

GTL Technology - Challenges and Opportunities in Catalysis

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Abstract

Worldwide demand for clean, reliable and affordable energy has never been greater. New technologies are needed to produce more oil and natural gas from remote or “stranded” locations. Gas to Liquids (GTL) conversion is an umbrella term for a group of technologies that can create liquid hydrocarbon fuels from a variety of feedstocks. The conversion of natural gas into liquid fuels is an attractive option to commercialize abundant gas reserves. GTL, with virtually unlimited markets, offers a new way to unlock large gas reserves, complementary to other traditional technologies such as Liquefied Natural Gas (LNG) and pipelines. GTL has the potential to convert a significant percentage of the world's estimated proved and potential gas reserves which today holds little or no economic value.

In essence, GTL uses catalytic reactions to synthesize complex hydrocarbons from carbon monoxide and hydrogen. There has been significant improvement in reactor design and technology over the last decade.

Fundamental research is essential to achieve new and improved catalysts. Such research is concerned with establishing reaction mechanisms, in understanding the surface science of catalysis and catalyst structure performance relationships, as well as searching for new techniques for scientific design of catalysts.

1. Introduction

What is Gas to Liquids (GTL)? using natural gas to make a clean, versatile liquid fuel. This is a complementary rather than competitive technology for the exploitation of stranded natural gas. In the present world energy scenario, the supply of oil and other natural resources are limited and not uniformly distributed [1]. This has been further complicated with the added pressure that OPEC puts on world economy by restricting the crude output and controlling the prices. The high cost of energy has caused inflation in many economies creating a burden on most countries. Natural gas is available in large quantity and the reserve is not used to the same

extent as petroleum crude. Although it does have some drawbacks compared to other fuels, mainly issues dealing with its volume, it promises to be an increasingly important energy source in the years to come. Methane is the principal component of natural gas currently being used for home and industrial heating as well as for generation of electrical power. Also, natural gas burns cleaner and produces fewer pollutants than other fossil fuels. It has the largest heat of combustion relative to the amount of CO₂ formed. It produces 45% less CO₂ than coal for a comparable amount of energy, and also emits considerably less NO_x and SO_x. There are many potentially rich gas fields that are not drilled, because of

the need to lay expensive pipes to transport the gas. If the field is far away from the storage reservoir, the cost of the pipeline could discourage any investors on the field. Transporting by ship, train, or truck is much less costly, but methane's high volume as a gas prevents it from being transported in bulk.

Although, liquid natural gas (LNG) is one way of accomplishing this, the need to constantly keep LNG at a very low temperature is a drawback, sometimes a serious one. This leads to the other area of GTL, chemically reacting methane with other compounds. GTL is the technology that allows the producer to convert the gas into a liquid fuel, allowing it to be transported much more compactly, and hence more easily. GTL diesel, in particular, is ultra-clean, sulphur free with a very high cetane number of 75-80 (cetane number is a measure of fuel combustion quality) compared with typical refinery diesel range of 45-50. Average emission benefits for 100% GTL in a current modern (Euro-3) light duty engine compared to current European fuel are approximately

particulates 40%
 nitrogen oxides 5%
 hydrocarbon 60%
 carbon monoxide 75%

Such emission benefits of GTL will vary in different engine types/technologies, for examples. light duty vs. heavy duty; Euro-3 vs. Euro-4. The additional advantage is that existing diesel engines can use GTL fuels without modification, which is a draw back for alternative fuels like CNG and LNG. Due to clean qualities, GTL fuels are excellent feedstock for fuel cells.

During the last five years, there has been a renewed interest in Gas-to-liquids (GTL) technology, in which natural gas is converted to liquids useful as fuels and chemicals feed stock through the Fischer Tropsch Synthesis (FTS). Methane resource can be further increased through the extraction of coal bed methane (CBM), biogas from waste and effluent anaerobic treatment, landfills and even gas hydrates. Thus, GTL technology has the potential to utilize natural gas or any other resource rich in methane i.e., refinery gas, gas hydrates, land fills & CBM for gainful utilization of the feed stock with value addition to yield middle distillates or any other fuel product, chemical or chemical feedstock. At present, methane is an underutilized resource for chemicals and fuels. The known resources (year 2000 basis) are shown in Table 1. However, it can be seen that the

Table-1: World Natural Gas Reserves (tcf)

Country/Region	Reserve	% share
Former Soviet Union	2000	40.0
Iran	744	14.9
Africa	337	6.7
Asia Pacific	330	6.6
South Africa	204	4.1
Europe	192	3.8
Saudi Arabia	186	3.7
Other (ME countries)	707	14.1
USA	163	3.3
Canada & Mexico	137	2.8
<i>Total (tcf)</i>	<i>5000</i>	<i>100.</i>

distribution is not uniform and is mostly concentrated in the former

Soviet Union block and in the Middle East. Even in the Middle East, some states like Qatar are oil deficient and rich in gas.

