^3$ per hr. were passed over a metallic Co catalyst at 130° and 250 atm. pressure to yield 47% of nonaldehyde, 45% of di-isobutylene, 4% of octane, 4% of condensed products, and 0.13% of Co in combined form.

TAYLOR, R. *See* abs. **2397, 2398.**

TEBBOTH, J. A. *See* abs. **203.**

3734. TECHNICAL OIL MISSION. [Process for the Production of Hydrocarbons.] German Patent Appl. —, no date. TOM Reel 101, Doc. PG–21,576–NID; Transl. of German Documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis, Part II, 1946, pp. 6–10.

This invention describes a procedure that is said to overcome previous difficulties connected with the use of Fe catalysts and makes possible the replacement of the Co catalyst without diminishing the hydrocarbon yields or shortening the lifetime of the catalyst. This development consists in pretreating the Fe catalyst with pure CO or CO-rich gases at a pressure of about 0.1 atm., a maximum temperature of 320°–340°, and a contact time of about 24 hr. H_2 should not be present. It is believed that the improvement in catalyst activity is due to the formation of Fe carbides and the dispersion of a well-defined pattern of C throughout the crystal lattice. After induction, the preferable synthesis procedure is to use a synthesis-gas mixture of composition $1.5–2CO+1H_2$ at a pressure of 10–30 atm. and a temperature of 200°–320°. Example: An Fe catalyst, precipitated from the nitrates and containing 0.1% of alkali, was inducted at 0.1 atm. for 24 hr. at 325°, with 4 l. CO per 10 gm. Fe. Then the catalyst was operated with a synthesis gas consisting of $CO+H_2$ in the ratio of 1.8 : 1 at a pressure of 15 atm. and a temperature of 235°. The gas contraction was 55%, corresponding to a complete conversion of the CO. The yields of solid, liquid, and gasol hydrocarbons were approximately 150 gm. per N $m.^3$ of synthesis gas. The activity of the catalyst was still constant at the same operating temperature after 3 mo. The liquid hydrocarbons consisted chiefly of relatively antiknock benzine boiling up to 180°. 20 to 30 gm. of the total yield were C_3 and C_4 hydrocarbons partly unsaturated.

TELEGIN, V. G. *See* abs. **1739, 1983.**

3735. TEMKIN, M. I., AND PYZHEV, V. M. [Catalyst for Ammonia Synthesis.] Russian Patent 64,607, Apr. 30, 1945. Chem. Abs., vol. 40, 1946, p. 5216.

When Fe oxide catalyst used for NH_3 synthesis is regenerated in a special apparatus outside the synthesis column, the catalyst becomes pyrophoric, and thereby loses its catalytic activity. To prevent this, the catalyst after regeneration is cooled in a mixture of N_2 and H_2 and is treated, while cold, with a mixture of N_2 and H_2 containing a small quantity (for example, 0.1–0.2% by vol.) of O_2. When the catalyst is placed in the synthesis apparatus, the passivating film wears off

under the influence of N_2 and H_2 and the temperature within the apparatus. The activity of such catalyst is fully equal to that of a catalyst regenerated within the apparatus. The O_2 is best supplied by adding air to the N_2–H_2 mixture.

3736. TETER, J. W. (Sinclair Refining Co.). Amines and Nitriles From Olefins and Ammonia. United States Patent 2,419,470, Apr. 22, 1947. Chem. Abs., vol. 41, 1947, p. 5144.

Amines and nitriles are prepared by the reaction of olefins and NH_3 in the presence of reduced Co oxide catalyst. The mixture of olefin and NH_3, molar ratio 1:5 to 1:10, is passed over the catalyst bed at 400°–725° F. and 1,000–3,000 p. s. i. pressure. The catalyst, which has an active life of 6–10 hr., is reactivated by passing H_2 over it at elevated temperature and pressure. When 2 or more catalyst beds are used, the process is continuous.

3737. ——— (Sinclair Refining Co.). Method of Reactivating Reduced Metal Oxide Catalysts. United States Patent 2,500,776, Mar. 14, 1950; appl. filed Oct. 12, 1944, Serial No. 558,483; 2 claims (*Cl. 252–411*). Chem. Abs., vol. 44, 1950, p. 4607.

Reduced Co or Ni oxide catalyst can be reactivated after use in reaction of ammonia with olefins at 450°–750° F. and 500–3,000 p. s. i. with H_2 at 450°–750° F. and 1,000–3,000 p. s. i. The N-containing tarry deposit is converted to volatilized hydrocarbons and ammonia. The catalyst can be purged of H_2 by passing ammonia over it. 12 United States patents cited.

3738. ——— (Sinclair Refining Co.). Reducing a Metal Oxide Catalyst. United States Patent 2,437,487, Mar. 9, 1948; appl. filed Oct. 12, 1944, Serial No. 558,487; 5 claims (*Cl. 252–257*). Chem. Abs. vol. 42, 1948, p. 4313.

In reducing a metal oxide catalyst in which the metal oxide is of the group consisting of Co and Ni, the catalyst is subjected to a number of alternate treatments with NH_3 and H_2 at a temperature within the approximate range of 450°–750° F.

3739. TETER, J. W., AND OLSON, L. E. (Sinclair Refining Co.). Amines and Nitriles From Ammonia and Olefins. United States Patent 2,520,181, Aug. 29, 1950. Chem. Abs., vol. 45, 1951, p. 638.

Pyrolytic decomposition in the reaction of NH_3 and olefins was repressed by the use of an improved catalyst, a mixture of reduced metal oxides containing Co and another metal, especially Ni or Zn, capable of forming spinel-type crystal structures with Co. Diatomaceous earth 540 gm. was suspended in aqueous Na_2CO_3 910 gm. per gal., the slurry settled, heated to 90°, an equal volume containing 1,275 gm. $CoSO_4.7H_2O$ and 597 gm. $NiSO_4.6H_2O$ per gal. added, the mixture stirred, filtered, dried, ground, washed, calcined 2 hr. at 660° F., pelleted with 4% graphite, purged with NH_3, reduced with H_2, and the Na content adjusted to 1.95% with NaOAc. A gas mixture of 10 mol. NH_3 and 1 mol. MeCH : CH_2 at 640° F., 1,500 p. s. i., and olefin space velocity 0.2 gave 27.8% EtCN.

See also United States Patent 2,419,470 (abs. **3736**).

3740. TEXACO DEVELOPMENT CORP. [Catalyst.] French Patent 938,564, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell. Leipzig, 1950, p. 155.

Active constituents precipitated in the pressure of Filter-Cel.

3741. ———. Separation of Water-Soluble Organic Compounds From the Carbon Monoxide-Hydrogen Reaction. British Patent 646,925, Nov. 29, 1950. Chem. Abs., vol. 45, 1951, p. 6826.

Aqueous mixture from CO and H_2 synthesis containing compounds with O_2 are extracted with liquid aliphatic hydrocarbons at 175°–300° F. and 100–300 p. s. i. The hydrocarbon phase may then be treated with aqueous $NaHSO_3$ to recover the aldehydes and ketones and then with a secondary solvent, such as $(CH_2OH)_2$, to recover the alcohols.

3742. ———. Synthesis Gas. British Patent 672,165, May 14, 1952. Chem. Abs., vol. 46, 1952, p. 9287.

Synthesis gas is produced from a high-boiling hydrobon having an initial b. p. >204°, such as a residual fuel oil, in a 2-stage process, which comprises (1) burning the oil with O_2 of high purity in a regulated amount substantially below that necessary to convert the hydrocarbon completely into CO and H_2, together with a solid carbonaceaus material; and (2) separating the C and gasifying it to produce more water gas by treatment with steam and pure O_2. The reactions are preferably carried out at 1,093°–1,316°. The synthesis gas thus produced contains a greater proportion of H_2 than would be produced by complete gasification of the oil in 1 step, by reason of the steam added.

3743. ———. Synthesis Gas Containing Hydrogen. British Patent 649,645, Jan. 31, 1951. Chem. Abs., vol. 45, 1951, p. 5912.

Hydrocarbon consisting essentially of CH_4 is reacted with O_2 in the absence of steam and of a catalyst at 1,093°–1,427° in a reaction zone with the ratio of interior surface to volume of about 0.65. The CH_4 is preferably preheated to about 649° without cracking and is charged at the rate of 1,000–3,000 cu. ft. per hr. per cu. ft. reaction space. The O_2 is separately preheated to about 427° or higher and is charged to the reactor at such a rate that the primary reaction occurs with a substantially nonluminous flame. The products from the reactor consist principally of CO and H_2, about 5 mol. % or less H_2O, less than 2 mol. % CO_2, and not over 4–5 mol. % CH_4. The gas contains less than 1 gm. suspended C per 1,000 cu. ft. standard gas. Preferably 95% O_2 should be used.

3744. ———. Synthesizing Gasoline Hydrocarbons. British Patent 655,843, 1951. Fuel Abs., 1951, abs. 2904.

Mixture obtained by the hydrogenation of CO is separated into a gas phase, a liquid hydrocarbon phase, and a H_2O phase, the latter 2 containing considerable amounts of O_2-containing compounds dissolved therein. The gas phase containing normally gaseous products of conversion and unreacted CO and H_2 is recycled at least in part to the reaction zone. The aqueous phase containing mainly low-molecular-weight O_2-containing compounds dissolved therein is extracted at elevated temperature and pressure with a hydrocarbon solvent to form a hydrocarbon-rich extract phase containing most of the nonacidic O_2-containing compounds and a H_2O-rich phase containing low-molecular weight organic acids. The hydrocarbon-rich extract phase is combined with the liquid hydrocarbon phase, which is initially separated from the products of conversion and which, in general, contains oxygenated compounds of higher molecular weight than the aqueous phase. The combined phases are fractionated into 2 components, a low-boiling fraction distilling <245° F. and a high-boiling fraction distilling > that temperature. A substantial portion of the low-boiling fraction is recycled to the reaction zone to effect conversion of the low-boiling oxygenated compounds to liquid hydrocarbons in the gasoline range.

———. *See* abs. **262, 774, 775, 776, 777, 787, 821, 835, 838, 1045, 1836, 2755, 2756, 2757, 2841, 3323, 3324, 3658.**

TEXAS CO. (THE). *See* abs. **29, 30, 31, 32, 47, 48, 49, 50, 52, 53, 54, 55, 56, 58, 59, 60, 61, 62, 126, 158, 159, 160, 161, 162, 263, 264, 313, 391, 392, 395, 588, 589, 590, 591, 592, 593, 594, 778, 779, 780, 819,**

820, 836, 837, 1043, 1044, 1046, 1047, 1742, 1835, 1837, 1838, 1839, 1840, 2105, 2210, 2340, 2341, 2342, 2394, 2498, 2499, 2500, 2632, 3326, 3327, 3328, 3329, 3331, 3332, 3333, 3350, 3639, 3640, 3870, 3871, 3872, 3873, 3874, 3875, 3876, 3877, 3988.

3745. THARSON, A. (Lazote, Inc.). Synthesis of Ammonia. Canadian Patent 285,189, Nov. 27, 1928. Chem. Abs., vol. 22, 1929, p. 937.

In the synthesis of NH_3 a mixture of N_2 and H_2 is passed over a catalyst containing oxides of Fe, K, and Mg, which is more active than Fe alone, at a temperature 400°–700°. An Fe catalyst containing a mixed promoter comprising 1% K_2O and 1% MgO will give 25–30% NH_3 under normal synthesis conditions for relatively long periods of time. Mixed promoters comprising Li_2O and MgO, Na_2O and MgO_2, Na_2O and CaO, or K_2O and BaO can also be employed advantageously.

THERMATOMIC CARBON CO. *See* abs. **3441.**

THIELE, E. W. *See* abs. **3337.**

3746. THIEME, C. [Producing Fatty Acids by Ozonizing Mixtures of Olefin-Containing Hydrocarbons.] German Patent 744,080, Jan. 11, 1944; appl. T 50,522, filed June 12, 1938; (*Cl. 12 o–11*). FIAT Reel E 29, frames 618–619; PB 70,432.

Olefinic products obtained by the hydrogenation of coal or CO are ozonized in the cold, the resulting oxonides cracked preferably under oxidation and in presence of alkalies, and the fatty acids thus formed separated from the soaps. Example: 100 gm. of a Fischer-Tropsch diesel oil of specific gravity 0.769, I No. 12.69, viscosity 1.20 at 20°, flame point 89°, and solidifying point —3.5° was ozonized to saturation at room temperature. The oil was saponified with NaOH with simultaneous passage of air therethrough until the aldehydes formed were oxidized to acids. The saponifiable oils were then separated by shaking with petroleum ether, the soaps extracted from the residue with 50% alcohol and decomposed with H_2SO_4. There were obtained 6.39 gm. of H_2O-insoluble, clear yellow, liquid fatty acid besides 1.13 gm. of H_2O-soluble fatty acid. The H_2O-insoluble fatty acid was completely soluble in petroleum ether, therefore, free from oxyacids. The amount of unsaponifiable, unozonized oils was 90 gm.

3747. THOMAS, C. L. (Universal Oil Products Co.). Hydrogenation-Isomerization Catalyst. United States Patent 2,406,864, Sept. 3, 1946; appl. filed May 31, 1939, Serial No. 276,553; 14 claims (*Cl. 260–449.6*). Chem. Abs., vol. 40, 1946, p. 7574.

In the synthesis of hydrocarbons of gasoline and higher boiling range from CO and H_2, a motor fuel with improved octane qualities may be produced directly by using catalyst that has in addition to the hydrogenation component a second catalytic component known to function as an isomerizing and cracking agent. In the preferred method the hydrogenation component is prepared by precipitating the hydroxides of the metals on kieselguhr. The isomerization cracking component is prepared in powdered form in a separate operation, and the two components are mixed and shaped into pellets. The catalyst contains thoria and at least one of the metals of group VIII associated with a major proportion of silica and a minor proportion of at least one of the compounds, alumina and zirconia.

THOMAS, E. B. *See* abs. **69, 70, 72, 73, 74, 2569, 2570.**

3748. THOMAS, E. B., AND ALCOCK, E. H. (British Celanese, Ltd.). Acetic Acid. British Patent 669,760, Apr. 9, 1952. Chem. Abs., vol. 46, 1952, p. 8354.

AcOH is obtained in good yields by treating MeOH with CO under pressure > 100 atm. and at a temperature < 200° in the presence of H_2O and an iodide of a carbonyl-forming metal, such as Ni, Co, and Fe. The crude MeOH obtained from H_2 and CO in the presence of a MeOH-forming catalyst (ZnO, Cr_2O_3) can be used in this process without purification.

3749. THOMPSON, W. I., AND TYSON, C. W. (Standard Oil Development Co.). Regeneration of Fluidized Catalysts. United States Patent 2,475,650, July 12, 1949. Chem. Abs., vol. 43, 1949, p. 9300.

Combustible contaminants are removed from finely divided catalysts by burning with O_2-containing regenerating gas. The regeneration is carried out in successive heated zones, with progressively increasing O_2 concentrations and total pressures in the individual stages. This technique tends to counteract the decreased reaction rate resulting from loss of combustible matter. Effluent regenerating gas from a particular regenerating zone is used as feed gas for the preceding zone. The contact material and gas are blown upward in each stage, so that the time of passage of the regenerating gas is materially less than that of the fluidized catalyst. Gives 1 diagram.

TOBIAS, G. D. *See* abs. **3825.**

3750. TOMPKINS, L. G. R. (Standard Oil Development Co.). [Removing Oxygenated Organic Compounds From Hydrocarbon Mixtures.] French Patent 969,444, Dec. 20, 1950; appl. filed July 21, 1948. Chem. Zentralb., 1951, I, p. 2109.

The fractionated mixture, b. 38°–204°, is contacted in vapor form with a H_2O-free melt of 80% NaOH and 20% Na_2CO_3 at temperature > 318°. The oxygenated compounds are thus fixed. Distillation gives a hydrocarbon mixture rich in alpha olefins and especially suitable for catalytic conversion.

TONGUE, H. *See* abs. **2399.**

3751. TOTZEK, F. (H. Koppers G. m. b. H.). [Continuous Process for Generating Water Gas.] German Patent 740,734, Sept. 9, 1943 (*Cl. 26 a–2*). Chem. Abs., vol. 40, 1946, p. 197.

Water gas is generated from lumps of a nonreactive coal by the method of internal heating with a steam-O_2 mixture heated over 900°. Incompletely gasified coke is being withdrawn continually.

TOWNSHEND, S. C. *See* abs. **3862.**

TRAEGER, K. *See* abs. **2361.**

TRAMM, H. *See* abs. **454, 505, 816, 817, 918, 1914, 2140.**

3752. TRAMM, H., AND KOLLING, H. (Ruhrchemie A. G.). [Catalyst Regeneration.] German Patent 740,535, no date. Kainer, p. 244.

To remove deposits of C from the catalyst, mixed air and steam are passed over it at a flow rate of 620 and 180 $m.^3$, respectively, per hr.

3753. TRAMM., H., AND WISCHERMANN, W. (Ruhrchemie A. G.). [Hydrogenation of Carbon Monoxide in a Liquid Medium Over Suspended Catalysts.] German Patent 744,185, Jan. 26, 1944; appl. R 109,563, R 559, filed Mar. 11, 1941 (*Cl. 12 o–1.03*). FIAT Reel E 29, frames 878–880; PB 70,432; FIAT Reel AA–89, frames 61–64; PB 70,274; TOM Reel 177 frames 1,762–1,768; Chem. Zentralb., 1944, II, p. 93; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 1, chap. 61, 1948, p. 154; Chem. Abs., vol. 39, 1945, p. 2861.

As catalyst is used Ni, Co, or Fe suspended in a liquid medium. The hydrogenation is carried out in successive stages at 150°–280° under nearly atm. pressure or under pressures up to 50 atm. The synthesis gas is introduced into the catalyst zone in a highly dispersed form by means of a fritted ceramic plate, such as glass. In this way the reaction can be carried out in several steps, in all of which the gas velocity must be maintained equal. To accomplish this, either

the cross section of the frits must be reduced from step to step in accordance with the reduced quantity of gas, or corresponding amounts of H_2O vapor or low-boiling hydrocarbons or synthesis gas must be introduced into the cycle. The conversion temperature is so chosen that CH_4 formation in each step amounts to not more than 1% of the converted CO, while at the same time the catalyst load is increased about 2–7 times higher than is usual for the hydrogenation of CO in the gaseous phase.

3754. TRAUTMANN, J. Hydrogenation of Coal and Oil; Synthesis of Oils From Carbon Monoxide and Hydrogen. British Patent 261,786, Nov. 21, 1925. Chem. Abs., vol. 21, 1927, p. 3740.

Heat required for various processes is supplied to the reacting substances by finely divided heated metal, which may be in the form of powder, liquid, or vapor. Coaxial nozzles may be used. The reagents pass through the inner nozzle, while the hot metal is supplied through the outer one.

3755. ———. Hydrogenation of Coal and Oil; Synthesis of Oils From Carbon Monoxide and Hydrogen. British Patent 261,787, Nov. 21, 1925. Chem. Abs., vol. 21, 1927, p. 3740.

Specifies carrying out reactions similar to British Patent 261,786 (abs. **3754**) while employing molten Sn or other suitable catalyzers that may be brought into contact with reacting substances by threshing or centrifugal action. Describes apparatus.

3756. TROĬTSKIĬ, K. V. [Catalyst for Carbon Monoxide-Hydrogen Synthesis.] Russian Patent 54,392, Jan. 31, 1939; appl. filed July 27, 1937.

For the synthesis of hydrocarbons by the Fischer-Tropsch process, the catalysts are made as follows: Metallic Fe or magnetite is melted with addition of activating substances, such as K_2O or Al_2O_3, in a stream of O_2. Just before setting, a powder of the same composition is added to the melt. Co or Ni catalysts can be produced in the same way. Such catalysts have a high porosity.

See also Russian Patent 42,060 (abs. **3757**).

3757. ———. [Catalyst for Synthesis of Ammonia.] Russian Patent 42,060, Mar. 31, 1935. Chem. Zentralb., 1935, II, p. 3961; Chem. Abs., vol. 30, 1936, p. 8538.

Fe or magnetite, together with an activator, is melted in a stream of O_2. A powder prepared in the same way is added to the melt just before solidification.

3758. ———. [Contact Apparatus for the Ammonia and Methanol Synthesis.] Russian Patent 44,239, Sept. 30, 1935. Chem. Abs., vol. 32, 1938, p. 2792.

Construction details of a catalytic chamber equipped with a powdered and granular catalyst.

3759. ———. [Contact Apparatus for the Synthesis of Ammonia and Methanol.] Russian Patent 51,150, May 31, 1937. Chem. Abs., vol. 33, 1939, p. 4748.

Construction details of a reaction chamber for use of powdered and granulated catalyst.

See also Russian Patent 44,239 (abs. **3758**).

TROPSCH, H. *See* abs. **695, 696, 697, 698, 699, 700, 701, 702, 703, 704, 705, 706, 707, 708.**

3760. TSCHUNKUR, E., AND KLAMROTH, A. (I. G. Farbenindustrie A. G.). Purifying Synthetic Methanol by Use of Permanganate. United States Patent 1,744,180, Jan. 21, 1930; appl. filed Oct. 12, 1927. Chem. Abs., vol. 24, 1930, p. 1393.

See French Patent 650,543 (abs. **1517**).

3761. ——— (I. G. Farbenindustrie A. G.). [Refining Methanol.] German Patent 625,324, Feb. 7, 1936 (*Cl. 12 o–5.01*). Chem. Abs., vol. 30, 1936, p. 2993.

MeOH prepared from CO and H_2 is treated in the presence of H_2O with small portions of $KMnO_4$ and $ZnCl_2$. With very impure MeOH, treatment with an organic base of high boiling point—for example, a phenylenediamine or aminophenol, may follow. The mixture is then fractionated.

TSUNEOKA, S. *See* abs. **758, 1875, 1878, 1879, 3707.**

TURNER, G. *See* abs **3733.**

3762. TUSSON, J. R. (Standard Oil Co. of Indiana). Catalytic Contacting Apparatus. United States Patent 2,550,948, May 1, 1951; appl. filed Mar. 24, 1948, Serial No. 16,720; 1 claim (*Cl. 23–289*). Chem. Abs., vol. 45, 1951, p. 6368.

Describes apparatus for contacting fluids with solids at elevated temperatures and pressures. Discusses its application to the production of synthetic hydrocarbons by catalytic reduction of CO with H_2 by the Fischer-Tropsch process.

3763. TUTUMI, S. (Director of Nenryo Kenkyuzyotyo). [Synthesis of Hydrocarbon Oils.] Japanese Patent 130,554, June 15, 1939. Chem. Abs., vol. 35, 1941, p. 1970.

Aqueous Ni and Cr salts (not $>$ 20% as much Cr as Ni), with or without carrier or kieselguhr, asbestos, pumice, are precipitated by adding carbonate or caustic alkali and reduced with H_2 at high temperature; CO and H_2 are passed at $<$ 50 atm. and $>$ 90°, preferably at 165°.

———. *See* abs. **124.**

3764. TYSON, C. W. (Standard Oil Development Co.). Starting-up Operation Using Powdered Catalyst. United States Patent 2,391,366, Dec. 18, 1945; appl. filed June 15, 1943; Serial No. 490,831; 7 claims (*Cl. 196–52*). Chem. Abs., vol. 40, 1946, p. 1016.

When powdered catalyst is used, the whole system must be heated to a temperature $>$ the condensation point of H_2O, before the powdered catalyst is introduced, to prevent massing of the catalyst particles. Heated air is passed through both the reaction and regeneration zones until a temperature of 225°–400° F. is reached. An auxiliary burner is then started, and the heated air on the regeneration side is replaced by hot combustion gases diluted with air. The air going to the reaction side is replaced by superheated steam. Then, combustion gases from the auxiliary burner at a temperature of 1,250° F. are quenched with the cold catalyst, which is then supplied to the regeneration side of the unit. In this way the cold catalyst is heated quickly, and heat is also supplied throughout the equipment.

See abs. **2151, 2439, 3749.**

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UFER, H. *See* abs. **3287, 3288.**

3765. UFER, H., AND SCHMIDT, O. (I. G. Farbenindustrie A. G.) [Methanol.] German Patent 565,880, Mar. 4, 1923. Chem. Abs., vol. 27, 1933, p. 2459.

Methanol is prepared by reducing CO with excess of H_2 in the presence of catalysts at 220°–250° and under pressure. The catalyst consists of elements of the Cr or B groups. Gives examples.

See also German Patent 544,665 (abs. **2364**).

UFER, J. *See* abs. **3289, 3290, 3291, 3292, 3293, 3294.**

3766. UHDE, F., AND PFIRRMANN, T. W. [Heating Oil

and Motor Fuel.] French Patent 819,660, Oct. 23, 1937. Chem. Abs., vol. 32, 1938, p. 2325.

Heating oil and diesel motor oil are obtained by dissolving primary bitumen and coal extracts in oils poor in H, adding an oil causing precipitation (gasoline, benzene, light oils obtained by hydrogenating coal extracts or primary bitumen, oils rich in H obtained from paraffin, such as those resulting from the Fischer-Tropsch synthesis), and removing the precipitating oil by distillation, or otherwise after removal of the precipitates obtained.

3767. ———. Motor Fuel. British Patent 482,783, Apr. 5, 1938. Chem. Abs., vol. 32, 1938, p. 7249.

See French Patent 819,659 (abs. **3769**).

3768. ———. Motor Fuel. British Patent 505,953, May 19, 1939; appl. filed Aug. 29, 1938. British Chem. Abs., 1939, B, p. 693; Chem. Abs., vol. 33, 1939, p. 9599.

Gasoline and diesel fuels are made from tars, such as brown coal, low- or high-temperature or producer tar, by treating them with a middle oil obtained in the reduction of CO with H_2 and separating the extract from the heavy-oil residue, the extract being then hydrogenated in the gas phase and the oil residue hydrogenated in the liquid phase to form fuels. The gas phase is carried out over rigid catalysts immune to S poisoning at 420°–440°, the liquid phase in presence of finely divided Mo or Sn catalysts at 450°–500° at higher pressures.

3769. ———. [Motor Fuel.] French Patent 819,659, Oct. 23, 1937. Chem. Abs., vol. 32, 1938, p. 2325.

Fuel suitable for diesel motors is made by hydrogenating carbonaceous materials such as coal, lignite, coal extracts, and primary bitumen to produce oils poor in H and adding oils rich in H. The oils rich in H may be obtained by synthesis from CO and H_2 or by hydrogenating carbonaceous materials. Solid bituminous hydrocarbons, such as coal extracts and primary bitumens obtained from coal, may also be added.

3770. ———. [Motor Fuel.] French Patent 841,528, May 22, 1939. Chem. Abs., vol. 34, 1940, p. 4544.

Tar products obtained by destructive distillation are separated into 2 layers by mixing with Kogasin. The upper layer, containing the Kogasin and non-aromatic hydrocarbons rich in H, is subjected to hydrogenation in gaseous phase. The lower layer, containing in greater part aromatic and asphaltic substances, is hydrogenated in liquid phase. The resulting products are motor and diesel fuels of high heating value.

ULLMANN, D. *See* abs. **1912**.

3771. ULLRICH, A. [Drying Oil.] German Patent Appl. Sch 127,903, no date (*Cl. 22 h–2*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 693.

Synthetic drying oil for paint is made from paraffin hydrocarbons of CO hydrogenation, with about 14–35 C atoms, plus oil-reactive phenol resins of the Resol type. Addition to German Patent Appl. Sch 126,583 (abs. **3234**).

3772. ———. [Improving Synthetic Waxes.] German Patent Appl. Sch 128,630, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 356.

Synthetic waxes from the oxidation of high-molecular paraffin hydrocarbons are improved by a subsequent hydrogenation.

3773. ———. [Substitute Fats.] German Patent Appl. Sch. 128,184, no date (*Cl. 12 o–11*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 355.

Substitutes for industrial fat are produced from the oxidation products of high-molecular paraffin hydrocarbons (acid No. at least 80, ester No. at least 70, b. p. >300°) by esterifying with univalent alcohols, which contain at least 3 C atoms in the molecule.

3774. ———. [Waxes.] German Patent Appl. Sch 128,228, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 355.

Wax exchange material is produced by oxidizing hard paraffin of the Fischer-Tropsch process under pressure, whereby the O_2 partial pressure decreases with increasing degree of oxidation, the total pressure however being kept constant by the addition of inert gases.

3775. UNDERWOOD, A. J. V. Production of Hydrocarbons. British Patent 516,555, July 21, 1938. Chem. Zentralb., 1941, I, p. 2894; British Chem. Abs., 1940, B, p. 189.

Coal, coke, or other carbonaceous material is gasified under pressure with steam, the products of gasification, chiefly CO and H_2, are passed through a H_2O-cooled synthesis chamber, and the low-pressure steam produced by heating of the cooling H_2O and/or contained in the products of the synthesis reactions is then converted by means of an injector thermocompressor into high-pressure steam, which is used for the gasification of further fuel.

3776. UNION CHIMIQUE BELGE. [Catalytic Reactions.] French Patent 672,898, Apr. 10, 1929. Chem. Abs., vol. 24, 1930, p. 2255.

In exothermic catalytic synthesis in the gaseous state, a regulated part of the gases to be treated is sent into the catalyst chamber without being submitted to an exchange of temperature with the products of reaction, a rational cooling of the reaction mass taking place. The gases to be treated are used to produce, by convection from metallic surfaces buried in the contact mass, an absorption of heat corresponding to the normal temperature most favorable to the reaction. Describes apparatus.

3777. ———. [Catalytic Synthesis in Gaseous Phase.] Belgian Patent 359,588, May 31, 1929. Chem. Abs., vol. 24, 1930, p. 930.

