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Creating Future Fuels


May 13, 2006

CERTIFICATE

This is to certify that the thesis entitled “**Preparation of novel FT catalysts for conversion of Synthesis gas to Middle distillates**” submitted by *Nimmagadda Veeresh* in partial fulfillment of the requirements for the award of the degree of Master of Technology (Petrochemical Engineering), at College of Engineering, University of Petroleum and Energy Studies, Dehradun, is a record of the work carried out by him at Indian Institute of Petroleum, Dehradun under my guidance and supervision.

To the best of my knowledge, the contents of this thesis did not form a basis of the award of any previous degree or published material by any one else.

The work is comprehensive of sufficient standard and here by recommended for the award of the degree of M. Tech. in Petrochemical Engineering.


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CERTIFICATE

This is to certify that the thesis entitled “**Preparation of Novel FT Catalysts for Conversion of Synthesis Gas to Middle Distillates**” submitted by **Nimmagadda Veeresh** in partial fulfillment of the requirements for the award of the degree of **Master of Technology in Refining & Petrochemical Engineering**, at College of Engineering, University of Petroleum and Energy Studies, is a record of the work carried out by him at Indian Institute of Petroleum, Dehradun.

This work is certified as bonafide.


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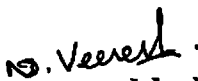
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Abstract

According to the Centre for Applied Energy and Research (CAER), Kentucky, the world petroleum reserve is anticipated to run out within next fifty years, therefore the twenty-first century is witnessing the establishment of a new global business based on natural gas processing. The Gas to Liquids (GTL) industry is entering a new phase of expansion based on the use of Fischer-Tropsch (FT) synthesis. While for many this might look like new technology but most of the fundamentals are not so new. GTL conversion is an umbrella term for a group of technologies that can create liquid hydrocarbon fuels from variety of feedstocks. GTL offers a new way to unlock abundant gas reserves, complimentary to others traditional technologies such as Liquefied Natural Gas (LNG) and pipelines. GTL has the potential to convert significant percentage of the world's estimated proved and potential gas reserves which today holds little or no economic value. On the other hand the prices of crude oil hovering around \$ 70 per bbl and it may continue to increase further. Under this scenario utilization of low value natural gas into valuable middle distillates is an attractive proposition.

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

Therefore, this work highlights some of these concepts, giving recognition to the FT technology pioneers.

1. Introduction

1.1 Introduction:

In the present state of world the global energy demand will be on increase with the passage of time this is because of the economic growth by virtue of industrialization. Also to meet stringent environmental regulations the fuel quality will also be a matter of great concern. Among the alternative source of energy, natural gas is emerging as a preferred fuel for this country. The natural gas resources are far from the consumers transporting gas from remote locations is not an easy task as compared to transporting oil due to its large volume. In the right situation, the conversion of natural gas to liquids (GTL) could create real economic value. The conversion of natural gas to liquid hydrocarbons by using Fischer-Tropsch process is viable and best option in present global energy scenario.

1.2 Gas to liquid (GTL):

Natural gas is an abundant resource in various part of the world. Methane is main constituent of natural gas, coal-bed gas and biogas. Methane is produced in huge quantities during oil production as associated gas and also produced in the petrochemical refining and petrochemical processes. It is also available in huge quantities as methane hydrate at sea beds. Since methane is available and produced mostly in remote places, its transportation is very costly or even impossible. Therefore, much of the natural gas associated with oil is flared causing not only a wastage of valuable energy under the present energy crisis but also global warming due to the release of very large quantity of CO₂ in the atmosphere. Even from the environmental consideration, the methane / natural gas produced in the remote places need to be converted into easily transportable and / or value added products. For this purpose, a new technology is being developed and applied to convert natural gas to liquids in gas to liquids technology (GTL). The projects are scalable, allowing design optimization and application to smaller gas deposits. The key influences on their

competitiveness are the cost of capital, operating costs of the plant, feedstock costs, scale and ability to achieve high utilization rates in production. As a generalization however, GTL is not competitive against conventional oil production unless the gas has a low opportunity value and is not readily transported.

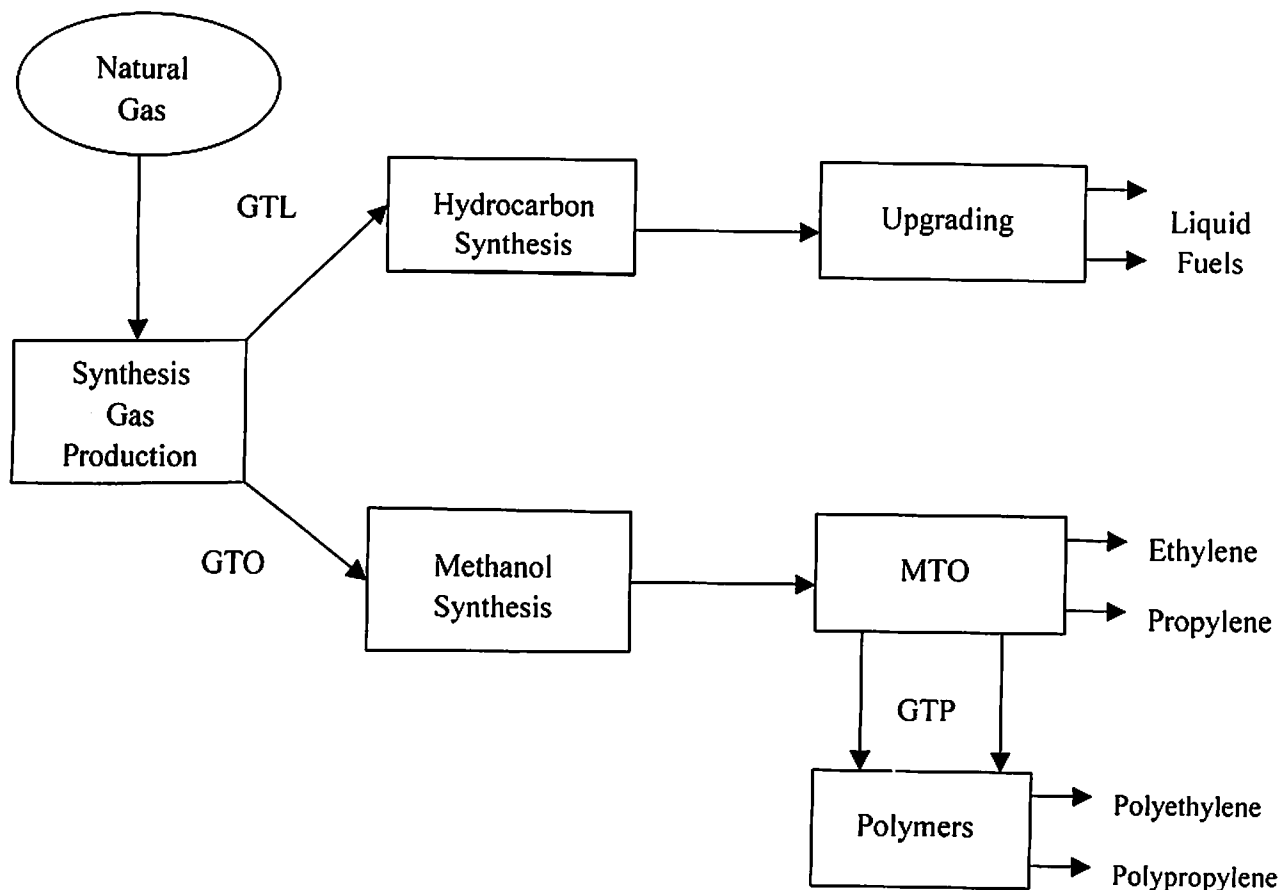


Figure 1, Conversion steps for natural gas to liquid & polyolefin

GTL not only adds value, but capable of producing products that could be sold or blended into refinery stock as superior products with less pollutants for which there is growing demand. Reflecting its origins as a gas, gas to liquids processes produces diesel fuel with an energy density comparable to conventional diesel, but with a higher cetane number permitting a superior performance engine design. Fine particulates are associated with respiratory problems, while certain complex aromatics have been found to be carcinogenic. Low sulfur content, leads to significant

reductions in particulate matter that is generated during combustion, and the low aromatic content reduces the toxicity of the particulate matter reflecting in a worldwide trend towards the reduction of sulfur and aromatics in fuel.

Today, natural gas based hydrogen has found new application as a fuel for the fledgling transport fuel cell industry. Historically, the drive to satisfy the ever-increasing global demand for energy in the form of oil (a readily transported liquid fuel) resulted in the accidental finding of massive quantities of dry and associated gas. To produce the oil associated with such gas, in the absence of a convenient local market or export pipeline, significant resources have been wasted through flaring. In response to environmental and economic pressures, gas re-injection has been practiced; Projects of this type are very capital intensive and require long term finance/supply contract arrangements and the backing of large world-class companies to make them happen. Consequently, alternative means of exploiting the large number of dry gas and remote wells are necessary and this has partly motivated development of gas-to-liquid processes. Certainly, Fischer-Tropsch (FT) liquids and methanol are feasible alternatives to LNG for remote gas transport. For smaller gas deposits, conversion to methanol can provide a relatively low cost route to commercializing natural gas, but this is currently subject to the short-term demands of the methanol market. For larger deposits, conversion to FT liquids provides access to the larger and more stable liquid fuels market.

1.3 GTL background and current direction:

The conversion of natural gas into hydrocarbon liquids has been a technological goal for many years. In 1923, Germans Franz Fischer and Hans Tropsch developed a process to convert coal or natural gas to hydrocarbon liquids. Their namesake process has been the primary focus of gas-to-liquids (GTL) research and development work to date and remains the basis for almost all commercially proven or viable GTL processes.

The historical Fischer-Tropsch (FT) process has three main steps. First, natural gas is combined with oxygen and steam in a catalytic reforming reaction to form a hydrogen and carbon monoxide mixture, or syngas. Second, the syngas is reacted in a catalytic FT reactor to form paraffinic hydrocarbons. Third, the paraffinic mix is hydrotreated and processed to convert, separate and purify the final synthetic petroleum products, including diesel fuel, kerosene, naphtha, and even waxes. Germany used the FT process to fuel its military during World War 2. South Africa installed the first world-scale GTL unit in 1955 during apartheid. Only a few other commercial-scale GTL plants are currently in operation in the world, each started-up in the 1990's. In fact, most, if not all, GTL plants to date would not have been built if it were not for governmental subsidies or political restrictions or influences. Enormous capital cost has always been the primary concern, necessitating huge plants to create the economy of scale needed for a venture to be economical. Of course, with a required capital investment of hundreds of millions of dollars for such a plant, controlling the technological risk becomes another major obstacle.