About 2500 tcf of proved natural gas, nearly half of proven reserves, is being left in the ground. In fact, despite strong world wide growth in demand for natural gas, more than doubling between 1973-1993, gas reserves continue to grow, but discovered and left 'in place' for lack of transportation or gas being less than pipe line quality. Natural gas markets have been expanded through improved pipeline technology, making long distance transportation feasible. In case of off shore reserve of high quality, where infrastructure is poor, it is converted to LNG and shipped. But for majority of world gas fields where gas extracted is not to support the investment on LNG, which is highly capital intensive, there remains a problem of utilization. Long distance pipelines are often saddled with too much geographic, economic and political risk to attract investment. Part of the produced gas never makes to the market because it is flared off as an unwanted byproduct of crude oil production, a practice that is increasingly opposed in many parts of the world as a threat to environment. In this backdrop GTL assumes importance since this technology appears to be the break through for stranded gas and shut in fields.

2. Technology overview

The strategy for GTL depends on the location of methane, demand for products, construction costs, the economic and geopolitical stability

etc. One should keep in mind that the capital cost involved in any GTL is very high. Where natural gas is extracted along with petroleum crude, there may not be buyers for the purchase of gas along with the crude in which case it becomes a liability, and the gas may be available at cheap cost. There is the other case where the gas extracted is in abundance and the utilization is poor. In such cases transportation through pipeline or conversion to LNG are expensive alternatives. At present in many fields, the excess gas is re-injected into the well and as the oil reserve gets depleted, an increasing amount of gas will be recycled per barrel of oil produced. In a free market economy, the profitability of these facilities will depend on the selling price of the product and the cost of alternative technologies, both of which may fluctuate significantly over a short period. The major driving forces for lifting up GTL are given in Table 2

The process of converting natural gas to marketable liquid hydrocarbons comprises three main steps, viz. i) synthesis gas, a mixture of CO and H₂ (syngas) production ii) GTL synthesis and iii) product work-up. The feed gas will typically be treated initially for removal of sulphur compounds which otherwise poison the catalyst, in addition to causing corrosion and environmental problems.

i) Syngas generation

In GTL technology, FT conversion process is employed which requires a specific molar ratio of hydrogen depending upon the product. One or more of several processes, working

in parallel, in a combined mode or with the addition or extraction of hydrogen, can achieve the appropriate syngas composition ratio. The established syngas production technologies are summarized in Table 3. Syngas for GTL though does not call for a unique process, the technology choice becomes critical in view of a) economy of (very large scale) of scale b) operating cost (energy efficiency) and c) investment economies (capital efficiency). Syngas generation dictates 2/3 of total energy usage and more than half of capital investment. The syngas technologies were described by Wilhelm *et al* [3].

Table 2: Factors favouring GTL

<i>Environmental</i>
-Legislation for lighter, cleaner alternative (syn) fuels
-Non-flaring policy for associated gas
<i>Economical</i>
-Better fuel efficiency
-Strategic investments in gas-rich locations
-Monetizing remote/ stranded gas reserves
- Refineries in future have to deal with excess bottom residues
<i>Market & political</i>
-Crude oil availability / price
-Exploitation of gas reserves against constrained markets

3.History of FTS

The FT process [3,4] had a lively history of about eight decades since its discovery in Germany by Franz Fischer and Hans Tropsch in the 1920s. During world war-II, two processes for converting coal to liquid transport fuels were tried in

Germany. The first, direct liquefaction (Bergius process) involves the direct catalytic hydrogenation of coal to liquids which are further refined. In contrast, indirect liquefaction involves conversion of coal by partial oxidation in the presence of steam to yield syngas, which after purification is reacted catalytically to form liquid hydrocarbon fuels. Both Bergius and FTS were discontinued after war because of easy availability of petroleum. However, FTS was started in a big scale at SASOL in South Africa in the 1950s. A brief history of FTS and the related events during the last century are given in Table 3. There had been several reviews recording the developments of FTS [5-9].

i)Fischer Tropsch Synthesis (FTS)

In the second step of the GTL process, syngas is converted into paraffinic and olefinic hydrocarbons of varying chain length. GTL can also produce methanol and DME. FTS typically uses iron or cobalt based catalysts. The process takes place at moderate temperature (200-300°C) and moderate pressure (10 – 40 bar). The basic reaction is:

$$n\text{CO} + (2n+1) \text{H}_2 = \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O} \quad \Delta H_R = -39.4 \text{ kcal/mol}$$

Other reactions also take place in the process, resulting in the formation of olefins and alcohols; besides, there are some side reactions. Much attention is focused on developing catalysts with appropriate selectivity and physical properties. Catalyst selectivity, syngas composition and process conditions (principally temperature) govern the product