Pressure tube is divided by tubular walls into 2 annular and 1 central compartment, the upper part of the latter being surmounted by an annular electrical resistance. The central compartment contains the catalyst through which passes a series of heat-exchanger tubes; these are closed at the bottom and each surrounds a central tube.

3778. ———. [Decomposition of a Mixture of Methane and Wator Vapor by Means of Heat.] Belgian Patent 361,718, July 31, 1929. Chem. Abs., vol. 24, 1930, p. 4615.

H_2 and CO are obtained by the decomposition, by means of heat, of a mixture of H_2O vapor and volatile or gaseous hydrocarbons, such as those contained in natural gas or in gases produced in the carbonization or gasification of fuels. The required heat is obtained by the combustion of part of the gas to be treated.

3779. ———. [Exothermic Catalyst Synthesis in Gaseous Phase.] Belgian Patent 360,405, June 29, 1929. Chem. Abs., vol. 24, 1930, p. 903.

Catalysis is carried out in successive and progressive stages, the amplitude of each stage being regulated so that at no point in the mass is a given predetermined temperature exceeded. The vertical walls of the vessel containing the catalyst are provided with horizontal protuberances, and the periphery of some of the protuberances is provided with openings for partial successive introductions of fluid.

3780. ———. [Hydrogen and Carbon Monoxide.] French Patent 682,549, Aug. 25, 1930; appl. filed Oct. 1, 1929. Chem. Abs., vol. 24, 1930, p. 4596.

H_2 and CO are produced by decomposing, under the action of heat, a mixture of steam, CH_4, and gaseous or volatile hydrocarbons, such as those contained in natural gases or in gases coming from the carbonization or gasification of fuel. The required heat is obtained by the combustion of a part of the gas to be treated, the circuit of gas to be treated and that of the gases in combustion being separated during the treatment.

UNION OIL CO. OF CALIFORNIA. *See* abs. **171, 172, 2496, 2752, 2753.**

UNION RHEINISCHE BRAUNKOHLEN KRAFTSTOFF A.-G. *See* abs. **2630, 2631.**

3781. UNITED ENGINEERS & CONSTRUCTORS INC. Synthesis of Gas Rich in Hydrogen and Carbon Monoxide. British Patent 685,359, Dec. 31, 1952. Chem. Abs., vol. 47, 1953, p. 6636.

Gases rich in H_2 and oxides of C are made in a cyclic, catalytic process utilizing steam and hydrocarbons. First, fuel is burned, and the hot products of combustion are passed through 2 successive heat-storage beds and a catalyst bed. Then, a gaseous hydrocarbon is introduced between the 2 heat-storage beds, admixed with steam, part of which may have been passed through the first heat-storage zone, and the mixture is converted in the catalyst zone to gas rich in H_2 and CO.

3782. ———. Water Gas. British Patent 689,762, Apr. 1, 1953. Chem. Abs., vol. 47, 1953, p. 8997.

Gas rich in H_2 and CO is manufactured from a fluid fuel in a cyclic process, which comprises: (1) Burning the fuel in a combustion chamber in 1 part of the cycle, dividing the hot combustion products into 2 streams, and passing each stream simultaneously and in parallel through a separate path, each of which comprises in series a 1st heat-storage zone of refractory material, a zone of reforming catalyst, and a 2d heat-storage zone of refractory material to store heat therein; (2) in another part of the cycle passing a hydrocarbon in the gaseous state and steam serially through both paths to form a gas rich in H_2 and oxides of C, mainly CO, and collecting the gas; and (3) in another part of the cycle passing a hydrocarbon in the gaseous state and steam serially through both paths in the opposite direction to the 2d step, to form a gas rich in H_2 and oxides of C, largely CO, and collecting this gas also. Air may also be added to the streams of gaseous hydrocarbon and steam.

UNITED STATES, ATTORNEY GENERAL. *See* abs. 2655.

UNITED STATES OF AMERICA, AS REPRESENTED BY THE SECRETARY OF THE INTERIOR. *See* abs. **451, 513, 947, 3897.**

3783. UNIVERSAL OIL PRODUCTS Co. [Catalyst] French Patent 938,605, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell., Leipzig, 1950, p. 155.

See United States Patent 2,406,864 (abs. **3747**).

3784. ———. Catalyst and Process for Synthesizing Organic Compounds. British Patent 626,071, July 8, 1949. Chem. Abs., vol. 44, 1950, p. 2205.

Catalyst for the synthesis of organic compounds from CO and H_2 consists of ThO_2 and at least 1 metal from Group VIII in combination with an isomerizing and cracking component, mainly SiO_2 mixed with Al_2O_3, and/or ZrO_2. The improvement is the addition of the isomerizing and cracking component to the hydrogenating catalyst to obtain high-grade motor fuels.

3785. ———. Cracking Oils. British Patent 495,477, Nov. 9, 1938. Chem. Abs., vol. 33, 1939, p. 3129.

Normally liquid or solid hydrocarbon materials of predominantly paraffinic character, for example, a paraffin-base stock containing hydrocarbon wax or a paraffinic hydrocarbon distillate, are converted into olefinic products suitable for polymerization into lubricating stocks by vaporizing the hydrocarbon materials and immediately, without separation, subjecting the vapors to cracking in a plurality of parallel-connected tubular elements, directly connected to the tubular vaporizing zone, in which additional heat is supplied to produce substantial yields of olefins, abruptly reducing the temperature of the cracked products by direct contact with a cooling fluid, and recovering the olefinic products by fractional condensation.

———. *See* abs. **910, 911, 1110, 1801, 1802, 2035, 2036, 2696, 3321, 3747, 3869.**

URBAN, W. *See* abs. **2372.**

3786. URQUHART, N. J., AND RIDER, C. A. (Combustion Processes Co.). Method of Reducing Iron Oxides. United States Patent 2,654,669, Oct. 6, 1953; appl. filed Oct. 2, 1951; Serial No. 249,323; 4 claims (*Cl. 75–33*).

Claim 1. The method of reducing Fe oxide by supporting a particulate batch of Fe oxide and C in the chamber of a rotable tubular furnace, sustaining a reducing atmosphere over the said particulate batch, repeatedly raising substance of the batch at the surface thereof to a crust-forming temperature below that at which free-flowing slag is formed, and by successive intermittent angular movements of the said furnace chamber turning under in the particulate batch successive crusts of reduction products formed at the surface of the batch, while repeatedly bringing fresh substance of the batch to the surface thereof for exposure to the crust-forming gases and temperature of the said furnace atmosphere.

3787. USINES DE MELLE. [Formaldehyde.] French Patent 811,038, Apr. 5, 1937. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesell. Leipzig, 1950, p. 230; Chem. Abs., vol. 31, 1937, p. 6981.

Mixture of H_2 with CO or CO_2 is passed through an electrical field under a reduced pressure not exceeding 0.15 atm. The electric charge may be 0.05–0.3 milliamps per $cm.^2$ of reaction tube cross section. Higher yields are obtained if an absorbent for CH_2O, for example, active C, is mounted between the electrodes. Describes apparatus.

———. *See* abs. **896, 2779.**

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3788. VAIL, W. E. (E. I. du Pont de Nemours & Co.). Aliphatic Carboxylic Acids. United States Patent 1,924,764, Aug. 29, 1933; appl. filed Dec. 31, 1931, Serial No. 584,294; 8 claims (*Cl. 260–116*). Chem. Abs., vol. 27, 1933, p. 5340.

Boron phosphate is used as a catalyst in the production of acids, such as propionic acid, by reaction of steam, CO, and an olefinic hydrocarbon, such as C_2H_4.

3789. ——— (E. I. du Pont de Nemours & Co.). Formic Acid. United States Patent 1,895,238, Jan. 24, 1933. Chem. Abs., vol. 27, 1933, p. 2457.

Gaseous mixture containing CO and steam is subjected to catalytic reaction in the presence of a B phosphate catalyst.

3790. ——— (E. I. du Pont de Nemours & Co.). Methyl and Ethyl Propionates, Ethyl Butyrate, and Other Similar Esters. United States Patent 1,979,717, Nov. 6, 1934; appl. filed Dec. 31, 1931, Serial No. 584,296;

16 claims (*Cl. 260–106*). Chem. Abs., vol. 29, 1935, p. 181.

Olefin, an alcohol, and CO (such as C_2H_4, EtOH, and CO for the production of ethyl propionate, or C_3H_6, EtOH, and CO for the production of ethyl butyrate) are caused to react (suitably in the presence of an activated charcoal catalyst, at a temperature of about 325° and <700 atm. pressure). MeOH containing 1% of NH_4Cl may be used, and as catalytic materials there also may be used inorganic acids of P, As, or B, or compounds, such as $CaCl_2$, Cd phosphate, silicotungstic acid, $ZnCl_2$, CaF_2, CaI_2, or NaBr. Gives several examples, with details of procedure.

3791. ——— (E. I. du Pont de Nemours & Co.). Producing Carboxylic Acids Such as Propionic Acid. United States Patent 2,000,053, May 7, 1935; appl. filed Aug. 24, 1931, Serial No. 559,132; 7 claims (*Cl. 260–116*). Chem. Abs., vol. 29, 1935, p. 4027.

Gaseous mixture containing an olefinic hydrocarbon, such as C_2H_4 (for the production of propionic acid) or C_3H_6 (for the production of butyric acid) steam, and CO is passed over a metal compound, such as K_2CO_3, which forms a salt with the carboxylic acid produced (suitably at 300° <700 atm. pressure).

——— *See* abs. **2010.**

3792. VALLALAT, K. H. [High-Pressure Gas Reactions.] German Patent 274,538, Jan. 24, 1913. Chem. Abs., vol. 8, 1914, p. 2930.

In carrying out high-pressure gas reactions, the reaction-gas mixture is divided in the reaction chamber into several streams, of which each flows through the reaction chamber only for a portion of its length. Specifies an apparatus.

3793. VANCE, F. P. (Phillips Petroleum Co.). Fluidized-Bed Reactor. United States Patent 2,546,570, Mar. 27, 1951; appl. filed Nov. 15, 1948, Serial No. 60,071; 9 claims (*Cl. 260–449.6*).

Apparatus and process particularly adaptable to the Fischer-Tropsch reaction are given. The depth and volume of the fluidized bed of catalyst may be adjusted in response to the flow rate and desired contact time. Gaseous reactant is introduced at the bottom of the reactor, containing sufficient fluidizable catalyst to maintain the catalyst in a dense, fluidized bed phase. Gaseous reactant is also introduced at least one point above the bottom at a sufficient rate to maintain the catalyst above the inlet zone in a less dense, fluidized-bed phase. The depth of the less dense phase is varied by varying the height of the reactant-gas inlet zone and by introducing or removing catalyst from the more dense phase when said depth is decreased or increased. 4 United States patents cited.

3794. VANDAVEER, R. F. (Stanolind Oil & Gas Co.). Hydrocarbon Synthesis. United States Patent 2,626,-274, Jan. 20, 1953; appl. filed June 19, 1948, Serial No. 34,147; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 47, 1953, p. 6123.

Finely divided Fe catalyst is impregnated with 0.1–2.5% of an alkali metal compound. An aqueous solution of an alkali metal salt of a sulfonic acid having at least 8 C atoms is used in quantity sufficient only to be absorbed by the catalyst. The catalyst is dried and reduced at temperature >700° F. under superatmospheric pressure. Enough surface active material is added to the alkali metal solution to reduce the surface tension of the solution to <40 d. per cm. 1 literature ref., 1 foreign patent, and 10 United States patents cited.

VAN DE PUTTE, W. L. *See* abs. **3301.**

3795. VAN DER WAALS, J. H. (N. V. de Bataafsche Petroleum Maatschappij). [Separating Hydrocarbons and Oxygenated Derivatives.] Netherlands Patent 69,028, Dec. 15, 1951. Chem. Abs., vol. 46, 1952, p. 9584.

Hydrocarbons and O-containing organic compounds, insoluble in H_2O, are separated by treating mixtures containing these substances (for example, obtained in the Fischer-Tropsch process or the Oxo synthesis from CO and olefins) with formic acid, optionally admixed with H_2O. Preferably, 78% formic acid, which is the maximum azeotropic mixture with H_2O, is used. For example, from a mixture of paraffinic hydrocarbons containing about 10% $MeCOCH_2CHMe_2$, the latter is isolated by countercurrent extraction with a mixture of 77.5 wt. % formic acid and 22.5% H_2O. The yield is 99%, and the degree of purity of the ketone is 99%.

3796. ——— (Shell Development Co.) Separation of Oxygenated Organic Compounds. United States Patent 2,644,006, June 30, 1953; appl. filed Mar. 7, 1949; Serial No. 80,104; 10 claims (*Cl. 260–450*).

Claim 1. A process of extracting H_2O-insoluble, oxyhydrocarbon compounds containing from 4–10 C atoms per molecule from a lower boiling range fraction of H_2O-insoluble products obtainable by the catalytic synthesis of hydrocarbons from a mixture of CO and H_2, utilizing the Fischer-Tropsch process, which process comprises subjecting a portion of said fraction of products to intimate contact with counterflowing solvent bodies of an extracting agent, comprising a major proportion of formic acid and of a liquid hydrocarbon having a substantially higher boiling range than the boiling range of the hydrocarbons present in said fraction of products, a minor proportion of H_2O, based on the formic acid, being added to the system of counterflowing solvent bodies at least at one point thereof during said contacting operation, separating resulting extract and raffinate phases, and recovering oxyhydrocarbon compounds from the separated extract phase.

3797. ——— (N. V. de Bataafsche Petroleum Maatschappij). [Separation of Oxygen-Containing Derivatives of Hydrocarbons.] Netherlands Patent 69,921, May 15, 1952. Chem. Abs., vol. 47, 1953, p. 1726.

Mixtures of O-containing compounds, which are insoluble or practically insoluble in H_2O, obtained in the manufacture of synthetic hydrocarbons (especially those formed in the Fischer-Tropsch or Oxo process), are separated into 2 fractions containing respective compounds with a more or less pronounced polar character by subjecting them to treatment with 2 solvents flowing countercurrent to each other, one being a liquid containing a substance with 2 or more polar groups (I) or 1 polar group and a highly polarizable remainder (II), and the other a liquid that consists entirely or substantially of 1 or more paraffinic hydrocarbons with a boiling range outside the boiling limits of the starting mixture (III). It is advantageous to subject mixtures boiling within a range of not more than 40° to the extraction process. Representatives of (I) are polyalcohols and polyalcoholic ethers, for example, glycols or glycol ethers, furfural, alkanolamines, hydroxy nitro compounds, and chlorohydrins, and of (II) $PhNO_2$, PhOH, cresols, phenyl glycide ether, sulpholenes, and substitution products thereof. Those with b. p. higher than those of the compounds to be separated are preferred. As (III), there may be used kerosine fractions poor in aromatics. In an example, a fraction (1 vol.) containing 60% alcohols and 40% aldehydes (b. 140°–160°), separated by distillation from a reaction mixture obtained in the oxo process starting from CO, H_2, and C_5–C_7 olefins, was fed to the 3d stage of a 7-stage extraction apparatus; $O(CH_2CH_2OH)_2$ (IV) (7 vol.) was fed to the 1st and a naphtha free of aromatics (V) (12 vol.), b. 90°–100°, to the 7th stage. After extraction, phase (IV) con-

tained 96.2% alcohols and 3.8% aldehydes and phase (V) only aldehydes.

VAN SCHAACK BROS. CHEMICAL WORKS. *See* abs. **3239.**

VAN'T SPIJKER, P. *See* abs. **1100.**

3798. VAN'T SPIJKER, P., AND HART, M. (Shell Development Co.). Synthesis of Carbinols. United States Patent 2,581,988, Jan. 8, 1952; appl. filed Oct. 17, 1950, Serial No. 190,523; 1 claim (*Cl. 260–638*).

In the multistep Oxo process the olefinic reactant is reacted with CO and H_2 in a 1st step to give a product consisting largely of aldehydic products, with minor amounts of higher boiling oxygenated products (thick oil), carbinol, unreacted olefin, diluents, soluble Co compounds, and suspended catalyst. The product from this so-called carbonylation step contains dissolved Co as impurity; therefore, it is passed through a decobalting step wherein the soluble Co compounds are decomposed to form insoluble metallic Co. The product, including the suspended Co, is finally passed through a hydrogenation stage wherein the aldehydic intermediate products are converted to carbinols. The catalyst for both stages, Co on "Celite", gradually loses its effectiveness, and it is recycled after separation from the product back to the carbonylation stage where it is replenished by addition of about 4% of fresh catalyst as a slurry in the olefin feed. It is now found that better results are obtained in maintaining the activity of the catalyst if the fresh catalyst used for replenishment is added at a point just preceding the hydrogenation stage. The yield of product is improved, and there is a lesser formation of the undesired thick oil. Details of the process are presented in a flowsheet.

3799. VAN'T SPIJKER, P., AND SHERRED, J. A. (Shell Development Co.). Method for the Synthesis of Carbinols. United States Patent 2,486,693, Nov. 1, 1949; appl. filed Jan. 2, 1948, Serial No. 434; in the Netherlands, Jan. 15, 1947; 3 claims (*Cl. 260–638*). Chem. Abs., vol. 44, 1950, p. 2544.

Describes an apparatus that has an inner vessel for the Oxo reaction and an outer vessel for hydrogenation of aldehydes. The space between removes CO and insulates the zones. Instead of synthesis gas, 2 gases are used, an H_2-containing gas relatively free of CO and a gas containing H_2 and CO relatively rich in CO or even pure CO. The gases, although separately used, are ultimately mixed, thereby providing an optimum composition of the synthesis gas in the respective stages and eliminating 1 gas recycle. The same pressure 100–300 atm. is used in both stages. The temperature in the hydrogenation stage is somewhat higher than in the Oxo stage. Throughput is 1–3 l. of liquid reactant per l. reaction space per hr. The gas mixture, recycle gas plus added gas rich in CO, for the Oxo stage contains CO and H_2 in a ratio corresponding to ratio in which they are used in the reaction. This is 1 : 1 for a pure reaction, but generally between 1 : 1 and 1 : 2 as a result of the accompanying hydrogenation of part of the aldehydes primarily formed. For the hydrogenation step, a H_2-containing gas, substantially free of CO, is used. 1 literature ref. and 4 United States patents cited.

3800. VAN'T SPIJKER, P., HART, M., AND WEEDA, K. A. (N. V. de Bataafsche Petroleum Maatschappiji) [Organic Compounds From Carbon Monoxide and Hydrogen.] Netherlands Patent 65,130, Feb. 15, 1950. Chem. Abs., vol. 44, 1950, p. 4229.

In the synthesis of O-containing compounds by the Oxo process, better results are obtained by preheating the olefins, together with gas containing CO and H_2 and Co catalyst, at 80°–130°. The reaction proceeds with greater rapidity than when the olefins and the $CO+H_2$ are preheated separately, so that the velocity of the gas stream through the reaction tower may be increased.

3801. VASALLI, F., AND FIORELLO, F. [Synthesis Gas From the Residues of the Pyrogenic Decomposition of Mineral Oils.] Italian Patent 373,346, May 10, 1939. Chem. Zentralb., 1940, II, p. 1678.

Residues are distilled at 800°–1,000°. The gas thus obtained is converted at 1,000°–1,100°, yielding a gas with high CO and H_2 content. Water gas made from the coke residue of the distillation is added thereto.

VELDE, H. *See* abs. **2141, 2142, 2143.**

3802. VEREIN FÜR CHEMISCHE INDUSTRIE A. G. [Effecting Reactions Between Gases.] Swiss Patent 127,-243, May 27, 1926. Chem. Abs., vol. 23, 1929, p. 1188.

Reactions between gases are effected by supplying 1 of the reagents to each side of a porous wall, the gases meeting and reacting in the pores of the wall. Suitable apparatus comprises a porous tube arranged within an impermeable tube, connections being provided for passing gases, preferably in countercurrent, through the porous tube and through the annular space between the tubes. The porous tube may be impregnated with a catalyst. Examples describe the preparation of (1) CH_4 from CO and H_2O; (2) MeOH from CO and H_2O; (3) MeOH from HCOOH and H_2; (4) MeOH from HCOOMe and H_2; (5) Ac_2O from ethylidene diacetate and air; (6) AcOH from CH_3CHO and air; (7) SO_2Cl_2 from SO_2 and Cl.

———. *See* abs. **3863, 3864, 3865.**

3803. VEREINIGTE OELFABRIKEN HUBBE & FARENHOLTZ. [Fatty Acids.] French Patent 838,243, Mar. 1, 1939. Chem. Abs., vol. 33, 1939, p. 7820.

Fatty acids obtained by oxidation of hydrocarbons are subjected to purification treatment comprising the steps of blocking the carboxyl groups by reactions depriving them of their acid character, for example, reactions leading to the formation of salts, and heating the salts or other compounds thus formed to temperatures of 280°–360°, in the absence of oxidizing gases, so as to remove their content of oxyacids, lactones, lactides, estolides, ester-acids, and malodorous compounds. Heating may be effected in presence of steam, CO, CO_2, or N_2.

3804. ———. [Fatty Acids and Fatty Alcohols.] German Patent 739,570, Aug. 12, 1943 (*Cl. 12 o–11*). Chem. Abs., vol. 40, 1946, p. 350.

These fatty compounds are produced by oxidation of synthetic, high-moleular, saturated or unsaturated hydrocarbons having boiling ranges above those of illuminating and gas oils. The oxidation is carried out at temperatures >100°, with an oxidizing gas containing molecular O_2. The preferred starting materials are the products of the Fischer-Tropsch synthesis. The lighter, more volatile intermediates, which are formed in the course of the oxidation process, are good promoters for the desired degree of oxidation and are retained in the reaction mixture for this purpose.

3805. ———. [Fatty Acids From Aliphatic Hydrocarbons.] German Patent 742,054, Oct. 7, 1943 (*Cl. 12 o–11*). Chem. Abs., vol. 40, 1946, p. 899.

Fatty acids are produced by oxidizing high-molecular, aliphatic hydrocarbons. Oxidation is brought about by intimate mixing of an O_2-containing gas with the hydrocarbons at a temperature above their m. p., preferably 100°–170°. The mixing of the reactants is achieved with a rapidly revolving stirrer, such as a slotted, perforated, or comblike paddle.

3806. ———. [Oxidation Products of High-Molecular Hydrocarbons.] German Patent Appl. V 35,896, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 377.

Alcohols and fatty acids are produced from high-molecular hydrocarbons by passing oxidizing gases or air through a series of reaction vessels containing the hydrocarbons. Paraffin gatsch from the catalytic hydrocarbon synthesis from CO and H_2 are suitable raw materials. Addition to German Patent Appl. H 145,293 (abs. **1104**).

3807. ———. [Oxidation Products of High-Molecular Hydrocarbons.] German Patent Appl. V 35,930, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 377.

Fatty acids or alcohols are obtained by steadily passing an oxidizing gas stream through the hydrocarbons in the reaction vessel. The gas stream is passed thruogh the reaction vessel at greater velocity than the hydrocarbons.

3808. ———. [Oxidizing Hydrocarbons.] French Patent 837,524, Feb. 13, 1939. Chem. Abs., vol. 33, 1939, p. 5865.

Higher hydrocarbons are oxidized to acids or alcohols by solid, liquid, or gaseous oxidizing agents in several reaction vessels, a gaseous current being led successively through the various vessels and a supplementary amount of gas being added to the 2d and succeeding vessels. Describes apparatus.

See also British Patent 506,104 (abs. **640**).

3809. ———. [Process and Apparatus for Producing Fatty Acids From Aliphatic Hydrocarbons.] German Patent Appl. V 36,427, PA 30,508; filed Jan. 15, 1940. FIAT Reel B–196, frames 147–155; PB 83,253.

In the process for producing fatty acids by oxidation of high-molecular aliphatic hydrocarbons and the like, the condensable portions of the liquor arising from the oxidation are precipitated in the apparatus following the oxidation vessel with hydrocarbons, organic solvent agents, or H_2O. The liquids, which serve for the precipitation of the condensable portions of the liquor in the adjoining vessel, are kept at a lower temperature than the raw material awaiting oxidation in the previous oxidation apparatus. Example: 144 kg. of paraffin gatsch was blown with air at 125° in a vessel containing 6% of catalyst, consisting of 2 parts of Mn stearate and 1 part of stearic acid. After 12 hr., 50% of the charge was oxidized and after a further 9 hr., 91%. The yield from the oxidation was 105%. Addition to German Patent Appl. H 145,334.

3810. ———. [Process for Obtaining Oxidation Products From High-Molecular Hydrocarbons.] German Patent Appl. V 34,745, PA 249,646; filed Apr. 4, 1938 (*Cl. IV d–12 o*). FIAT Reel B–196, frames 156–172; PB 83,253.

An improvement is given for the process for obtaining oxidation products, such as fatty acids, alcohols, or the like, from high-molecular hydrocarbons, such as the paraffin gatsch, from the Fischer-Tropsch synthesis in the presence of catalysts, at temperatures 80°–130°. To obtain the maximum amount of homogeneous oxidation products from the raw material, the troublesome cyclic, heterocyclic, and pseudocyclic compounds, such as naphthenes and terpenes, asphalts and resins, the S-containing compounds, and other troublesome impurities are removed before the oxidation is performed. Their removal may be accomplished by means of 85–95% H_2SO_4 at 60°–90°, followed by washing with H_2O or alkalies to remove the residual acid, by adsorption on bleaching earths or the like, or by treatment with solvents, such as ether, methyl alcohol, acetone, chloroform, or mixtures of these with ethyl alcohol. To obtain fatty acids suitable for soaps or for technical and edible fats and to increase the homogeneity of the oxidation products, those portions of the raw material b. <310°–320° are distilled off, and/or the raw materials are subjected to distillation at a temperature up to 500°.

3811. ———. [Process for the Production of Oxidation Products From Material Containing Paraffin.] German Patent Appl. V 40,421, PA 560,884; filed Sept. 7, 1943. FIAT Reel B–196, frames 783–790; PB 83,253.

Material to be oxidized is first treated at a temperature above its melting point in known manner with concentrated (85–100%) H_2SO_4 or oleum. It is finally washed with dilute alkali (1–5% NaOH) at a temperature between the melting point of the paraffin and the boiling point of H_2O. The lye is washed out, and the material subjected to oxidation. Before or after the treatment with H_2SO_4, a treatment with bleaching earth or a selective solvent may take place. The treatment with concentrated H_2SO_4 at a temperature 150°–200° is so arranged that a part of the cyclic-unsaturated and the pseudocyclic compounds and the like is coked. After a final treatment with bleaching earth and filtration, the material may be treated with dilute alkalies, preferably caustic soda. Paraffins which are brought by distillation to a boiling range of 320°–330° up to 450°, calculated at 760 mm. Hg column, are used in the process.

3812. ———. [Production of Fatty Acids.] Italian Patent 364,452, Jan. 19, 1938. Chem. Zentralb., 1940, I, p. 1274.

High-molecular aliphatic hydrocarbons are oxidized with O_2-containing gases in presence of catalysts, which consist of compounds of elements of groups 6–8, if desired, together with alkali, earth alkali, or Mg compounds. Example: 3 parts Mn strearate, 1 Mg Stearate, and 1 stearic acid. The catalyst used is 1–2% of the hydrocarbons.

3813. ———. [Production of Fatty Acids by Oxidation of Paraffin Hydrocarbons.] French Patent 837,251, Feb. 7, 1939. Chem. Abs., vol. 33, 1939, p. 6880.

Hydrocarbons are oxidized in presence of a catalyst consisting of a salt of a metal of group 6, 7, or 8 of the periodic system, together with a fatty, resinic or naphthalenic acid, and preferably together with a compound of an alkali or alkaline earth metal including Mg. Only a part of the catalyst mixture is added to the paraffins at the beginning of the oxidation, the remainder being added during the course of the reaction. The catalyst mixture may contain Mn stearate, Co resinate, or Fe naphthenate. Oxidation may be effected at 90°–150°.

VEREINIGTE STAHLWERKE A. G. *See* abs. **3305.**

3814. VERGASUNGS INDUSTRIE, A. G. [Apparatus for the Production of Water Gas.] French Patents 819,591 and 819,592, Oct. 21, 1937. Chem. Abs., vol. 32, 1938, p. 2327.

3815. ———. [Catalyst for Conversion of Carbon Monoxide Into Hydrocarbons.] French Patent 815,351, July 10, 1937; appl. filed Dec. 22, 1936. Chem. Zentralb., 1937, II, p. 3666.

Composition is Fe_3O_4 84.5%, AlO(OH) 10%, KOH 0.5%, and Kaolin 5%.

3816. ———. [Gas From Bituminous Lumpy Fuels.] German Patent 742,272, Nov. 26, 1943; appl. filed May 15, 1940 (*Cl. 24 e–1.07*). TOM Reel 36, bag 3,541, item 8; Oel Kohle Erdoel Teer, Schriftumschau, vol. 40, No. 13/14, Apr. 1, 1944, p. 53; Chem. Abs., vol. 40, 1946, p. 2961.

In producing a synthesis gas from bituminous, lump fuel by means of O_2 or enriched air, the out gas produced is reintroduced into the gasification chamber of the gas producer as cycle gas through several points in the circumference at which O_2 is admitted. The 2 gases meet each other close to the fuel bed, and the

resulting combination raises the temperature of the cycle gas and efficiently cracks the hydrocarbons contained therein, at the same time effecting a rapid heating of the fuel bed and preventing undesired premature ignition. The process assures a uniform gas composition, complete gasification of the fuel, and a high gas yield.

VERGILIO, J. H. *See* abs. **2342, 2499, 2500.**

VERGUES, J. *See* abs. **299.**

3817. VESTERDAL, H. G. (Standard Oil Development Co.). [Catalyst for Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 962,998, June 26, 1950; appl. filed Mar. 10, 1948; in United States, May 29, 1947. Chem. Zentralb., 1950, II, p. 2271.