There are many incentives to continue to pursue an economical GTL process. Rising energy prices and the need for a new source of fuel to replace depleting oil reserves are often cited. Gas converted into liquids transportable to end markets would be a significant help. Over 75 percent of the world's known gas reserves are not currently accessible by pipeline, and the majority of those reserves exist in remote locations where gas pipelines can not be economically justified. Approximately 15.5 trillion cubic feet of stranded natural gas is flared, vented, or reinjected each year. Other incentives to pursue an economical GTL process continue to appear and grow. Governmental restrictions on flaring and emissions are increasing. In some cases, production of oil from certain fields may stop or at least decrease due to lack of options for handling the associated gas. Environmental concerns are gaining support. Laws for cleaner fuels are being enacted and enforced. More often of late, a government may desire to monetize its country's resources that may have been considered worthless or even wasted (flared).

Mega-scale GTL plants have been garnering much attention and study. However, while there are over 15,000 natural gas fields outside North America, less than 200 of them are large enough to support mega-scale GTL plants. Liquefied natural gas (LNG) and methanol projects have also attracted attention as means of liquefying gas for transport and use. LNG has extremely high capital costs and requires long term agreements to be profitable. On the other hand, LNG can be used on much smaller gas fields, even ones located offshore. Methanol-only plants have been around for decades, but their economics do not match those of GTL.

In recent years, companies have spent billions of dollars in research and development of gas-to-liquids (GTL) technology, almost all of which is based upon Fischer-Tropsch technology. The companies are planning to spend billions of dollars in the next few years to construct mega-scale GTL plants at the world's largest gas fields in Qatar. Several other projects have also been announced by various partnerships in locals such as Nigeria, Malaysia, and the Middle East. However, the costs and economics will likely keep most such GTL projects in the planning stages longer, and few of them will actually be constructed near term.

1.4 Existing Technology:

There are two broad technologies for gas to liquid (GTL) to produce synthetic petroleum products, (syncrude): direct conversion from gas, and an indirect conversion via synthesis gas (syngas). The direct conversion of methane, (typically 85 to 90 per cent of natural gas), eliminates the cost of producing synthesis gas but involves a high activation energy and is difficult to control. Several direct conversion processes have been developed but none have been commercialized being economically unattractive. Long experience in methanol plant design has shown that reliability is crucial for reforming as plants must be in constant operation at optimized processing conditions to provide an acceptable return on such investment. This, however, resulted in a plant with significantly increased complication and, as has been

revealed with recent startups, a not inconsiderable cost to reliability – especially in the early days of a plant’s life where good performance is crucial to plant economics. Further, the cost effectiveness of such an approach has not been fully demonstrated. Another approach has been the use of well-proven catalytic rich gas (CRG) pre reforming technology. This was formerly developed by British Gas and in 1997, a new high temperature, stable and more robust catalyst was introduced. CRG converts the higher carbon number compounds in natural gas to methane and partially reforms this to carbon.

1.5 The GTL Process:

The GTL process is based on two primary steps:

1. The conversion of natural gas into synthesis gas - In the first step in the process, natural gas is reacted with oxygen using proprietary catalytic partial oxidation to produce synthesis gas, consisting primarily of carbon monoxide and hydrogen.
2. The conversion of synthesis gas into synthetic crude - In a reaction based on Fischer-Tropsch chemistry, the synthesis gas flows into a reactor containing a proprietary catalyst, converting it into hydrocarbons

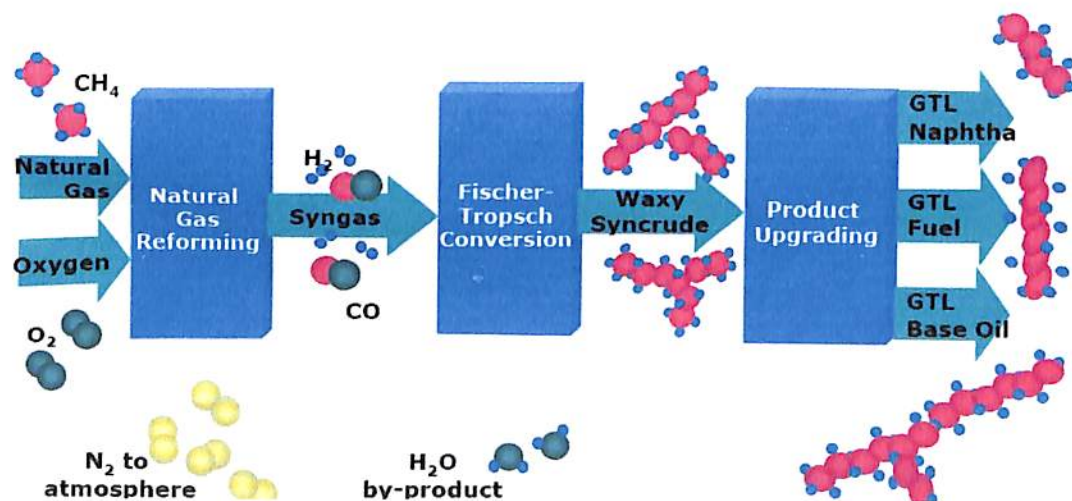


Figure 2, The overview of GTL process

1.6 Factors Favoring GTL Technology:

GTL technology offers a number of significant benefits, including:

Monetizing stranded natural gas reserves –

The world's proved and potential natural gas reserves are estimated to be more than 14,000 trillion cubic feet (tcf). Most of these reserves are considered as "stranded" because they are too far from the consumers and difficult to transport. GTL has the potential to convert a significant percentage of this gas into several hundred billion barrels of hydrocarbon liquids-enough to supply the world's energy needs for the next 25 years. GTL offers tremendous economic value to the countries and/or companies that control these reserves. GTL will permit the economic development of these remote natural gas discoveries that currently are deemed too far from market to be of economic value. Therefore, GTL is a very attractive option to produce hydrocarbon liquids with respect to monetize the abundant gas reserves.

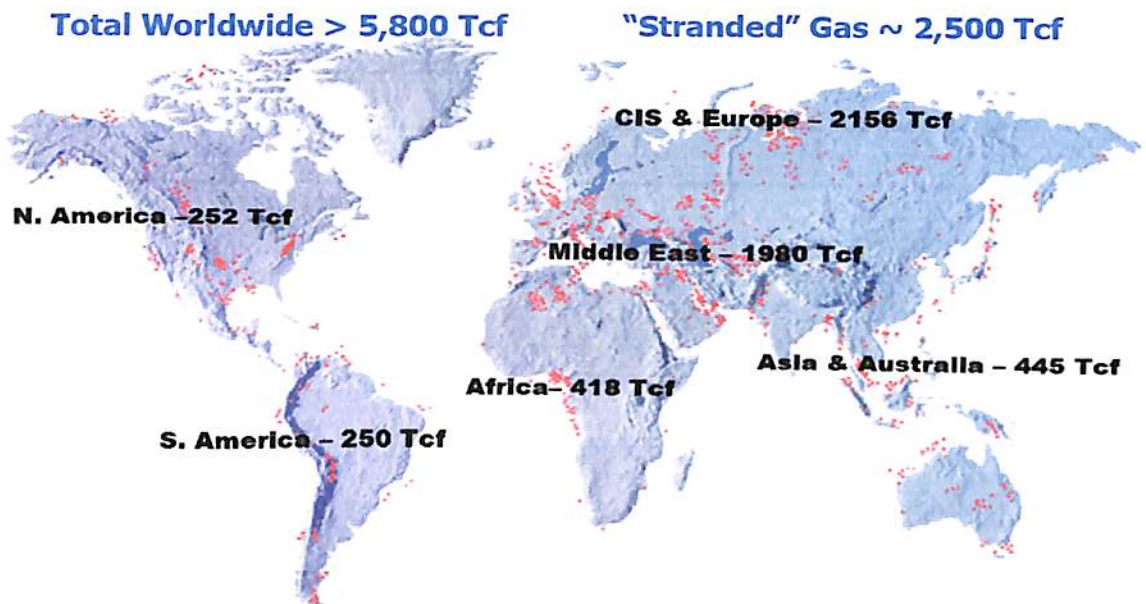


Figure 3, World wide overview of natural gas

Eliminating costly and/or environmentally disadvantageous practices –

GTL will help to eliminate the need for flaring natural gas, associated with oil production, which will permit earlier development and production of oil fields shut in

by the inability to dispose of the associated natural gas, and reducing the negative environmental impact of flaring.

Production of environmentally superior liquid fuels –

GTL will yield synthetic hydrocarbons of the highest quality that can either be used directly as fuels or blended with lower quality crude oil derived fuels to bring them up to compliance with increasingly stringent environmental and performance specifications. GTL fuels has virtually no sulphur, aromatics, or toxics. It can be blended with non-complying diesel fuel to make the fuel cleaner so it will comply with new diesel fuel standards. The characteristics of GTL diesel fuel over conventional petroleum diesel are summarized in table 1¹.

Sr.no.	Characteristics	Conventional	GTL
1.	Sulphur	>350	<5.0
2.	Cetane Number	45-50	>70.0
3.	Density	0.85	0.78
4.	Flash Point (°C)	71	81
5.	Cloud Point (°C)	-17	-12
6.	Aromatics	10	<1

Table 1, GTL diesel quality

Economics:

Due to the low density of neat GTL fuel, there may be a slight loss of fuel economy of upto 3.3 percent. However, diesel engines are 20-40% more efficient than gasoline engines. Therefore, synthetic diesel fuel appears to be the most economical fuel product from the GTL process, compared to producing gasoline. A preliminary testing of unmodified diesel engines, fueled with neat GTL diesel fuel, shows the following average emission reductions.

Sl.no.		
1.	Particulates	<40 %
2.	Nitrogen Oxides (NO _x)	<05 %
3.	Hydrocarbons	<60 %
4.	Carbon-monoxide	<75 %

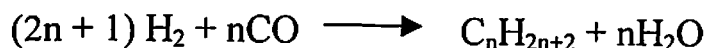
Table 2, Average emission analysis of GTL fuel

Therefore, GTL fuel offers a new opportunity to use non petroleum-based fuels in diesel engines without compromising fuel efficiency, increasing capital outlay, or impacting infrastructure cost.