Table 3: Syngas Production Technologies currently adopted

Techno-logy	Description /Features	Developers/ Licensors
Steam Reforming (SMR)	Steam & natural gas are reacted at 800-900°C and moderate pressure (20-30 bar) in presence of nickel catalyst $\text{CH}_4 + \text{H}_2\text{O} = 3\text{H}_2 + \text{CO}$ $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$	-Haldor Topsoe AS -Foster Wheeler Corp -Lurgi AG -International BV -Kinetics Technology -Uhde GmbH
Partial Oxidation (POX)	Can also be used for the production of syngas from coal or heavy oil products. Natural gas is burned at higher temperature (1200-1500°C) and pressure (140+ bar). Catalyst is not used. Gives near-ideal H ₂ /CO ratio. $2\text{CH}_4 + \text{O}_2 = 2\text{CO} + 4\text{H}_2$	-Texaco Inc. -Royal Dutch/Shell.
Auto-thermal reforming (ATR)	A hybrid process, concurrently reacts natural gas with steam and oxygen in the optional presence of CO ₂ . Partial oxidation occurs first, followed by steam reforming in the catalyst bed, all in a single reactor. $2\text{CH}_4 + \text{H}_2\text{O} + 1/2 \text{O}_2 = 5 \text{H}_2 + 2 \text{CO}$	-Lurgi -Haldor Topsoe

The other utilities required are 1) Oxygen Plant 2) Power Station and 3) Water treatment Plant.

Table 4: Brief History of Commercial Fischer Tropsch Synthesis

1902:	Methanation reaction with Syngas over Ni catalyst (Sabatier & Senderens).
1923:	Franz Fischer & Hans Tropsch reported hydrocarbon synthesis at higher pressure using Co, Fe Ru catalysts.
1936	4 FT Plants commissioned in Germany (total cap. 0.2 MMTA)
1944	Capacity of 9 plants (5 plants added) was increased to 0.7 MMTA. Although Fe catalyst development continued, Co was not replaced until after World War II.
1950	Hydrocol plant operated for sometime based on Fixed Fluidized Bed reactor with Fe-K catalyst, Cap. 5000 bpd at Brownsville, Texas.
1950-53	In Germany, Koelbel set up 1.5 m dia. slurry phase reactor at Rheinpreussen and operated successfully
1950s:	US Bureau of Mines operated a plant in Louisiana, Missouri with Fe catalyst (FB Reactor).
Mid 1950s	German plants were shut down after brief operation using petroleum residue. Interest in FTS declined worldwide, when oil deposits were discovered in abundance in the Middle East.
1955	However, in South Africa the first plant Sasol I was commissioned, based on Fe catalyst in ARGE tubular fixed bed (TFB) and circulating fluidized bed-Synthol (CFB) reactors. This was followed by Saol II (1980) and Sasol III (1982) based on Synthol-CFB. Later CFB has been replaced with Fixed Fluidized Bed (SAS Reactor).
1970-80	Renewed interest in FTS due to increased oil prices and fear of oil shortage
1990s	Further revival of FTS or GTL due to discoveries of huge stranded natural gas reserves and requirement for clean fuels.
1992	First natural gas based plant (Mossgas) set up in S.Africa, based on Sasol's Synthol reactor.
1993	Shell Middle Distillate Synthesis (SMDS) plant (12,500 bpd) was set up in Malaysia (natural gas based) using TFB reactor and Co catalyst
1993	Sasol Slurry Phase reactor (2,500 bpd) with Fe catalyst commissioned

distribution and the limit of the paraffinic chain length. The mechanisms proposed to explain the chain length with the help of ASF distribution and other data were discussed in detail by Davis [10]. The exact mechanism is complex and is still a subject of much debate. However, it can be described in a simplified manner in the following steps.

i) Initiation or C_1 compound formation ii) Hydrocarbon chain growth by successive insertion of the C_1 building blocks and iii) Chain termination by a) desorption of unsaturated surface species and b) hydrogenation and desorption of saturated species.

The types of catalysts employed in syngas conversion are shown in Table 5. FT process typically involves the recycle of unconverted gases to the reactor, CO_2 removal from the recycle loop and dehydration of the recycle gas. In some cases, the process separates H_2 for using in the product-upgrading unit. The recycle gas may be used as fuel gas. In addition to distillates, Fischer-Tropsch GTL plants can also produce a range of specialty products, such as normal paraffins (C_{10} to C_{13} range), a feedstock used in the detergent industry for the production of linear alkyl benzene sulphonate (LAS), one of the world's most widely used surfactants. Some plants however, may not produce paraffins suitable for LAS and suitability will depend on GTL catalyst selection and process conditions. Compared to the traditional route of extracting normal paraffins from kerosene, the GTL route is simpler and has significant capital and operating cost

advantages. Normal paraffins made by the Shell GTL plant at Bintulu have been successfully marketed in Asia since the start-up of the plant in 1993. In the future, GTL technology could largely replace traditional technology to meet the growth in demand for normal paraffins.