Catalyst consists of Fe oxide and a small amount of a hydrogenation catalyst, such as Cu chromite, W oxide, or Pt, with a small amount of an activator in the form of a K compound, such as K_2CO_3. It is made by mixing 89 kg. of red Fe oxide with 5 l. of an aqueous solution of 200 gm. K_2CO_3 per l. The mixture is dried in air at 150°, and then 10 kg. of powdered $CuCr_2O_4$ is added. The product is formed into balls and reduced in a stream of H_2 for 4 hr. at 482°.

3818. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,471,129, May 24, 1949; appl. filed Sept. 7, 1946, Serial No. 695,564; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 317.

A superior promoter for Fe catalyst is obtained by combining fluoboric acid with such a metal as K and Na to form metal fluoborates. $NaBF_4$ may be used, but KBF_4 is preferred. The promoter may be added to pure Fe oxide or hydroxide or to Fe ores, such as magnetite, hematite, limonite, and others, in amounts 0.2–10.0% based on the Fe present. Example: 9.11 gm. KBF_4 were dissolved in 225 cc. hot distilled H_2O. The solution was poured onto 491 gm. powdered Fe oxide while mixing to form a paste. The paste was dried at 220° F., then pilled in the presence of 2% hydrogenated vegetable oil, such as cotton, corn, or peanut oil, which was used as a lubricant for the pilling operation. The vegetable oil was burned from the pills by heating in air at 850° F. for 3 hr. The catalyst was reduced by heating for 4 hr. at 900° F. with H_2 at atmospheric pressure, 1,000 vol. H_2 per vol. catalyst per hr. 3 United States patents cited.

3819. ——— (Standard Oil Development Co.). Process of Preparing an Iron Catalyst Promoted With an Alkali Metal Fluoborate. United States Patent 2,471,130, May 24, 1949; appl. filed July 12, 1947, Serial No. 760,691; 3 claims (*Cl. 252–433*). Chem. Abs., vol. 44, 1950, p. 317.

The process is similar to that described in United States Patent 2,471,129, (abs. **3818**).

3820. ——— (Standard Oil Development Co.). Process of Reducing Iron Group Metal Oxides. United States Patent 2,479,435, Aug. 16, 1949; appl. filed May 14, 1946, Serial No. 669,530; 6 claims (*Cl. 252–472*). Chem. Abs., vol. 43, 1949, p. 9419.

Finely divided O compounds of ferro-magnetic metals, particularly Fe group metal oxides and carbonates, are subjected in the form of a suspension in a reducing gas, to reducing temperatures for a time sufficient to cause partial reduction but insufficient to decrease the activity of the reduced catalyst. Particles of the desired degree of reduction are separated by means of a magnetic field, and the particles insufficiently reduced are recycled to the reduction zone. 2 foreign patents and 5 United States patents cited.

3821. ——— (Standard Oil Development Co.). Reactivation of Catalysts Containing Iron. United States Patent 2,541,680, Feb. 13, 1951; appl. filed Nov. 20, 1947, Serial No. 787,259; 3 claims (*Cl. 252–416*). Chem. Abs., vol. 45, 1951, p. 6653.

K promoted Fe oxide catalyst that has been used in a dehydrogenation reaction may be reactivated in situ. The catalyst is allowed to cool to 200°–500° F.; then a stream of gas containing CO is passed through the catalyst for 0.5–5 hr. The CO-containing gas is cut off, and the temperature of the catalyst is raised >1,000° F. The gas-feed rate is not important. The pressure may be above atmospheric. Since the rise in catalyst temperature should be as rapid as is feasible and since the reaction should contain steam at the beginning of the productive phase, steam is passed through the catalyst after the CO is cut off. 6 United States patents cited.

3822. ——— (Standard Oil Development Co.). Synthesis of Hydrocarbons. United States Patent 2,553,433, May 15, 1951; appl. filed May 29, 1947, Serial No. 751,445; 6 claims (*Cl. 260–449.6*).

Fluidizable CO–H_2 synthesis catalyst having a decreased tendency toward carbonization is made up of a reduced mixture consisting essentially of 75–99 parts by weight of Fe, 1–20 parts by weight of a hydrogenation catalyst, such as Cu chromite, WO_2, or Pt, and 0–5 parts by weight of an alkali metal compound promoter. 4 United States patents cited.

3823. VESTERDAL, H. G., AND KONRAD, W. A. (Standard Oil Development Co.). Separation of Straight-Chain From Branched-Chain Hydrocarbons. United States Patent 2,586,889, Feb. 26, 1952; appl. filed Aug. 23, 1949, Serial No. 111,946; 18 claims (*Cl. 196–148*).

Normally liquid straight-chain hydrocarbon in a mixture, with at least 1 normally liquid branched-chain aliphatic hydrocarbon and cyclic hydrocarbons, is separated therefrom by contacting the mixture with an activated C prepared by treating acid sludge coke with steam at 1,350°–1,500° F., until a yield of 70–90 wt. % of activated C based on the weight of acid sludge coke is obtained, and then preferentially adsorbing the straight-chain hydrocarbon thereon.

3824. VESTERDAL, H. G., AND SYKES, H. J. (Standard Oil Development Co.). Synthesis of Hydrocarbons in the Presence of an Iron-Type Catalyst. United States Patent 2,533,071, Dec. 5, 1950; appl. filed Oct. 1, 1947, Serial No. 777,308; 3 claims (*Cl. 260–449.6*).

Synthesis conditions include temperature 550°–750° F., pressure 200–650 p. s. i. H_2: CO ratio 0.8–3 : 1 and catalyst 0.2–1% carbonyl Fe supported on subdivided Zn-alumina spinel containing 0.5–10% K carbonate. The catalyst may be fluidized at a gas velocity of 0.3–3 ft. per sec., with a bed density of 30–100 lb. per cu. ft. 1 literature ref. and 5 United States patents cited.

3825. VESTERDAL, H. G., AND TOBIAS, G. S. (Standard Oil Development Co.). [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 968,351, Nov. 24, 1950; appl. filed June 25, 1948. Chem. Zentralb., 1951, I, p. 2220.

Synthesis is performed in presence of an Fe catalyst at 260°–370° and a maximum of 4.2 atm. pressure. The ratio of CO : H_2 is 1 : 0.5–3, preferably 1 : 1. If desired, N_2 is added to the catalyst bed as inert gas. Ethylene and propylene are formed by the synthesis.

3826. VESTERDAL, H. G., SYKES, H. J., AND MATTOX, W. J. (Standard Oil Development Co.). [Iron Catalyst for the Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 971,859, Jan. 23, 1951; appl. filed Sept. 21, 1948. Chem. Zentralb., 1952, I, p. 3273.

Fe carbonyl is precipitated to the amount of 0.2–10 wt. % upon an active support, such as Zn–aluminate, which has been treated with a small quantity of an alkaline activating agent. The carbonate of a metal

of group 2 is used as the support. The catalyst will contain 0–7% of K_2CO_3.

VIDSTRAND, E. H. *See* abs. **632, 633.**

3827. VIDSTRAND, E. H., AND HULTGREN, N. F. [Synthetic Benzine.] Netherlands Patent 1,260, Apr. 2, 1916. Chem. Abs., vol. 10, 1916, p. 1788.

Mixtures of the more or less pure hydrocarbons, gaseous at ordinary temperatures and containing CH_4, ethylene, or acetylene, to which H_2 has been added, are heated to a temperature of 2,000°.

3828. ———. [Synthetic Benzine.] Swiss Patent 71,769, Feb. 16, 1916. Chem. Abs., vol. 10, 1916, p. 1928.

Mixture of H_2 and a C and O compound is heated to a temperature of at least 2,000°, whereby a chemical reaction takes place, resulting in the formation of condensible hydrocarbons, which, upon cooling, separate as a readily volatile benzinelike liquid.

3829. VIDSTRAND, E. H., HULTGREN, H. B., AND HULTGREN, N. F. Liquid Hydrocarbons. British Patent 17,919. Chem. Abs., vol. 9, 1915, p. 376.

See French Patent 457,174, (abs. **3830**).

3830. ———. [Synthetic Benzine.] French Patent 457,174, Apr. 26, 1913. Chem. Abs., vol. 9, 1915, p. 148.

Manufacturing a combustible liquid like benzine by heating hydrocarbons of the CH_4, ethylene, or acetylene series (with the addition of H_2) in the electric arc furnace, at least to 2,000°. Such gases may be obtained, for example, by the dry distillation of turf. A mixture of CO and CO_2 with H_2 serves the same purpose. The product has a sp. gr. of 0.723, b. at 85.5°, and has a constitution between that of the paraffins and olefins.

3831. ———. [Synthetic Benzine.] Swedish Patent 41,210, Aug. 23, 1916. Chem. Abs., vol. 10, 1916, p. 3156.

Gaseous hydrocarbons of the CH_4, ethylene, and acetylene series are heated without increased pressure to 2,000°, at which temperature a reaction takes place producing a condensable gas, which, on cooling, condenses to a volatile liquid consisting in the main of hydrocarbons, like benzine, and belonging to the CH_4 and ethylene series.

See also Swiss Patent 71,769 (abs. **3828**).

3832. VINDEVOGEL & CIE. [Catalyst.] French Patent 664,996, Mar. 14, 1928. Chem. Zentralb., 1930, I, p. 3383.

Reaction of $CO+H_2$ at 80° over the double sulfate of Ce and Co.

3833. VLUGTER, J. C., KEULEMANS, A. I. M., AND HART, M. (Shell Development Co.). Decobalting Procedure in Carbonylation of Olefins. United States Patent 2,564,456, Aug. 14, 1951. Chem. Abs., vol. 46, 1952, p. 1582.

In the carbonylation of olefins by the Oxo process, decobalting is effected by treating the reaction products, consisting mainly of aldehydes, with H_2 at about 50 atm. and 150°–200° (170°–190° is preferred). Describes apparatus.

See United States Patent 2,464,916 (abs. **2**).

VOGT, E. *See* abs. **453.**

3834. VOGT, E., AND SMEYKAL, K. (W. E. Currie). Breaking Mineral Oil Emulsions. United States Patent 2,216,257, Oct. 1, 1940. Chem. Abs., vol. 35, 1941, p. 1212.

For breaking the emulsions, there is added to them a sulfonation product of a polymerized mixture of olefins obtained by dehydrating high-molecular alcohols from the hydrogenation of C oxides, the polymerized mixture containing olefins with from 10 to about 20 C atoms in the molecule.

3835. VOLK, F. [Fuel Gas.] Austrian Patent 156,280, June 10, 1939 (*Cl. 26a*). Chem. Abs., vol. 33,, 1939, p. 7996.

Fuel gas free from tar and hydrocarbons is obtained by gasifying bituminous fuel and passing the gas, without intermediate cooling, through a heated chamber containing a catalyst known to promote the conversion of tar vapors and hydrocarbons into CO and H_2. An oxidizing agent, for example, O_2, CO_2, or steam, may be fed to the chambers, if necessary. Describes apparatus.

3836. ———. [Operation of Water-Gas Generators.] Austrian Patent 146,939, Sept. 10, 1936; appl. filed Jan. 19, 1935. Chem. Zentralb., 1937, I, p. 1341.

Gas containing at least 2 times as much by volume of H_2 as CO suitable for synthesis of MeOH is obtained.

3837. ———. [Water Gas.] Austrian Patent 146,202, June 25, 1936 (*Cl. 24 e*). Chem. Abs., vol. 30, 1936, p. 6172.

In a system in which bituminous fuel is coked and the coke is then converted into water gas, the water gas is collected separately from the volatile coking products, and the latter are subjected to partial combustion to yield a mixture of H_2 and CO, which is added to the water gas. Describes plant.

3838. VON BETHMANN, M. F. AND STIEBLING, E. (Ruhrchemie A. G.). [Production of Soaps.] German Patent 817,483, Oct. 18, 1951; appl. filed Oct. 2, 1948 (*Cl. 23 e*). Chem. Zentralb., 1952, I, p. 943.

Olefinic hydrocarbon fractions, comprising at most 2–3 consecutive C numbers, obtained from the primary, cracked, or dehydrogenated products of the catalytic hydrogenation of CO, are converted by gases containing CO and H_2 into alcohols. From these is separated the fraction passing over closely below the high-boiling compounds (heavy oil) and converted by means of alkali fusion into soaps.

3839. VON DER HORST, H. D. (I. G. Farbenindustrie A. G.). [Organic Compounds Containing Sulfur.] German Patent 719,059, Mar. 5, 1942 (*Cl. 12 q–21*). Chem. Abs., vol. 37, 1943, p. 1722.

Aliphatic hydrocarbons or halohydrocarbons, with at least 1 C not linked with a halogen, are exposed to the action of halogen, SO_2, and short-wave light. The products containing O, S, and halogen are caused to react with phenols in the presence of NH_3 or amines.

See abs. **1041, 1042.**

VON FUENER, W. *See* abs. **2336, 2337.**

3840. VOORHEES, V. (Standard Oil Co. of Indiana). Process of Applying Promoters to Catalyst Particles. United States Patent 2,500,331, Mar. 14, 1950; appl. filed Dec. 5, 1947, Serial No. 790,011; 4 claims (*Cl. 252–473*). Chem. Abs., vol. 44, 1950, p. 4655.

Preparation is given for a fluid Fe catalyst containing 0.1–2.5% of an alkali or alkaline earth metal compound as promoter. The Fe catalyst is classified into relatively fine and relatively coarse particles. A dilute solution of the promoter is applied to the fine particles, and a strong solution of the promoter is applied to the coarse particles. The concentration of the solution is correlated with the weight of the Fe particles in direct proportion. The 2 sizes of promoted catalyst are dried separately. The particles recombined to give a mixture 15% smaller than 45 μ, 65% 60–125 μ, 20% 150–300 μ. The mixture is reduced at 600°–900° F. 4 United States patents cited.

See abs. **3356.**

3841. VOORHIES, A. (Standard Oil Development Co.). Catalytic Improvement of Hydrocarbon Synthesis Product. United States Patent 2,600,452, June 17, 1952; appl. filed July 1, 1947, Serial No. 758,329;

8 claims (*Cl. 260–450*). Chem. Abs., vol. 46, 1952, p. 8360.

Octane number of synthetic gasoline produced from CO and H_2 over an Fe catalyst is raised by passing the gasoline in the vapor phase at 900°–950° F. and a space velocity of 2–5 vol. of cold oil per vol. of catalyst over a spent SiO_2–Al_2O_3 cracking catalyst composed of SiO_2 86–88 and Al_2O_3 12–14, and containing Fe 0.3–1 part by weight. The catalyst should have an activity index ($D+L$ value) <20. The activity index is measured by cracking gas oil for 2 hr. at 850° F. over the catalyst at a space velocity of 0.6 vol. of oil per vol. of catalyst per hr., distilling 100 vol. of the product b. up to 400° F., determining the vol. of overhead distillate (D) and residue (L) and subtracting $D+L$ from 100. Treatment of a synthetic gasoline raised its research octane No. from 80 to 94.1 and the motor octane No. from 68.6 to 81.1. The improvement is due to the isomerization of the olefins present in the synthetic gasoline by shifting their double bond from the 1 position to the center of the molecule.

3842. ——— (Standard Oil Development Co.). [Fluidized Synthesis Process.] French Patent 918,720, Feb. 17, 1947; appl. filed Dec. 11, 1945; in United States, Dec. 14, 1944. Kainer, p. 204; Chem. Zentralb., 1947, II, p. 861.

Powdered catalyst with a grain size of 30- to 400-mesh is kept suspended in the synthesis zone by the synthesis gas. Simultaneously, a part of the catalyst is periodically removed and new catalyst admitted so that the catalyst level remains constant.

3843. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,479,439, Aug. 16, 1949; appl. filed Apr. 27, 1948. Chem. Abs., vol. 43, 1949, p. 9420.

In the synthesis of hydrocarbons from CO and H_2 an unpromoted fluidized Fe catalyst is used; 1 mol. H_2O vapor per 7–15 mol. H_2 is introduced with the feed gas, and an alkali metal promoter, specifically KF, is gradually introduced to obtain a slow and even impregnation of the catalyst with the promoter up to the point where the optimum amount is present, generally, when the catalyst reaches a KF content of 0.5–2.5%. The H_2O vapor prevents excess carbonization of the catalyst caused by the promoter, and an increase in the amount of H_2O vapor may be used to reduce excess carbonization. In an example, KF is introduced as a 0.1% aqueous solution over a period of 150 hr. until the Fe catalyst contains 1% KF. The process is also applicable to hydrocarbon synthesis with Co or Ni catalysts.

See also United States Patent 2,475,214, (abs. **135**).

3844. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis. United States Patent 2,533,072, Dec. 5, 1950; appl. filed June 5, 1947, Serial No. 752,801; 4 claims (*Cl. 260–449.6*).

Catalyst carbonized in the Fischer-Tropsch synthesis is withdrawn from the reactor at synthesis temperature 550°–750° F. and decarbonized with H_2 at a higher decarbonization stage, 900°–1,200°. The additional heat is supplied by addition of CO to the decarbonization stage. The CO comes from synthesis feed gas added to the H_2 in suitable proportion. In general, about 10–50 *n* cu. ft. of H_2 and 1–5 *n* cu. ft. of CO are required to remove 0.05–0.20 lb. C per lb. catalyst. 6 United States patents cited.

3845. ——— (Standard Oil Development Co.). [Production of Gas Mixtures Containing Carbon Monoxide and Hydrogen.] United States Patent 2,526,521, Oct. 17, 1950; appl. filed May 29, 1948, Serial No. 30,134; 6 claims (*Cl. 48–196*). Chem. Abs., vol. 45, 1951, p. 333.

To produce a desired H_2: CO ratio and at the same time prevent C formation, hydrocarbon gases are passed with steam and CO_2 in amounts corresponding to an excess of O_2 at temperatures of about 900°–1,700° F. through an extended catalyst zone, the great part of the CO_2 requirement being supplied to those portions of the catalyst zone having a temperature substantially > 1,175° F. No refs. cited.

3846. ——— (Standard Oil Development Co.). [Production of Synthesis Gas by the Catalytic Conversion of Hydrocarbons With Steam and Carbon Dioxide.] French Patent 978,834, Apr. 18, 1951; appl. filed Jan. 11, 1949. Chem. Zentralb., vol. 123, 1952, p. 4714.

O_2 contained in the added steam and CO_2 should essentially exceed that in the end gas. An essential part of the CO_2 is added at that point in the conversion column where the temperature is about 650°–704°. At this temperature, CO_2 and CH_4 are added in the proportion of 1.5 : 1.7, if a mixture of 1 H_2 : 1 CO is to be obtained. A gas mixture of 2 H_2 : 1 CO requires an initial gas of 0.5 CO_2 : 0.7 CH_4.

3847. ——— (Standard Oil Development Co.). [Removing Carbon From Synthesis Catalysts.] French Patent 964,635, Aug. 21, 1950; appl. filed Apr. 13, 1948. Chem. Zentralb., 1951, I, p. 281.

C-coated catalysts are regenerated in a regeneration chamber which is continuous with the reaction chamber. The catalyst is in a suspended state in both chambers and circulates from one chamber to the other. The catalyst is kept suspended by a boiling gas stream. The temperature in the regenerating chamber is kept at a higher point than that in the reaction chamber.

3848. ——— (Standard Catalytic Co.). Simultaneous Hydrogenation and Fischer Synthesis. United States Patent 2,365,029, Dec. 12, 1944. Chem. Abs., vol. 39, 1945, p. 4443.

In an outlined system natural gas and steam are supplied to a reformer to produce CO and H_2. The reaction products are passed through a scrubber to remove impurities, and the purified stream is combined with a feed oil admitted through another part of the system. The feed oil is of the kerosine or gas oil boiling range. The mixture passes through a heat exchanger and enters a reactor where the high-boiling feed is destructively hydrogenated and simultaneously the CO is hydrogenated, the product of both reactions being a fraction boiling in the gasoline range. The reaction product is fractionated, the gaseous and heavy fraction being recycled. The reaction in the reformer is carried out at 1,400°–1,500° F. with a Ni on Kaolin catalyst. The reactor operates at 500°–800° F. and suitable pressures using an Fe group (Ni, Co, Fe) catalyst supported on active cracking catalyst. A desirable catalyst is Ni supported on H_2SO_4- and HF- treated bentonite.

3849. ——— (Standard Oil Development Co.). [Synthesis of Hydrocarbons.] French Patent 955,939, Jan. 20, 1950; appl. filed Nov. 24, 1947, in United States, Nov. 29, 1946. Chem. Zentralb., 1950, II, p. 2368.

CO and H_2 are reacted in the presence of a catalyst consisting of Fe, Ni, or Co and a promoter, such as the oxide of Na, K, Cr, Zn, Al, or Mg. Further activating agents are the salts and hydroxides of K, Na, and Li, but particularly KF. Synthesis is begun with an inactive catalyst in the presence of H_2O under gradual addition of the promoting agent and at a temperature of 300°–400°. At intervals a 0.1% solution of KF is injected by spraying until about 1% of KF, calculated on the amount of catalyst, is present.

3850. ——— (Standard Oil Development Co.). Synthesis of Hydrocarbons From Carbon Monoxide and

Hydrogen With an Iron-Type Catalyst. United States Patent 2,469,755, May 10, 1949; appl. filed May 1, 1948, Serial No. 24,684; 13 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 6397.

Fe catalysts with excellent disintegration resistance are prepared by fusing a promoted Fe oxide and contacting the molten mass with a low-boiling liquid, such as H_2O. The melt may be poured in a fine stream into a relatively large amount of the cooling agent. In this way particles of the desired size may be recovered directly from the cooling liquid. When obtained in large aggregates, the catalyst is ground to the desired size, 30–100 μ, and reduced. 1 literature ref. and 4 United States patents cited.

———. *See* abs. **273.**

3851. VOORHEES, A., AND KREBS, R. W. (Standard Oil Development Co.). Hydrocarbon Synthesis Plant. United States Patent 2,556,861, June 12, 1951; appl. filed Sept. 15, 1948, Serial No. 49,426; 7 claims (*Cl. 260–449.6*).

High yields of hydrocarbons, unaccompanied by excessive C formation and catalyst disintegration, are obtained by operating a plurality of fluid synthesis reactors in parallel, each reactor being charged with catalyst of different average age. The amount of feed gas and recycle tail gas to enter each reactor is adjusted to the age of the catalyst, so that maximum quantities of C_4+ hydrocarbons and minimum C formation occurs. 4 United States patents cited.

3852. VOORHEES, A., AND OWEN, J. J. (Standard Oil Development Co.). Hydrocarbon Synthesis Process Catalyzed by Oxidized and Reduced Iron. United States Patent 2,483,512, Oct. 4, 1949; appl. filed Jan. 26, 1946, Serial No. 643,796; 3 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 1672.

Fe catalysts that give synthesis products unusually rich in oxygenated compounds, such as alcohols and ketones, may be prepared by keeping the finely divided metal particles constantly agitated in the oxidizing gas. The reduction also takes place with the Fe in dense suspension. The oxidation- and reduction-temperature range is 600°–900° F. A promoter may be added to the Fe before or after the oxidation step. 1 literature ref. and 14 United States patents cited.

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3853. WADLEY, E. F. (Standard Oil Development Co.). Method for Removing Oxygenated Organic Compounds From Hydrocarbons. United States Patent 2,494,371, Jan. 10, 1950; appl. filed Oct. 17, 1947, Serial No. 780,504; 2 claims (*Cl. 196–41*).

The following example illustrates the invention. Product from CO: H_2 synthesis using Fe catalyst was washed with aqueous NaOH solution. The solution was then distilled to obtain a fraction b. 85°–450° F., representing about 74% of the treated naphtha. 3 vol. of the distilled fraction was agitated for 1 hr. with 2 vol. of a MeOH–KOH solution containing 106 gm. KOH per l. MeOH at 350° F. The mixture was then cooled to room temperature, >85° F. On cooling, the mixture separated into 2 phases, hydrocarbon and alcoholic. The hydrocarbon phase represented 83% by vol. of the distilled naphtha. This was washed with H_2O and distilled to give 91% yield as an overhead fraction, the remainder being a high-boiling polymer boiling above 450° F. The alcoholic phase was diluted with H_2O to form aqueous solution containing 80–83% MeOH. This solution separated into hydrocarbon and aqueous alcoholic layers. The hydrocarbon layer was withdrawn, H_2O washed and distilled to give a fraction corresponding to 95 vol. % overhead, the remainder again being a heavy polymer outside the boiling range of the original naphtha. The 2 hydrocarbon fractions were separately extracted with aqueous MeOH (80 vol. %). The extracted oils were washed with H_2O and blended. The amount of oxygenated organic compounds had been reduced to a negligible figure. 3 United States patents cited.

3854. ——— (Standard Oil Development Co.). Removal of Oxygenated Compounds From Synthetic Naphthas. United States Patent 2,497,967, Feb. 21, 1950; appl. filed Dec. 17, 1947, Serial No. 792,249; 8 claims (*Cl. 260–450*).

Synthetic crudes from the Fischer-Tropsch reaction are treated with a mixture including oil, and alkali metal sulfonate, and an alkali metal hydroxide to remove oxygenated organic compounds. The mixture is diluted with H_2O and cooled to 80°–400° F. to cause phase separation. The hydrocarbon phase is distilled to obtain fractions free of oxygenated organic compounds including ketones. 1 foreign patent and 2 United States patents cited.

———. *See* abs. **1055, 1056, 1057.**

3855. WAGNER, A. (Braunkohle-Benzin A. G.). [Fischer-Tropsch Synthesis.] German Patent 739,569, Oct. 4, 1943; appl. B 178,085, filed Apr. 15, 1937 (*Cl. 12 o–1.03*). FIAT Reel AA–90, frames 1,433–1,434; PB 70,275; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. V, chap. 161, 1949, p. 49; Chem. Abs., vol. 39, 1945, p. 5439.

Tail gases are recycled to regulate the temperature. For this purpose, tail gases that contain an appreciable volume of vaporous, volatile reaction products are used.

WAINWRIGHT, G. E. *See* abs. **28.**

3856. WALDEN, G. H., PIERCE, J. A., AND SEGURA, M. A. (Standard Oil Development Co.). Preparation and Regeneration of a Hydrocarbon Synthesis Catalyst. United States Patent 2,488,150, Nov. 15, 1949; appl. filed Nov. 8, 1946, Serial No. 708,630; 6 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 1673.

Catalyst particularly suitable for use in hydrocarbon synthesis process is prepared by mixing finely powdered Al_2O_3 with Fe powder. The mixture is impregnated with a solution of K carbonate so as to obtain 3% alumina and 1% K_2CO_3 on the Fe. The mixture is passed through the flame of an O_2 torch and sintered. The powder is separated from the combustion gases and cooled. Effective flame temperature is 2,500°–3,500° F. If spheres are desired, the flame temperature must be above the fusion point of the fusible powder used. 2 foreign patents and 12 United States patents cited.

3857. WALDEN, G. H., PIERCE, J. A., SEGURA, M. A., WATTS, R. N., AND SPICER, W. L. (Standard Oil Development Co.). [Catalytic Production of Hydrocarbons From Carbon Monoxide and Hydrogen.] French Patent 952,815, Nov. 24, 1949, appl. filed Sept. 9, 1947; in the United States, Nov. 27, 1946. Chem. Zentralb., 1950, II, p. 961.

To produce hydrocarbons from CO and H_2, a reduced fluidized catalyst of Fe, Ni, or Co metals is used. When using Fe, KF or K_2CO_3 is added as promoter. To produce an active catalyst, it is oxidized at 1,650°–1,925° to form the oxide and then reduced at about 480°. A suitable catalyst contains, for example, 96% powdered Fe, 3% Al_2O_3 and 1% K_2CO_3, or 91% powdered Fe, 4.45% $KMnO_4$, 2.27% SiO_2, and 2.27% TiO_2.

3858. WALKER, S. W. (Stanolind Oil & Gas Co.). Hydrocarbon Synthesis Process and Catalyst. United

States Patent 2,485,945, Oct. 25, 1949; appl. filed Aug. 26, 1947, Serial No. 770,749; 8 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 1672.

Catalyst is prepared from a magnetic Fe oxide in laminar form produced on metallic Fe subjected to hot-milling operations. The oxide scale is ground to 100-mesh or finer and impregnated with a promoter, such as K_2CO_3 or $NaNO_3$. 0.5–2% based on the alkali metal oxide is effective. The oxide is reduced in H_2 at 700°–800° F. for 48–72 hr. The catalyst may be sintered by heating in H_2 for 2–12 hr. at 1,200°–1,400° F. In an example, 15 lb. of catalyst was charged to a reactor with an internal diameter of 2 in. and a height of 20 ft. A feed-gas mixture of H_2 30, CO 10, CO_2 17, N_2 23, and CH_4+ 20 vol. % was passed through the reactor for 350 hr. The temperature was 600° F. and the pressure 200 p. s. i. The conversion of CO rose from 63% to 85%. The rate of gas input was 80 cu. ft. per hr. per lb. of catalyst based on the volume of gas calculated at normal temperature and pressure. The density of the catalyst bed remained high, dropping from an initial 100 lb. per cu. ft. to 30 lb. per cu. ft. after 400 hr. The loss of catalyst was very slight. A table gives the effect of temperature change on Bloom scale catalyst when all other operating variables were held constant. 5 United States patents cited.

3859. ——— (Stanolind Oil & Gas Co.). Separation of Organic Oxygenated Compounds From Hydrocarbons. United States Patent 2,535,071, Dec. 26, 1950; appl. filed Aug. 12, 1948, Serial No. 43,947; 12 Claims (*Cl. 260–450*).