2. Literature Review

2.1 Literature Review:

Fischer-Tropsch process: The **Fischer-Tropsch process** is a catalyzed chemical reaction in which carbon monoxide and hydrogen are converted into liquid hydrocarbons of various forms. Typical catalysts used are based on iron and cobalt. The principal purpose of this process is to produce a synthetic petroleum substitute for use as synthetic. The original Fischer-Tropsch process is described by the following chemical equation:



The mixture of carbon monoxide and hydrogen is called synthesis gas or syngas. The resulting hydrocarbon products are refined to produce the desired synthetic fuel. The carbon dioxide and carbon monoxide is generated by partial oxidation of coal and wood-based fuels. The utility of the process is primarily in its role in producing fluid hydrocarbons or hydrogen from a solid feedstock, such as coal or solid carbon-containing wastes of various types. Non-oxidative pyrolysis of the solid material produces syngas which can be used directly as a fuel without being taken through Fischer-Tropsch transformations. If liquid petroleum-like fuel, lubricant, or wax is required, the Fischer-Tropsch process can be applied. Finally, if hydrogen production is to be maximized, the water gas shift reaction can be performed, generating only carbon dioxide and hydrogen and leaving no hydrocarbons in the product stream. Fortunately shifts from liquid to gaseous fuels are relatively easy to make. Since the invention of the original process by the German researchers Franz Fischer and Hans Tropsch, working at the Kaiser Wilhelm Institute in the 1920s, many refinements and adjustments have been made, and the term "Fischer-Tropsch" now applies to a wide variety of similar processes (**Fischer-Tropsch synthesis** or **Fischer-Tropsch chemistry**). The process was invented in petroleum-poor

but coal-rich Germany in the 1920s, to produce liquid fuels. It was used by Germany and Japan during World War II to produce alternative fuels. Germany's yearly synthetic fuel production reached more than 124,000 barrels per day from 25 plants ~ 6.5 million tons in 1944. After the war, captured German scientists recruited in Operation Paperclip continued to work on synthetic fuels in the United States in a United States Bureau of Mines program initiated by the Synthetic Liquid Fuels Act.

Currently, two companies have commercialised their FT technology. Shell in Bintulu, Malaysia, uses natural gas as a feedstock, and produces primarily low-sulfur diesel fuels. Sasol in South Africa uses coal and natural gas as a feedstock, and produces a variety of synthetic petroleum products. The process is today used in South Africa to produce most of the country's diesel fuel from coal by the company Sasol. The process was used in South Africa to meet its energy needs during its isolation under Apartheid. This process has received renewed attention in the quest to produce low sulfur diesel fuel in order to minimize the environmental impact from the use of diesel engines. A small US-based company, Rentech, is currently focussing on converting nitrogen-fertiliser plants from using a natural gas feedstock to using coal or coke, and producing liquid hydrocarbons as a by-product. Also Choren in Germany and CWT (Changing World Technologies) have built FT plants or use similar processes.

The FT process is an established technology and already applied on a large scale, although its popularity is hampered by high capital costs, high operation and maintenance costs, and the relatively low price of crude oil. In particular, the use of natural gas as a feedstock only becomes practical when using "stranded gas", i.e. sources of natural gas far from major cities which are impractical to exploit with conventional gas pipelines and LNG technology; otherwise, the direct sale of natural gas to consumers would become much more profitable. There are several companies developing the process to enable practical exploitation of so-called stranded gas reserves. It is expected by geologists that supplies of natural gas will peak 5-15 years after oil does.

There are large coal reserves which may increasingly be used as a fuel source during oil depletion. Since there are large coal reserves in the world, this technology could be used as an interim transportation fuel if conventional oil were to become more

expensive. Combination of biomass gasification (BG) and Fischer-Tropsch (FT) synthesis is a very promising route to produce renewable or 'green' transportation fuels.

2.2 History of Fischer-Tropsch synthesis:

The history of Fischer-Tropsch synthesis started with the discovery by Sabatier and Senderens in 1902. They reported the production of methane from hydrogen and carbon monoxide on reduced nickel and cobalt catalysts. Later, BASF showed that a mixture of hydrocarbons and oxygenated compounds could be formed from hydrogen and carbon monoxide over cobalt catalysts using high pressures. Fischer and co-workers further developed the process, and in 1923 the synthesis of mainly oxygenated products and liquid hydrocarbons over alkalized iron catalysts was reported. The research effort was concentrated on Co, Fe and Ni as potential catalysts. Nickel was discarded due to its high tendency to produce methane and loss of nickel as nickel carbonyl and Fe because it deactivated rapidly at low pressures. Thus, the early German Fischer-Tropsch plants commissioned in 1936 used cobalt catalysts. The German commercial catalysts used during the war, consisted of 100 Co: 5 ThO₂: 8 MgO: 200 kieselguhr (in relative mass units). Fixed-bed reactors and low pressures were used and the catalyst had a lifetime of about six months. Germany's special situation at this time led to considerable interest in the development of the Fischer-Tropsch process. Germany had large coal reserves and the coal-based Fischer-Tropsch plants together with the Bergius direct coal liquefaction provided Germany with transportation fuels during the Second World War. Pichler discovered that the lifetime of iron catalysts could be substantially improved by increasing the pressure to about 15 bars. However, this did not lead to replacement of the cobalt catalysts in the commercial plants during the war. In 1944, the total capacity of the nine Fischer-Tropsch plants in Germany amounted to 700,000 tons per year. Many of these plants were destroyed towards the end of the war.

Research on the Fischer-Tropsch process was continued in Germany and the USA after the Second World War, but with the discovery of large oil fields in the Middle East, the production of fuels and chemicals from coal became economically unattractive. Also factors as the multi-step nature and the relative inefficiency of the process contributed to a decreasing interest in the synthesis. In 1955 political reasons led to the

construction of the Sasol 1 plant in South Africa. This was the first large Fischer-Tropsch plants based on iron catalysts, and Arge fixed bed and Synthol circulating fluid bed reactors were used. The main technical development from now on proceeded at Sasol in South Africa. Sasol-ii, which became operational in 1980, had a capacity of 50,000 barrels per day, and in 1982 Sasol-iii was put into operation. The Sasol-ii plant produces mainly gaseous olefins and light oils in Synthol recirculated fluidized bed reactors.

The Middle East oil embargo during the 1970's triggered new research activity on Fischer-Tropsch processes also outside South Africa. The research effort was mainly aimed at maximizing the production of fuels and light olefins directly from the Fischer-Tropsch synthesis. However, high selectivity towards hydrocarbons in the gasoline range (C5-C11) or to light olefins (C2-C4) are restricted by the Anderson-Schultz-Flory (ASF) polymerization kinetics. Attempts have been done to circumvent the ASF product distribution through the use of promoters, reacting supports and combination with other catalysts.

In the development of second generation Fischer-Tropsch processes in recent years, the focus has been turned from direct production of gasoline or light olefins to maximizing the yield of heavy liquids and wax. These heavy products can then be hydrocracked to middle distillates at relatively mild conditions. In this way the nature of ASF polymerization kinetics is properly utilized. The Shell SMDS process belongs to this type of processes. It was commissioned in 1993 in Bintulu, Malaysia and produces liquid fuels and specialties. This is only commercial Fischer-Tropsch plant in operation outside South Africa, but many of the large oil companies such as Exxon, Statoil and Gulf have developed F-T processes that are not yet have been commercialized. The SMDS process is based on natural gas as feedstock and uses tubular fixed-bed (Arge) reactors and cobalt catalysts. The catalyst is reported to have a lifetime of up to 5 years with several regenerations during that time. As opposed to the fixed-bed reactors of the SMDS process, other companies such as Statoil and Exxon have chosen slurry reactors due to superior heat removal properties and much higher capacity potential. In 1992, the Moss Gas plant in South Africa producing transportation fuels from natural gas came on stream. Sasol's Synthol reactor technology and iron catalysts are used. In 1993 Sasol commissioned a new slurry bed Fischer-Tropsch reactor.

Presently, the Fischer-Tropsch hydrocarbons cannot directly compete economically with crude oil fractions. The superior quality of the Fischer-Tropsch fuel products and emerging environmental regulations may though increase the economic feasibility. The assessment of gas conversion technologies has traditionally been focused on land-based location of plants. Recently a new approach to utilizing Fischer-Tropsch technology has emerged. The possibility of small Fischer-Tropsch plants placed on a platform or a ship has been proposed. Such a plant can be used to process gas on gas fields or associated gas on oil fields, to process gas that is normally flared and to remove the need to provide reinjection facilities on fields where the gas would be reinjected for disposal purposes. This seems promising in view of the increasing concern about environmental protection and optimal utilization of unrenewable resources. This can also make the development of small or remote fields more attractive. A brief history of Fischer-Tropsch Synthesis is summarized in table 3.

1902	Methanation reaction with syngas over Ni catalyst (Sabatier & Sendeerens)
1923	Franz Fischer & Hans Tropsch reported hydrocarbon synthesis at higher pressure using Co, Fe, Ru catalyst
1936	4 FT plants commissioned in Germany (total capacity: 0.2 MMTA)
1944	Capacity of plants (5 plants added) was increased to 0.7 MMTA. Although Fe catalyst development continued, Co was not replaced until world war II
1950	Hydrocol plant operated for sometime based on fixed fluidized bed reactor with Fe-K catalyst, capacity 5000 bpd at Brownsville, Texas
1950-53	In Germany, Koelbel Setup 1.5 diameter slurry phase reactor at Rheinpreussen & operated successfully
1950's	US Bureau of Mines operated plant in Louisiana, Missouri with Fe catalyst (FB reactor)
Mid 1950's	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 Sasol-II (1980) and Sasol-III (1982) based on synthol –CFB has been replaced with fixed fluidized bed (SAS reactor)
1970-80	Renewed interest in FTS due to increased oil prices & fear of oil shortage
1990's	Further revival of FTS or GTL due to discoveries of huge stranded natural gas reserves & requirements for cleaner fuels
1992	First natural gas based plant (Mossgas) setup in South Africa based on Sasol's synthol reactor

Table-3, A brief history of Fischer-Tropsch Synthesis

2.3 Syngas Overview:

Synthesis gas (commonly known as syngas), a mixture of hydrogen and carbon monoxide, can be produced from natural gas, coal, petroleum, biomass and even from organic wastes, so that sources of syngas are ubiquitous in nature. The availability and flexibility of the resource base are keys to the present and future uses of syngas and of its separate components, hydrogen and carbon monoxide. Syngas is a present and increasing source of environmentally clean fuels and chemicals and is also a potentially major fuel for the production of essentially pollution-free electricity, as sulfur and nitrogen in parts per million (ppm) can be removed from syngas relatively easily. The early utilization of syngas started in the earlier part of the 20th century by the production of methane from the hydrogenation of carbon monoxide in 1902, followed by the discovery of Fischer-Tropsch synthesis and subsequent manufacture of methanol and higher alcohols.