Table 5: Potential FT catalysts

Source of carbon	Catalyst	Property
Any	Ni	Methanation
Carbon rich (coal)	Fe	WGS with CO_2 production
Hydrogen rich (natural gas)	Co	Highly active and gives linear hydrocarbons
-do-	Ru	Very active but expensive

ii) Product work-up

The hydrocarbon products from FTS have various chain lengths. They are predominantly paraffins and alpha olefins if the product is aimed at middle distillates. Some oxygenates also may be present. The mixture can be shipped as syncrude, as a feedstock for refineries. Transportation through conventional tankers may not be feasible because of high pour point of syncrude, particularly for plants operated for maximum distillates. Alternatively, the syncrude may be separated and further processed at the production site, producing fuels, fuel blending components or specialty products (like waxes, lube bases) for local use or export. A mild hydro cracking / hydro isomerization breaks down long chain paraffins into short chain normal and iso paraffins with

improved cold properties and boiling range. By this route, high quality jet fuel and diesel fuel blending components can be prepared. Mild hydrotreating can be used to eliminate olefins and alcohols. This type of finishing is not necessarily an integral part of a GTL plant. The decision to include this module is based on economic and market options. The quality of GTL diesel can be seen from the Table below.

Table 6: GTL diesel quality

Sulphur	<5 ppm
Aromatics	<1
Cetane No	>70
CFPP	- 25 ⁰ C
Density	<0.78

4. Catalyst Development

The role of the catalyst is a) to hasten those CO hydrogenation reactions for the desired products b) avoid wide varieties of competing reactions c) to do so at high enough velocity (catalyst activity) to be commercially useful d) to do so at relatively low temperature and pressure and e) to continue to be active and selective in stable operation for long periods of time. Although the catalyst development in FTS has been extensive, a review of the data suggests that the choice is limited, and only two types are commercially practiced. These are: Fe based and Cobalt based catalysts. However, due to high capital cost, cheap iron based catalysts are preferred. Cobalt based catalysts gave higher selectivity for any specific product. With high product selectivity, the high cost of the

catalyst can be partially compensated. The development on the technology for the catalytic conversion of syngas to hydrocarbons has been periodically reviewed [11-13]. Initial development was based on cobalt catalyst, which was commercially employed during World War II for producing 10,000 bpd gasoline in Germany. At the same time, Fe catalyst was also developed but was not commercialized. Iron catalyst was commercially used first in the Hydrocol Process (Table 4) at medium pressure (100-150 psig) fixed fluidized bed reactor with syngas produced from natural gas.

Several other significant discoveries were also made during this period. It was found that Ru is particularly capable of making high yields of wax. Higher selectivity to desired product should be the primary objective in catalyst improvement. In some cases, in addition to CO hydrogenation, accelerating the water gas reaction is also desired. This makes possible more economical syngas with lower H₂/CO ratio [14]. The catalysts must be able to split the carbon-oxygen bond of carbon monoxide. On Cr, Mo, W etc. CO is dissociatively adsorbed whereas on Pd, Pt and Cu associative adsorption is favoured while metals like Rh favour both. Catalysts such as alkali-iron are good water gas shift (WGS) catalysts and these catalysts deplete the concentration of CO to form H₂ thereby the apparent H₂/CO usage becomes smaller. On the other hand cobalt, which is not a good WGS catalyst, does not affect the feed ratio releasing water as a by-product. One has to take into

account these properties while formulating a catalyst composition for a particular product. Proven catalyst chemistry has to be applied in the front-end syngas making and the back-end hydro-cracking steps [15]. A number of innovative ideas for improved catalyst preparation have been investigated [6,11]. Iron nitrides and metal borides were investigated, although the tests were not promising [16,17]. Bimetallic clusters, which have been sulphided, were demonstrated to be sulphur-tolerant CO hydrogenation catalysts [18]. The concept of epitaxial deposition has been used to prepare a novel non-magnetic Fe on Cu 111 and Cu 110. The Fe has remarkable electronic properties and interesting preliminary catalytic properties for syngas conversion [19]. Spinel $MgAl_2O_4$ has been tested as a support for Ce-Co [20].

Alloys have also been investigated. Alloys of Fe, Co and Ni on a support were shown to generally enhance catalytic activity and suppress methane formation [21]. Also, special porous and amorphous $Ni_{67}Zr_{33}$ alloys have been prepared and tested for catalytic properties [22]. It has been shown that the particle size is important for supported Ru. Small particles (1 nm), produced significant proportions of higher hydrocarbons, and large single crystals, (11 nm), gave mainly methane [23].

The concept of partial poisoning provides a powerful means of improving catalyst selectivity, interpreted in terms of ensemble control [24]. Decreased methane formation by sulphur poisoning of fused magnetite FT catalyst was

reported [25]. Fe catalysts treated with a sub-monolayer of chemisorbed sulphur were examined and found that the treated catalysts had a three-fold reduction in methane selectivity relative to the untreated fused iron, when tested with 2:1 H_2/CO syngas at 300°C and atmospheric pressure. The C_2 olefin selectivity approached 100%. McCarty and Wilson demonstrated the improvement in selectivity with Fe, treated with low levels of sulphur [26]. All these developments remained at experimental level and are yet to be tested at higher scale.