Charging stock containing organic oxygenated compound and hydrocarbon is countercurrently contacted with aqueous extractant solution containing in excess of 30% by weight of the defined class of solubilizer salts, and a hydrocarbon reffinate is withdrawn containing a greatly reduced proportion of organic oxygenated compound. The resulting aqueous extract contains the organic oxygenated compound, heavily contaminated with hydrocarbon. This mixture is stripped from the extract and is then contacted with a 2d aqueous extractant solution containing <30% by weight of the defined class of solubilizer salts. A 2d hydrocarbon raffinate-containing organic oxygenated compound is withdrawn and recycled to the 1st extraction stage. The 2d aqueous extract contains the organic oxygenated compound in greatly purified form. It is withdrawn, and the depleted extractant is recycled to the 2d extraction stage. 2 United States patents cited.

———. *See* abs. **2314.**

3860. Walker, S. W., and Eickmeyer, A. G. (Stanolind Oil & Gas Co.). Catalyst Regeneration. United States Patent 2,544,574, Mar. 6, 1951; appl. filed Sept. 25, 1947, Serial No. 776,156; 6 claims (*Cl. 260–449.6*). Chem. Abs., vol. 45, 1951, p. 4912.

Used Fe catalyst containing about 30% total C as carbide, coke, or wax is treated with a mixture of H_2 and steam (5–40 vol. %) at 900°–1,400° F. The regeneration takes place in fixed bed with pelleted catalyst and in fluid bed with fluid catalyst. The time required will vary with the operation but will ordinarily be 2–20 hr. In continuous operation 5–85% of the volume of catalyst maintained in the reactor may be regenerated in a separate zone and recycled to the reactor after being cooled to synthesis temperature, or about 20% of the catalyst may be treated batchwise for about 5 hr. at 1,000°–1,100° F. Regeneration may take place in 2 or more stages, with progressively increasing temperature. The 1st stage for C removal may be at 900°–1,000° F., the subsequent stages for coke and wax removal may be 1,100°–1,400° F. In general, the proportions of H_2 and steam and the temperature of the treating step can be correlated in terms of the equation: Maximum % H_2O=10+0.05 (T °F., 700). T is the regeneration temperature in °F. 6 United States patents cited.

3861. Walker, S. W., and Latta, J. E. (Stanolind Oil & Gas Co.). Separation of Organic Oxygenated Compounds From Hydrocarbons. United States Patent 2,535,070, Dec. 26, 1950; appl. filed Aug. 12, 1948, Serial No. 43,946; 8 claims (*Cl. 260–450*).

Charging stock of organic oxygenated compound and hydrocarbon is countercurrently contacted with an aqueous extractant solution containing <30% by weight of the defined class of solubilizer salts. A 1st aqueous extract is withdrawn containing the principal product fraction, consisting mainly of organic oxygenated compound, with only a small proportion of hydrocarbon contaminant. The resulting hydrocarbon raffinate, still containing organic-oxygenated compound is then countercurrently contacted with an aqueous extractant solution containing in excess of 30% by weight of the defined class of solubilizer salts. A 2d aqueous extract containing organic oxygenated compound, which is heavily contaminated with hydrocarbon, is withdrawn. This mixture of organic oxygenated compound and hydrocarbon, when stripped from the 2d aqueous extract, may be recycled to the 1st-extraction stage. The 2d hydrocarbon raffinate contains comparatively little of the organic oxygenated compound. 3 United States patents cited.

3862. Wallis, A. E., and Townshend, S. C. (International Nickel Co. of Canada, Ltd.). Iron Carbonyl. Canadian Patent 453,853, Jan. 4, 1949. Chem. Abs., vol. 44, 1950, p. 1659.

Iron ore (I) is immersed in $NiSO_4$ until the (I) absorbs an amount of $NiSO_4$ equal to not above 2% by weight (I). (I) is reduced by H_2 at about 500°, and the mixture is caused to react with CO at about 200 atm. pressure at about 140° to effect 100% conversion to Fe carbonyl in 4 hr.

3863. Walter, H. (Verein für chemische Industrie A. G.). Diffusion Reactions Between Gases. United States Patent 1,685,759, Sept. 25, 1928; appl. filed May 1, 1926. Chem. Abs., vol. 22, 1928, p. 4677.

Gases, such as H_2 and CO, which slowly react in simple mixture, are separated by a diffusion partition, which may be formed of catalytically metallized asbestos, and the gases diffuse into this partition, and the product formed, for example, MeOH, emerges from the partition under the diffusion pressure.

3864. ——— (Verein für chemische Industrie A. G.) [Effecting Chemical Reactions.] German Patent 471,267, May 23, 1924. Chem. Abs., vol. 23, 1929, p. 2229.

See Swiss Patent 127,243 (abs. **3802**).

3865. ———. (Verein für chemische Industrie A. G.) [Effecting Chemical Reactions.] German Patent 474,283, Apr. 12, 1927. Chem. Abs., vol. 23, 1929, p. 3283.

Method of German Patent 471,267 (abs. **3864**) is modified by supplying both the reagents to 1 side of the porous wall and supplying to the other side a gas, which may be an indifferent gas serving merely to stimulate the diffusion or may be a reagent or a mixture of the reagents or a gas intended to react with the initial reaction product. Thus, in preparing MeOH, CO and H_2 may be passed through a porous tube surrounded with petroleum ether vapor, with which CO and/or H_2 may be mixed. Describes apparatus for conducting the process cyclically.

Ward, J. T. *See* abs. **1825.**

3866. Ward, W. J. V., and Imperial Chemical Industries, Ltd. Methanol. British Patent 309,708, Mar. 21, 1928. British Chem. Abs., 1929, B, p. 845; Chem. Abs., vol. 24, 1930, p. 630.

MeOH obtained by the catalytic hydrogenation of oxides of C is purified by treatment with a salting-out solution, such as brine, and a solvent for hydrocarbons, such as C_6H_6, which is substantially immiscible with the mixture of MeOH and salting-out solution. The treatment may be effected in a distilling column. Gives various details and modifications.

3867. WARNER, B. R. (Gulf Research & Development Co.). Fischer-Tropsch Catalyst and Its Preparation. United States Patent 2,467,283, April 12, 1949; appl. filed Feb. 27, 1947, Serial No. 731,403; 9 claims (*Cl. 252–474*). Chem. Abs., vol. 43, 1949, p. 5573.

A H_2O-soluble alkaline compound, such as K carbonate, is added to a warm aqueous solution of a H_2O-soluble Fe salt, such as ferric nitrate, to the point of incipient precipitation. At this point, an aqueous solution of gallic acid is added, with stirring, and precipitation takes place. The precipitate is filtered, washed with H_2O, and dried. The catalyst may be reduced or may be used directly in the synthesis. Various promoters or activators may be added, and various supporting materials may be used. Example: To 607 parts $Fe(NO_3)_3 \cdot 9\ H_2O$ dissolved in 3,000 parts H_2O and heated to 70°–90° C. was added, with stirring, a solution of 290 parts K carbonate dissolved in 450 parts H_2O. At the point of incipient precipitation, 15 parts of gallic acid dissolved in 1,000 parts of hot H_2O were added, and precipitation took place. The precipitate was filtered, washed with H_2O until the washing showed negligible nitrate content, and oven dried at 110° C. 2 literature refs. and 4 United States patents cited.

3868. ——— (Gulf Research & Development Co.). Hydrocarbon Synthesis. United States Patent 2,467,282, Apr. 12, 1949; appl. filed May 19, 1948, Serial No. 28,060; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 43, 1949, p. 5573.

Gives process for the synthesis of hydrocarbons from H_2 and CO in molecular ratio 2:1–1:1 at temperature 200°–350° C., using an Fe catalyst described in United States Patent 2,467,283 (abs. **3867**). The catalyst may be reduced with H_2 before used in the synthesis, or it may be reduced directly in the synthesis operation.

WARREN PETROLEUM CORP. *See* abs. **2440.**

WASSERBACH, T. B. *See* abs. **2092.**

3869. WATKINS, C. H. (Universal Oil Products Co.). Removal of Carbon Monoxide From Hydrocarbons. United States Patent 2,570,615, Oct. 9, 1951. Chem. Abs., vol. 46, 1952, p. 729.

Mixture is brought into contact with a catalyst prepared by reducing an Fe oxide ore at 800°–1,200° F. The catalyst is selective and completely hydrogenates the CO without effecting substantial hydrogenation of the olefins.

3870. WATSON, C. W. (The Texas Co.). Catalyst Regeneration. United States Patent 2,635,110, Apr. 14, 1953. Chem. Abs., vol. 47, 1953, p. 6637.

A catalyst, which has accumulated objectionable deposits of C during its use for the synthesis of hydrocarbons from CO and H_2, is regenerated by contact with CO_2 at a temperature materially above the temperature of the synthesis reaction and at which the CO_2 and C are caused to react to form CO, preferably in the range 760°–816°. The upper temperature limit is controlled only by the adverse effect of the high temperature upon the catalyst. The CO_2 supplied to the regenerator is preheated by direct heat exchange with the hot-regenerated catalyst, and the contaminated catalyst supplied to the regenerator is preheated by indirect heat exchange with the gaseous products from the regenerator. The temperature in the regenerator is maintained by introducing a limited amount of O_2 into the regenerator. Small amounts of H_2 in the CO_2, for example, 2%, are beneficial, but the moisture content is best maintained as low as possible—for example, not over 0.01%.

3871. ——— (The Texas Co.). Catalytic Conversion With a Fluidized Solid Catalyst. United States Patent 2,567,259, Sept. 11, 1951; appl. filed Mar. 7, 1946, Serial No. 652,834; 6 claims (*Cl. 260–449*). Chem. Abs., vol. 46, 1952, p. 711.

Catalytic conversion of a stream of $CO+H_2$ into compounds of higher molecular weight by contact with a solid particle catalyst is effected by passing the reactants upwardly through a reaction zone comprising a relatively constricted, vertical tube having an hydraulic radius of not more than 1 in. and occupied by a relatively coarse dispersing fraction, consisting of solid particles of diameter 0.05–0.35 times the diameter of the tube, and a relatively fine catalytic fraction, consisting of particles of not more than 0.1–0.001 times the diameter of the particles of the dispersing fraction. The effluent reaction products are withdrawn from the upper part of the reaction zone, and the catalyst particles are separated therefrom and reinjected into the reactant gas stream passing upwardly through the reaction zone. Enough fine catalyst particles are suspended therein, and the linear velocity is such that the coarse dispersing particles are continuously in contact with the reactants and the fine catalyst particles in the reaction zone to maintain the catalyst in a state of uniform fluidization at high bed density throughout its vertical extent, with the reactants dispersed throughout the mass of catalyst particles. Reaction zone pressures may range from atmospheric to 700 atm., and the temperatures from 200°–700° F. With an Fe catalyst, the effective pressures may be 150–300 p. s. i. g. and temperatures 500°–600° F. Space velocity of reactant gas flow may range 500–5,000 vol. gas per hr. per vol. reactor space occupied by fluidized catalyst. The process is useful for the production of both hydrocarbons and oxygenated compounds.

3872. ——— (The Texas Co.). Process for Catalytic Conversion of Carbon Oxides. United States Patent 2,486,894, Nov. 1, 1949; appl. filed Nov. 2, 1945, Serial No. 626,425; 3 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 1675.

In catalytic conversion of CO and H_2 into hydrocarbons, the production of CO_2 and CH_4 is reduced, and the yield of higher molecular weight hydrocarbons is increased by the addition of CO_2 to the feed gas and maintenance of a temperature gradient throughout the reaction zone. CO_2 is added in such amounts that the ratio of molecules of H_2 to the sum of the molecules of CO_2 and CO passing to the reaction zone is 0.6–1.0. The initial contact between the synthesis gas and the catalyst is at a temperature 10°–100° F. lower than the temperature of final contact. Conversion of CO is 95–99.5%. 6 United States patents cited.

3873. ——— (The Texas Co.). Process for Catalytic Conversion of Carbon Oxides. United States Patent 2,486,895, Nov. 1, 1949; appl. filed Dec. 7, 1945, Serial No. 633,481; 6 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 1675.

In a conversion similar to that described in United States Patent 2,486,894 (abs. **3872**), a synthesis catalyst is used in which is incorporated or with which is associated a catalyst for promotion of the water-gas shift reaction. The active agent for catalyzing the shift reaction is an oxide of a metal, such as Cr, and the agent for the synthesis of hydrocarbons from CO and H_2 is a metal of the Fe group in a form available for carbide formation during the conversion reaction. The feed gas is contacted with the fluidized catalyst mixture at 550°–700° F. until 95–99.5% of CO has been converted. The composition of the feed gas is kept at a molar ratio of $H_2:CO::2:1$, the amount of H_2O not more than that corresponding to saturation at

atmospheric temperature. The proportion of CO is such that the molar ratio

$$\frac{CO_2(H_2-COA)}{CO\times H_2O}$$

is greater
than the equilibrium constant K for the water-gas shift reaction at the temperature in the reaction zone. *A* is a fraction 0.95–0.995 representing the conversion of CO. 1 literature ref. and 8 United States patents cited.

3874. ——— (The Texas Co.). Process for Catalytic Conversion of Carbon Oxides. United States Patent 2,585,981, Feb. 19, 1952; appl. filed Nov. 23, 1945, Serial No. 630,521; 1 claim (*Cl. 260–449.6*).

In the production of synthetic hydrocarbons by the catalytic hydrogenation of CO, the process is so carried out that substantially all of the CO feed is converted and the formation of CO_2 is repressed to the greatest possible extent. This is accomplished by contacting a gaseous mixture of CO, H_2, H_2O vapor, and CO_2 with a fluidized Fe catalyst at 550°–700° F. and 200 p. s. i. g. until about 0.95–0.995% of the CO feed has been converted. The composition of the gaseous feed mixture is so maintained that the molar ratio of H_2: CO is at least 2:1, the amount of H_2O vapor is not more than what corresponds to saturation at 100° F., and the proportion of CO_2 is enough to repress action of the water-gas shift in that direction, which consumes CO and H_2O vapor with formation of CO_2, and substantially to inhibit the conversion of the feed CO into unwanted CO_2.

3875. ——— (The Texas Co.). Production of Liquid Hydrocarbons, Oxygenated Hydrocarbons and the Like. United States Patent 2,583,164, Jan. 22, 1952; appl. filed Sept. 8, 1949, Serial No. 114,620; 21 claims (*Cl. 260–449.6*).

Carbonaceous material containing H, such as crude oil or natural gas, is converted into synthesis gas by treatment at 1,000°–2,000° F. with a readily reducible oxide of a hydrocarbon synthesis catalyst containing a catalytic metal, such as Fe, Co, Ni, or Ru, capable of forming readily reducible oxides. The resulting synthesis gas and the reduced metal oxide particles are subsequently contacted at a lower temperature 350°–800° F., at which the particles become catalytically effective to convert the synthesis gas into desired product fractions. The catalyst particles are reconverted to a highly oxidic form, providing a continuous source of O_2 for gasification of carbonaceous feed material and largely or completely obviating the requirement for rectified molecular O_2 otherwise encountered in the production of pure synthesis gas. Moreover, the hydrocarbon synthesis operates with greatly reduced production of undesired byproduct gases, such as CH_4, CO_2 and H_2O vapor, thus enabling increased yield of desired liquid product fractions.

3876. ——— (The Texas Co.). Stabilization of Fluidized Iron Synthesis Catalyst. United States Patent 2,616,915, Nov. 4, 1952; appl. filed Oct. 30, 1947, Serial No. 783,064; 5 claims (*Cl. 260–449.6*). Chem. Abs., vol. 47, 1953, p. 1361.

Catalyst particles, < 400-mesh, are recovered from the gaseous products. They are cemented by mixing with 25% by weight of Ca aluminate refractory cement and sufficient H_2O to form a mortar. After the mix sets, it is ground and graded to 150- to 300-mesh. The graded particles are continuously returned to the reaction zone. After treating the recovered fines over a period of approximately 200 hr., the proportion of fines in the stream of reaction products is reduced to a negligible factor, and the stabilization treatment can be discontinued. The invention is particularly applicable to hydrocarbon synthesis using Fe catalysts. The catalyst may contain any of the usual promoters, but K oxide (0.5–1.5%) and Al oxide (1.5–5%) are preferred. 12 United States patents cited.

3877. ——— (The Texas Co.). Synthesis of Hydrocarbons. United States Patent 2,537,496, Jan. 9, 1951; appl. filed Mar. 26, 1947, Serial No. 737,326; 7 claims (*Cl. 260–676*).

In this process, the 1st stage consists of carbiding Fe catalyst by reacting the Fe with synthesis gas comprising H_2 and CO at such a temperature that there is almost complete consumption of the CO and only H_2O vapor is produced as a byproduct. In the 2d stage the Fe carbide is reacted with the H_2, which is now substantially free of CO in a decarbiding zone at a temperature at which liquid hydrocarbons are formed.

3878. WATSON, J. R. Retort for Effecting Synthetic Reactions Under High Pressure. United States Patent 1,169,893, Feb. 1, 1916. Chem. Abs., vol. 10, 1916, p. 833.

Retort described is used for the synthetic production of phenol, α-naphthol, toluene, and pyrocatechol, or for reactions with alkalies and HCl, in which high pressures are used. The retort is formed with a seamless flask of drawn metal rotatably mounted on journals and carrying electric resistance heaters insulated from the retort itself. The temperature is controlled by a thermostat, and a safety plug limits the maximum pressure. Gives illustration.

3879. WATTS, R. N. (Standard Oil Development Co.). [Catalysts for Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen.] French Patent 961,419, May 11, 1950; appl. filed Feb. 18, 1948, in United States, Apr. 2, 1947. Chem. Zentralb., 1950, II, p. 2270.

Catalyst consists of Fe balls, the core of which is metallic Fe and the surface Fe oxide. To produce the balls, pure melted Fe in the form of a thin round band is sprayed by means of a spray pistol through a combustible atmosphere of O_2 and C_2H_2 at a certain distance, about 90 cm., at an angle of 30° into H_2O with the formation of balls. The catalyst balls consist of 74% Fe_3O_4 and 26% Fe. They are activated by spraying with a solution of 17.3 gm. $K_2CO_3\cdot 1.5\,H_2O$ in 20 cc. H_2O. C_3- and C_4-hydrocarbons are mainly formed with the dried catalyst.

3880. ——— (Standard Oil Development Co.). Hydrocarbon Synthesis With Spherical Catalyst Particles. United States Patent 2,530,344, Nov. 14, 1950; appl. filed Sept. 6, 1947, Serial No. 772,595; 3 claims (*Cl. 260–449.6*).

Spherical catalyst particles with Fe cores and oxidized surfaces are produced by using Fe wire containing <0.2% C and a metallizing gun. A reduced atmosphere existed in front of the gun for 6 in. When metal is impinged upon a surface within this distance, no oxidized metal is deposited upon this surface. When the surface is withdrawn beyond the 6 in. limit, the extent to which the metal is oxidized is a function of the distance the surface is withdrawn beyond the reducing atmosphere. The distance may be made a function of the O_2 concentration of the atmosphere in which the operation is conducted. The particle size of the Fe spheres is 20–200 μ; the thickness of the oxide Fe surface is <20 μ. 1 literature ref. and 3 United States patents cited.

3881. ——— (Standard Oil Development Co.). Preparation of a Spheroidal Fischer-Tropsch Catalyst. United States Patent 2,530,345, Nov. 14, 1950; appl. filed Sept. 30, 1948, Serial No. 51,987; 10 claims (*Cl. 252–443*).

Catalyst in the form of small spheres is obtained by passing Fe wire containing <0.2% C through a metallizing gun. The promoter, 1–5 wt. % based on Fe, is incorporated with the Fe particles either by precoating

the wire before passing it through the gun or by using an uncoated wire and quenching the molten particles issuing from the gun in a solution containing the promoter. The oxidized coating on the Fe cores has a thickness up to 20 μ. The depth is controlled by using an atmosphere in which O_2 concentration is controlled, 5–60% O_2 and the distance of travel for the particles 0.5–3 ft. The extent of oxidation is a function of the distance of its travel path beyond the reducing atmosphere. 9 United States patents cited.

———. *See* abs. **3857.**

3882. WATTS, R. N., AND SPICER, W. E. (Standard Oil Development Co.). Hollow Magnetite Bead Catalyst. United States Patent 2,583,452, Jan, 22, 1952; appl. filed Dec. 31, 1947, Serial No. 794,980; 2 claims (*Cl. 252–474*).

Hydrocarbon synthesis catalysts comprising hollow metal microspheres are prepared from an oxide of metal belonging to the group consisting of Fe, Co, or Ni by heating a wire or rod of the relatively pure metal in conjunction with a metallizing gun to a temperature of about 2,000°–4,000° F., causing a moving stream of the metal to impinge upon a convex baffle located in the path of the stream in an oxidizing atmosphere at a temperature 100°–300° F. The stream of molten metal is thus formed into hollow microspheres having a particle size predominantly within the range of 40–120 μ. The catalysts thus formed are utilized either alone or with carriers, such as kieselguhr, synthetic gels, silica, and alumina, and with promoters, such as oxides of Na, K, Cr, Zn, Al, Mg, and the rare earth metals, and under fixed-bed or fluidized conditions.

3883. WEARN, R. B. (Food Machinery & Chemical Corp.). Process For Production of Methane Aldehyde. United States Patent 2,501,200, Mar. 21, 1950; appl. filed Dec. 26, 1926, Serial No. 718,610; 4 claims (*Cl. 260–598*). Chem. Abs., vol. 44, 1950, p. 5911.

Limonene or dipentene is reacted with H_2 at 75°–150° C. and 200–2,000 p. s. i. with Co-kieselguhr catalyst until the side chain double bond is saturated. CO is introduced and the pressure raised to 1,000–4,000 p. s. i. until an aldehyde group is substituted on the 2-position. 1 foreign patent and 4 United States patents cited.

WEAVER, J. C. *See* abs. **610.**

3884. WEBB, G. M., AND MOEHL, R. W. Catalyst. United States Patent Appl. 584,728, no date. Official Gaz., vol. 665, 1952, p. 1313; Chem. Abs., vol. 47, 1953, p. 11603.

Shaped catalysts of good physical strength, useful in hydrogenation-dehydrogenation reactions, are produced by forming an aqueous slurry of a carrier (kieselguhr, clay, or silica gel) with at least 1 H_2O-soluble metal salt ($NiNO_3$ or $NiSO_4$) and at least 1 H_2O-soluble metal salt whose metal in the oxide form is difficult to reduce (Cr, Al, Mg, or Ca nitrate or sulfate), precipitating the metal carbonates with $(NH_4)_2CO_3$, separating and drying at 100°–250° F., and calcining at 300°–800° F. The calcined material is mixed with 5 percent by wt. of soap and formed into pellets which are reduced in a H_2 atmosphere at 575°–750° F.

3885. WEBSTER, H. A. (one half to E. T. Schuler). Hydrocarbons and Alcohol From Natural Gas. United States Patent 1,711,913, May 7, 1929. Chem. Abs., vol. 23, 1929, p. 3333.

An apparatus is specified comprising 2 retorts, to 1 of which a portion of the gas is supplied while the other retort is heated by the other portion of the gas; connections are provided for supplying steam alternately to the retorts and for supplying air alternately with the steam supply, and a catalyzer chamber is connected to the retorts and supplied with gases from them.

3886. WEBSTER, H. G. (one-half to J. W. G. Winnett). Mixed Fuel Derived From Mineral Oil and Natural Gas. United States Patent 1,839,362, Jan. 5, 1932; appl. filed May 15, 1930, Serial No. 452,584. Chem. Abs., vol. 26, 1932, p. 1419.

Heavy residues from the distillation of crude petroleum are cracked into free C and H_2, the C is reacted with H_2O vapor to form CO, and the CO and H_2 are synthesized over a catalyst of ZnO, Ni, and platinized asbestos to form MeOH, which is mixed with the distilled fractions to form a motor fuel.

WEEDA, K. A. *See* abs. **937, 3800.**

WEGENER, E. *See* abs. **2822.**

WEGERICH, A. *See* abs. **2761.**

WEINGAERTNER, E. *See* abs. **2434.**

3887. WEINGAERTNER, E., AND KUNZE, H. (Braunkohle-Benzin A. G.). [Removing Sulfur Compounds From Gases and Vapors.] German Patent 724,911, July 23, 1942 (*Cl. 26 d–8.04*). Chem. Abs., vol. 37, 1943, p. 5850.

Gases are treated with solid, finely subdivided salts capable of yielding O carried on a vehicle having large surface area, for example, activated C, SiO_2 gel, or bog Fe ore at approximately 80°. The process is particularly suitable for removing CS_2, mercaptans. H_2S should be removed before this treatment.

3888. WEINGAERTNER, E., AND SEEMANN, W. (Ruhrchemie A. G.). [Regeneration of Used Adsorption Agents.] German Patent 749,793, December 9, 1944; appl. filed Dec. 30, 1938. TOM Reel 42, bag 3,439, item 58, frame 1,049.

Adsorption agents, which have been used for separating the light hydrocarbons from the residual gases of the Fischer-Tropsch synthesis, are treated with steam at about 300°–500° and then cooled suddenly by trickling cold H_2O over them. The process is applied to regeneration of active C.

3889. WEINROTTER, F. (Österreichische Stickstoffwerke A. G.). [Industrial Gas.] Austrian Patent 173,675, Jan. 10, 1953. Chem. Abs., vol. 47, 1953, p. 1919.

Gas consists of a mixture of H_2 and CO containing optionally small amounts of CO_2 or N_2. It is produced by treating liquid or meltable gasoline refinery products with an excess of O_2 or air, preferably in the presence of steam, and mixing the obtained gas mixture without cooling with other industrial gases or with natural gas, so that the hydrocarbons contained in the latter are transformed into H_2 and CO. The heat necessary for this transformation is furnished by exothermic reaction of the gasoline gasification.

WEISS, B. *See* abs. **1847.**

WEISSBACH, H. *See* abs. **157.**

WEITKAMP, A. W. *See* abs. **207.**

WEITTENHILLER, H. *See* abs. **1030.**

3890. WEITZEL, G., AND HEUNICKE, W. (I. G. Farbenindustrie A. G.). [Decomposing Hydrocarbons.] German Patent 554,551, July 11, 1932; appl. filed Aug. 15, 1928. Chem. Abs., vol. 26, 1932, p. 5962.

Hydrocarbons are catalytically decomposed with H_2, CO_2, O_2, or air or mixtures of these, into a mixture of H_2 and CO or H_2, CO and N_2 by heating in the presence of a catalyst containing a metal of the Fe group and burned $Al_2(SiO_3)_3$ or kaolin. In the examples, catalysts formed from kaolin and $Ni(NO_3)_2$ or MgO are used.

3891. WEIZMANN, C. Aromatic Hydrocarbons. British Patent 574,973, Jan. 29, 1946; appl. filed Mar. 11, 1941. Chem. Abs., vol. 42, 1949, p. 1955.

Aromatic hydrocarbon product is produced from a hydrocarbon oil, boiling within the range 150°–400°, originating from the Fischer-Tropsch synthesis process.

The hydrocarbon oil is subjected, in the form of its vapor, to the action of a hydrogenation-dehydrogenation catalyst, at 500°–800°, at about atmospheric pressure, and at a space velocity of 0.1–0.5 l. of the oil per l. of catalyst vol. per hr. The reaction product is cooled and condensed, and the liquid phase obtained is fractionally distilled.

WELLER, —. *See* abs. **2054.**

3892. WELTY, A. B. (Standard Oil Development Co.). Apparatus for Conversion of Hydrocarbons. United States Patent 2,550,741, May 1, 1951; appl. filed June 28, 1946, Serial No. 679,886, divided and this appl. filed May 19, 1948, Serial No. 27,879; 5 claims (*Cl. 23–288*).

In the conversion of gaseous hydrocarbons into synthesis gas by contact with a fluidized mixture of metal oxide and reformer catalyst, the reduced metal oxide is separated from the reformer catalyst by centrifugal force, reoxidized and mixed with the separated reformer catalyst, the mixture being used again for conversion. The apparatus used comprises a conversion vessel and a reoxidizing vessel, a connecting pipe with a curved section to effect separation of the catalysts by centrifugal force, means for conducting the separated reformer catalyst back to the conversion chamber, and means for conducting the separated reduced catalyst to the reoxidizer from which it is conveyed back to the conversion chamber to be mixed with the reformer catalyst. 1 United States patent cited.

3893. ——— (Standard Oil Development Co.). Coal Gasification. United States Patent 2,538,219, Jan. 16, 1951; appl. filed Sept. 27, 1946, Serial No. 699,656; 27 claims (*Cl. 48–206*).

Coal or coke added to the water-gas generator is of large enough size particles that it will not be fluidized under conditions used in the water-gas generator. Nonfluidizable ash is removed continually from the bottom of the water-gas generator. There is thus provided a moving solids bed of coal or coke through which a much finer relatively inert heat-carrying solid is circulated. This circulating solid is the same as that being circulated between the water-gas generator and heater. The inert material is mixed with the carbonaceous fines from the water-gas generator as it passes to the heater. The fines of low concentration are burned in the heater with air or O_2 to generate heat by formation of CO_2 Conditions are so controlled as to increase O_2 consumption and decrease CO formation, the final result being that the ratio of CO_2: CO in the combustion fumes is 15–20 volumes to 1. The foreign material thus heated is returned to the generator. A commercial mixture of CO and H_2 is obtained.

3894. ——— (Standard Oil Development Co.). Continuous Process for the Production of Hydrocarbons. Canadian Patent 468,409, Sept. 26, 1950; appl. filed Jan. 23, 1946. Chem. Zentralb., 1951, I, p. 1406.

CO and H_2 mixed with CH_4 are treated in a fluidized bed in presence of a reducible heavy metal oxide, a mixture of Fe- and Ni-oxides, at 1,200°–2,000° F. The catalyst is regenerated with a O_2-containing gas.