Syngas is now used in a host of different ways. The use of synthesis gas (syngas) offers the opportunity to furnish a broad range of environmentally clean fuels and chemicals. There has been steady growth in the traditional uses of syngas. Almost all hydrogen gas is manufactured from syngas and there has been a tremendous spurt in the demand for this basic chemical; indeed, the chief use of syngas is in the manufacture of hydrogen for a growing number of purposes. Methanol not only remains the second largest consumer of syngas but has shown remarkable growth as part of the methyl ethers used as octane enhancers in automotive fuels. The Fischer-Tropsch synthesis remains the third largest consumer of syngas, mostly for transportation fuels but also as a growing feedstock source for the manufacture of chemicals, including polymers. Future growth in Fischer-Tropsch synthesis may take place outside the continental United States. The hydroformylation of olefins (the oxo-reaction), a completely chemical use of syngas, is the fourth largest use of carbon monoxide and hydrogen mixtures; research and industrial application in this field continue to grow steadily. A direct application of syngas as fuel (and eventually also for chemicals) that promises to increase is its use for Integrated Gasification Combined Cycle (IGCC) units for the generation of electricity (and also chemicals) from coal, petroleum coke or heavy residuals. In the period 2005-2015, the amount of syngas employed in this manner may approach that used for all other specific

purposes. Syngas is the principal source of carbon monoxide, which is used in an expanding list of so-called carbonylation reactions.

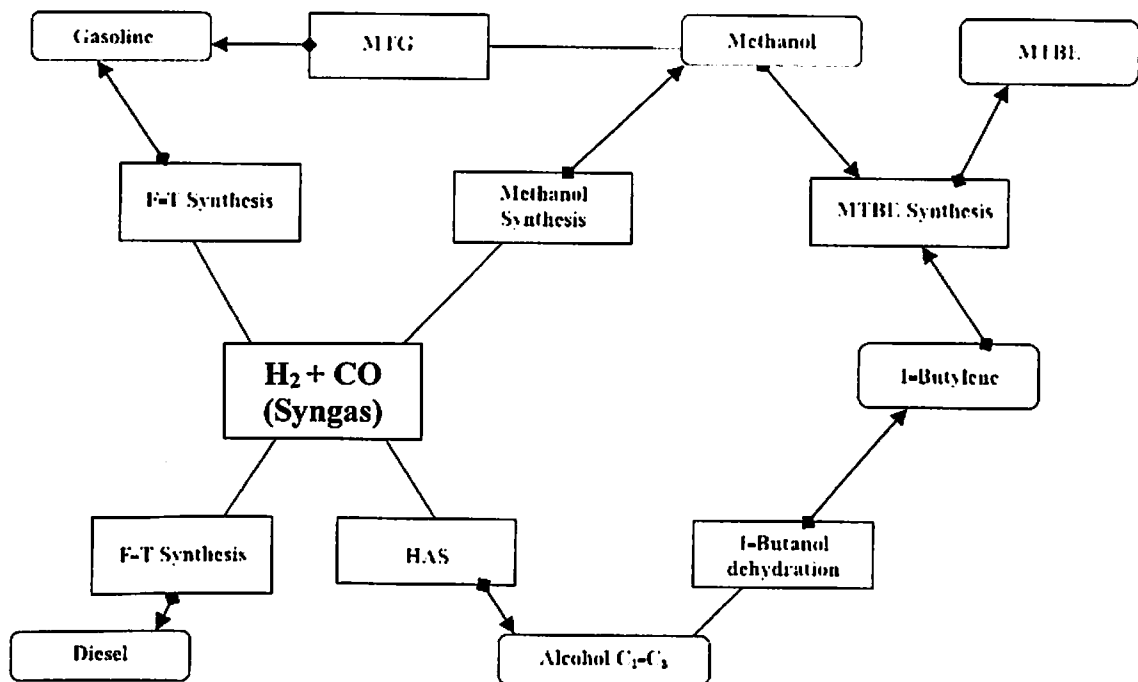


Figure 3, Application of Syngas as fuels, Additives, or Intermediate Products for further Synthesis

2.4 Engineering a GTL Technology:

A GTL plant for the production of F-T products can be divided into three sections:

1. Syngas generation.
2. Syngas conversion (F-T synthesis)
3. Hydrocarbon upgrading

1. Syngas generation:

Synthesis gas is a versatile feedstock for methanol and ammonia syntheses and oxo-processes and also for a F.T.synthesis for the production of liquid fuels, olefins and oxygenates. Hence, the conversion of methane to value added products via its conversion to syngas is highly promising one, provided the syngas from methane is produced economically. The principal technologies for producing syngas from natural gas are:

- Steam Methane Reforming (SMR)
- Partial Oxidation (POX)

- Autothermal Reforming (ATR)
- CO₂ reforming of methane

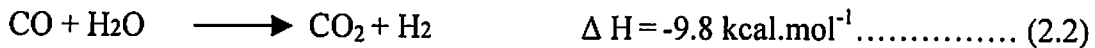
Steam Reforming of Methane to Syngas (SMR):

Steam reforming is established process for converting methane or natural gas and other hydrocarbons into syngas. It has been used for several decades since its first development in 1926 and over the years substantial improvement has been introduced. In this process, methane is reacted with steam over a Ni / α -Al₂O₃ catalyst in a primary reformer to produce syngas at an H₂: CO ratio of 3:1. The catalytic reactions are as follows:

Main reaction



Side reaction



Equation (2.1) is the reforming reaction (endothermic) and equation (2.2) is the water gas shift reaction (slightly exothermic). The heat of reaction (ΔH) was also indicated. The comparison of the heat of reaction values indicates that the net reaction is endothermic. For this reason, additional energy has to be provided by external heating (as shown in figure 4). The reaction is highly endothermic and is carried out in a fired tube furnace at 900 °C at pressure of 15-30 atm. The superficial contact time (based on feed gases at STP) is 0.5-1.5 Seconds, which corresponds to residence times of several seconds. Excess of steam is used to prevent carbon formation on the catalyst, and the feed H₂O/CH₄ mol. ratios are typically 2-6, depending on the syngas end use. Potassium compounds or other bases (CaO and MgO) are typically used to accelerate carbon removal reactions. The methane conversion at the exit of the primary reformer is typically 90-92 % and the product mixture contains CO₂ and H₂O along with CO and H₂.

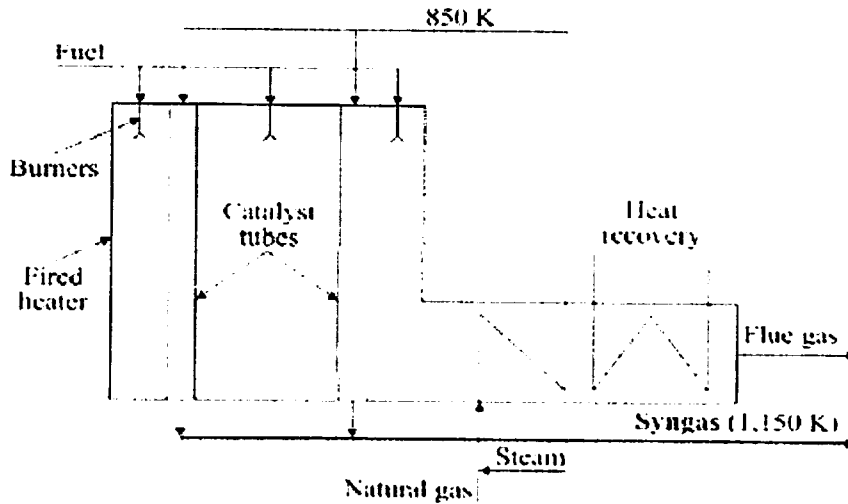


Figure 4, Typical SMR Process Scheme Diagram

The primary reformer is followed by a secondary auto-thermal reforming stage in which the unconverted methane (8-10 %) is reacted with oxygen at the top of a refractory lined vessel. The product mixture is then equilibrated over a packed bed of Ni catalyst below the oxidation zone. The exothermicity of the oxidation reactions is used to produce high-pressure steam to drive the turbines for the syngas compressor. In newer configurations, better energy integration allows heat evolved in the secondary reformer to be used for the primary reformer in which the fired tube furnace is replaced by a heat exchange reformer. Over the years, the steam reforming process has been optimized with the design of better burners for the furnaces, highly creep resistant materials for the reformer tubes, and new sulphur passivated catalysts, which inhibit carbon formation. Depending on the end use, the secondary reformer is usually followed by two Water Gas Shift (WGS) reactors to adjust the H₂/CO ratio of the reformer product gases, as sketched in fig 5.

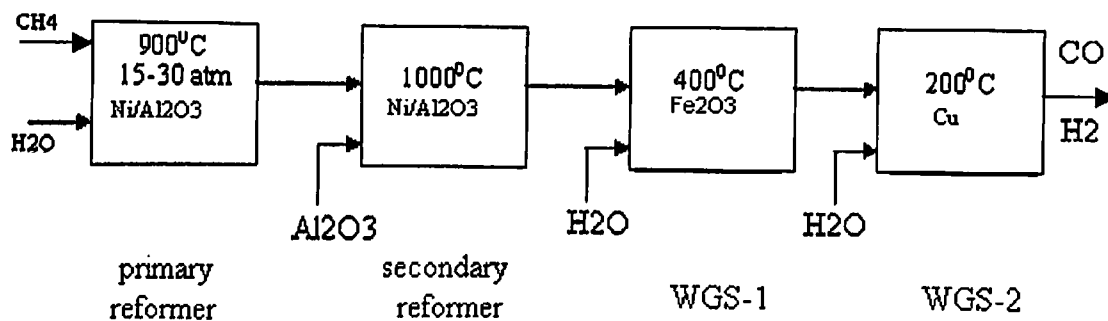


Figure 5, Block diagram for conventional steam reforming

A high temperature shift over iron-oxide (Fe_2O_3)/Chromia catalysts at 400°C is followed by a low temperature shift at 200°C on a copper based catalyst to attain favorable equilibrium in WGS. Both WGS stages have superficial contact times greater than one second. The syngas is then exported after subsequent purification stages.

Advantages and Disadvantages:

The Steam Methane Reforming (SMR) process has following advantages:

- It is most extensive industrial experience
- Oxygen not required
- Lowest process temperature requirement
- Best H_2/CO ratio for hydrogen production application

Today, steam reforming is a principal process for the production of H_2 and synthesis gas. More than 80% of world ammonia production is based on steam reforming.