The MTG process (14,500 bpd) has first demonstrated the activity of a new class of catalysts, viz., Zeolites in the synfuels synthesis. Much research has been devoted to understanding the scientific aspects of MTG reaction chemistry [27,28] to develop alternatives or improved catalysts, to process simplification, to changing process products from conventional FT operation and to develop a hybrid slurry FT/MTG process. Catalysts have been investigated in which Al in the ZSM-5 crystal framework has been replaced by other ions. Exchange with Zn or Ga is said to increase the selectivity to aromatic compounds. These developments have resulted in improvements in classical FT technology and represent opportunities for additional improvements. US company Catalytica is developing special catalysts which will allow natural gas to be converted directly to methanol through direct methane oxidation process. The methanol can be further converted to gasoline by MTG route. Catalytica claims to

have achieved 70% yield per single pass in experimental units.

An area of considerable interest is the potential production of dimethyl ether (DME) from natural gas via syngas. DME is a clean fuel similar to LPG and is also suitable as diesel for general fuel purpose. It is environmentally acceptable fuel. Amoco and Haldor-Topsoe are developing DME technology.

A variety of catalysts have been tested in the slurry reactor. Fine particles composed of Fe-Co-Ni or pure Fe were found to be more active than precipitated catalysts. A new concept of combining slurry phase followed by upgrading over zeolites is regarded as a significant improvement over classical FT. The potential active catalyst constituents successful in commercial trials are shown in Table 5. It may be noted that most of the formulations are proprietary and very little information regarding preparation or characterization is available.

5. Bio-Catalysis:

Bio-catalysis may find an application for conversion of syngas to fuels [11]. The biological production of fuels from coal-derived gas has been reviewed by Gaddy [29]. Some exploratory research was carried out. A preliminary evaluation indicated that microorganisms could produce alcohols (up to C3), acetic/propionic acid and acetone from syngas [30]. A detailed study with *clostridium thermoautotrophicum* (derived from sludge) produced acetate and butyrates from $\text{CO} + \text{H}_2 + \text{CO}_2$ substrate. Preliminary results with

other strains showed slow CO conversion to alcohols (40 %) predominantly ethanol. If bio catalysis were successful, it would help utilizing natural gas from very small fields where setting up commercial units would be uneconomical. Biogas generated from landfills or anaerobic treatment of wastes can also be harnessed.

To sum up, the catalytic improvements that could contribute significantly to more economical manufacture of synthetic liquid fuels are:

- Catalysts, which have higher selectivity to molecular species, which are useful as high performance fuels. For hydrocarbons, this means conversion, preferably in one step, to high-octane gasoline components, namely isoparaffins and aromatics, or to olefins, which can be converted to liquid fuels. For oxygenates, this means octane enhancing ethanol or higher mixed alcohols.

- Catalysts, which eliminate or greatly reduce methane formation, particularly in the FT process or higher alcohol manufacture.

- Catalysts, which provide for operation of process modes, which are engineered to improve plant investment and operating costs, e.g., catalytic slurry system which can control heat release and decrease requirements for syngas recycle.

- Catalysts systems capable of providing for process integration for better energy efficiency.

- Catalysts with higher stability, resistant to deactivation by carbon deposition or by sulphur or halides.

For those under development the thought is that further advances

Table 7: Typical Catalyst Constituents

Company	Typical Catalyst Constituents			
	Primary	Reduction Promoter	Activity/Selectivity Promoter	Support
Conoco	Co	Re, other	N/A	alumina, other
Gulf (Shell)	Co	Ru	Oxide promoters	alumina
Exxon	Co	Re/Ru	Oxide promoters	titania or TiO ₂ /silica
IFP	Co			
Intevp	Co	-	Oxide and carbide promoters	silica
Rentech	Fe	N/A	N/A	-
Shell	Co	with or w/o a noble metal	ZrO ₂	silica, silica/alumina
Statoil	Co	Re	Oxide promoters	alumina
SASOL	(Fe) Co	Pt	-	alumina
Williams	Co	with or w/o a noble metal	with or w/o oxide promoters	doped alumina

Table 8: GTL Reactors in commercial practice

Reactor	Features	Advantages / Disadvantages
Tubular Fixed Bed (TFB)	TFB was used in Sasol I (ARGE reactor) and in SMDS (Shell) Plant. Catalyst pellets are packed in the tubes and the cooling medium flows around the outside of the tubes, similar to a shell & tube exchanger. Tube dia. limited to 25-50 mm because of heat transfer limitations within the tubes. -	Relatively simple design, but expensive construction due to large No. of tubes. Temp. gradient in the tubes may cause sintering. May give high pressure drop in the tubes. Catalyst replacement, a major undertaking. Fe catalysts, which are inherently unstable, have to be replaced periodically. Co catalysts can be regenerated in-situ.
Fluidized Bed i) Circulating Fluidized Bed (CFB)	Used in Sasol I & II (Synthol Reactor). Fused iron catalyst is circulated with syngas through a complex reactor / hopper / standpipe system and heat is removed as steam through coils suspended in the reactor section. The reactor needs a complex support system to cope with the circulating catalyst loads and temperature differences.	Better heat removal and temperature control. Less pressure drop problems. On-line catalyst removal/addition. Physically complex and suspended in a complex structure. Circulation of large tonnage of catalyst results in considerable recycle gas compression with added costs. CFB operates normally at higher temperature and if the H ₂ / CO ratio decreases this would lead to carbon