3895. ——— (Standard Oil Development Co.). Conversion of Hydrocarbon Gases to Hydrogen and Carbon Monoxide. United States Patent 2,550,742, May 1, 1951; appl. filed June 28, 1946, Serial No. 679,886; 5 claims (*Cl. 48–196*).

In the conversion of gaseous hydrocarbons to CO and H_2 by passing the hydrocarbons over a fluidized mixture consisting of a metal oxide and a Ni-containing reformer catalyst, the catalyst mixture is withdrawn from the conversion zone and passed through a curved, confined path to cause a separation of the reduced catalyst from reformer catalyst by centrifugal action. The reduced catalyst is passed to an oxidizing zone where it is reoxidized and both it and the reformer catalyst are returned to the conversion zone. 7 United States patents cited.

———. *See* abs. **714.**

3896. WELZ, —., AND BARKOW, —. (I. G. Farbenindustrie A. G.). [Process for Producing Aromatic, Antiknock Gasoline From Aromatic, Hard-to-Split Middle Oils.] German Patent Appl. —, OZ 14,426, filed Oct. 11, 1943. TOM Reel 20, frames 2,686–2,690, item 168.

Process is given for producing aromatic, antiknock gasoline from aromatic, hard-to-split middle oils, such as coal-tar middle oils with high naphthalene content b. 170°–310°. The middle oil is first passed over catalyst made up of the sulfides or oxides of metals of groups 2–8 (active Al_2O_3 with 10% MoO_3) on carriers of low cracking ability, such as Al_2O_3, silica gel, active C, at temperatures of 480°–550°, pressures of 100–700 atm. and H_2 partial pressure of >50 atm. with maintenance of the aromatic content and removal of the O, S, and N-compounds and the unsaturates from the products. The gasoline obtained is separated, and the hydrocarbons boiling above the gasoline boiling range are cracked into aromatic gasoline by contact with strongly cracking, artificially produced Al or Mg silicates, which contain small amounts of the oxides or sulfides of metals of groups 2–8, at temperatures of 350°–550° and pressures of 40–300 atm. The gasolines obtained in the 2 steps may be combined. The gasoline has aromatic content of 50–58% and octane No. 81–82, motor method.

WELZ, H. *See* abs. **1806, 1807.**

3897. WENDER, I., AND ORCHIN, M. (United States of America, as represented by the Secretary of Agriculture). Reduction of Carbonyl Compounds. United States Patent 2,614,107, Oct. 14, 1952. Chem. Abs., vol. 47, 1953, p. 5,422.

R^1COR^2 (R^1=alkyl, aryl, cycloaliphatic, or heterocyclic group, R^2=H, or similar to R^1) is reduced with H_2 in the presence of $[Co(CO)_4]_2$ (prepared from CO and Co or Co salts) at 150°–300° and under pressure to give alcohols. The presence of double bonds in other than the α, β-position to the carbonyl leads to new carbonyl groups at the double bond by the Oxo reaction. An autoclave containing $Co(OAc)_2 \cdot 4\ H_2O$ 7, PrCHO 61.2 gm., H_2 and CO (1:1) under 3,000 lb. at room temperature was heated 3 hr. to 160°–180°; distillation of the reaction mixture gave 36 gm. BuOH (I). Similarly BzH gives $PhCH_2OH$, which is dehydrated under the reaction conditions to $(PhCH_2)_2O$, and MeCH: CHCHO yields (I).

3898. ———. Reduction of Oxygenated Thiophene Compounds. United States Patent 2,587,671, Mar. 4, 1952; appl. filed May 15, 1951, Serial No. 226,520; 9 claims (*Cl. 260–332.8*).

Method is described for reducing the O-containing group in an oxygenated thiophene compound selected from the class consisting of thiophene aldehydes, thiophene ketones, and thenyl alcohols, wherein the O atom of the O-containing group is attached to a C atom α to the thiophene nucleus. The compound is reacted with H_2 in the presence of a catalyst chosen from the group consisting of carbonyls of Co and Fe. The preferred temperature and pressure are respectively 110°–200° and 100–300 atm. A concentration of CO in the reaction zone is maintained sufficient to prevent decomposition of the carbonyl catalyst under the reaction conditions. The catalysts for the reaction are cheap and may be formed in situ by adding an organic or inorganic salt of the metal to the reaction mixture where it reacts with CO to form the Co or Fe carbonyl. In the case of Co the active catalyst is probably either dicobalt octacarbonyl $[Co(CO)_4]_2$ or Co hydrocarbonyl $HCo(CO)_4$. Cheap hydrogenating

gases, such as unpurified water gas or coke-oven gas, may be employed. 3 examples.

WENT, J. J. *See* abs. **3365.**

3899. WENZEL, —. (I. G. Farbenindustrie A. G.). [Foam Reduction Agent.] German Patent Appl. I 76,932, OZ 14,609, filed Feb. 23, 1944. TOM Reel 23, item 15, frames 167–171; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 5, 1949, chap. 154, p. 29.

Oxygenated synthesis product obtained by the reduction of CO with H_2 to olefins and subsequently hydrogenated is used as a foam-reducing agent. Example: 3% of a finely divided catalyst containing 30% Co is added to an oil containing 30% of olefins besides saturated hydrocarbons, which was obtained by cracking the hydrocarbons from the hydrogenation of CO and which b. 75°–90°. Then a $CO:H_2$ mixture is allowed to react at 200 atm. and 130° until the reaction is complete and then heated under the influence of H_2 at 200 atm. and 180°. The catalyst is then filtered off, the mixture heated to 170° and the saturated hydrocarbons separated. The fraction 175°–195° is used as a foam-reducing agent in the fermentation industry.

———. *See* abs. **1035, 2763.**

3900. WENZEL, —, AND WINTZER, —. (I. G. Farbenindustrie A. G.). [Removing the Heat of Conversion.] German Patent Appl. I 71,916, OZ 13,345, filed Mar. 28, 1942 (*Cl. IV d–12 o*). FIAT Reel 172, frame 289; PB 25,616; TOM Reel 19, item 140, frames 1,640–1,646; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, 1948, chap. 99, p. 74.

Cooling of the converter by the faster removal of the excess heat of conversion by methods other than by H_2O-cooled tubes in the catalyst bed or by wetting the catalyst bed is discussed. The methods suggested depend mainly on variations in gas circulation or in H_2O cooling.

3901. WENZEL, —, REISINGER, —, AND MENSEL, —. (I. G. Farbenindustrie A. G.). [Clarifying the Products of Carbon Monoxide Hydrogenation.] German Patent Appl. I 75,356, OZ 14,260, filed June 23, 1943 (*Cl. IV d–23 b*). TOM Reel 15, bag 3,043, item 18, frames 2,397–2,404; TOM Reel 243; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, 1948, chap. 102, p. 84.

High-boiling portions of the products of $CO+H_2$ conversion are treated with solvents consisting mainly of saturated or mildly unsaturated aliphatic or cyclic hydrocarbons. Further clarification can be obtained by catalytic hydrogenation. Example: 20 kg. of that portion of the products b. >350° are dissolved in 35 l. of triisobutane and the solution stirred for 3 hr. at 105° with 4 kg. of Tonsil. The mixture is filtered and the filtrate freed from the solvent in vacuum. The high-boiling mass remaining shows a very extensive clarification over the original distillation residue from brown to light yellow. Triisobutylene and the decahydronaphthalene are also good solvents. Treatment of the same product, after solution in decahydronaphthalene and bleaching with Tonsil, at 280° in presence of 10% by weight of a Cu–Ba–Cr catalyst under 200 atm. H_2 pressure for 2 hr. yields a virtually white product. The alcohol content is increased, obviously by the cracking hydrogenation of the esters.

3902. WENZEL, —, REISINGER, —, AND WINTZER, —. (I. G. Farbenindustrie A. G.). [Process for Reacting Carbon Monoxide With Hydrogen.] German Patent Appl. I 70,488, OZ 13,005, filed Sept. 24, 1941 (*Cl. IV d–12 o*). FIAT Reel 172, frames 249–250; PB 25,616; TOM Reel 17, item 32, frames 855–865; TOM Reel 19, item 137, frames 1,608–1,618; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 2, 1948, chap. 97, p. 65.

In catalytically converting CO and H_2 into liquid and solid oxygenated organic compounds, besides multibranched hydrocarbons, under conditions which cause the O not entering into these compounds to form CO_2, only so much gas is converted in 1 passage through a stage that <20%, suitably not >15%, of CO_2 is formed, calculated on the end gas freed from liquid and solid products. The conversion is carried out in several stages, and before further conversion of the gas is effected the CO_2 contained therein is wholly or extensively removed. Example: A gas mixture, consisting essentially of $CO:H_2=1:0.8$, containing 3% CO_2 is passed under 25 atm. pressure through 2-plate converters filled with a fused Fe catalyst with additions of Al and K oxides. The rate of throughput is 150 $m.^3$ of gas per $m.^3$ of catalyst per hr. The temperature in the 1st converter is 180°, in the 2d 200°. The gas from each converter, after separation of the liquid and solid products, contains 12.5% of CO_2. The contraction is respectively 22% and 15%. The average alcohol content of the fractions of the 1st stage is about 45%, that of the 2d stage about 32%. A considerably higher alcohol content results when a 2-stage, rather than a single-stage process is used. Similar to German Patent appl. I 70,503 (abs. **3905**).

3903. WENZEL, —, WINTZER, —, AND BREYWISCH, —. (I. G. Farbenindustrie A. G.). [Separation of the Synthesis Products of Carbon Monoxide Conversion.] German Patent Appl. I 74,241, OZ 13,974, filed Feb. 4, 1943 (*Cl. IV d–12 o*). FIAT Reel 172, frame 363; PB 25,616; TOM Reel 19, item 142, frames 1,665–1,674; transl. TOM Reel 243; Meyer Transl. PC-S-II, Fischer-Tropsch, vol. 3, 1948, chap. 116, p. 28.

In producing oxygenated compounds by the hydrogenation of CO in presence of Fe catalysts at raised pressure, the low-boiling products are separated by adsorption or absorption agents which are then regenerated by steam. After condensation of the steam and the low-boiling synthesis products, the aqueous layer of the condensate is treated for the recovery of the oxygenated compounds by distillation or extraction.

3904. WENZEL, —, WINTZER, —, AND REISINGER, —. (I. G. Farbenindustrie A. G.). [Conversion of Carbon Monoxide With Hydrogen to Liquid and Solid Oxygenated Hydrocarbons.] German Patent Appl. I 71,725, OZ 13,281, filed Mar. 2, 1942 (*Cl. IV d–12 o*). FIAT Reel 172, frames 284–285; PB 25,616; TOM Reel 17, item 32, frames 872–880; TOM Reel 19, item 139, frames 1,631–1,639; Meyer Transl. PC-S-II, Fischer-Tropsch, vol. 2, 1948, chap. 96, p. 61.

In the conversion of CO with H_2 under increased pressure and such conditions that the O of the converted CO is not combined in the form of the oxygenated derivatives but chiefly in the form of CO_2, maintenance of a low conversion temperature holds the rate of conversion at so low a point that at most only 50% or less of the heat of conversion is generated, the effect of which is the formation especially of multibranched hydrocarbons instead of an inadmissibly high CH_4 formation. The temperature is some 10°–20° lower than that generally observed for the conversion to products consisting mainly of multibranched hydrocarbons. The lower the rate of conversion is maintained through the choice of a relatively low temperature, the greater is the proportion of oxygenated organic compounds in the products. These may be present up to 50 or 60% or more in the various fractions of the products. The use of increased pressure (12–50 atm.), and Fe catalysts of practically any origin is preferred with a gas ratio of $CO:H_2=1:1–1:0.5$ and a temperature 170°–250°.

3905. ——— (I. G. Farbenindustrie A. G.). [Conversion of Carbon Monoxide With Hydrogen to Liquid

and Solid Oxygenated Organic Compounds.] German Patent Appl. I 70,503, filed Sept. 25, 1941; OZ 13,010 (*Cl. IV d–12 o*). FIAT Reel 172, frames 250–251; PB 25,616; TOM Reel 19, item 138, frames 1,619–1,630.

Gas containing at least 30% CO is converted at 180°–230° and ordinary or increased pressure, preferably 12–25 atm., over an Fe catalyst which has been reduced at a gas velocity of >800 $m.^3$ per $m.^3$ of catalyst 370°–800°. The temperature of conversion is maintained such that the content of CO_2 in the tail gas should not amount to >15%. The Fe catalyst may be of the sintered, skeleton or precipitated type. The conversion is carried out in 4 furnaces in series. The contact time of synthesis gas on the catalyst is generally 4–400 sec. calculated on all stages and at the preferred hourly throughput of 70–500 $m.^3$ of gas per $m.^3$ of catalyst space, the depth of catalyst bed being 0.5–5 m. The liquid and solid products contain 42% alcohol, the fraction b. 230°–350°, 51.5%.

3906. WENZEL, W. [Carrying Out Exothermic Reactions.] German Patent Appl. —, filed Jan. 10, 1941; APC 373,942.

In carrying out exothermic catalytic reactions in the gaseous or vapor stage, excess heat of reaction may be carried away by introducing a finely dispersed liquid, such as hydrocarbon oils, into the catalyst space during the conversion. The boiling point of the oil, under the pressure of the gases prevailing in the reaction space, should be lower than the temperature to be attained by this cooling step.

———. *See* abs. **119, 120, 3224, 3956.**

3907. WENZEL, W., HEROLD, P., AND GEMASSMER, A. (Badische Anilin- u. Soda-Fabrik). [Production of Alcohols.] German Patent 767,223, Mar. 3, 1952; appl. filed Apr. 2, 1943 (*Cl. 12 o*). Chem. Zentralb., vol. 123, 1952, p. 5814.

Alcohols are produced by reacting CO and H_2 under pressure and in presence of carbonyl-forming metals as catalysts with carbonaceous compounds containing olefinic double bonds and reducing the resulting products. O_2-containing organic compounds and products containing olefins are used as the raw materials. They have been obtained by the reaction of CO and H_2 at <250° and by aid of catalysts of the Fe group, preferably Fe and under raised pressure, preferably medium pressure. The alcohols thus obtained are mainly branched chain.

3908. WERNER, E. G. G., KEULEMANS, A. I. M., AND HOOG, H. (N. V. de Bataafsche Petroleum Maatschappij). [Purification of Aliphatic Alcohols Prepared From Olefins.] Netherlands Patent 64,011, Sept. 15, 1949. Chem. Abs., vol. 44, 1950, p. 1525.

Alcohols prepared from olefins with CO and H_2, with subsequent hydrogenation of the aldehydes first formed, are purified by a final catalytic hydrogenation. The alcohols are used for the preparation of esters with phthalic, maleic, adipic, or other dicarboxylic acids, suitable as plasticizers. Only after purification by hydrogenation of the alcohols can plasticizers be obtained which are clear and colorless. For example, a mixture of alcohols prepared from olefins with 6–8 C atoms is hydrogenated during 2 hr. at 180° and 200 atm. H_2, with a Ni catalyst; the color changes from light brown to pale yellow. The phthalates prepared from this product are clear and only slightly colored. The best results are obtained with a mixture of alcohols which is freed from unchanged initial products and high-boiling fractions by distillation.

WESTINGHOUSE ELECTRIC CORP. *See* abs. **2049.**

WESTON, P. E. *See* abs. **3311.**

3909. WHITE, A. H. Methane Synthesis. United States Patent 1,772,652, August 12, 1930; appl. filed Oct. 5, 1925, Serial No. 60,684. Chem. Abs., vol. 24, 1930, p. 5045.

Gases such as blue water gas which contain CO, H_2, and S compounds are subjected to the action of a catalyst comprising Ni on a material largely composed of MgO at a temperature at 230°–760°. CH_4 is thus formed and the MgO is converted to $MgCO_3$, and sulfide, which are then dissociated by heat to regenerate MgO.

WHITE, D. E. *See* abs. **2075, 2076.**

3910. WHITE, P. C. (Standard Oil Co. of Indiana). Method for the Recovery of Hydrocarbon Synthesis Products. United States Patent 2,476,788, July 16, 1949; appl. filed Sept. 28, 1945, Serial No. 619,245; 7 claims (*Cl. 260–450*).

The hydrocarbon-synthesis products are separated by fractional condensation. The products from the reacting zone are cooled in stages, with separation of phases between the cooling stages. The residual gas fraction is scrubbed for removal of oxygenated compounds before recycle to the system. The product stream, after removal of waxes, can be cooled 20°–100° F. below the boiling point of H_2O at the partial pressure of H_2O existing in the product stream following the wax knockout trap. The mol fraction of the H_2O in the effluent stream will be a function of the gas mixture used as feed, the conversion level, and the product distribution. Ordinarily the mol fraction of H_2O will be 10–50%. The scrubbed residual gases which predominate in H_2, CO, CO_2, and light hydrocarbons may be recycled to the reactor or to the gas-preparation step. Optionally these gases can be sent to hydrocarbon recovery by means such as charcoal, oil, or H_2SO_4 adsorbers. Where air has been used in the synthesis-gas preparation, the tail gases containing N_2 should be vented.

3911. ——— (Standard Oil Co. of Indiana). Preparation of a Raney Catalyst Surface. United States Patent 2,583,619, Jan. 29, 1952; appl. filed Mar. 15, 1944, Serial No. 526,661; 2 claims (*Cl. 252–477*).

Method is devised for preparing catalytically active heat-exchange surfaces for promoting synthesis by exothermic reaction of H_2 with CO. There is a reaction zone with heat transferred from the catalytic surfaces through a gas-impermeable metal wall to a cooling medium instead of from the catalyst surface through the gas phase to the metal wall. An alloy layer is produced on the reaction-zone side of a catalyst-forming metal chamber fabricated of at least 1 metal of the Fe group to a thickness of about 0.015–0.125 in., with an alloying element such as Si, Al, or Zn, the alloy layer comprising 35–65 wt. % of the alloying element. The alloy layer is leached with an aqueous solvent capable of dissolving the alloying element, but not the catalyst-forming metal and leaving the latter in the form of a fixed skeleton layer integrally bonded to the reaction zone side of the gas impermeable metal chamber. The fixed catalyst skeleton is then activated by treatment with H_2.

3912. ——— (Standard Oil Co. of Indiana). Separation of Hydrocarbon-Synthesis Products. United States Patent 2,501,115, Mar. 21, 1950; appl. filed Oct. 30, 1945, Serial No. 625,552, 5 claims (*Cl. 260–450*). Chem. Abs., vol. 44, 1950, p. 5082.

Gaseous effluents from the Fischer-Tropsch synthesis are cooled to 50°–250° F. 2 liquid phases form in the separator, aqueous and liquid hydrocarbons. The uncondensed stream of rich gas goes over to a 2-phase absorber. Organic oxygenated compounds are removed from the aqueous phase. A lean absorber-oil fraction is recovered from the liquid-hydrocarbon phase. The lean aqueous phase and the lean absorber-oil fraction are used with the gas phase. Organic oxygenated com-

pounds are absorbed in the aqueous phase, and the normally gaseous hydrocarbons selectively absorbed in the oil fraction. 6 United States patents cited.

3913. WHITMAN, G. M. (E. I. du Pont de Nemours & Co.). Method for the Catalytic Production of Oxo-Carbonyl Compounds. United States Patent 2,462,448, Feb. 22, 1949; appl. filed Sept. 5, 1946, 13 claims (*Cl. 260–599*). Chem. Abs., vol. 43, 1949, p. 4287.

An olefinic hydrocarbon, such as cyclohexene, is reacted under super atmospheric pressure and at a temperature of at least 100° C. with a mixture of CO and H_2 in the presence of a group II metal having an atomic number of 12–30, such as Ca or Zn. Oxo-carbonyl compounds such as hexahydrobenzaldehyde are obtained. 2 United States patents cited.

WIENER STADTWERKE. *See* abs. **1783.**

3914. WIETZEL, G. (I. G. Farbenindustrie A. G.). Combustible Gas Containing Hydrogen and Carbon Monoxide. United States Patent 1,751,117, Mar. 18, 1930. Chem. Abs., vol. 24, 1930, p. 2583.

In an exothermic process of manufacturing gas which has a high calorific value and which is rich in H_2 and CO, pulverulent solid fuel is gasified in a continuous process with the aid of a gas containing a higher % of free O_2 than atmospheric air.

———. *See* abs. **1118, 1119, 2674, 2685, 2686, 2687, 2688, 3265, 3890.**

3915. WIETZEL, G., AND STARKE, A. (I. G. Farbenindustrie A. G.). Unsaturated Gaseous Hydrocarbons and Hydrogen From Saturated Hydrocarbons. United States Patent 1,892,973, Jan. 3, 1933; appl. filed Apr. 9, 1927. Chem. Abs., vol. 27, 1933, p. 2,101.

Gas such as natural gas is subjected to the action of an electric arc to form C_2H_2 and other unsaturated hydrocarbons, which are separated from the gas mixture, and the residual gas is converted into a mixture substantially composed of CO and H_2 by treatment at a high temperature with steam of O_2 or both in suitably restricted proportions.

3916. WIETZEL, G., AND WIETZEL, R. (Badische Anilin- u. Soda-Fabrik). Synthesizing Aldehydes, Acids, or Similar Compounds. United States Patent 1,562,480, Nov. 24, 1925; appl. filed Feb. 25, 1925, Serial No. 11,557. Chem. Abs., vol. 20, 1926, p. 424.

In synthesizing higher alcohols, aldehydes, acids, or similar higher molecular compounds containing O, CO is caused to act on vaporized MeOH, EtOH or other vaporized aliphatic alcohol at an elevated pressure and temperature; for example, 200 atm. and 420°, and in the presence of a catalyst such as one containing alkali, Cr, and Mo.

3917. WIETZEL, G., AND WINKLER, K. (I. G. Farbenindustrie A. G.). [Oxygenated Organic Compounds.] German Patent 488,156, Apr. 12, 1923. Chem. Zentralb., 1930, I, p. 2,040; Chem. Abs., vol. 24, 1930, p. 2,137.

Water gas and like mixtures of CO and H_2 to be used for the manufacture of MeOH by catalytic reaction at a high temperature and pressure are preliminarily purified by treatment with steam in the presence of a catalyst promoting the production of H_2 and CO_2 from CO and H_2O. This treatment decomposes organic S compounds in the gas mixture and yields H_2S, which is removed with the CO_2. Gives example. Addition to German patent 396,115 (abs. **113**).

3918. WIETZEL, G., HALLER, W., AND HENNICKE, W. (I. G. Farbenindustrie A. G.). [Decomposing Hydrocarbons.] German Patent 578,824, June 17, 1933. Chem. Abs., vol. 28, 1934, p. 866.

In subjecting hydrocarbon gases to decomposition by treatment with steam, CO_2, and O_2, or air in the presence of a catalyst, to obtain a mixture of H_2 and CO, the hydrocarbons and the steam are pretreated to remove inorganic or organic S componnds. Gives examples.

3919. ——— (I. G. Farbenindustrie A. G.). [Hydrogen-Carbon Monoxide Mixtures.] German Patent 570,026, June 28, 1927. Chem. Abs., vol. 27, 1933, p. 2,539.

Hydrocarbon gases, such as purified coal gas, are led with steam or CO_2, with or without air or O_2, over an activated catalyst in long narrow tubes which are heated externally to 600°–800° and made of resistant steel, for example, Cr–Ni steel, or of Cr–Ni alloy. The catalyst may be Ni activated with Al_2O_3 or MgO. The process may be effected in 2 stages.

3920. WIETZEL, G., STARKE, A., AND EISENHUT, O. (I. G. Farbenindustrie A. G.). [Carbon Monoxide and Hydrogen From Hydrocarbons.] German Patent 488,502, Apr. 16, 1926. Chem. Abs., vol. 24, 1930, p. 2,251.

Gaseous hydrocarbons or gas mixtures containing them are partly oxidized or electrically treated to form, in part, unsaturated hydrocarbons; these may be removed and the remaining gas made to react with H_2O vapor or O_2 or both to form mixtures of CO and H_2 for synthesis of MeOH and higher alcohols, or the CO may be oxidized to CO_2 and removed, leaving only H_2.

3921. WIETZEL, G., WIETZEL, R., AND HALLER, W. (I. G. Farbenindustrie A. G.). [Catalytic Production of Hydrocarbons.] German Patent 505,459, Aug. 19, 1930; appl. I 28,474, filed July 6, 1926 (*Cl. 12 o–1*). Chem. Abs., vol. 24, 1930, p. 5,764.

See British patent 279,347 (abs. **1185**).

WIETZEL, R. *See* abs. **2088, 2374, 2682, 2683, 2684, 3916, 3921.**

3922. WIETZEL, R., AND FISCHER, K. (Standard-I. G. Co.). Hydrocarbons From Carbon Oxides and Hydrogen. United States Patent 1,801,382, Apr. 21, 1931; appl. filed August 17, 1928, Serial No. 300,381. Chem. Abs., vol. 25, 1931, p. 3,357.

Reaction between C oxides and gases containing H_2 is effected in the presence of catalysts containing a metal of group 8 of the periodic system, such as Fe and Co, together with a quantity of an alkali metal equivalent to less than about 0.6 part by weight of alkali calculated as alkali metal per 100 parts by weight of the group 8 metal.

3923. WIETZEL, R., AND KÖHLER, O. (I. G. Farbenindustrie A. G.). [Higher Aliphatic Acids From Catalytic Reduction of Carbon Oxides.] German Patent 441,272, Sept. 26, 1924. British Chem. Abs., 1927, B, p. 924.

The oily products from the catalytic reduction of C oxides or from the condensation of alcohols with or without CO, preferably freed from lower alcohols, are heated with alkali or alkaline-earth hydroxides. Mixture of higher acids is obtained.

3924. WIETZEL, R., AND LUTHER, M. (I. G. Farbenindustrie A. G.). [Organic Compounds Containing Oxygen.] German Patent 628,557, Apr. 7, 1936 (*Cl. 12 o–5.01*). Chem. Abs., vol. 30, 1936, p. 6005.

High-molecular alcohols are obtained by passing oxides of C over contact masses containing a greater amount of hydrating than hydrogenating catalyst. Thus, a contact mass containing $CdCrO_3$ is heated and CO and H_2 passed over at 200 atm. At 420°, MeOH is the chief product. At 250°, with a reduction in the amount of H_2 used, a mixture of alcohols, ketones, esters, and acids is obtained. Instead of $CdCrO_4$, MnO_2, $Cu_3(NO_4)_2$, $PbMoO_4$, Ag aluminate, or mixtures of the corresponding oxides may be used as the hydrating catalyst.

See also German Patent 625,757 (abs. **2374**).

3925. ——— (I. G. Farbenindustrie A. G.). [Oxygenated Organic Compounds.] German Patent 492,427, Jan. 23, 1924. Chem. Zentralb., 1930, I, p. 3848; Chem. Abs., vol. 24, 1930, p. 2755.

Preparation of oxygenated organic compounds by the catalytic hydrogenation of CO by the method of German Patent 479,829 (abs. **2088**) is modified by removing the H_2O formed, together with some of the constituents, in solid form, by cooling to low temperatures.

See also German Patent 492,245 (abs. **3286**).

3926. WIETZEL, R., AND SPEER, W. (I. G. Farbenindustrie A. G.). Hydrogenation of Oxides of Carbon. Canadian Patent 284,235, Oct. 23, 1928. Chem. Abs., vol. 23, 1929, p. 604.

Catalysts for the reduction of oxides of C, in addition to Fe, Ni, or Co or compounds of these, contain Cd, Tl, or their compounds or mixtures of these substances. Such catalysts are effective at 180°–200°, but preferably the process is carried out at 250°–350°; the catalysts may be used at temperatures of about 400°. Admixture of the Cd or Tl prevents deposition of soot on the catalyst. Elements of group 8 of the periodic system also give, in combination with Cd or Tl, a similar action to that given by Fe, Ni, or Co. The activity of the catalysts is assisted by addition of substances such as Cu, Au, Ag, Ce, Zr, Al, V, U, Cr, Mo, W, Mn, alkali metals and alkaline-earth metals, or compounds of these, provided the metal compounds containing O, which are difficultly reducible to the metal are absent or present in amount not exceeding 5%, preferably <1% of the catalytically active material. The process may be carried out at ordinary or elevated pressure. According to the conditions of working as regards temperature, pressure, composition of the gases, catalysts, and the like, solid liquid or gaseous hydrocarbons may be produced or also products containing O or mixtures of these.

3927. WIETZEL, R., SPEER, W., AND KAEHLER, H. (I. G. Farbenindustrie A. G.). Hydrocarbons of High-Boiling-Point Range Suitable for Use As Lubricating Oils. United States Patent 1,798,288, Mar. 31, 1931; appl. filed Aug. 23, 1928, Serial No. 301,698. Chem. Abs., vol. 25, 1931, p. 3160.

Mixture of oxides of C and H_2 is subjected to treatment with a catalyst containing, in addition to a metal of group 8 of the periodic system such as Fe and Co, a quantity of an alkali-metal compound, such as Na having, an alkalinity not substantially greater than that of Na_2CO_3 and comprising less than 0.5 part, calculated as alkali metal, per 100 parts of the group 8 metal; the treatment is effected at temperatures of 270°–350°, and the resulting hydrocarbons of low-boiling-point range are subjected to a treatment under pressure at temperatures <250° in the presence of an inorganic anhydrous halide having a condensing action such as $AlCl_3$ which, when treated with H_2O, causes strong evolution of heat.

3928. WIETZEL, R., SPEER, W., AND MOEGENBURG, H. (I. G. Farbenindustrie A. G.). [Production of Liquid Hydrocarbons by the Catalytic Reduction of Carbon Oxides.] Russian Patent 13,145, Mar. 31, 1930; appl. filed June 21, 1927. Chem. Zentralb., 1931, II, p. 2248.