Though steam reforming is a well – established process, it suffers from the following disadvantages.

- It is highly endothermic process and hence, energy requirements are very high.
- H_2/CO ratio obtained in the product stream is very high (>3) and therefore is unsuitable for methanol and Fisher – Tropsch synthesis
- The CO selectivity obtained is very poor because of the water gas reaction.
- The catalyst undergoes deactivation very fast due to coke deposition on the surface of the catalyst, which results in the poor heat transfer from wall of the reactor.

Partial Oxidation of Methane to Syngas (POX):

The conventional process for syngas ($\text{CO} + \text{H}_2$) production from methane, which is based on the steam reforming of methane (SRM), is highly endothermic and hence highly energy intensive process. Catalytic partial oxidation of methane to syngas offers the most viable alternative to the steam reforming. It is mildly exothermic reaction, which produces H_2 and CO with the desirable H_2/CO ratio of 2.0, suitable for various down stream processes such as Fischer–Tropsch and methanol synthesis processes. The reactions, which occur during the partial oxidation of methane to syngas, are given below.

Main reaction



Side reactions



Since the direct oxidation reaction is slightly exothermic, a reactor based on this reaction would be much more energy efficient than the energy intensive steam reforming process. Oxidation reactions are also much faster than reforming reactions, suggesting that a single stage process for syngas generation would be a viable alternative to steam reforming and also result in a smaller reactors and higher throughput.

A recent study showed that there are significant economic incentives for onsite methanol plant based on catalytic partial oxidation of natural gas. An estimated 10-15% reduction in the energy requirement and 25-30% lower capital investment is expected for catalytic partial oxidation compared to typical steam reforming processes.

However, the direct oxidation process has not yet been commercially, and it is difficult to study fundamentally because it involves pre-mixing of CH_4 / O_2 mixtures which can be flammable or even explosive. Homogeneous reactions in a highly reducing environment can lead to soot formation and carbon deposition on the catalyst. In addition, flames in the reaction zone can also lead to very high local temperature that can destroy catalyst. However, recent discovery of highly selective direct oxidation catalysts have renewed interest in direct oxidation process. These catalysts overcome the problem of carbon deposition without any steam input (total dry oxidation). The absence of homogeneous reactions also prevents the formation of unwanted oxidation products or flames, which can lead to soot formation. The typical POX reactor shown in Figure 6.

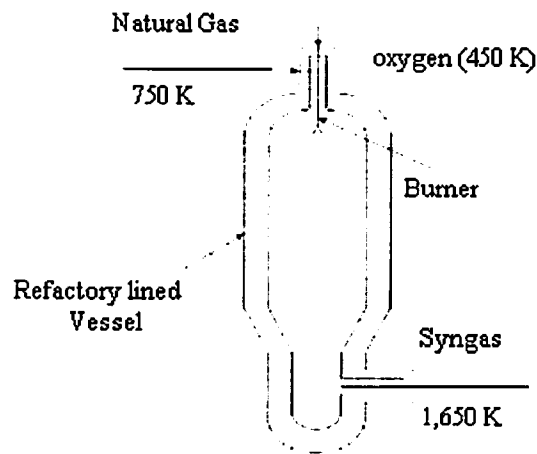


Figure 6, Typical POX Reactor

Advantages and Disadvantages of POX process:

Partial oxidation process has the following advantages:

- Feedstock desulphurization not required
- Absence of catalyst permit carbon formation and therefore operation without steam, significantly lowering syngas CO₂ content
- Low methane slip
- Low natural H₂/CO ratio is an advantage for application requiring ratio less than 2.0

Partial oxidation process has also the following disadvantages

- Low natural H₂/ CO ratio is a disadvantage applications requiring ratio greater than two
- Very high process operating temperature
- Usually requires oxygen
- High temperature heat recovery is soot formation / handling adds process complexity
- Syngas methane content is inherently low and not easily to meet downstream process requirement.

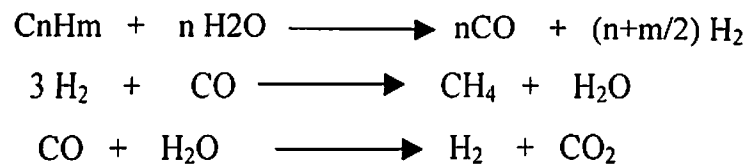
Autothermal Reforming to Syngas(ATR):

Neither SMR nor partial oxidation is ideally suited to GTL applications. This is due to the fact that F-T synthesis calls for an H₂/CO ratio of about 2, a value higher than that achievable with partial oxidation and lower than that obtainable with SMR.

A solution to this dilemma is to use both technologies i.e. partial oxidation and SMR may be used in parallel to produce syngas streams that have differing compositions but, when mixed, form a total F-T feedstock of the desired composition. An alternative to this approach is autothermal reforming (ATR).

Autothermal Reforming process is a combination of homogeneous partial oxidation and steam reforming and was first developed in the late 1970s with the aim of carrying out reforming in a single reactor. A Typical process concept for the production of synthesis gas based on ATR is shown in figure 2.4. The key steps in the process scheme are desulphurisation, adiabatic pre-reforming, ATR and heat recovery.

In the desulphurisation section the sulphur present in the natural gas feedstock is removed to avoid poisoning of the downstream pre-reforming catalyst. Steam is added to the desulphurised natural gas, and after further heating, the resultant mixture is passed to the adiabatic pre-reformer. In the pre-reformer, all higher hydrocarbons (C₂+) are converted into a mixture of methane, hydrogen and carbon oxides according to the following reactions:



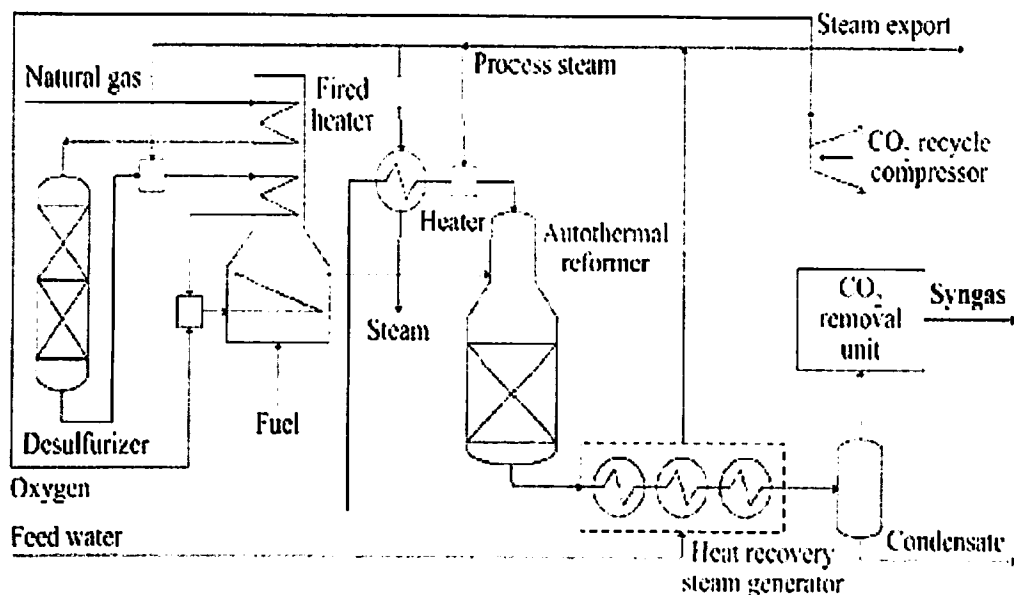


Figure 7, Typical ATR process Scheme

The pre-reformer is an adiabatic, fixed-bed reactor with highly active nickel catalysts. The use of a pre-reformer in the process (Figure 7) upstream the ATR reactor reduces the oxygen consumption per unit of the product produced.

The key part of the synthesis gas unit in a GTL plant is the autothermal reformer. The ATR reactor has a compact design consisting of a burner, combustion chamber and a catalyst bed placed in a refractory-lined pressure vessel. The pre-reformed natural gas reacts with oxygen and steam in a sub-stoichiometric flame. The reactions, which occur during the autothermal reforming of methane to syngas in autothermal reformer, are given below:

Main reaction



Side reaction



In the catalyst bed, the gas is equilibrated with respect to the methane steam reforming and shift reactions. The composition of the product gas is determined by the thermodynamic equilibrium of these reactions at the exit temperature is given by the adiabatic heat balance based on the composition and flow of the feed, steam and oxygen added to the reactor. The produced synthesis gas is completely free of soot and oxygen.

This process requires an inexpensive source of oxygen. An undesired side reaction in the combustion zone is the formation of carbon or soot which leads to solid carbon deposition on the catalysts and subsequent coking and deactivation. Gas phase carbon forms soot on downstream surfaces thereby causing equipment damage and heat transfer problems. Excessive local temperatures also lead to burner damage. This also calls for a catalyst of high thermal stability and mechanical strength. In newer configurations catalytic burners have been tested.

In another process the combustion and reforming may be carried out in separate reactors. A CH₄/O₂/H₂O mixture is ignited in a burner to produce partial oxidation products which are then catalytically steam reformed in a second reactor to give equilibrated products.