ii) Fixed Fluidized Bed (FFB)	Used in Sasol II & III (SAS Reactor) Basically a vessel with a gas distributor at the bottom and heat exchange tubes suspended in the F.B Catalyst inventory and product selectivity (low M.W) is same as Synthol reactor.	deposition limiting the reaction rates and catalyst life due to decrease of catalyst surface available for reactor. Improved stability and less catalyst consumption. Less erosion than CFB reactor Product must be volatile at the reaction conditions since non-volatile hc. may decrease bed fluidization.
Slurry Phase Bubble Column Reactor (SBCR)	Most accepted future reactor for GTL. Syngas is bubbled up through a slurry made of paraffinic high boiling liquid with the catalyst suspended in 50-80 µm.	Simple design and construction Ease of addition & removal of catalyst Good heat transfer & temp. control Good selectivity control Low Pressure drop Ideal for high boiling products Potentially high capacity (10,000-20,000 bpd) Improved catalyst economy and low turn down ratio. Slurry - phase reactor is about 45% cheaper in construction than TFB.

Table: 9 Commercially operated FT plants

Company	Capacity, (b/d)	Product	Starting
* SASOL I	2,500	F/S	1955
* SASOL II	85,000	F/S	1980
* SASOL III	85,000	F/S	1982
NZ Synfuels	12,000	F	1985
Mossgas	12,500	F/S	1992
Shell	30,000	F/S	1993

* = coal based; F= Fuels; S= specialty chemicals

Table: 10 Planned Commercial Plants

Company	Location	capacity	product	Starting
Exxon/Mobil	Qatar	80,000	F/S	2005
Sasol/Qatar	Qatar	34,000	F	2005
Sasol/Chevron	Nigeria	34,000	F/S	2005
Syntroleum/Ivanhoe	Australia	11,500	S	2005
Shell/Qatar	Qatar	140,000	F/S	2008/10

could be very valuable in justifying their industrial installation. For the mid-and longer-term projects, it is expected that these have the potential for even greater improvements.

6. Research - current application

-Wax and Crack: Research should be carried out to find catalysts which synthesize a high wax hydrocarbon product having a narrower and hence improved molecular weight distribution. Already this route is followed by Shell.

-Slurry synthesis: Reasons for loss of catalyst stability in slurry operation, and improved catalysts and procedures for some stable operation.

-More selective catalysts should be sought for direct conversion to ethanol using syngas.

-Improved catalytic systems should be found to increase energy efficiency in use of methanol fuels.

7. Research for the future

- Biocatalysts for conversion of syngas to liquid fuels offer an essentially new research approach, which merits support.

-Technique of partial poisoning of metal catalysts with sulphur or other agents, and so restrict unwanted reactions and improve overall selectivity.

-The effect of metal particle size needs to be better understood and techniques for controlled particle size established, with the objective of determining if the selectivity observed can be put to practical use.

-The use of metal organic complexes, including metal clusters, has the potential for unusually high selectivity attained by control of

geometric and electronic factors through choice of metal and ligands. Investigations with transition metal complexes need to be carried out.

-Research is needed to find a catalyst, which controls chain grown synthesis beyond a certain stage, by finding catalytic chemistry, which avoids the polymerization type mechanism or limits it from proceeding beyond a certain stage.

-Modification of supported metals is a field of great potential with opportunities in the use of special supports, chemical modifiers, and utilizing multi-metal components.

-Dual function catalysts, which activate hydrogen and carbon monoxide on separate sites, offer a new means for control of catalytic performance.

-Melt catalysts are in an exploratory phase and proffer opportunities for synthesis of particular molecules of interest as fuels or fuel precursor. This is a new research direction.

-Epitaxial deposition offers a means of providing novel metals unusual chemical characteristics and therefore, catalytic properties.

-Inorganic structures such as layered smectites, new zeolites with different pore structure, and new ceramic solids, carbonitrides or ion implantation systems, are research topics for improved catalytic properties.

8. Developments in FT Reactors & Technology

(i) Technology

One of the major advances in FT technology is the methods developed for separation / purification of the products including the syngas generated through gasification or reforming.

These developments at Sasol enabled to separate and utilize the petroleum feedstock components of the product such as ethylene, propylene and also chemicals such as ethanol, acetic acid and acetone. The projected distribution of products by this development is expected at, -motor fuels - 15,000, ethylene - 195,000; chemicals - 85,000, tar products - 185,000; ammonia - 100,000 and sulphur - 90,000 TPA. Currently Sasol II & III are estimated to produce nearly 7 million tons / year of marketable fuels & chemicals.