See French Patent 635,950 (abs. **1190**).

WILBOR, O. J. *See* abs. **906**.

3929. WILCOX, W. D. (Oil & Gas Research, Inc.). Carbon Black, Carbon Monoxide, and Hydrogen From Hydrocarbon Gases. United States Patent 2,322,989, June 29, 1943; appl. filed Aug. 11, 1939. Chem. Abs., vol. 38, 1944, p. 242.

Process is employed for producing C black, CO, and CO–H_2 gas mixtures having a ratio of the H_2 to the CO of 2:1, which involves the steps of pyrolysis within a dissociation chamber, at a temperature of 2,800°–3,000° F., of a hydrocarbon gas to which has been added a volume of CO_2 <½ the volume of the hydrocarbon gas, separation of the resultant gas mixture, and the C particles not retained within the chamber and then introducing into the chamber a volume of CO_2 which, together with the CO_2 added in the first step of the process, equals approximately ½ the volume of the hydrocarbon gas, and treating the CO_2 at a high temperature with the residual C to form CO, which is added to the resultant gas mixture obtained in the 1st step.

3930. ———. Carbon Monoxide and Hydrogen. United States Patent 1,905,326, Apr. 25, 1933; appl. filed June 28, 1930. Chem. Abs., vol. 27, 1933, p. 3,567.

For converting hydrocarbon gases and vapors into a mixture of CO and H_2 in the volumetric proportions of 1:2, respectively, there is added a volume of steam more than sufficient to oxidize the C content of the gases to CO and the mixture is passed through a conduit heated externally to >980° and the heating is continued until a dissociation of about 80% has been effected and there is added to the gases a volume of O_2 enough to oxidize the C in the undercomposed residue of hydrocarbon gases to CO and to convert to H_2O vapor all H_2 in excess of 2 times the volume of CO.

3931. ———. Converting Natural Gas or the Like Into a Mixture of Carbon Monoxide and Hydrogen in Controlled Proportions. United States Patent 1,903,845, Apr. 18, 1933; appl. filed Aug. 29, 1928. Chem. Abs., vol. 27, 1933, p. 3,321.

Interior of a conduit, having a filling of refractory material, is heated to >1,090° by burning combustible gas within the conduit, and there is then admitted to the conduit a mixture of hydrocarbon gases with a controlled volume of steam and it is passed through the conduit in a direction countercurrent to the travel of the combustion gases in the conduit, thence through a regenerator chamber having a filling of refractory material, and the gases are then withdrawn; in the reheating cycle, the air that supports combustion is passed through the regenerator in a direction countercurrent to the travel of the conserved gas.

3932. ———. Methanol Production From Carbon Oxides and Hydrogen. United States Patent 2,279,153, Apr. 7, 1942; appl. filed May 19, 1938, Serial No. 208,840; 11 claims (*Cl. 260–449*). Chem. Abs., vol. 36, 1942, p. 5,188.

In a process utilizing high pressures and catalysts, the gases are 1st passed at 200°–325° through a layer of catalyst material predominantly composed of finely divided metallic Cu, and then passed, at 300°–450°, through a layer of catalyst material predominantly composed of ZnO.

3933. ———. Mixture of Carbon Monoxide and Hydrogen in Controlled Proportions Suitable for Methanol Synthesis. United States Patent 2,256,333, Sept. 16, 1941; appl. filed Jan. 6, 1938, Serial No. 185,646; 6 claims (*Cl. 252–373*). Chem. Abs., vol. 36, 1942, p. 250.

Process is employed that involves heating the interior of a refractory walled dissociation chamber filled with refractory heat-absorbing masses to a temperature >2,500° F., by a combustion of fuel gas in the chamber, conveying the combustion gas through a heat exchanger and preheating the air which supports the combustion of the fuel gas, then passing hydrocarbon gases, to which have been added a volume of steam in excess of that, which if dissociated, would oxidize the C of the hydrocarbon gas to CO, through the dissociation chamber, in a direction of travel countercurrent to the travel of the heating gas, with a time of contact with the heated refractories within the chamber such as

effects a nearly complete dissociation of the hydrocarbon gas; then bringing about an increase in the ratio of CO : H_2 in the gas, by passing the gas from the dissociation chamber through a body of coke previously heated, to incandescence, in a connected generator and converting the undecomposed steam in the gas to CO and H_2 by union with the coke.

3934. ———. Producing a Carbon Monoxide-Hydrogen Mixture. United States Patent 2,199,475, May 7, 1940; appl. filed July 15, 1937, Serial No. 153,722; 3 claims (*Cl. 23–212*). Chem. Abs., vol. 34, 1940, p. 6,049.

Process of obtaining a mixture of CO and H_2 in controlled proportions by the dissociation of a hydrocarbon gas such as CH_4 consists in subjecting a mixture of the hydrocarbon gas, steam and CO_2 in controlled proportions to a dissociating temperature, effecting a partial dissociation, and thereafter adding to the product gas in a refractory-walled combustion chamber O_2 in a volume adequate to oxidize to CO the C in any undecomposed hydrocarbon gas, to burn to H_2O vapor any excess of H_2 in the gas and to create by the partial combustion such a rise in the temperature of the gas as will assure the complete dissociation of the hydrocarbon gas.

3935. ———. Synthesis Gas. United States Patent 1,929,665, Oct. 10, 1933; appl. filed Aug. 13, 1930. Chem. Zentralb., 1934, I, p. 612.

Apparatus and process for cracking hydrocarbons with steam and O_2 or air in the presence of catalysts. Synthesis gas suitable for MeOH production or NH_3 synthesis can be obtained.

3936. WILDE, H. D. (Standard Oil Development Co.). Continuous Method of Catalytic Reactions. United States Patent 2,534,092, Dec. 12, 1950; appl. filed Aug. 21, 1948, Serial No. 45,526; 1 claim (*Cl. 23–1*). Chem. Abs., vol. 45, 1951, p. 3100.

Catalyst supported on a belt of wire gauze is moved continuously by means of suitable reels through a reaction zone where it is brought into contact with the reactants for a short time, after which it is moved out of the reaction zone to a point where the catalyst may be regenerated or renewed. This endless-belt arrangement may be used for any catalytic reaction requiring short contact times. For example, $AlCl_3$ may be deposited on a metallic gauze belt and used to catalyze the reaction between CO and H_2 at the proper temperature and pressure.

WILHELMI, F., FABRIK CHEMISCHER PRODUCTE. *See abs.* **2017.**

3937. WILKE, E., AND FRIED, F. (I. G. Farbenindustrie A. G.). [Hydrogen and Carbon Monoxide From Methane.] German Patent 525,556, May 26, 1931; appl. filed Sept. 12, 1929. Chem. Abs., vol. 25, 1931, p. 4672.

H_2 and CO are prepared by passing CH_4 over metallic oxides, except those of Fe, which can pass to a lower stage of oxidation. TiO_2 and CrO_3 are mentioned in examples.

See also British patents 336,635 and 336,944 (abs. **1308** and **1309**).

WILLFROTH, E. *See* abs. **1064.**

WILLIAMS, C. E. *See* abs. **165**, **166.**

WILLIAMS, K. *See* abs. **3445.**

3938. WILLIAMS, K., PRING, P., AND ANDREW, T. Synthesis of Hydrocarbons. British Patent 545,695, June 9, 1942; appl. filed Apr. 29, 1940. Chem. Abs., vol. 37, 1943, p. 2163.

Hydrocarbons or their hydroxyl derivatives can be produced synthetically by passing a mixture of H_2 and CO through an alternating electric field in which the frequency is 6,000,000–37,000,000 cycles per sec., and the potential difference is 60,000–100,000 v., in the presence of a hydrogenating catalyst.

3939. WILLIAMS, K., PRING, P., AND LAWRIE, T. A. [Synthesis of Hydrocarbons, Alcohols, and Aldehydes.] French Patent 865,262, Apr. 27, 1940. Chem. Zentralb., 1941, II, p. 2021.

Gas mixture of H_2 and CO are subjected in the presence of catalysts to high frequency electric current at 250°–450° and 18–250 atm.

3940. WILLIAMS, N. H., AND HUMPHREYS & GLASGOW, LTD. Manufacture of Water Gas or Gas Consisting Largely of Carbon Monoxide and Hydrogen. British Patent 616,811, Jan. 27, 1949. Fuel Abs., vol. VI, No. 1, abs. 290; Chem. Abs., vol. 43, 1949, p. 4837.

In a cyclic process of gas manufacture in which air and steam and, if desired, other gases passed upward through the generator are preheated in a heat exchanger by the gaseous products of their respective upward passage through the generator, cyclic fluctuations in the temperature of the gaseous products and the undecomposed steam passing from the top of the generator to the heat exchanger are reduced in extent and rapidity, and more constant conditions at the hot end of the heat exchanger are insured by passing the uprun gaseous products from the generator 1st through a regenerator in a constant direction and then through the heat exchanger.

3941. WILLIAMS, R. (Du Pont Ammonia Corp.). Ammonia Synthesis. United States Patent 1,820,417, Aug. 25, 1931. Chem. Abs., vol. 25, 1931, p. 5739.

Gaseous mixture containing CO, together with H_2 and N_2 in NH_3-forming proportions, is subjected, preliminarily and at reacting temperature, to the action of a catalyst, such as one containing Cu, Mn, and Mg capable of converting CO in the presence of H_2 into oxygenated hydrocarbon derivatives; the latter are condensed and removed from the associated gases, and the gases are then subjected to the action of an NH_3-forming catalyst at reacting temperature. Describes arrangement of apparatus.

See also British Patent 344,119 (abs. **3943**).

3942. ——— (Du Pont Ammonia Corp.). Apparatus for Synthetic Reactions Such As Ammonia Synthesis. United States Patent 1,809,291, June 9, 1931. Chem. Abs., vol. 25, 1931, p. 4153.

U-shaped tube extends into a receptacle for the main body of catalyst, and heat exchange is permitted between the entering gaseous mixture and the main body, the tube enclosing another portion of catalyst in the path of the gaseous mixture.

3943. ——— (Du Pont Ammonia Corp.). Catalytic Ammonia Synthesis of Production of Oxygenated Organic Compounds. British Patent 344,119, Dec. 31, 1928. Chem. Abs., vol. 25, 1931, p. 4667.

In a cyclic process, the reacting materials are brought into contact with the hot catalyst, makeup gases are then added, and the mixture formed is brought into contact with purifying material, reaction products are removed, and the gases are recirculated. Various details of apparatus are described, in 1 form of which a single catalyst chamber may be used and the makeup gases introduced at the junction of a layer of purifying material and main catalyst, which may be similar in composition and formed by fusion and reduction of a mixture of Fe, K, and Al oxides, for NH_3 synthesis, or a mixture of Cu, Cr and Zn oxides for production of oxygenated organic compounds from H_2 and C oxides.

3944. ——— (Lazote, Inc.). Purifying Hydrogen; Ammonia Synthesis; Hydrogenation of Oils. British Patent 258,887, Sept. 24, 1925. Chem. Abs., vol. 21, 1927, p. 3109.

CO is removed from H_2-containing gases by passage under pressure over a catalyst such as Zn, Zn and Cr,

and Zn and Cu (or Fe, if the formation of some CH_4 is not detrimental) capable of forming oxygenated organic compounds such as MeOH, which are then removed from the gas by condensation while the gas is still under pressure. The pressure used is preferably that under which the purified gas is to be used. Residual CO can be removed from the gas by use of a CH_4-forming catalyst. Oily products and higher alcohols are produced when the gas speed is reduced, the temperature increased or alkali oxides are added to the catalyst. A mixture of H_2 and N_2 may be passed under a pressure of 900 atm. over heated ZnO or a mixture of Zn and Cr oxides and then passed to an NH_3-forming catalyst, formed from Fe_3O_4 containing 2% Al_2O_3 by fusing, cooling, crushing, and screening.

3945. WILLIAMS, T. S. (M. W. Kellogg Co.). Synthesis of Organic Compounds. United States Patent 2,615,911, Oct. 28, 1952; appl. filed Mar. 21, 1947, Serial No. 736,323; 10 claims (*Cl. 260–449.6*). Chem. Abs., vol. 47, 1953, p. 9346.

Difficulty of fluidizing finely divided material, such as Fe catalyst, during activation or reactivation is solved by mixing the catalyst with diluent material, such as silica, quartz, alumina, bentonite-type clay, diatomaceous earth, bauxite, kieselguhr, or super Filtrol. These materials retain a fluidized condition in either an oxidizing or reducing atmosphere at 2,000° F. or above. The fluidization characteristic of the diluent is imparted to the entire mass. The diluent should comprise 50–95% by weight of the mixture. Pressure equivalent to that in the reaction zone and a linear velocity of 0.1–40 ft. per sec. are maintained. 12 United States patents cited.

WILLIAMSON, E. H. *See* abs. **616, 617, 618, 619, 620, 621.**

WILSON, D. W. *See* abs. **1825, 2527, 2787, 2788.**

3946. WINKLER, F. (I. G. Farbenindustrie A. G.). [Active Carbon.] German Patent 463,772, July 19, 1928. Chem. Abs., vol. 22, 1928, p. 4212.

Active C is prepared by action of hot gases on carbonaceous materials in a blast furnace.

———. *See* abs. **569, 570, 571, 572, 573, 574, 575, 808, 809, 2055, 2056, 2057.**

3947. WINKLER, F., AND LINCKH, E. (I. G. Farbenindustrie A. G.). [Fuel Gas.] German Patent 647,142, June 29, 1937 (*Cl. 24 e–1.03*). Chem. Abs., vol. 31, 1937, p. 6853.

Continuously replenished bed of finely granular fuel is treated from below with a gasifying agent, for example O_2, in such a manner that the bed is kept in constant motion, resembling the motion of a boiling liquid. This movement is facilitated by introducing into the bed, from the side or from below, a separate stream of a fuel gas, preferably gas produced in the process. Describes apparatus.

3948. ——— (I. G. Farbenindustrie A. G.). Gasifying Fine-Grained Solid Fuels. United States Patent 2,111,579, Mar. 22, 1938. Chem. Abs., vol. 32, 1938, p. 3938.

Through an incandescent body of fine-grained solid fuel, such as fine coke, a gasifying agent, such as O_2, is blown at 1 place of introduction (in a described apparatus) and at the same time, from another relatively distant place of introduction, there is blown through the fuel a combustible gas, such as water gas and steam, having a lower temperature than the incandescent fuel body, the gasifying agent and combustible gas being introduced with such speed that a boiling action is established in the incandescent fuel body.

WINKLER, K. *See* abs. **2365, 2366, 2367, 2368, 2369, 2370, 2371, 2372, 2675, 2682, 2683, 2684, 2685, 2686, 2687, 2688, 3917.**

WINNETT, J. W. G. *See* abs. **3886.**

WINTERSHALL, A.-G. *See* abs. **3279, 3280, 3281, 3282, 3283.**

WINTZER, —. *See* abs. **2763, 3900, 3902, 3903, 3904, 3905.**

3949. WIRTH, —. (I. G. Farbenindustrie A. G.). [Tubular Chamber for Conducting Chemical Conversions.] German Patent Appl. —, OZ 13,712, filed Oct. 13, 1942. TOM Reel 19, item 149, frames 1,722–1,730; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 3, 1948, chap. 119, p. 40.

Describes apparatus with diagram for carrying out exothermic or endothermic chemical reactions, such as the catalytic conversion of CO with H_2 to multibranched hydrocarbons, and liquid and solid oxygenated compounds which require special measures for the removal or introduction of heat. The apparatus is characterized by the use of horizontal or slightly inclined tubes, through which flows a liquid or gaseous cooling or heating agent. The reaction chamber is supported on only 1 side, and the tube bundle so formed and reinforced that it is able to carry its own weight. The cooling or the heating agent, the raw, untreated material, and the reaction products are all conveyed to the supported side of the chamber. The jacket around the reaction chamber is so arranged that it is freely removable from the supported part of the chamber.

———. *See* abs. **3568.**

3950. WIRTH, G. (I. G. Farbenindustrie A. G.). [Catalytic Reaction between Carbon Monoxide and Hydrogen.] German Patent 734,218, Mar. 11, 1943; appl. I 62,510 filed Sept. 24, 1938 (*Cl. 12 o–1.03*). FIAT Reel AA88, frames, 3,465–3,467, PB 70,273; Chem. Abs., vol. 38, 1944, p. 1343.

The reaction is conducted in cold-jacketed, narrow tubes. Within these tubes the catalyst is arranged in such a manner that the gases can flow unhindered along the walls, while the center of the tubes offers no passage to the gases.

3951. ——— (W. E. Currie). Catalytic Reaction of Carbon Monoxide With Hydrogen. United States Patent 2,238,240, Apr. 15, 1941; appl. filed Mar. 23, 1940, Serial No. 325,517, in Germany Apr. 29, 1939; 5 claims, (*Cl. 260–449*). Chem. Abs., vol. 35, 1941, p. 4940.

Apparatus used is described and a process for the production of hydrocarbons containing >1 C atom in the molecule by catalytic conversion of CO and H_2 in a plurality of reaction systems from which the heat evolved is removed by indirect heat-exchange relation with a cooling liquid, which comprises bringing each of the systems into indirect heat-exchange relation with a separate amount of cooling liquid, condensing the vapors formed from each of the separate amounts of cooling liquid in a separate system by indirect heat-exchange relation with the same body of a secondary liquid and recycling each condensate to the heat-exchange relation with the reaction system from which it is desired.

3952. ——— (I. G. Farbenindustrie A. G.). [Conversion of Carbon Monoxide With Hydrogen.] German Patent 741,826, Nov. 18, 1943; appl. I 63,658, filed Jan. 31, 1939 (*Cl. 12 o–1 03*). FIAT Reel AA–90, frames 1,638–1,640; PB 70,275; Chem.-Ztg., Chem.-Tech. Übersicht. vol. 68, No. 6, June 14, 1944, p. 35; Meyer Transl. PC–S–II, Fischer-Tropsch, vol. 6, 1949, chap. 166, p. 8; Chem. Abs., vol. 39, 1945, p. 2636.

Tube furnace is described for the catalytic conversion of CO with H_2 to hydrocarbons in which the excess heat is removed by a cooling liquid surrounding the catalyst tubes. Describes arrangement of the tubes.

3953. WIRTH, G., AND LAUDENKLOS, H. Conversion of Carbon Monoxide and Hydrogen Into Hydrocarbons of More Than One Carbon Atom. United States Patent 2,345,957, Apr. 4, 1944. Chem. Abs., vol. 38, 1944, p. 4778.

In the process of conversion of CO and H_2 into hydrocarbons or more than 1 C atom, the major portion of the gaseous product, issuing from the catalytic conversion zone, is recycled to the entrance of the fresh feed stock, without change in temperature. This recycled gas is maintained in amounts of 4 or 5 times the fresh gas. The remaining portion of the gases issuing from the reaction zone is separated into liquid and solid components. The increase in yield of the desired hydrocarbons is up to 38% by this method.

3954. WIRTH, G., SABEL, F., AND LAUDENKLOS, H. (International Hydrocarbon Synthesis Co.). [Production of Hydrocarbons From Carbon Monoxide and Hydrogen.] Swedish Patent 101,635, May 27, 1941; appl. filed Dec. 18, 1939. Chem. Zentralb., 1942, I, p. 702.

See Italian patent 379,797 (abs. **1669**).

3955. ———. Synthesis of Hydrocarbons From Hydrogen and Carbon Monoxide. United States Patent 2,351,248, June 13, 1944. Chem. Abs., vol. 38, 1944, p. 5385.

Hydrocarbons having more than 1 C atom per molecule are produced by catalytic conversion of CO with H_2 in a plurality of consecutive reaction vessels with removal behind each reaction vessel of the liquid hydrocarbons formed, while maintaining in all the reaction vessels substantially the same throughput within the range of 200–600 $m.^3$ of gas per $m.^3$ of catalyst per hr.

3956. WIRTH, G., WENZEL, W., SABEL, F., AND LAUDENKLOS, H. Hydrocarbons From Carbon Monoxide and Hydrogen. United States Patent 2,338,475, Jan. 4, 1944. Chem. Abs., vol. 38, 1944, p. 3801.

In the production of hydrocarbons containing more than 1 C atom in the molecule, with removal of excess reaction heat by indirect heat exchange with a cooling medium coming into contact with the walls of the reaction space, the gas, comprising CO and H_2, is passed through the reaction space with a linear velocity of flow of at least about 0.6 m. per sec., and there is maintained a ratio of the space velocity of the gas to the height of the catalyst layer, expressed in meters, of not greater than about 100. Operation under these conditions serves to produce a benzine relatively stable to knocking.

WISCHERMANN, W. *See* abs. **3753**.

WISNIEWSKI, J. *See* abs. **1985**.

3957. WITT, D. Desulfurizing Fuel Gases. German Patent 671,189, Feb. 1, 1939 (*Cl. 26 d–8.04*). Schmidt, J., Das Kohlenoxyd, Akademische Verlagsgesellschaft, Leipzig, 1950, p. 168; Chem. Abs., vol. 33, 1939, p. 3568.

Distillation gases from coal or brown coal are freed from H_2S in known manner and then led through active C, whereby benzene and part of the organic S compounds are removed. The residual gas is treated with steam at 300°–500° in the presence of a catalyst to convert part of the CO into CO_2 and H_2 and the bulk of the residual organic S compounds into H_2S. The latter is removed in known manner, and the residual gas is led again through active C, to complete the removal of organic S compounds. The gas may then be subjected to known catalytic treatments. Gives an example.

3958. WOBKER, B. F. (Phillips Petroleum Co.). Treatment of Fluids With Comminuted Solids. United States Patent 2,456,035, Dec. 14, 1948; appl. filed Jan. 2, 1948, Serial No. 222; 11 Claims (*Cl. 196–52*). Chem. Abs., vol. 44, 1950, p. 5,579.

Two similar chambers each containing powdered catalyst are used alternately on conversion and on reactivation. A 3d chamber is used for catalyst storage. The conversion step is started in 1 chamber containing approximately ⅓ of the total catalyst that is to be used ultimately. The activity is maintained by means of added fresh catalyst continuously introduced with the feed. The catalyst is kept in a fluidized state. Conversion continues until the catalyst level has risen to a predetermined maximum. Conversion is diverted to the 2d chamber, and the 1st is purged and the catalyst reactivated. Reactivation gases carry catalyst to the supplementary storage chamber until the catalyst level in the 1st chamber is lowered sufficiently for the next conversion step. In Fischer-Tropsch synthesis the Fe catalyst that has been deactivated by wax deposits is reactivated by treatment with H_2 at temperatures up to 800° C. 5 United States patents cited.

WOEBCKE, H. N. *See* abs. **168**.

WOERNER, A. *See* abs. **1039**.

3959. WOHLERS, H., AND PERSIEL, H. (I. G. Farbenindustrie A. G.). [Esters of Synthetic Alcohols.] German Patent 704,775, no date. Kainer, p. 289.

Esters from alcohols of CO hydrogenation b. 140°–200° and dicarboxylic acids are suitable for making pigment paste with high pigment content.

3960. WOODALL-DUCKHAM, LTD. Continuously-Operating Vertical Retort for the Production of Synthetic Gas. British Patent 531,289, Jan. 1, 1941. Chem. Abs., vol. 35, 1941, p. 8,262.

Retort is provided at the region of transition of the preheating zone to the carbonization zone where the temperature is in the region of 300° with a gas-collecting space into which surplus gases flow. The gases generated in the preheating zone and in the carbonizing zone are led down through the reaction zone. The term "synthetic" gas refers to a gas consisting essentially of H_2 and CO in such proportions as to make it suitable for production of hydrocarbons, alcohols or NH_3 by catalytic synthesis processes, the gas having been freed from hydrocarbons.

3961. WOODHOUSE, J. C. (E. I. du Pont de Nemours & Co.). Accelerating Vapor-Phase Reactions Involving Carbon Monoxide. United States Patent 2,003,477, June 4, 1935; appl. filed Feb. 28, 1931, Serial No. 519,276; 17 Claims (*Cl. 260–116*). Chem. Abs., vol. 29, 1935, p. 4854.

Reaction promoters such as the halogens, hydrohalides, alkyl halides and N oxides are used in accelerating reactions such as the synthesis of HOAc from CO and MeOH or the synthesis of HCN from CO and NH_3 (suitably in the presence of a thoria catalyst) or various other reactions involving use of CO.

3962. ——— (E. I. du Pont de Nemours & Co.), Aliphatic Carboxylic Acids. United States Patent 1,924,762, Aug. 29, 1933; appl. filed Nov. 11, 1932, Serial No. 642,238; 18 claims (*Cl. 260–116*). Chem. Abs., vol. 27, 1933, p. 5,339.

Preparation of acids such as propionic, butyric, or valeric acid from steam, CO and an olefinic hydrocarbon such as C_2H_4, C_3H_6 or C_4H_8 is effected by reaction in the presence of a volatile inorganic acid, such as HCl, formed in situ from Cl in the presence of activated charcoal.

3963. ——— (E. I. du Pont de Nemours & Co.). Carboxylic Acids Such as Acetic or Propionic Acid. United States Patent 1,946,256, Feb. 6, 1934; appl. filed June 28, 1932, Serial No. 619,735; 13 claims (*Cl. 260–116*). Chem. Abs., vol. 28, 1934, p. 2,369.

This patent relates to production of a carboxylic acid such as HOAc from an aliphatic alcohol and CO with employment of a volatile halide, such as HCl, and Mn chloride associated with activated C as a catalyst.

3964. ——— (E. I. du Pont de Nemours & Co.). Denatured Alcohol. United States Patent 2,085,779, July 6, 1937; appl. filed Nov. 7, 1932. Chem. Zentralb., 1937, II, p. 2608; Chem. Abs., vol. 31, 1937, p. 5940.

There is used as a denaturant a mixture consisting essentially of aldehydes, esters and ketones of the liquid dehydrogenation products of O-containing compounds boiling above MeOH obtainable in the synthesis of MeOH and higher alcohols by catalytic hydrogenation of CO under pressure.

3965. ——— (E. I. du Pont de Nemours & Co.). Formic Acid. United States Patent 2,001,659, May 14, 1935. Chem. Abs., vol. 29, 1935, p. 4379.

Preparation of HCOOH from CO and steam is effected in the presence of a volatile inorganic acid catalyst such as Cl or HCl which may be continuously formed in situ, in the presence of activated charcoal.

See British Patents 406,344 (abs. **581**) and 406,345 (abs. **582**).

3966. ——— (E. I. du Pont de Nemours & Co.). Removing Color and Aldehyde From Ketone-Aldehyde-Hydrocarbon Mixtures From the Hydrogenation of Carbon Monoxide. United States Patent 2,076,607, Apr. 13, 1937; appl. filed Oct. 27, 1934. Chem. Zentralb., 1937, II, p. 665; Chem. Abs., vol. 31, 1937, p. 3940.

Mixture is treated with alkali metal such as Na at 80° for 2 hr. while subjected to vacuum distillation and refluxing.

3967. ——— (E. I. du Pont de Nemours & Co.). Synthesis of Esters Such as Methyl Acetate. United States Patent 2,135,447, Nov. 1, 1938; appl. filed Apr. 23, 1936, Serial No. 76,018; 10 claims (*Cl. 260–496*). Chem. Abs., vol. 33, 1939, p. 992.

Process for the preparation of an aliphatic organic ester at elevated temperatures and pressures comprises treating an aliphatic organic ether with CO in the presence of active C and of HCl, HBr, HF, HI, NH_4Cl, NH_4Br, NH_4I, chloramine, EtCl, MeBr, sulfuryl chloride, B fluoride or phosphoryl chloride as the catalyst.

3968. ——— (E. I. du Pont de Nemours & Co.). Synthesis of Organic Compounds Such as Acetic Acid. United States Patent 2,053,233, Sept. 1, 1936. Chem. Abs., vol. 30, 1936, p. 7124.

Vapor-phase synthesis in which CO is one of the reacting materials, such as the production of HOAc from CO, MeOH, H_2O and H_2, is conducted in the presence of a H halide such as HCl or NH_4Cl, and of active C (suitably at 325° under 700 atm. pressure).

3969. ——— (Commercial Solvents Corp.). Methanol Synthesis. British Patent 279,377, Oct. 25, 1926. Chem. Abs., vol. 22, 1928, p. 2756.

Catalysts are prepared by treating a reducible Ni compound such as the hydroxide, oxide, nitrate, oxalate or tartrate with H_2 at 300°–950°, preferably 500°–600°, suitable after forming into tablets with a binder such as dextrin. MeOH may be produced from C oxides and H_2 by use of the catalysts at 250°–450° under a pressure of 50 atm. or higher.

3970. Woodruff, J. C., and Bloomfield, G. Catalyst for Methanol Production. United States Patent 1,608,643, Nov. 30, 1926. Chem. Abs., vol. 21, 1927, p. 250.

ZnO and $Fe(OH)_3$ are used together in the synthesis of MeOH from CO, CO_2, and H_2.

3971. ———. Catalyst for Synthesis of Methanol. United States Patent 1,609,593, Dec. 7, 1926; appl. filed May 26, 1926. Chem. Abs., vol. 21, 1927, p. 250.

MgO and $Fe(OH)_3$ are used together.

3972. ———. Catalyst for Synthetic Methanol Production. United States Patent 1,625,924, Apr. 26, 1927; appl. filed May 26, 1926. Chem. Abs., vol. 21, 1927, p. 1993.

ZnO, Cr oxide, or other difficultly reducible metal oxide is used together with an easily reducible oxide such as Cu, Ag, Fe, Ni, or Co oxides and with $ZnCl_2$, $MgBr_2$, or other metallic halide.