Advantages and Disadvantages of Autothermal Reforming process:

Autothermal Reforming has the following advantages:

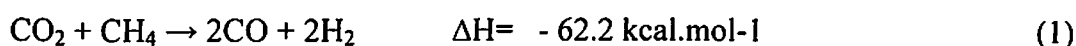
- Natural H₂/CO ratio often is favorable
- Lower process temperature requirement than POX
- Low methane slip
- syngas methane content can be tailored by adjusting by reformer outlet temperature

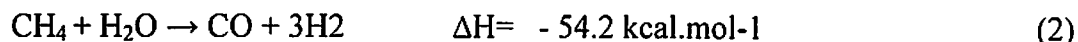
This process also has following disadvantages:

- Limited commercial experience
- Usually requires oxygen

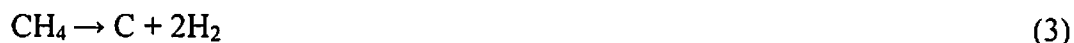
CO₂ Reforming of Methane to Syngas:

Release of large quantities of CO₂ in the atmosphere has created a large green house effect causing a global warming. Hence worldwide efforts are being made for conversion of CO₂ to useful products. CO₂ reforming of methane to syngas has been considered as an important process for the utilization of CO₂. In the last few years the research activities on the CO₂ reforming of methane have gained a lot of momentum. The CO₂ reforming of methane involves a highly endothermic reaction (Equation-1). The thermodynamics and equilibrium characteristics of CO₂ reforming of methane are similar to the widely employed steam reforming of methane (Equation – 2) except that the former reaction produces synthesis gas with lower H₂/CO ratio,





The CO₂ reforming of methane has been used in conjunction with steam reforming process and the coupled reactions are likely to be conducted under conditions where carbon formations via reactions,



is thermodynamically feasible. Other reactions, which could also have an important influence on the overall product spectrum, are:



Thus, the CH₄/CO₂ reforming reaction (Eq. – 1) can be seen as consisting of reactions (3) and the reverse reaction (4). The carbon formed in reaction (3) should be rapidly consumed by the reverse of reaction (4) and, to a lesser extent, by the steam carbon gasification reaction (i.e. reaction 6). Reaction (6) can play a role in CO₂/CH₄ reforming because steam is almost always formed via the reverse water gas shift (RWGS) reaction (Eq. – 5). If the reaction (3) is faster than the carbon removal rate(s), there will be a net build-up of carbon to pose serious problems and reactor blockages. Apart from reaction (3), reaction (4) and the reverse of reaction (6), both, which are favored at low temperatures, are also potential sources of carbon. It may also be noted that reaction (5), which consumes product hydrogen, represents a disadvantage unless both reactions (5) and (6) are made to take place efficiently in tandem so that the overall stoichiometry of the CO₂/CH₄ reforming reaction is maintained. But a very serious problem associated with the CO₂ reforming of methane is a rapid carbon deposition on the catalyst. In general, the rate of carbon deposition is very high for the Ni-based catalysts and relatively slower for the Cobalt and noble metal based catalysts. It is therefore of great practical importance to develop a non-noble metal-based catalyst, which allows only a little or no carbon formation in the CO₂ reforming reaction.

Capital and Operating Costs:

The most capital-intensive part of the GTL plant is the preparation of synthesis gas, which may account for 50-75 % of the capital cost. Ongoing Research & Development efforts to develop lower-cost syngas generation technologies include the following:

- The development and application of “compact reformers” and of “heat exchange reformers”, in which a portion of the heat of reaction is provided by heat recovery from the reformed gas, rather than by burning fuel. Potential advantages over conventional tubular reactors include improved efficiency, smaller plant footprint, lower capital cost, and reduced emissions. Companies active in this area have included Air Products, KTI, ICI, BP/Kvaerner, Kellogg, Haldor Topsoe, Krupp Uhde, and Lurgi.
- Development and application of air-blown autothermal reformer technology, thereby eliminating the need for an oxygen plant. (Air-blown secondary reforming is well established, being commonly utilized for syngas production for ammonia plants). The chief proponent of the air-blown approach is Syntroleum.
- New reformer reactor approaches, most notably that employed by Exxon’s AGC-21 process for converting natural gas to liquids. The first step in this process is syngas generation via oxygen-blown catalytic autothermal reforming in a fluidized bed reactor. The process has been demonstrated at large pilot scale—about 200 b/day.
- “Ceramic membrane reactors”, based on the use of ionic or oxygen transport membranes, which would couple air separation and partial oxidation in one unit operation, thereby eliminating the need for a conventional oxygen plant.

Future improvements:

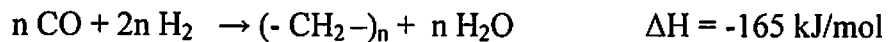
In order to have the greatest impact on the economics of the process, future breakthrough should be in areas that decreases the capital cost of syngas generation and/or improve the thermal efficiency of the plant as whole. An obvious way of improving the thermal efficiency of the plant is to combine it with a power generation plant. The use of feed/product heat exchanger to recover energy from the reformer outlet can increase the thermal efficiency of the process.

Other potential improvements:

- Increasing the catalyst life by making it more resistant to irreversible sulphur poisoning.
- Changing the selectivity dependency on the H₂/CO ratio to such an extent that high diesel yields can be obtained at H₂/CO ratios similar to the usage ratio. The advantage of such a catalyst would be that, due to the increase in reaction rate at higher H₂/CO ratios, much less catalyst would be needed for the same conversion.

2. Synthesis gas conversion (F-T process):

In the Fischer-Tropsch (F-T) process, one mole of CO reacts with two moles of H₂ to afford a hydrocarbon chain extension (-CH₂-). The oxygen from the CO is released as product water:



The reaction affords mainly aliphatic straight-chain hydrocarbons (C_xH_y). Besides these straight-chain hydrocarbons also branched hydrocarbons, unsaturated hydrocarbons (olefins), and primary alcohols are formed in minor quantities. The kind of liquid obtained is determined by the process parameters (temperature, pressure), the kind of reactor, and the catalyst used. Typical operation conditions for the FT synthesis are a temperature range of 200-350°C and pressures of 15-40 bar, depending on the process

3. Hydrocarbon upgrading:

The subsequent FT chain-growth process is comparable with a polymerization process resulting in a distribution of chain-lengths of the products. In general the product range includes the light hydrocarbons methane (CH₄) and ethane (C₂), LPG (C₃-C₄), gasoline (C₅-C₁₂), diesel (C₁₃-C₂₂), and light and waxes (C₂₃-C₃₂ and >C₃₃, respectively). The distribution of the products depends on the catalyst and the process operation conditions (temperature, pressure, and residence time). The (theoretical) chain length distribution can be described by means of the Anderson-Schulz-Flory (ASF) equation, which is represented as:

$$\log \frac{W_n}{n} = n \cdot \log \alpha + \log \frac{(1 - \alpha)^2}{\alpha}$$

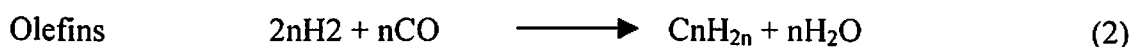
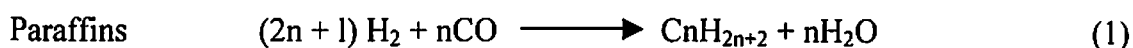
where W_n is the mass fraction of a product consisting of n carbon atoms and the chain growth probability factor (α). A plot of the relative mass fractions of products formed as function of the ASF chain growth factor α is given in Figure below. As can be seen from this plot, higher values of α give higher molecular weight products.

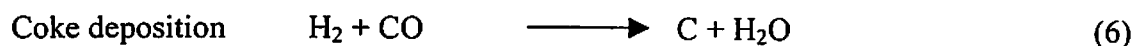
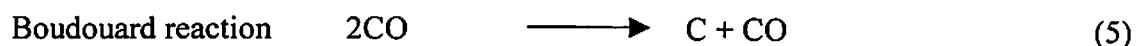
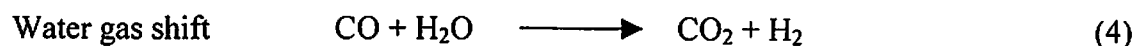
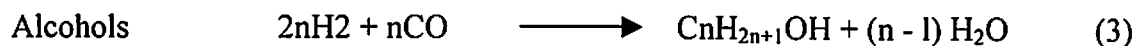
With respect to the production of green diesel, process conditions can be selected to produce maximum amounts of products in the diesel-range. However, an even higher yield of diesel can be achieved when the FT synthesis is optimized towards production of wax (i.e. high α). Subsequently, the wax can be selectively cracked to yield predominantly diesel.

2.5 Chemistry of Fischer-Tropsch Synthesis:

The scientific and industrial importance of the chemistry of carbon monoxide has increased rapidly since about 1925. More recent advantages include the F-T process for synthesis of chiefly liquid aliphatic hydrocarbons, alcohols and minor amounts of aldehyde, acids, and ketones by hydrogenation of carbon monoxide.

The Fischer-Tropsch synthesis (FTS) is catalyzed heterogeneously on metal catalysts which are extremely sensitive to poisoning by sulfur, on which CO is strongly chemisorbed, and which form metal carbonyls at high pressures but at temperatures too low for the FTS. These metal catalysts must be able to dissociate CO (split the carbon-oxygen bond). On certain catalysts under certain conditions, dissociative adsorption of CO is the main route; on Pd, Pt and Cu, associative adsorption is most likely, and on some catalysts (rhodium is probably the best example) CO is adsorbed in both ways. The FT reaction yields a wide spectrum of hydrocarbons and oxygenated compounds. The major constituents of the hydrocarbons are paraffins and olefins, and primary alcohols are usually the chief oxygenated products. Straight-chain paraffins, along with some 2-methyl-branched paraffins, predominate among the saturated hydrocarbons; the major olefin components are terminal olefins. A large number of reactions occur during the FT reaction; the major ones are given below:





For catalysts that are good water gas shift (WGS) catalysts, such as alkalized iron, the water formed in equations (1), (2) and (3) reacts with CO to form H₂ so that the apparent H₂/CO usage becomes smaller. For a catalyst such as cobalt, which is not a good WGS catalyst, water is the main reaction byproduct.

The carbon number distribution of organic compounds is extremely wide and much effort has been expended in finding ways to improve the selectivity of the Fischer-Tropsch synthesis for desirable products: gasoline, diesel fuel, C₂-C₄ olefins and alcohols. Glycols are not produced in the FT reaction. Aromatic products become significant only at high reaction temperatures.

When several reactions involving the same reactants are thermodynamically possible, the yields of various products depend upon their relative reaction rates and on the rates of ensuing reactions. At the temperatures usually employed in the FTS, the actual selectivity found differs very much from that expected from thermodynamic calculations.