Air products & chemicals who are already in the LNG market are investigating alternatives. Eltron Research Inc. developed a ceramic membrane reactor to separate oxygen from air. The oxygen passes through the membrane as reactive ions, which combine with natural gas in the partial oxidation. This technology eliminates the cryogenic plant for extraction of oxygen from air and reduces around 25% of the estimated cost of syngas generation. DoE sponsored the work to Air Products Inc. to work in collaboration with Babcock & Wilcox and ARCO.

The existing FT-GTL plants are land based. Sasol and Statoil are however trying to setup floating GTL plants. Gas that is flared has no value at present, which can be effectively utilized by the floating plants, which may become economically viable when some of the recent technological developments are adapted with more active catalysts replacing the conventional catalysts. Syntroleum is developing a horizontal fixed bed reactor for easy mounting on floating platforms or barges designed by them.

(ii) Reactor Design

In addition to the advances in product optimization and value addition, there has been a substantial improvement brought out by the companies involved in GTL in the reactor design. The major features and the types of reactor in commercial practice are shown in Table 8. There have been extensive reviews on the FT reactors [31,32]

A preliminary economic analysis of the SAS and CFB reactors indicated that the SAS will be a leading contender for future synthetic fuels.

A second advanced technology employs a slurry system. The slurry phase reactor is the outcome of the improvement in the process engineering for better heat control. Indeed, removal of the heat of reaction (about 25% of the calorific value of the Syngas) probably is the chief problem in practical application of the synthesis. A slurry FT reactor operates with finely divided catalyst suspended in an oil medium. Using a precipitated Fe catalyst, the slurry reactor has been demonstrated to yield higher single pass H_2+CO conversion with low (0.6) H_2/CO ratio. These developments led to the introduction of Sasol Slurry Bed Process (SSBP) reactor at Sasol in 1993. This resembles a SAS reactor except that the catalyst is suspended in a liquid. Although great potential exists to alter the product pattern by change of operating conditions of catalyst properties, the slurry reactor is mostly used for FT waxes. Slurry reactors are also going to be used commercially for distillates in the future commercial plants coming up in Qatar and Nigeria.

It is likely that any new commercial venture may adopt some variant of SSBP or SAS reactor depending upon the type of product. SAS reactors are to be erected for high yields of olefins, low boiling range gasoline and substantial quantity of oxygenates. Diesel fuel can be produced from the product by oligomerization of olefins. For paraffins, linear products and waxes the multi-tubular reactor used by Sasol and Shell may be replaced by slurry reactors.

9.GTL Joint Ventures

GTL plants may come up in Qatar and Nigeria in the next 5 years. Qatar General Petroleum Corporation (QP) and Shell signed an agreement for 140,000 bpd GTL facility to produce primarily naphtha and transport fuels with some normal paraffins and lube bases. The first phase (70,000 bpd) may become operational by 2008/09 and the second phase two years later. QP has also another venture with Sasol to produce 34,000 bpd transport fuel and naphtha and some LPG.

QP and Exxon Mobil are carrying out a feasibility study for AGC-21 technology for an 80,000 bpd fuels and lubricants. Ivanhoe Energy has completed a feasibility study for a 156,000 bpd in two phases (78,000 each) with QP. Ivanhoe is offering the Syntroleum process. QP has also approached Conoco for an 80,000 bpd project, with the idea of developing an olefin complex along side it.

Sasol-Chevron and Nigerian National Petroleum Corporation (NNPC) are likely to set up 34,000 bpd GTL plant at Escravos. Sasol's slurry phase process is likely to be adopted. For syngas

manufacture. Haldor Topsoe's ATR is likely to be licensed. The plant is scheduled for 2005.

The potential processes that are yet to be commercialized are described below.

Exxon process: The advanced Gas Conversion for the 21st century (AGC-21) of Exxon is a two-stage process where syngas is converted to a high molecular product, which is upgraded by mild hydro isomerization. A 200 bpd plant operated at Baton Rouge, Louisiana. Syngas is produced by simultaneous partial oxidation and steam reforming in a single fluidized-bed reactor. Economies of a scale are achieved by the use of a single, large reactor vessel.

Rentech Process: Rentech operated a plant of 235 bpd liquid hydrocarbons in 1992 utilizing the methane gas from the landfill at Pueblo (Colorado). Subsequently the plant was shut down the same year for want of sufficient methane from the landfill. This experience has encouraged DoE to have another look at the untapped natural gas resource in Alaska's North Slope. Rentech process involves steam reforming of methane to make synthesis gas that is bubbled through a slurry containing a synthesis reactor using proprietary iron catalyst powder to produce straight chain hydrocarbons.