3973. ———. Catalyst for Synthetic Methanol Production. United States Patent 1,625,925, Apr. 26, 1927; appl. filed May 26, 1926. Chem. Abs., vol. 21, 1927, p. 1993.

Difficultly reducible group 2 metal oxides are used, such as ZnO and MgO, together with difficultly reducible metal oxides from the 3d to 7th groups, for example, Cr oxide and a metallic halide such as $ZnCl_2$.

3974. ———. Catalyst for Synthetic Methanol Production. United States Patent 1,625,926, Apr. 26, 1927; appl. filed May 26, 1926. Chem. Abs., vol. 21, 1927, p. 1993.

Plurality of difficultly reducible metal oxides such as ZnO and Cr oxides are used together with Ni oxide and a metallic halide.

3975. ———. Catalyst for Synthetic Methanol Production. United States Patent 1,625,927, Apr. 26, 1927; appl. filed May 26, 1926. Chem. Abs., vol. 21, 1927, p. 1993.

Difficultly reducible metal oxide such as Co oxide is used.

3976. ———. Catalyst for Synthetic Methanol Production. United States Patent 1,625,928, Apr. 26, 1927; appl. filed May 26, 1926. Chem. Abs., vol. 21, 1927, p. 1993.

Difficultly reducible metal oxide, such as Cu oxide is used instead of Ni oxide.

3977. ———. Catalyst for Synthetic Methanol Production. United States Patent 1,625,929, Apr. 26, 1927; appl. filed May 26, 1926. Chem. Abs., vol. 21, 1927, p. 1993.

Difficultly reducible metal oxides, such as Zn oxide, Cr oxide, Fe oxide and $ZnCl_2$, are used together.

3978. ——— Methanol. British Patent 271,840, May 26, 1926. Chem. Abs., vol. 22, 1928, p. 1596.

Catalysts for the production of MeOH from C oxides and H_2 at elevated temperature and pressure comprise a mixture of (*a*) 1 or more difficultly reducible oxides of metals of groups 2 or 6, such as Zn, Mg, Cd, Cr, V and W; (*b*) 1 or more easily reducible oxides, such as those of Cu, Ag, Fe, Ni and Co; and (*c*) a metallic halide, such as chloride or bromide of Zn or Mg or chloride of Cu or Cr. Gives numerous details of preparing the catalyst mixtures.

See also Canadian Patents 274,911, 274,912, and 274,915 (abs. **3983, 3979, 3980**).

3979. ———. Methanol Catalyst. Canadian Patent 274,912, Oct. 25, 1927. Chem. Abs., vol. 22, 1928, p. 1220.

MeOH catalyst consists of 750 gm. ZnO and 82 gm. $Fe(OH)_3$ the $Fe(OH)_3$ being formed by precipitation in aqueous solution from a soluble ferric salt.

3980. ———. Methanol Catalyst. Canadian Patent 274,915, Oct. 25, 1927. Chem. Abs., vol. 22, 1928, p. 1220.

MeOH catalyst is prepared by combining 4,500 gm. ZnO, 7,200 gm. $Cr(NO_3)_3.9\ H_2O$, 4,300 gm. $Fe(NO_3)_3.9$

H_2O and 450–820 gm. $ZnCl_2$ in aqueous mixture and converting the nitrates to oxides.

3981. ———. Methanol Synthesis. British Patent 272,864, June 21, 1926. Chem. Abs., vol. 22, 1928, p. 1782.

For synthesis of MeOH from C oxides and H_2 at elevated temperature and pressure, there are employed catalysts comprising 1 or more difficultly reducible metal oxides to which a metal halide is added. The metal oxides are preferably those of the 2d periodic group and an oxide of a metal of groups 3 and 7 is added as a promoter. Among the catalysts that may be used are: Oxides of Zn and Cr with Zn or V chloride, oxides of Zn and Mn or V and $MgCl_2$, oxides of Mg and V with MgF_2, oxides of Mg and Cr with Cr chloride and oxides of Sr and Cr with $ZnCl_2$. Various details of preparing the catalysts are given.

See also Canadian Patents 274,911, 274,912, 274,915 (abs. **3979**, **3980**, **3983**).

3982. ——— (Commercial Solvents Corp.). Methanol Synthesis. British Patent 279,378, October 25, 1926. Chem. Age, vol. 17, 1927, p. 579; Chem. Abs., vol. 22, 1928, p. 2756.

In preparing catalysts for MeOH synthesis such as those of the general type described in British Patent 271,840 (abs. **3978**) ZnO may be stirred into an aqueous solution containing Cr nitrate, $Fe(NO_3)_3$, and $ZnCl_2$ and the mass evaporated and heated to decompose the nitrates, the product then crushed and treated with an aqueous solution of $ZnCl_2$ and allowed to harden spontaneously. Other similar examples also are given and reference is made to the use of oxides of Zn, Mg, Cd, Cr, V, W, U, Zr, Ti, Al, Mn, Mo, Th, and Ce, as difficultly reducible oxides, which may be used with more easily reducible oxides such as those of Cu, Ag, Fe, Ni and Co.

See also British patent 272,864 (abs. **3981**).

3983. ———. Methanol Synthesis. Canadian Patent 274,911, Oct. 25, 1927. Chem. Abs., vol. 22, 1928, p. 1220.

MeOH catalyst consists of 750 gm. MgO and 82 gm. $Fe(OH)_3$, the $Fe(OH)_3$ being formed by precipitation in aqueous solution from a soluble ferric salt.

3984. Woodruff, J. C., Bloomfield, G., and Bannister, W. (Commercial Solvents Corp.). Synthetic Methanol. United States Patent 1,695,447, Dec. 18, 1928; appl. filed Oct. 25, 1926. Chem. Abs., vol. 23, 1929, p. 851.

See British Patent 279,377 (abs. **3969**).

3985. Worsham, C. H. (Standard Oil Development Co.). Method of Minimizing Ester Formation in Hydrocarbon Synthesis. United States Patent 2,537,178, Jan. 9, 1951; appl. filed Feb. 20, 1948, Serial No. 9,644; 5 claims (*Cl. 260–449.6*).

Steam introduced into the stream of hot reaction products immediately after it emerges from the reactor decreases the amount of ester (40%) in the final product and increases the yield of low molecular weight acids (30%) and alcohols (40%) recoverable from the aqueous layer. The steam is added at substantially the same temperature and pressure as in the reaction zone. 1 literature ref. and 5 United States patents cited.

3986. Worsham, C. H., and Holder, C. H. (Standard Oil Development Co.). Fatty-Acid Production in Hydrocarbon Synthesis. United States Patent 2,521,436, Sept. 5, 1950; appl. filed Sept. 3, 1948, Serial No. 47,706; 2 claims (*Cl. 260–449.6*). Chem. Abs., vol. 44, 1950, p. 11069.

High yields of fatty acids, mainly acetic acid, may be formed at low C formation ratio when the hydrocarbon synthesis process is operated at pressure of 500–700 p. s. i. g. recycle: fresh feed of 1.0–1.3 : 1= H_2 : CO and a synthesis gas conversion level of about 93% is maintained. CO_2 concentration >30% is maintained in the total feed to the reactor as well as H_2 partial pressure >175 p. s. i. Low H_2 : CO ratio, ordinarily associated with high C production, under condition of this invention is not conducive to high C deposition. 3 United States patents cited.

3987. Wrightson, J. M. (M. W. Kellogg Co.). Separation of Organic Compounds. United States Patent 2,583,620, Jan. 29, 1952; appl. filed June 28, 1947, Serial No. 757,912; 16 claims (*Cl. 260–450*).

To separate the mixture of hydrocarbons and oxygenated organic compounds present in the oil product obtained from the condensation of the reactor gases produced in the catalytic hydrogenation of CO, it is first extracted with a glycol solvent for the oxygenated organic compounds present in the oil. Glycols, which boil higher than the oxygenated compounds under extraction, such as ethylene glycol, 1,3-butanediol, or 1,6-hexanediol are preferred. The extract, comprising oxygenated organic compounds and a minor portion of hydrocarbons and a raffinate made up of a major portion of hydrocarbons, is distilled to recover the solvent and the mixture of oxygenated organic compounds and hydrocarbons remaining is contacted with a light alcohol treating agent to form a minimum boiling azeotrope with the hydrocarbons. Suitable alcohols are MeOH, EtOH, and PrOH. The resulting mixture of alcohol-hydrocarbon azeotropes and oxygenated organic compounds is distilled to separate the latter constituent from the azeotropes which are then extracted with H_2O to obtain the alcohol treating agent and H_2O and a raffinate comprising the separated hydrocarbons. This extract is next distilled to separate the alcohol from the H_2O, the former being recycled to the 2d distillation step and the latter to the 2d extraction step. The raffinate from the 1st extraction step is itself extracted with H_2O to obtain an extract comprising the solvent treating agent and H_2O and a raffinate made up of the separated hydrocarbons. The solvent treating agent is separated from the H_2O by distillation and both are returned to the process.

Y

3988. Yarnall, W. A. (The Texas Co.). Treatment of Hydrocarbons. United States Patent 2,257,082, Sept. 23, 1941; appl. filed Mar. 18, 1939 (*Cl. 260–683*). Chem. Abs., vol. 36, 1942, p. 94.

Olefins are formed from normally gaseous hydrocarbons and low boiling liquid hydrocarbons by contacting the hydrocarbons at low pressures and at temperatures of about 350°–600° in the vapor phase and in presence of a substantial amount of CO with a mixture of catalysts including a dehydrogenation catalyst such as Al_2O_3–Cr_2O_3 and a catalyst strongly promoting the interaction of CO and H_2 in the ratio of 1 : 2, such as the oxides of Co, Mg, and Th.

Yoshioka, Y. *See* abs. **1873**.

3989. Yosimura, R. (Isii Tekkozio K. K.). [Catalyst for Preparation of Hydrogen by the Water–Gas Reaction.] Japanese Patent 132,592, Oct. 11, 1939. Chem. Abs., vol. 35, 1941, p. 3400.

Limonite, micaceous hematite and siderite, not containing over 1.5% P_2O_5 and not heated >690°, are used as carrier for Fe_2O_3 or Cr_2O_3 prepared by precipitation.

Z

3990. ZANLEONI, C., AND CIAMPI, C. [Oxygenated Compounds.] Italian Patent 368,351, no date. Schmidt, J., Das Kohlenoxyd, Akad. Verlagsgesselschaft, Leipzig, 1950, p. 230.

Oxides or hydroxides of metals of the Si-group are used as catalyst.

3991. ZEISBERG, F. C. (E. I. du Pont de Nemours & Co.). Ethyl Acetate. United States Patent 1,708,460, Apr. 9, 1929. Chem. Abs., vol. 23, 1929, p. 2449.

EtOH vapor is passed over a dehydrogenation catalyst at a temperature of 250°–500° and under a pressure >10 atm., producing EtOAc and some associated products including normal BuOH. As catalysts, there may be used metals such as Cu, Ni, Co, and Fe, alone or in admixture or with additions of oxides such as those of Mn, Cr, Mg or Ca, or oxides alone may be used such as those of Zn, Mg, Cr or Mn.

See abs. **2033.**

ZEITSCHEL, F. *See* abs. **473.**

3992. ZERBE, C. (Rhenania-Ossag Mineralölwerke A. G.). [Catalyst for Cracking Hydrocarbons.] German Patent 738,752, July 29, 1943 (*Cl. 23 b–1.04*). Chem. Zentralb., 1944, I, p. 841; Chem. Abs., vol. 38, 1944, p. 4789.

Residues from synthesizing hydrocarbons, aldehydes, and carboxylic acids from dehydrogenation, from addition, condensation, and polymerization reactions carried out with $AlCl_3$ are used as catalysts for the cracking processes. These residues consist predominantly of organic compounds containing Cl, inorganic compounds containing S and Cl, oxidation products and small amounts of metal chlorides.

3993. ZHENOCHKIN, M. N. [Methanol.] Russian Patent 53,868, Sept. 30, 1938. Chem. Abs., vol. 35, 1941, p. 1606.

CH_4-containing gases from wood distillation are converted to $CO+H_2$, and from this mixture MeOH is synthesized.

ZIESECKE, K. *See* abs. **711, 712.**

ZIMMERMANN, W. *See* abs. **736.**

ZISSON, J. *See* abs. **3313.**

NO NAME

3994. [Carrying Out Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen in a Cycle.] German Patent Appl. B 205,171, no date (*Cl. 12 o–9.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 18.

Fresh gas is introduced between the catalyst furnace and the active C vessel in the cycle.

3995. [Catalyst Tubes for Synthesis Furnaces.] German Patent Appl. B 197,857, no date (*Cl. 12 g–4.02*). Auszüge deut. Patent Anmeldungen, vol. 7, p. 192.

Catalyst tube in furnaces for carrying out the synthesis of hydrocarbons from CO and H_2 consists of a perforated tube for introducing the reacting substances, extending axially over a part of the total length and imbedded in the catalyst mass.

3996. [City Gas From Carbon Monoxide and Hydrogen.] German Patent Appl. M 150,846, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 275.

City gas consisting essentially of hydrocarbons obtained by conversion through pressure gasification of a mixture of CO and H_2 in the presence of a hydrogenation catalyst, the final gas having an end content of 4–8% CO.

3997. [Fatty Acids.] German Patent Appl. M 144,558, no date (*Cl. IV d–12 o*). Auszüge deut. Patent Anmeldungen, vol. 6, p. 271.

Hydrocarbons from paraffin or gatsch are oxidized under pressure to fatty acids, at first in small stirring autoclaves arranged in series until the oxidation has progressed so far that it continues to go on at lower temperature with sufficient velocity.

3998. [Fatty Acids.] German Patent Appl. R 117,923, no date (*Cl. 12 o–11*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 317.

Aliphatic hydrocarbons are oxidized to fatty acids and alcohols under pressure. After the oxidation is finished the crude oxydate is treated with the tail gases from the oxidation to remove the low-molecular fractions.

3999. [Furnace for Carbon Monoxide Hydrogenation.] German Patent Appl. B 196,838, no date (*Cl. 12 g*). Auszüge deut. Patent-Anmeldungen, vol. 7, p. 192.

Tubes containing the catalyst for the hydrogenation of CO are provided with inserts which divide the tube interiors into several parts and permit free passage of the gas from 1 part of the tube to another.

4000. (Possibly Braunkohle-Benzin A. G.). [Gasoline.] German Patent Appl. B 195,200, no date (*Cl. IV d–23 b*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 743.

Normal gasoline is obtained from the hydrocarbons produced by synthesis from CO and H_2 by passing them with H_2 180°–200° over the catalyst used for the synthesis.

4001. [High-Molecular Hydrocarbons From Carbon Monoxide and Hydrogen.] German Patent Appl. B 197,998, no date (*Cl. 12 o–1.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 11.

High-molecular hydrocarbons are synthesized from CO and H_2 under medium pressures of 5–20 atm. and temperatures < 250° by the use of Fe, Cu, and Zn catalysts.

4002. [Hydrocarbon-Synthesis Process.] German Patent Appl. B 205,533, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 19.

Hydrocarbons are synthesized from CO and H_2 at medium pressure with precipitated Fe catalysts which contain essential amounts (10–20%) of $BaCO_3$ besides other desired additions.

4003. [Hydrocarbons Rich in Olefins.] German Patent Appl. B 196,014, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 9.

Olefin-rich hydrocarbon mixtures are obtained from CO and H_2 with Fe catalysts which contain > 5% of alkali carbonate. The process is at first operated without pressure and later under pressure. Addition to German Patent appl. B 194,712.

4004. [Hydrogenation of Carbon Monoxide.] German Patent Appl. M 151,313, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 276.

Hydrocarbons are obtained by hydrogenating CO in the presence of Fe catalysts and pressures of 5–25 atm., using gases that contain more H_2 than corresponds to the ratio $CO : H_2 = 1.8 : 1$, the operation being carried in more than 1 step with gas recycle.

4005. [Improving Solid Paraffins.] German Patent Appl. B 206,125, no date (*Cl. 23 b–2.01*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 745.

Solid paraffins from CO hydrogenation are improved by pressing them at temperatures below their melting points.

4006. [Lubricants.] German Patent Appl. R 114,137, no date (*Cl. 12 o–1.01*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 312.

Lubricants are produced by the polymerization of olefins with $AlCl_3$ in several steps. Olefins from the vapor-phase cracking of paraffin hydrocarbons are suitable.

4007. [Polishing Agent.] German Patent Appl. Sch 127,766, no date (*Cl. IV c–22 g*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 641.

Waxes from the hard paraffin produced in the Fischer-Tropsch synthesis are used as polishing agents. Acid number about 30–40, ester number 30–50, and saponification number 60–90.

4008. [Polymerization of Olefins.] German Patent Appl. R 113.835, no date (*Cl. 12 o–1.01*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 312.

Acid sludge occurring in the polymerization of olefins with $AlCl_3$, are processed by extracting with solvents and refining the oils which pass over into the extraction medium.

4009. [Process for the Production of Substitutes for Industrial Fats.] German Patent Appl. Sch 128,189, PA 621,715, filed October 8, 1943. FIAT Reel B–196, frames 545–547; PB 83,253.

In producing a substitute material for industrial fats, the oxidation products of a high-molecular paraffin hydrocarbon, such as the hard paraffin produced by the Fischer-Tropsch synthesis, with a b. p. of about 300°–400°, an acid number >100 and an ester number >90, is directly, without previous treatment, esterified with some H_2SO_4 mixed with monovalent alcohols with at least 3 C atoms to the molecule, also produced by the Fischer-Tropsch process and b. 120°–150°. After esterification the excess alcohol is distilled off in a vacuum, washed with H_2O and bleached with active C. A brownish, nonsticky product is obtained which is suitable for many purposes such as lubricating oils and fats, softeners, and leather oils.

4010. [Reduction of Hydrogenation Catalysts.] German Patent Appl. B 187,134, no date (*Cl. 12 o*). Auszüge deut. Patent Anmeldungen, vol. 6, p. 6.

Hydrogenation catalysts, which contain metals of the Fe group, are reduced by means of H_2 which has been freed of all C oxides by being passed over a methanizing catalyst.

4011. [Refining Synthetic Paraffin.] German Patent Appl. B 206,246, no date (*Cl. 12 o–7.03*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 19.

Cracked product of synthetic paraffin obtained by the hydrogenation of CO is improved in quality by compressing at temperatures below the melting point.

4012. [Regenerating Catalysts.] German Patent Appl. B 205,505, no date (*Cl. IV, d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 19.

Exhausted Co hydrogenation catalysts are worked up by being dissolved in HNO_3, after being treated with neutral, weak acids or alkali nitrate solutions.

4013. [Regenerating Synthesis Catalysts.] German Patent Appl. B 205,241, no date (*Cl. IV d–12 o*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 18.

Exhausted catalysts in the hydrogenation of CO are regenerated by treatment with H_2 or H_2-containing gases in the synthesis furnace at approximately synthesis temperature. The temperature of the H_2 is regulated by mixing with it the exothermic reacting material, such as the C oxides, on the catalyst.

4014. [Regenerating Used Hydrogenation Catalysts.] German Patent Appl. B 201,899, PA 292,062, Mar. 23, 1943. FIAT Reel B 196, frames 743–745; PB 83,253.

Method is given for regenerating used Co hydrogenation catalysts by dissolving them in HNO_3 after removal of the greater part of the organic substances by treating while warm, with solvents, gases or vapors. Before the catalysts are dissolved in acid at temperatures < about 700° they are oxidized with air. By this means a considerable saving of acid is reported.

4015. (Possibly Byk-Guldenwerke chemische Fabrik A.-G.). [Ski Wax.] German Patent Appl. B 196,993, no date (*Cl. 22 g–6.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 594.

Wax contains high-molecular paraffins melting >90° from the catalytic hydrogenation of CO and/or their high-molecular oxidation products.

4016. (Possibly Byk-Guldenwerke chemische Fabrik A.-G.). [Ski Wax.] German Patent Appl. B 198,323, no date (*Cl. 22 g–6.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 594.

Acids of the high-molecular oxidation products of the paraffins melting >90° and occurring in the catalytic hydrogenation of CO are neutralized wholly or partially with bases of earth alkali or earth metals (also Mg). Addition to German patent appl. B 196,993 (abs. **4015**).

4017. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] German Patent Appl. B 203,592, no date (*Cl. 12 o–1.02*). Auszüge deut. Patent-Anmeldungen, vol. 6, p. 16.

Synthesis of hydrocarbons from CO and H_2 is carried out in 2 or more steps. Calculation of the residence time of the gas in each step is discussed.

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618, 455	188	641, 266	3460	656, 560	2202	671, 490	3557
620, 775	3521	641, 332	2467	657, 014	3494	671, 552	3456
621, 902	3474	641, 333	2467	657, 224	3532	671, 573	2384
623, 815	3466	641, 945	3496	657, 269	3486	671, 608	3550
624, 869	1828	643, 503	2487	657, 526	2461	671, 652	734
625, 841	3471	643, 606	3499	657, 528	3504	672, 165	3742
626, 069	3475	643, 610	2489	657, 585	3538	672, 259	2245
626, 070	3564	644, 239	2165	658, 458	3544	672, 349	3454
626, 071	3784	644, 665	2473	658, 542	2760	672, 365	966
626, 742	3476	646, 424	2523	658, 848	3469	672, 405	2881
626, 743	3539	646, 532	2777	659, 002	1121	672, 421	2462
627, 905	3507	646, 557	3491	659, 315	3468	672, 880	262
628, 160	255	646, 744	2474	659, 712	3530	673, 170	2703
629, 915	3528	646, 925	3741	659, 727	350	673, 332	2704
630, 142	2588	647, 052	3479	659, 981	2488	673, 333	2705
630, 950	3508	647, 079	3483	660, 737	3463	675, 719	2472
631, 316	577	647, 155	900	660, 773	3541	676, 635	1120
631, 319	3492	647, 363	3455	661, 148	112	676, 658	3488
631, 322	3477	647, 467	1122	661, 916	2491	676, 710	1045
631, 325	511	647, 489	1829	662, 528	2475	677, 470	2896
631, 457	3478	647, 706	1985	662, 706	583	677, 643	427
631, 682	3553	648, 317	1771	662, 907	181	677, 878	85
632, 231	2204	649, 464	3511	663, 240	3561	678, 963	3001
632, 386	3537	649, 645	3743	664, 127	3563	678, 997	3522
632, 961	3558	649, 680	278	664, 205	2492	680, 241	2882
633, 184	3733	650, 571	2464	664, 525	3548	680, 281	2883
633, 718	3366	650, 794	3555	664, 974	3518	680, 545	3493
634, 534	3554	651, 144	2470	665, 218	2871	680, 865	1070
634, 882	3498	651, 250	3452	665, 698	584	681, 296	3542
634, 933	3523	651, 559	3500	665, 705	586	681, 551	2636
635, 219	2638	652, 477	3516	666, 066	3536	682, 154	2188
635, 909	35	653, 834	3515	667, 093	1986	682, 177	3546
635, 913	3517	653, 915	3559	667, 617	3562	683, 516	2241
636, 206	3524	654, 492	3501	667, 824	2463	684, 968	3565
636, 401	34	654, 667	3480	668, 140	3533	685, 359	3781
637, 389	3527	655, 024	2481	668, 309	2823	685, 485	77
637, 776	2479	655, 237	852	668, 419	2968	685, 962	886
637, 999	878	655, 339	3731	668, 592	2466	688, 096	827
638, 087	2714	655, 454	3566	668, 866	3187	688, 228	2298
638, 754	869	655, 685	3502	668, 941	3497	688, 915	624
640, 115	3529	655, 690	3567	668, 963	3453	689, 672	3782
640, 311	2465	655, 698	3549	669, 382	1830	690, 214	498
640, 455	2764	655, 827	3503	669, 760	3748	690, 432	2919
640, 907	3495	655, 843	3744	669, 831	2637	690, 925	2257
640, 965	26	655, 869	206	670, 299	2284	692, 176	1801
641, 121	3470	655, 976	3732	670, 336	2195		
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251, 485	2688	276, 300	2037	315, 876	2026	453, 853	3862
251, 486	3290	280, 008	737	319, 121	475	464, 217	1984
254, 987	2689	281, 814	1114	329, 226	3311	464, 546	835
264, 324	3441	282, 392	793	333, 861	561	468, 409	3894
264, 600	2604	284, 235	3926	343, 080	559	469, 242	2437
265, 063	704	285, 189	3745	343, 563	323	475, 545	897
266, 382	696	286, 288	3637	343, 564	324	476, 474	1817
267, 008	337	286, 289	601	343, 740	325	476, 475	1819
271, 569	760	286, 290	603	359, 414	630	479, 511	1765
273, 983	2591	299, 868	2216	371, 802	2056	481, 962	1740
273, 984	2592	300, 962	596	411, 292	2527	487, 256	1790
274, 911	3983	300, 963	597	421, 168	1836		

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25, 371	2619	457, 174	3830	606, 381	1340	635, 777	580
31, 551	97	468, 427	2357	606, 596	3434	635, 950	1190
31, 758	831	492, 154	557	610, 649	3433	636, 337	398
32, 175	98	519, 649	370	612, 505	1342	636, 568	795
32, 666	833	521, 054	637	613, 146	832	636, 882	1304
33, 568	719	540, 543	2616	613, 200	706	638, 109	1242
34, 348	3435	550, 720	2603	613, 470	299	639, 058	404
34, 361	399	551, 222	959	613, 541	410	639, 441	64
35, 096	3390	554, 529	2722	613, 542	406	641, 195	3381
36, 719	3406	571, 285	2686	613, 896	3432	641, 580	470
37, 076	721	571, 354	2670	614, 127	1522	642, 318	1626
37, 720	3407	571, 355	3291	615, 972	409	643, 784	1543
38, 825	423	571, 356	2369	617, 426	521	643, 923	3396
47, 814	2959	574, 173	24	617, 428	523	644, 147	1306
48, 512	3208	575, 913	99	617, 431	526	644, 189	1627
48, 739	1599	580, 905	100	617, 433	524	644, 266	3386
48, 876	1279	580, 949	83	618, 439	2602	644, 420	1292
49, 333	1266	581, 816	101	620, 653	3447	644, 525	400
49, 424	1297	585, 169	2356	621, 145	2058	647, 730	1384
50, 928	2540	590, 744	3404	621, 550	1145	647, 981	931
51, 588	3611	593, 648	2608	623, 068	2034	648, 946	1268
51, 974	2225	593, 649	2620	628, 107	1613	649, 295	1385
52, 734	1557	593, 650	2617	629, 407	844	649, 296	1307
52, 826	1577	593, 942	1381	630, 483	3388	649, 711	3382
52, 993	1246	594, 121	2609	630, 757	1267	650, 543	1517
53, 200	1650	598, 447	2622	631, 882	1187	651, 167	3392
53, 324	1577	598, 966	2594	631, 927	720	651, 194	1002
53, 488	3237	599, 588	2615	632, 011	1489	651, 406	1531
53, 821	1577	601, 163	2721	632, 259	411	652, 574	3387
345, 649	544	602, 467	339	632, 660	342	652, 595	1194
355, 900	3221	605, 349	1503	633, 139	412	652, 898	1338
400, 656	3219	605, 530	2606	634, 747	845	653, 554	545

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658, 643	422	764, 836	3397	827, 761	2962	855, 270	1711
658, 788	2524	770, 608	2550	828, 334	359	855, 378	1689
659, 582	1250	774, 157	401	828, 893	677	855, 381	1737
660, 108	3377	783, 732	1628	830, 289	3534	855, 515	1588
660, 133	1269	784, 337	3693	830, 560	2450	855, 812	1220
660, 560	1244	784, 742	2724	830, 871	2307	855, 815	1217
660, 678	1233	784, 885	3663	832, 038	1831	856, 933	1705
664, 420	1270	787, 896	3411	832, 546	999	857, 174	1547
664, 996	3832	788, 286	3661	832, 967	2265	857, 177	1597
669, 643	2397	790, 873	1356	833, 064	996	858, 330	1723
669, 872	1746	791, 729	1339	834, 328	2090	858, 789	2446
670, 396	3322	791, 950	2960	834, 686	2716	858, 790	2453
670, 763	2512	792, 021	3702	835, 899	469	859. 121	1598
670, 878	403	797, 902	3696	836, 273	3149	859, 198	1658
671, 241	1360	797, 934	20	836, 701	3201	859, 686	2444
672, 797	1625	799, 058	1272	836, 937	2256	860, 007	1914
672, 898	3776	799, 270	1530	837, 002	3182	860, 289	2796
673, 337	417	800, 735	2849	837, 251	3813	860, 360	1636
674, 457	1240	800, 956	1572	837, 524	3808	860, 383	1637
675, 596	2218	801, 771	3378	837, 904	2223	861, 415	1865
677, 973	1607	802, 208	1383	838, 010	1276	861, 745	1703
680, 585	722	802, 536	2887	838, 243	3803	862, 105	1706
680, 619	1271	803, 293	2635	838, 841	799	862, 171	1651
680, 849	3373	805, 696	1539	838, 918	4	862, 536	1652
681, 147	2513	807, 703	2113	839, 061	815	862, 870	1653
681, 345	1137	809, 226	3204	839, 874	1324	862, 926	123
681, 958	3408	810, 012	1939	840, 568	3682	863, 311	1645
682, 549	3780	811, 038	3787	841, 008	1963	863, 473	1654
683, 320	2502	812, 290	1273	841, 030	1196	863, 503	1410
683, 615	3402	812, 376	2045	841, 043	3665	863, 521	792
684, 181	1277	812, 598	1305	841, 528	3770	863, 687	1655
686, 040	675	812, 883	2920	841, 898	1605	864, 161	1656
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689, 342	546	814, 082	1529	842, 278	2969	865, 262	3939
689, 757	1629	814, 101	1249	842, 463	1526	866, 256	1334
690, 091	1603	814, 434	3369	842, 507	1604	866, 308	2942
691, 210	520	814, 636	1274	843, 305	2966	866, 360	1826
692, 395	3405	814, 853	1275	843, 306	2894	868, 102	3162
692, 736	517	815, 200	798	843, 370	419	869, 162	3205
696, 163	443	815, 351	3815	843, 515	2244	869, 163	3155
697, 539	1313	815, 716	1280	843, 844	1479	869, 341	431
697, 726	547	815, 894	242	843, 847	1942	870, 211	1657
697, 727	548	816, 928	997	843, 874	1937	870, 212	1693
697, 896	549	817, 291	995	844, 575	2860	870, 213	1664
698, 094	550	817, 767	930	845, 108	1389	870, 679	2301
699, 438	3431	817, 862	998	845, 301	3163	870, 896	3436
700, 034	2551	818, 056	2911	845, 361	1730	871, 230	2227
701, 003	1147	818, 078	1725	845, 492	1732	871, 499	2700
705, 590	3383	819, 591	3814	845, 962	1735	871, 536	2226
705, 683	3393	819, 592	3814	846, 588	2560	871, 909	1712
705, 845	444	819, 659	3769	846, 605	2559	871, 999	2701
706, 504	3400	819, 660	3766	847, 409	756	872, 069	2915
706, 505	3401	819, 701	3198	847, 617	2152	872, 238	3608
706, 506	3399	819, 808	3343	849, 158	3607	873, 645	1696
707, 607	2706	820, 576	2984	849, 527	304	874, 063	3335
712, 092	3415	820, 757	3450	850, 756	992	874, 483	915
713, 707	519	822, 636	3200	851, 182	2292	874, 890	483
722, 850	558	822, 818	2505	852, 170	1243	874, 918	477
726, 045	458	823, 262	1221	852, 269	1215	877, 010	445
729, 357	2742	823, 302	1199	853, 302	1661	877, 257	1894
731, 052	16	824, 002	309	854, 402	1709	877, 672	1578
733, 248	353	824, 135	303	854, 439	1734	877, 792	1895
734, 032	354	824, 216	2928	854, 502.	1804	879, 959	606
734, 065	2827	824, 893	3681	854, 617	1617	882, 450	1568
742, 760	525	825, 379	661	854, 903	1736	883, 454	1230
746, 640	1520	825, 839	1333	854, 962	1733	884, 257	484
748, 584	1949	826, 820	3171	855, 049	421	884, 394	1001
755, 493	3376	826, 821	2961	855, 122	1596	885, 784	2302