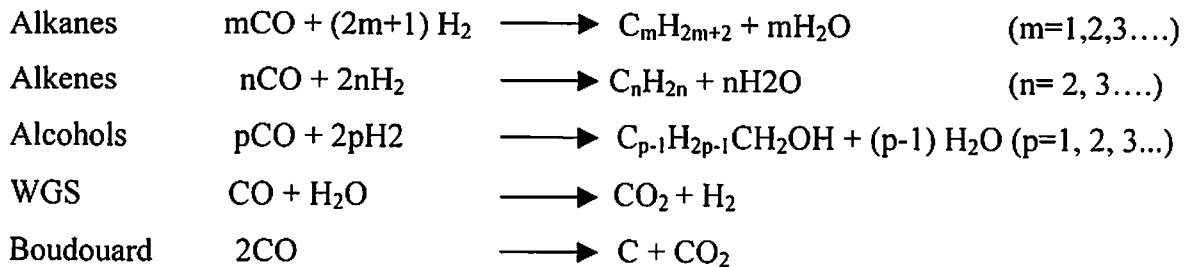
The FTS is usually carried out at pressures from 0.1 to 4 MPa with approximately 425°C as the upper temperature limit. As FT reactions involve a decrease in the number of moles, conversions at a given temperature increase rapidly with increase in pressure. The pressure and temperature limits of the reaction are determined by changes in selectivity and in the rate of catalyst deterioration. Excessive catalyst temperature can lead to undesirable products, carbon deposition, catalyst deactivation or catalyst disintegration. The heats of reaction per carbon atom of the products vary only slightly with temperature, increasing with increasing carbon number for paraffin and decreasing with increase in the carbon number of the olefins formed. The heat of reaction, for the formation of alcohols, is also somewhat independent of temperature. As kinetic rather than equilibrium considerations are controlling in the F-T synthesis, only limited amounts of useful information are furnished by thermodynamics. The products obtained depend

largely on the selectivity of the catalyst. But certain conclusions derived from thermodynamics help us understand these syngas reactions:

- Methane is the preferred product at all FTS conditions.
- The relative stability of various compounds varies with the temperature of the FTS (25-425°C). The order is paraffins > olefins > alcohols.
- Although methane is the preferred paraffin, for olefins the favored products are compounds with the highest carbon number. Above nearly 425°C at 0.1 MPa this reverses and light olefins are favored.
- The equilibrium conversion of syngas increases with pressure. Owing to the effect of pressure (and temperature) on the activity and selectivity of the catalyst, the upper limits of usefulness for iron catalysts are 3-4 MPa and approximately 400°C.
- The water gas shift reaction is favored under FIS conditions; iron is a particularly good catalyst for this reaction.
- The reaction of ethylene and of ethanol with syngas is thermodynamically possible at FT temperatures. Incorporation of higher olefins or higher alcohols is less favored. Thermodynamically, methanol incorporation is favored over that of ethanol. The term “incorporation” denotes the building-in of an organic molecule together with CO and H₂ in the FTS.
- The amounts of oxygenated compounds (alcohols, aldehydes, acids, ketones) are also formed in much higher concentrations than predicted from thermodynamic calculations.
- Olefin hydrogenation and alcohol dehydration are thermodynamically favored under FT conditions. Olefins and paraffins may be formed by dehydration of alcohols and hydrogenation of the olefins, respectively, and by primary reactions.
- The Boudouard reaction, in which CO can form free carbon and CO₂, is favored under all synthesis conditions.

2.6 The Fischer-Tropsch Reaction Mechanism:

The stoichiometry describing the conversion of synthesis gas to typical methanation and Fischer-Tropsch products can be represented by the following equations:



The Fischer-Tropsch synthesis on Fe, Co, and Ru, results in the range of products from methane to long chain hydrocarbon waxes. The secondary water-gas-shift (WGS) reaction produces hydrogen, and is useful when the H_2/CO feed ratio differs from that required by the stoichiometry of the desired products. The Boudouard reaction results in carbon deposition and is favored by high temperatures and low H_2/CO ratios. It is generally accepted that the formation of hydrocarbons is governed by a stepwise growth mechanism, involving one carbon entity at a time being added to the growing chain.

The probability (α) for any chain C_n to propagate rather than to terminate is defined by the ratio of the rates:

$$\alpha = r_p / (r_p + r_t)$$

where r_p = chain propagation rate

r_t = chain termination rate

It is assumed that α is independent of the chain length, and that chain growth occurs only in one direction, the distribution of the hydrocarbon products can be described by the chain polymerization kinetics model of Anderson-Schultz-Flory (ASF). The ASF polymerization equation is written as :

$$W_n / n = (1-\alpha)^2 \cdot \alpha^{(n-1)}$$

Where n = number of carbon atoms in the product

W_n = weight fraction of product containing n carbon atoms

α = chain growth probability

and on logarithmic form :

$$\ln(W_n / n) = \ln(1-\alpha)^2 - (n-1) \cdot \ln \alpha$$

A linear relation between $\ln(W_n / n)$ and n , with slope $\ln \alpha$, is expected if the product distribution among the carbon numbers follows the polymerization equation described above. Figure shows how the theoretical product distribution of hydrocarbons depends on the chain growth probability. The figure indicates that high yields are only possible for the extreme ends of the hydrocarbon product spectrum, CH_4 and waxes.

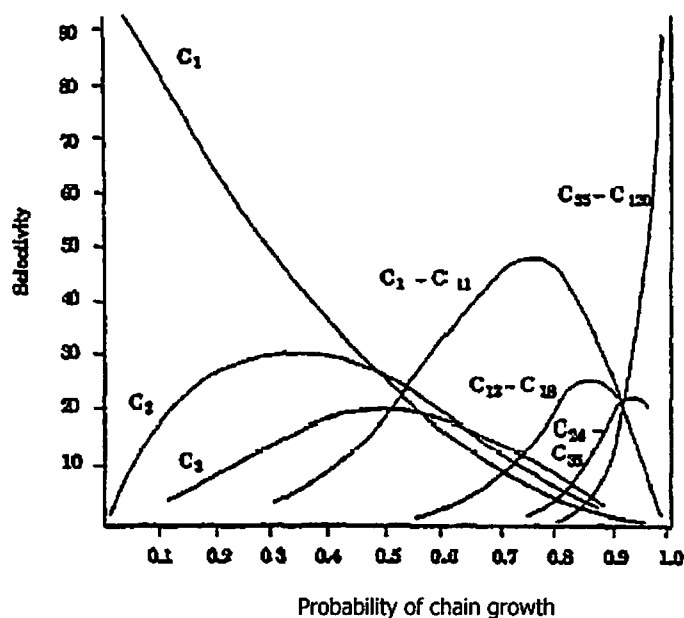


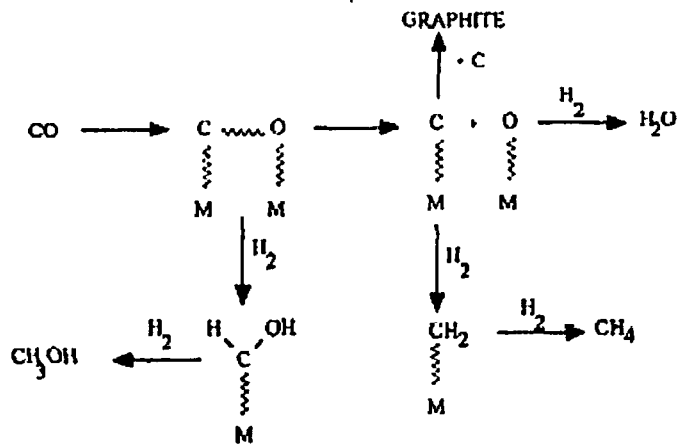
Figure 8, Selectivity of hydrocarbon fractions as a function of chain growth probability, α (from Dry, M.E in: *Catalysis: Science & Technology*, Anderson, R.B., and Boudart, M. (Eds.), 1 (1981) 159)

The formation and nature of the “monomeric” unit taking part in the chain growth has been a subject of controversy during the years. The discussion have been focused on three main types of reaction pathways:

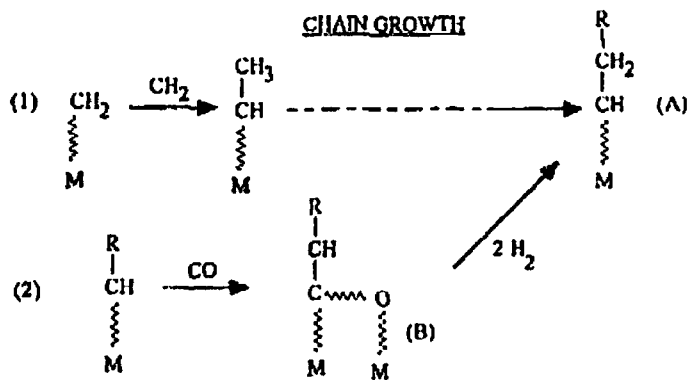
- Surface carbide mechanism (dissociative adsorption of CO)
- Hydroxycarbene mechanism (hydrogenation of associated adsorbed CO to $\text{M}=\text{CH}(\text{OH})$)
- Carbonyl mechanism (insertion of CO in growing chains)

At present the surface carbide mechanism is most accepted, but it does not account for the production of oxygenates. To account for this Dry has proposed a general reaction scheme including elements from both the carbide insertion theory and the CO insertion theory. This scheme is shown below:

INITIATION AND C₁ COMPOUNDS



CHAIN GROWTH



CHAIN TERMINATIONS

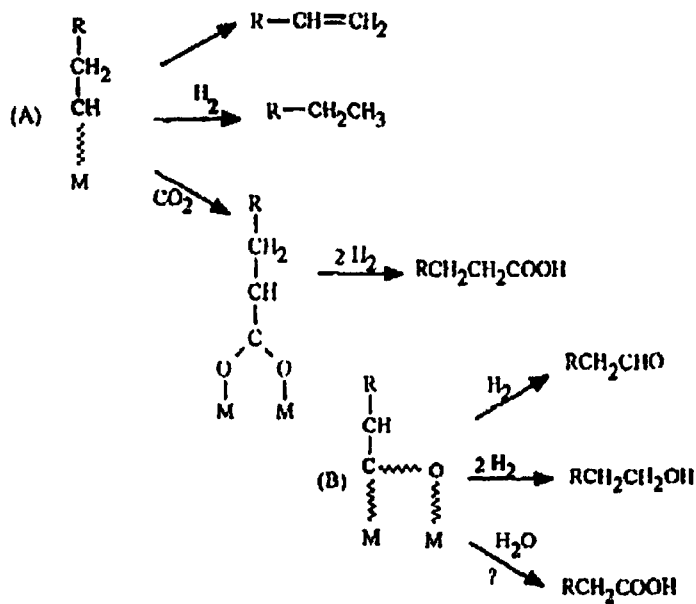


Figure 9, Mechanism of FT reaction, (Dry,1990)

2.7 Catalysts for the Fischer-Tropsch Synthesis:

Already in 1920-30's Fe, Co, Ni and Ru were identified as the most promising catalysts for the Fischer-Tropsch Synthesis. These are still main components of today's Fischer-Tropsch catalysts, but the composition and activity have changed throughout the years. Ni has high selectivity to methane. Fe has high water-gas-shift (WGS) activity and is therefore suitable when low H₂/CO feed ratios are used, i.e. when coal is used for synthesis gas production. The H₂/CO ratio obtained from natural gas is close to the stoichiometric ratio of the Fischer-Tropsch reaction and the water-gas-shift reaction is therefore not desirable. Co and Ru are therefore the catalysts of choice due to low water-gas-shift activity and high selectivity to long chain hydrocarbons and waxes when natural gas based feeds are used for synthesis gas production. Co is the preferred metal due to its relatively low cost compared to Ru.