Syntroleum Process: The Syntroleum process uses autothermal reforming for syngas generation and claims that a refractory lined carbon steel vessel, employing a nickel based catalyst serving as the reformer costs much less than a conventional steam reformer. Furthermore, the syngas

from autothermal reforming produces a near ideal H_2/CO ratio. Instead of oxygen, air is used in the partial oxidation. A high capacity fixed bed horizontal reactor is under development. The new reactor would be useful for barges, ships and platform-mounted installations. Syntroleum air-based design is inherently safer than oxygen-based design, which is an important consideration for off shore applications.

The commercial plants already in operation or ready for commissioning are shown in Table 9 and planned plants in Table 10.

10. National Scenario:

FTS was carried out in the past at CFRI (Dhanbad), IIT (Kharagpur), IIT (Chennai), IIT (Mumbai) and IICT (Hyderabad). At present a Task Force has been set up by CSIR with IIP (Dehradun), CFRI and NCL (Pune) for developing new generation fuels (DME and FT diesel) by GTL. The objective is to develop catalyst / process that would lead to indigenous technology development. CFRI worked on all the aspects of FTS, viz. middle distillates, olefins and alcohols at different scales, but the emphasis was on middle distillates [33,34] with high selectivity for diesel. The activity of Fe/Cu/MgO/ThO₂/K catalyst was initially studied in a single tube reactor (150 ml) followed by tests in a multi-tubular reactor (3.5 L). The results are compared (Table 11). Even though the multi-tubular reactor was operated at lower temperature and pressure, the syngas conversion was higher in terms of

conversion and middle distillate selectivity.

Subsequent investigations were based on precipitated iron catalysts in which thorium, which is, hazardous has been replaced with kieselguhr(KG). The Fe/Cu/Mn/KG catalyst was tested only in a single tube reactor, which showed good conversion and selectivity for middle distillates. In Table 12, the results of the study on development of catalysts for middle distillates and wax are shown. The results are satisfactory for middle distillates with 47.6 % and 64.4 % selectivity for diesel oil and middle distillates respectively.

Based on these results, conceptual flow sheets were drawn for 20,000 bpd GTL unit, with syngas generation by CO₂/CH₄ reforming [35].

11. CONCLUSION

We are slowly moving from a position of total dependence on oil refining to one which co-exists with gas refining, built around GTL facilities. Catalyst in FTS is the heart of the plant because it is only on the catalyst performance, the technology providers try to distinguish themselves in the global competition. The catalysts used in the new generation GTL are mostly cobalt based usually on alumina supports and often with precious metal promoters. Every company has their view of what the formulation should be and secretive about the same. For the catalyst scientists, the challenge is enormous and the opportunities are many for exploring new catalytic compositions /preparatory

techniques within the currently practiced systems as also in novel concepts.

Table 11: GTL – Middle Distillates

Reactor	Single Tube (150ml)	Multi-tube (10) 3500ml
Catalyst - (Fe/ Cu/ MgO/ ThO ₂ /K)		
Temp ^o C	210-222	180-200
Pressure, kg/cm ²	21.0	13.0
Time, h	177	25
GHSV, h ⁻¹	350	275
H ₂ /CO ratio	1.71	1.76
Syngas conv. %	70.0	79.3
<i>Product yield (g/Nm³ syngas consumed)</i>		
C ₁ -C ₄	19.5	3.4
C ₂ -C ₄	6.5	3.9
C ₅ +	120.5 (59.3)	135.0 (78.8)
Total	146.5	142.3

Figures in the parentheses denote 160-360^oC fraction

Synfuels technology is ready for a take off by the end of this decade on its own merits aided by other energy compulsions. Recent advances in reactor technology and catalyst development make GTL economics favourable at \$25/bbl and upwards subject to control of natural gas prices. The fuels are ultra pure with zero aromatics, sulphur and nitrogen compounds complying the Euro 4 specifications. A separate distribution infrastructure is not necessary since it can integrate with the existing refinery distribution network.

Future innovative developments such as ceramic membranes for in-situ O₂

generation, POX with air and CO₂/methane reforming would further improve the economics.

Today, syngas reactions are significant on the basis of stranded gas and heavy fuels and might gain priority when ultimately the reserves of oil, gas and solid organic mater would be consumed, and progressively hydrogen technology will govern the fuel energy scene.

This article does not endorse the superiority of any particular technology amongst those mentioned, rather highlights the special features of each technology.

Table 12: CFRI Iron based Catalysts for GTL

Yield of Products g/Nm ³ CO + H ₂ converted.			
Catalyst	Fe/Kieselguhr	Fe/Kieselguhr	Fe/Clay
Selectivity	Diesel Oil	Middle Distillate	Wax
C ₁ – C ₄	15.3	15.3	4.5
C ₂ – C ₄	4.0	4.0	1.7
C ₅ +	122.7	122.7	135.9
Total HC	142.0	142.0	142.1
Selectivity % C ₅ + hc	47.6	64.4	53.2
% CO + H ₂ conversion	71.7	71.7	87.5

Acknowledgement

I dedicate this article to my beloved teacher and guide Prof. L.M. Yeddanapalli who not only taught me catalysis, but also influenced me in many ways.

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