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888, 604	3276	919, 065	3254	955, 429	2103	964, 635	3847
889, 079	1567	921, 299	3545	955, 836	2044	964, 636	461
890, 980	2258	922, 493	2436	955, 866	885	964, 693	655
891, 202	626	924, 109	3395	955, 939	3849	964, 694	653
892, 152	295	924, 909	1833	956, 067	2484	965, 313	2485
892, 365	1386	925, 684	3248	956, 192	2288	965, 316	2486
892, 974	1582	930, 178	3543	956, 586	2970	966, 139	2480
892, 978	1576	930, 214	142	957, 262	2415	967, 234	2460
893, 155	348	933, 719	3535	957, 315	2381	968, 351	3825
893, 371	1974	934, 109	3520	957, 372	2382	968, 691	3713
893, 372	1975	934, 110	3482	957, 415	2385	969, 444	3750
893, 663	2183	934, 111	3526	958, 160	746	969, 523	3443
896, 627	1694	937, 565	3490	959, 193	976	969, 716	654
896, 955	1649	938, 437	3506	959, 599	2642	969, 735	25
897, 240	1695	938, 564	3740	959, 863	2482	970, 001	3272
899, 044	2864	938, 605	3783	960, 312	3268	970, 040	144
899, 045	3207	939, 910	3457	960, 314	2564	970, 823	192
899, 332	1606	943, 220	140	960, 868	969	970, 850	1056
900, 832	485	943, 408	1849	961, 419	3879	971, 154	1055
901, 970	1169	943, 737	818	961, 524	1851	971, 859	3826
902, 029	482	944, 450	3359	962, 568	2100	973, 289	352
905, 913	1708	945, 103	2690	962, 660	1787	973, 322	896
906, 299	1170	952, 262	2478	962, 947	2563	976, 166	351
908, 013	612	952, 815	3857	962, 948	984	976, 553	2552
912, 575	3462	953, 152	986	962, 998	3817	977, 108	1994
912, 759	1690	953, 180	3263	963, 290	2471	977, 109	1995
914, 030	3505	953, 248	2156	963, 334	2582	978, 243	2158
914, 125	3464	953, 555	902	963, 448	460	978, 270	2194
914, 577	3458	953, 616	1773	963, 475	1065	978, 834	3846
915, 433	3334	953, 667	3714	963, 531	296	996, 442	479
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I 63, 257	1165	I 70, 108	1328	I 73, 795	1453	K 142, 695	1916
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I 63, 487	1497	I 70, 151	1542	I 73, 820	1500	K 148, 007	1935
I 63, 572	1540	I 70, 190	1411	I 73, 882	1232	K 148, 919	1969
I 63, 658	3952	I 70, 230	1319	I 74, 059	1481	K 149, 907	1927
I 63, 778	1490	I 70, 282	2763	I 74, 060	1405	K 150, 067	1962
		I 70, 366	1460	I 74, 066	1807	K 152, 169	1928
I 63, 779	1177	I 70, 367	1461	I 74, 142	1471		
I 63, 810	1204	I 70, 455	1462	I 74, 150	1442	K 154, 575	1972
I 63, 879	1944	I 70, 488	3902	I 74, 240	1476	K 155, 451	1832
I 63, 924	2662	I 70, 498	1153	I 74, 241	3903	K 155, 906	929
I 64, 187	1171	I 70, 503	3905	I 74, 320	1375	K 160, 334	1970
I 64, 241	571	I 70, 527	1532			K 161, 058	66
I 64, 482	1312	I 70, 640	1335	I 74, 390	1126	K 162, 061	1924
I 64, 683	1183	I 70, 663	2316	I 74, 440	1395	K 162, 062	1925
I 64, 693	1595	I 70, 739	1419	I 74, 465	1488	K 162, 172	1929
I 65, 343	2633	I 70, 917	2324	I 74, 468	568	K 162, 979	1967
I 65, 518	1458			I 74, 495	1197	K 163, 068	1971
I 65, 560	1430	I 70, 918	2325	I 74, 496	1259	K 163, 111	1930
I 65, 742	1434	I 71, 524	1428	I 74, 553	1400	K 163, 252	1965
I 65, 845	1172	I 71, 558	1545	I 74, 591	1534	K 163, 511	1931
I 66, 084	1363	I 71, 700	1504	I 74, 594	1515	K 163, 512	1932
		I 71, 725	3904	I 74, 630	1396	K 165, 060	1966
I 66, 146	1364	I 71, 756	1444	I 74, 732	1156		
I 66, 305	1615	I 71, 916	3900	I 74, 733	1157	K 165, 274	1933
I 66, 308	1888	I 71, 941	1154	I 74, 736	1035	L 99, 223	1979
I 66, 476	1248	I 71, 966	1472	I 74, 790	1166	M 132, 610	2769
I 66, 643	1496	I 72, 009	1437	I 74, 834	1552	M 133, 836	2119
I 66, 644	1429	I 72, 047	1514	I 75, 006	1537	M 134, 467	2767
I 66, 711	1409	I 72, 249	1315	I 75, 051	1482	M 134, 700	2117
I 67, 079	1149	I 72, 407	1544	I 75, 063	1468	M 135, 302	2124
I 67, 082	2315	I 72, 531	1498	I 75, 218	1464	M 135, 840	2127
I 67, 099	1408	I 72, 605	1505	I 75, 246	1467	M 136, 500	1018
I 67, 223	1846	I 72, 625	1573	I 75, 247	1465	M 136, 573	1006
I 67, 224	1533	I 72, 695	1350	I 75, 356	3901	M 136, 644	2279
I 67, 281	1847	I 72, 741	1502	I 75, 412	1478	M 136, 645	1024
I 67, 375	1150	I 72, 810	1546	I 75, 423	1371	M 136, 681	2261
I 67, 460	1414	I 72, 813	1564	I 75, 440	1206	M 136, 878	2259
I 67, 516	1484	I 72, 850	1407	I 75, 540	1401		
I 67, 560	1036	I 72, 919	1228	I 75, 541	1397	M 136, 915	1763
I 67, 690	1431	I 72, 925	1473	I 75, 563	1155	M 136, 921	2271

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M 137, 625	2128	N 44, 653	2534	R 105, 067	2844	R 110, 168	3141
M 138, 086	1004	N 44, 666	2535	R 105, 206	2142	R 110, 169	2977
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M 138, 824	2129			R 105, 508	3180	R 110, 308	3103
M 139, 097	2120	R 95, 050	3148			R 110, 396	3011
M 139, 142	2237	R 95, 051	2916	R 105, 615	3069	R 110, 530	3007
M 139, 149	2114	R 95, 052	2913	R 105, 623	3070	R 110, 690	3087
		R 95, 118	2791	R 105, 624	3106	R 110, 734	3119
M 139, 309	1019	R 95, 973	2904	R 106, 263	3054	R 110, 735	3098
M 139, 535	1010	R 95, 984	2813	R 106, 554	2843	R 110, 978	3115
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M 140, 004	2770	R 96, 036	2935	R 106, 698	2997	R 111, 074	3113
M 140, 068	3241	R 96, 288	2979	R 106, 704	3184	R 111, 103	2890
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M 143, 569	2224	R 97, 949	3197	R 106, 876	2948	R 112, 068	3144
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M 151, 313	4004	R 103, 362	2800	R 108, 555	3107	R 115, 125	2995
M 151, 366	2290	R 103, 371	3178	R 108, 639	3147	R 115, 133	2996
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M 154, 098	2282	R 103, 714	2821	R 109, 371	3027	R 115, 709	2945
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		St 56, 470	684	St 60, 647	3575	St 63, 341	3596
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Assignee	Abstract No.
Braunkohle-Benzin A.-G	224.
Ibing, G., and Schacht, W	1124a.
I. G. Farbenindustrie A.-G	1417, 1432, 1443, 1445, 1450, 1452, 1454, 1589.
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OZ 11, 123	1887	OZ 13, 043	1335	OZ 14, 074	249	R 415	3023
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R 576	3012	R 621	2980	R 659	2907	R 699	3065
R 578	3103	R 622	2981	R 660	3112	R 700	3057
R 579	3011	R 625	2952	R 662	3128	R 701	3018
R 581	3007	R 626	2978	R 664	3090	R 702	3019
R 582	3087	R 629	3031	R 665	3136	R 703	3045
R 583	3119	R 630	3078	R 667	2945	R 704	3077
R 584	3098	R 632	3003	R 668	3047	R 705	3067
R 587	3115	R 634	3127	R 669	3083	R 707	3095
R 589	3044	R 635	3005	R 670	3000	R 710	3022a
R 593	3113	R 636	3132	R 673	3099	R 713	3049
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30, 508	3809	162, 433	1075	408, 888	3601	621, 715	4009
41, 561	2304	199, 203	3148	411, 292	1972	705, 256	3599
53, 099	2280	230, 288	3597	467, 032	2228	755, 183	3147
61, 045	3158	249, 646	3810	483, 418	3073	852, 505	904
62, 092	3079	250, 501	3619	486, 632	2274	884, 658	3086
62, 096	3058	292, 062	4014	551, 590	232	899, 335	3600
86, 822	3056	294, 891	2971	560, 882	2294	913, 619	2285
94, 674	3064	325, 783	3604	560, 884	3811	967, 306	3150
98, 309	2766	336, 742	3602	568, 242	3152		
109, 780	1072	337, 431	3605	602, 820	3078		

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183, 412	617	366, 791	2361	458, 756	736	492, 245	3286
185, 932	76	370, 975	694	462, 837	1380	492, 427	3925
190, 201	616	390, 861	87	463, 772	3946	499, 652	840
191, 026	614	396, 115	113	467, 930	2727	502, 768	209
237, 499	349	408, 811	1162	471, 267	3864	505, 319	2430
249, 447	86	411, 216	695	474, 283	3865	505, 459	3921
259, 030	176	411, 389	1239	479, 829	2088	507, 917	1310
274, 538	3792	415, 469	1163	482, 925	1624	508, 953	2379
283, 895	248	415, 686	2368	484, 166	2648	510, 302	2683
293, 787	2360	430, 623	2433	484, 337	699	512, 718	1088
295, 202	111	441, 272	3923	487, 379	2431	514, 394	2555
295, 203	2359	441, 433	2371	488, 156	3917	518, 389	2082
307, 380	82	442, 125	1251	488, 502	3920	520, 154	1089
337, 503	246	442, 840	1252	489, 280	2728	520, 222	269
339, 946	247	452, 066	2428	489, 938	742	522, 559	3306
362, 462	3309	456, 979	1253	490, 248	2679	523, 032	1623

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524, 468	702	633, 389	3422	709, 582	989	729, 059	274
525, 556	3937	636, 682	2354	709, 667	1901	729, 060	2792
528, 740	736	637, 446	2355	709, 843	3296	729, 290	2334
531, 004	700	640, 472	2046	710, 128	2107	729, 339	164
534, 551	413	646, 928	2516	710, 677	305	729, 729	184
535, 068	2080	647, 142	3947	710, 766	308	729, 962	2126
535, 254	1090	647, 720	941	710, 963	212	730, 346	1799
535, 853	480	651, 462	2812	711, 316	1180	730, 409	1889
538, 012	116	654, 373	118	711, 422	1961	730, 853	1903
539, 572	2084	659, 133	2376	711, 719	3302	730, 897	1227
539, 990	2372	659, 407	2805	712, 505	3299	730, 968	174
540, 316	512	660, 619	2367	712, 693	2108	730, 995	918
542, 616	1521	664, 055	1883	713, 627	3308	731, 295	3684
544, 665	2364	664, 817	3655	713, 913	3278	732, 684	3232
546, 336	669	669, 434	492	713, 915	1893	732, 719	2122
548, 188	2087	671, 189	3957	714, 489	2577	732, 957	1762
548, 434	1378	671, 261	802	714, 775	2125	733, 401	1611
551, 167	2086	671, 606	1945	715, 323	1561	733, 749	914
552, 446	1119	672, 731	693	715, 531	151	733, 841	2434
553, 785	1946	675, 182	2807	715, 759	152	734, 218	3950
554, 551	3890	676, 919	3678	715, 846	1041	734, 993	1024
556, 309	2657	677, 111	11	716, 078	1926	735, 276	2328
557, 650	3389	677, 222	1921	716, 239	454	735, 469	1788
558, 745	2851	678, 191	119	716, 506	155	735, 569	2109
559, 892	1377	679, 601	3223	716, 747	180	735, 662	1029
564, 045	1357	679, 961	244	716, 836	2715	736, 094	1806
564, 208	494	681, 979	800	716, 853	691	736, 471	2121
565, 309	2351	682, 018	2060	717, 247	1923	736, 528	2676
565, 459	1064	683, 373	2097	717, 693	2816	736, 617	1074
565, 880	3765	683, 691	3088	718, 509	2794	736, 701	1008
567, 069	701	683, 927	2818	719, 059	3839	736, 702	2139
568, 627	2672	684, 016	3210	719, 375	646	736, 839	2833
570, 026	3919	685, 291	670	719, 449	929	736, 844	1006
571, 898	666	685, 319	471	719, 539	2016	736, 922	1005
574, 000	3419	685, 371	1195	719, 652	1763	736, 977	1031
577, 069	697	685, 372	1964	719, 874	659	737, 351	456
578, 311	667	686, 456	1579	720, 107	2137	737, 620	1013
578, 824	3918	692, 226	2525	720, 685	3241	738, 091	679
580, 695	1996	692, 836	905	720, 733	805	738, 368	3228
581, 123	1952	693, 370	3281	720, 830	1899	738, 461	455
583, 851	662	693, 985	2680	720, 928	1134	738, 709	2326
585, 278	3420	694, 152	757	721, 359	2057	738, 752	3992
587, 818	2664	695, 647	157	721, 603	241	738, 813	3231
589, 014	938	695, 860	1761	721, 929	2913	739, 445	3225
590, 433	2828	695, 925	2681	721, 945	1843	739, 569	3855
593, 064	2215	697, 756	1040	722, 553	1884	739, 570	3804
593, 369	3421	698, 654	2017	722, 591	2117	740, 294	1845
594, 167	2652	699, 489	790	722, 706	2821	740, 347	1020
596, 093	1951	699, 843	713	722, 707	2845	740, 535	3752
597, 515	211	700, 940	459	723, 116	1042	740, 634	3656
600, 625	1343	701, 501	17	723, 215	1979	740, 677	1036
600, 677	3288	701, 758	808	724, 054	1902	740, 734	3751
608, 361	3287	701, 846	2810	724, 518	210	741, 280	66
612, 046	3375	702, 605	809	724, 873	173	741, 826	3952
612, 229	1379	703, 101	2678	724, 911	3887	741, 998	2874
612, 267	2519	703, 225	2852	725, 000	2949	742, 054	3805
614, 928	2509	703, 561	2061	725, 113	2118	742, 154	2699
614, 975	2647	703, 562	2842	725, 485	1844	742, 272	3816
616, 466	15	704, 428	2131	725, 488	10	742, 376	1010
617, 565	1834	704, 775	3959	726, 197	2848	742, 666	2748
622, 595	2352	705, 311	2813	726, 870	2979	743, 089	3298
625, 324	3761	705, 528	688	726, 885	2654	743, 569	1908
625, 757	2374	706, 951	2132	726, 894	2904	743, 995	3582
626, 787	1842	707, 079	1800	727, 289	3354	744, 022	3303
628, 427	2353	707, 227	2081	727, 676	1916	744, 075	2633
628, 557	3924	708, 125	2085	727, 750	2817	744, 076	1004
630, 824	2650	708, 500	674	728, 217	1904	744, 077	1017
630, 828	1594	708, 512	2051	728, 547	3222	744, 078	1019
631, 382	3353	708, 889	3677	728, 766	3230	744, 079	1846

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744, 136	1847	749, 079	2094	759, 843	2235	766, 110	2850
744, 184	13	749, 391	363	759, 895	2880	766, 149	1910
744, 185	3753	749, 424	2938	761, 883	1018	767, 223	3907
744, 224	2071	749, 793	3888	762, 301	2271	800, 400	2531
744, 713	2077	749, 972	3576	763, 022	2124	801, 988	2072
744, 970	504	750, 018	1912	763, 232	2261	802, 876	1909
745, 069	261	750, 072	1555	763, 233	1025	803, 352	271
745, 242	2822	750, 581	1665	763, 307	1905	804, 571	743
745, 444	1026	752, 475	2934	763, 553	2114	808, 836	430
745, 557	3133	752, 480	1906	763, 689	1600	809, 334	2707
745, 634	1135	753, 234	2275	763, 831	3004	809, 807	3307
745, 859	3134	753, 433	3603	763, 855	2236	811, 347	3481
745, 919	2576	753, 948	2224	764, 106	2268	811, 348	839
746, 304	945	754, 367	2281	764, 165	2987	812, 073	108
746, 887	1030	754, 368	2286	764, 166	3580	815, 038	276
747, 398	2308	754, 540	1071	764, 325	2260	817, 010	1117
747, 399	1015	754, 821	2279	764, 394	1136	817, 483	3838
747, 401	1897	755, 822	1907	764, 590	2237	817, 596	3300
747, 730	1016	756, 066	3233	764, 643	3120	819, 854	2630
747, 731	1027	756, 242	2287	764, 766	1586	824, 793	2761
748, 156	1011	756, 243	2272	765, 189	3613	844, 891	2532
748, 287	2791	756, 488	1107	765, 512	1911	848, 947	834
748, 312	3297	756, 609	1580	765, 515	3572		
748, 373	3229	756, 725	1172	765, 687	2229		
748, 374	2819	758, 861	2276	766, 024	1962		

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22, 982	3704	24, 210	2905	24, 733	2230	25, 276	2246
23, 278	3153	24, 309	2865	25, 177	3203	25, 835	3169

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267, 698	2515	352, 611	3683	373, 833	1863	383, 206	1320
268, 367	3379	352, 746	2386	374, 024	1713	384, 203	658
272, 064	3374	356, 468	2522	374, 071	1714	384, 545	1681
278, 927	3391	361, 595	1590	374, 226	1698	385, 590	1483
283, 343	2517	362, 514	2153	374, 244	1715	385, 693	1158
334, 877	1344	362, 725	2247	374, 321	1591	386, 631	1549
340, 547	2921	363, 468	1329	374, 322	1716	386, 654	2154
341, 317	432	363, 948	673	374, 615	1201	387, 038	1638
342, 930	2506	363, 973	3672	374, 759	3168	387, 040	2299
344, 270	2963	363, 997	3689	375, 265	2941	389, 201	1697
345, 471	1299	363, 998	3670	376, 947	1345	389, 594	3156
345, 513	1300	364, 452	3812	378, 208	1663	389, 688	2964
345, 671	1301	364, 488	1581	378, 638	3727	390, 152	1672
345, 674	3368	364, 629	2300	378, 812	1646	390, 187	1480
346, 263	1934	366, 213	1943	379, 250	1686	390, 547	1717
346, 389	2885	367, 118	2868	379, 797	1669	390, 888	2248
346, 769	1541	367, 973	3671	379, 825	1941	391, 251	1642
349, 478	2859	368, 351	3990	380, 045	1670	392, 831	608
349, 685	1726	370, 762	2426	380, 542	1639	439, 334	2383
351, 291	3283	371, 292	2427	381, 194	1330	446, 318	842
351, 470	2906	371, 909	953	381, 276	1671	448, 038	644
351, 674	3282	373, 277	1618	381, 315	1666	450, 478	643
351, 714	1528	373, 346	3801	382, 921	1687		
352, 074	1198	373, 532	1720	382, 942	1707		
352, 319	2886	373, 541	933	382, 962	1667		

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	871	2554						

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96, 341	1853	132, 543	1091	144, 803	1867	156, 456	759
98, 205	1868	132, 592	3989	144, 921	1891	156, 987	1892
98, 954	3347	133, 237	1092	147, 086	1876	157, 787	2533
98, 957	2497	133, 533	124	147, 087	1873	162, 927	1978
102, 118	1976	134, 661	1866	147, 126	1877	175, 929	604
106, 560	758	134, 662	1879	150, 548	1871	176, 614	3705
126, 845	3707	139, 563	1896	150, 952	1875	287, 840	1848
129, 242	1869	142, 908	3706	154, 262	1872		

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34, 085	1346	50, 858	1677	54, 877	2249	65, 130	3800
41, 919	3673	51, 930	1728	55, 196	1682	66, 312	2493
42, 296	3668	52, 257	1685	55, 360	1684	66, 313	2494
43, 321	3669	52, 326	1729	55, 463	2797	67, 010	2477
43, 369	2922	52, 418	1229	57, 692	1691	68, 159	2490
46, 377	2866	52, 657	1662	58, 224	1722	68, 486	499
47, 123	1258	52, 832	420	58, 695	1679	68, 491	500
48, 189	3674	53, 095	1673	60, 033	1692	69, 028	3795
49, 151	2110	53, 262	1683	60, 321	1719	69, 049	1087
49, 169	3342	53, 298	1700	63, 799	2469	69, 921	3797
49, 555	2857	53, 451	1699	64, 011	3908	70, 261	497
49, 595	3675	53, 471	2459	64, 137	2476	71, 499	3301

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24, 576	633	62, 024	3676	63, 361	1640	64, 995	1641
41, 140	2362	62, 414	1702	63, 409	3438	65, 217	916
56, 163	3701	62, 581	1647	64, 344	2798	66, 363	1570
57, 461	1382	63, 292	1688	64, 956	1989	77, 199	2741

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10, 025	1038	44, 240	2729	52, 802	1981	58, 217	2725
13, 145	3928	46, 889	3340	52, 888	503	58, 699	2781
38, 135	1980	47, 287	2558	52, 907	1739	64, 607	3735
42, 060	3757	47, 687	1797	53, 249	67	65, 854	265
42, 990	1795	48, 259	3325	53, 868	3993	66, 698	1915
44, 237	784	51, 150	3759	54, 392	3756	66, 906	789
44, 238	785	52, 384	1983	54, 406	765	68, 429	764

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53, 822	1084	99, 689	1648	104, 476	954	130, 256	2212
53, 824	1085	101, 547	2802	104, 645	2867	130, 726	2631
58, 458	102	101, 635	3954	106, 009	917	130, 809	2163
59, 281	957	102, 819	1990	127, 239	1099	134, 706	2536
91, 811	3690	103, 374	2250	127, 678	1954		

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71, 769	3828	110, 740	1583	125, 266	3410	150, 613	1808
77, 933	1913	110, 746	106	125, 468	708	162, 458	3371
91, 562	1164	118, 972	266	125, 971	343	162, 460	3372
99, 281	960	119, 470	2599	127, 243	3802	188, 881	1167
102, 236	2520	119, 717	2621	127, 251	334	204, 840	478
107, 200	2669	119, 979	2612	136, 373	1524	205, 523	2296
107, 201	103	119, 980	2613	137, 206	3427	211, 487	2251
107, 391	107	120, 509	2597	140, 093	2514	211, 489	1668
107, 853	3292	121, 809	2614	141, 673	1560	223, 963	1571
108, 071	104	121, 969	1159	141, 827	2510	229, 187	3448
110, 286	105	122, 810	1523	147, 151	2503	267, 907	2012
						273, 952	371

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22, 205	820	1, 757, 441	2726	1, 908, 484	2004	2, 056, 911	3265
22, 415	130	1, 757, 826	125	1, 908, 696	501	2, 059, 495	3352
23, 145	146	1, 757, 830	257	1, 915, 473	2743	2, 061, 470	2006
23, 433	2134	1, 762, 100	2542	1, 917, 323	2682	2, 063, 623	2659
191, 026	615	1, 766, 763	2685	1, 919, 857	2675	2, 066, 153	2028
943, 627	613	1, 770, 165	2600	1, 920, 858	942	2, 067, 729	2710
956, 734	3220	1, 772, 652	3909	1, 921, 478	2649	2, 076, 607	3966
983, 199	165	1, 773, 970	539	1, 921, 776	2780	2, 079, 216	2009
989, 755	166	1, 774, 432	738	1, 924, 762	3962	2, 083, 125	3257
1, 169, 893	3878	1, 775, 674	781	1, 924, 763	318	2, 083, 213	117
1, 201, 850	2358	1, 779, 092	940	1, 924, 764	3788	2, 085, 779	3964
1, 228, 818	2644	1, 784, 583	516	1, 924, 765	2010	2, 086, 582	3569
1, 355, 105	302	1, 788, 170	2674	1, 924, 766	319	2, 099, 475	804
1, 431, 047	2836	1, 790, 853	332	1, 924, 767	320	2, 110, 240	2811
1, 460, 244	958	1, 791, 568	2363	1, 924, 768	321	2, 110, 241	2793
1, 558, 559	2366	1, 793, 350	68	1, 924, 769	322	2, 111, 469	728
1, 562, 480	3916	1, 794, 232	1113	1, 925, 389	1747	2, 111, 579	3948
1, 563, 587	2744	1, 797, 569	602	1, 927, 414	2568	2, 115, 553	803
1, 569, 775	2350	1, 798, 288	3927	1, 929, 665	3935	2, 116, 081	2665
1, 591, 526	782	1, 799, 858	2343	1, 930, 442	2543	2, 117, 554	927
1, 602, 846	280	1, 801, 382	3922	1, 930, 443	2544	2, 127, 127	2144
1, 605, 761	2528	1, 803, 306	3635	1, 936, 563	127	2, 128, 994	671
1, 608, 643	3970	1, 809, 291	3942	1, 936, 564	128	2, 132, 533	1918
1, 609, 593	3971	1, 812, 372	2738	1, 936, 565	129	2, 132, 613	726
1, 618, 004	841	1, 812, 399	783	1, 937, 728	3647	2, 135, 447	3967
1, 625, 924	3972	1, 815, 677	2518	1, 939, 708	2003	2, 135, 450	1997
1, 625, 925	3973	1, 818, 165	3293	1, 940, 209	687	2, 135, 451	2066
1, 625, 926	3974	1, 820, 417	3941	1, 942, 021	565	2, 135, 453	2067
1, 625, 927	3975	1, 823, 468	2646	1, 942, 530	70	2, 135, 459	2069
1, 625, 928	3976	1, 824, 896	1754	1, 945, 812	1744	2, 147, 268	2732
1, 625, 929	3977	1, 829, 046	2032	1, 946, 256	3963	2, 148, 299	1919
1, 628, 190	2745	1, 831, 179	1753	1, 946, 918	3310	2, 148, 545	505
1, 631, 823	1764	1, 832, 762	270	1, 949, 825	326	2, 149, 515	664
1, 640, 668	2723	1, 833, 331	2580	1, 959, 219	2751	2, 151, 106	1003
1, 643, 663	1882	1, 834, 621	1748	1, 962, 301	627	2, 151, 121	1922
1, 667, 322	1999	1, 836, 085	2618	1, 963, 119	563	2, 151, 329	2569
1, 667, 323	2000	1, 839, 362	3886	1, 964, 001	2030	2, 154, 676	944
1, 668, 838	199	1, 841, 201	2546	1, 970, 695	747	2, 158, 650	156
1, 679, 256	2429	1, 841, 910	2684	1, 972, 937	1751	2, 159, 077	570
1, 681, 750	3648	1, 843, 063	281	1, 973, 662	3239	2, 159, 140	595
1, 681, 751	3649	1, 844, 129	2008	1, 977, 718	560	2, 159, 148	944a
1, 681, 752	3650	1, 844, 857	2002	1, 979, 717	3790	2, 161, 974	2626
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