Sr.No.	Catalysts	Source of Carbon	Property
1.	Ni	Any	Methanation
2.	Fe	Carbon rich (coal)	WGS with CO ₂ production
3.	Co	Hydrogen rich (natural gas)	Highly active and gives linear hydrocarbons
4.	Ru	Hydrogen rich (natural gas)	Very active but expensive

Table 2.5, Potential of FT catalysts

Four types of catalysts can be used for the Fischer-Tropsch synthesis (as shown in table) - the most important are based on iron (Fe) or cobalt (Co). Cobalt catalysts have the advantage of a higher conversion rate and a longer life (over five years). The Co catalysts are in general more reactive for hydrogenation and produce therefore less unsaturated hydrocarbons and alcohols compared to iron catalysts. Iron catalysts have a higher tolerance for sulphur, are cheaper, and produce more olefin products and alcohols. The lifetime of the Fe catalysts is short and in commercial installations generally limited to eight weeks. The cobalt catalysts used in the first commercial Fischer-Tropsch plants had very low activity. The cobalt Fischer-Tropsch catalysts developed in recent years have approximately an order of magnitude of higher activity than the early German catalysts. The development of improved supported Co catalysts has been and is of major

importance in the development of new Fischer-Tropsch technology. Many recently developed catalysts system consists of 4 parts: the cobalt metal, a second metal (typically noble), oxide promoter(s) and the support.

Deactivation of catalysts:

Supported catalysts can be deactivated through one or several of the mechanisms leaching, sintering, poisoning, solid state reactions, fouling and coke formation. Leaching, i.e. loss of active material can be a problem with Ni catalysts due to the formation of volatile nickel carbonyl. Sintering occurs mainly at elevated temperatures and causes a decreased dispersion due to migration and agglomeration of the catalytically active material and hence loss of activity. Sulfur compounds have long been known to rapidly poison Fe, Ni and Co catalysts, but also other compounds can adsorb strongly and block the active sites (O, Se, Te, N, and P). The main effect of poisoning is loss of activity, but the selectivity may also be affected through ensemble size effects or selective poisoning which is used on purpose in some systems. The poison may be reversibly adsorbed and in this way inhibit the reaction, or it may be irreversibly adsorbed leading to permanent poisoning of the catalyst. The poison can block the active sites or it can react with the active site forming some compound.

Catalysts can also loose activity by fouling and coke formation. High molecular mass waxes are formed during Fischer-Tropsch synthesis and will fill the pores of the catalyst particles. This will slow down the diffusion of reactants (and products) and also in certain cases the reaction rate. The Fischer-Tropsch synthesis is normally operated at relatively low temperatures (< 523K) and little carbon deposition occurs.

The catalysts may also loose activity by transformation into an inactive phase. Catalytic materials are often dispersed on a support to increase the surface area of the active materials. Such supports should ideally be able to keep the catalytic phase in a highly dispersed phase without interacting to strongly with this phase. Supports as alumina, and silica, can react with the active (precursor) phase during preparation or pretreatment of the catalyst to form inactive phases with low reducibility. The formation of such phases will lead to catalysts with lower activity. It is also possible that similar

reactions between support and active phase can occur during synthesis resulting in a decline of activity.

Fe catalysts are known to deactivate through reoxidation by H_2O and CO_2 to iron oxides, but the possibility of reoxidation of cobalt catalysts during synthesis has received little attention in the past. It was speculated that reoxidation of the active metal could be the cause of deactivation for cobalt catalysts.

2.8 Development of Fischer-Tropsch Reactors:

Fischer-Tropsch Reactors have shown considerable development since the first reactors were used even before the Second World War. Presently, there are three types of reactors that are considered to meet the requirements for modern commercial applications.

Originally, fixed bed reactors, later in the form of multi tubular fixed bed reactors, were used, all for low Temperature Fischer-Tropsch (LTFT) operations. In the multi tubular form these reactors are commercially used by Sasol in South Africa and by Shell in Malaysia. They typically operate between 180-250 °C at pressures ranging from 10-45 bar. Under these conditions the reactor operates in the three phase- gas-liquid-solid trickle bed mode. A new development is the slurry bubble column or Sasol only uses slurry phase reactor, which is under development by several companies but at this stage, commercially.

There is also the high temperature Fischer-Tropsch (HTFT) process that has been operated by Sasol in South Africa since 1955. The HTFT process, called Synthol, up to a few years ago used a circulating fluidized bed reactor operating at a pressure of about 25 bar and temperature of about 330-350 C. At these conditions the reactor is operated in the two-phase gas-solid mode. The circulating fluidized bed reactors have now all been replaced by Sasol Advanced Synthol (SAS) reactors, which make use of conventional solid-gas fluidization.

Low Temperature Fischer-Tropsch Reactors:

Low temperature Fischer-Tropsch Reactors (LTFT) can be classified as:

- Multi tubular fixed bed reactor
- Slurry phase reactor

Multi Tubular Fixed Bed Reactors:

The multi tubular fixed bed reactors (MTFBR) which have been used since World War-2 are still used by Sasol in their Arge process and Shell in the Shell Middle Distillate Synthesis (SMDS) process. The FT reaction takes place over an iron based catalyst (Sasol) or over cobalt based catalyst (SMDS) in a reactor which resembles a tubular heat exchanger, as shown in figure10, with the catalyst packed in the tubes. The heat is removed through the tube walls to generate steam on the shell side of the reactor. The interaction between the generation of heat and heat removal through the walls gives rise to axial and radial temperature profiles. The axial temperature peaks are associated with the highest conversion rates. In effect this means that in the first few meters of the 10-12 metre long bed, most of the reaction takes place and that after the peak relatively little conversion is achieved and the catalyst is under utilized. It is possible to distribute the conversion more evenly over the tube length by either reducing the activity of the catalyst or by reducing the average temperature or by a combination of the two.

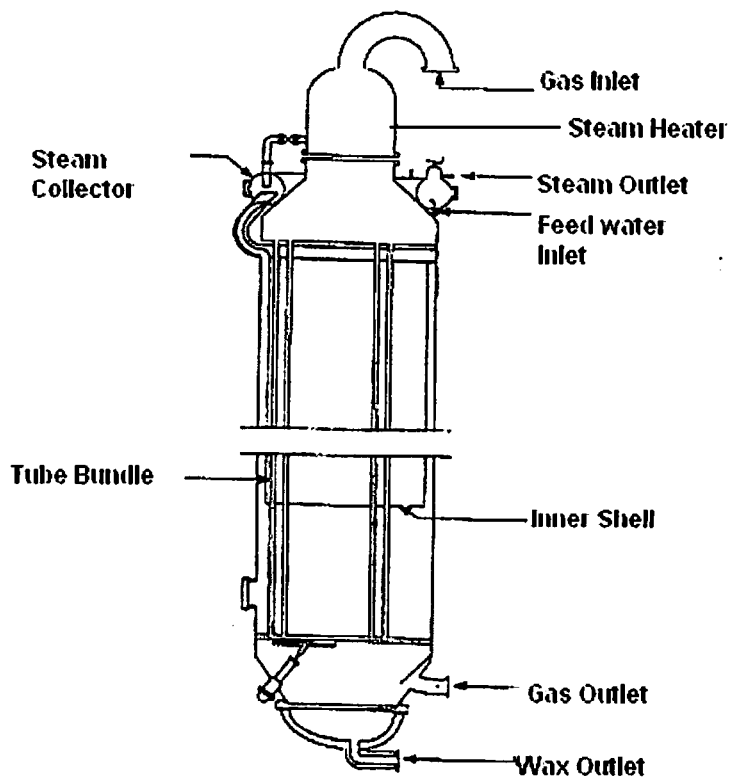


Figure 10, Multi Tubular Fixed Bed Reactor (Arge)

In order to obtain good conversions, a high average temperature is required but this is subject to a maximum temperature for the peaks above which selectivity is negatively affected and the catalyst may be damaged especially in the extreme case of temperature run-a-ways.

Efficient heat removal and effective temperature control at higher levels of temperature is therefore very important. Heat transfer in the bed and through the tube walls is much improved by increasing the gas and liquid flows in the bed. In the case where this is achieved by gas recycle, the conversion per pass is decreased but the overall conversion benefits in a large way by the recycle of reagents and the higher reaction rates possible at the higher average tube temperatures. This comes at the cost of recompression of the recycle gas. Recycle of liquid products also helps in improving the heat transfer and hence the heat removal processes. For this an effective liquid distribution is a prerequisite as uneven distribution can readily cause temperature run-aways and blockages in “dry” tubes.

The effective controls of temperatures and prevention of unstable conditions becomes more critical with increasing activity of the catalyst. When the contributions to improved heat transfer possible through recycle of gas and liquids have been exhausted, further improvements can only be achieved by decreasing the tube diameters. This comes at increased reactor costs but makes it possible to make higher pressure steam.

The pressure drop over the tube tends to be high compared to those obtained in fluidized systems. With relatively high recycle flows, this gives rise to increased recompression costs. In a tubular fixed bed, plug flow conditions are obtained which allow for optimal use of reagent concentrations. This benefit is however to a significant extent lost by recycle of the tail gas that has a diluting effect on the fresh feed.

The reactor is complex and expensive. The scale-up of the reactor is mechanically difficult and is complicated by the fact that the iron-based catalyst has to be replaced periodically and the design of the reactor has to provide for this. This replacement is cumbersome and maintenance and labor intensive. Cobalt based catalyst has a long life and replacement is a less important factor.

Slurry Phase Reactors:

The slurry phase reactor, as shown in figure 11, consists of a vessel containing slurry consisting of process-derived wax with catalyst dispersed in it. Syngas is bubbled through this slurry bed and is converted to hydrocarbons. The heat generated is passed from the slurry to the cooling coils inside the reactor to generate steam. The light hydrocarbons in the vapor phase are removed from the freeboard in the top of the slurry phase reactor with the unconverted reactants and are condensed in the downstream condensing train. The heavier liquid hydrocarbons are mixed into the slurry from which they must be removed by means of a solid separation process. Internal devices, in a proprietary separation process developed by Sasol, achieve this. The successful development of an effective and a relatively cheap liquid-solid separation step was crucial to the development of the slurry phase reactor. Precipitated catalyst, especially iron-based catalyst, tends to be weak. It is important that the catalyst is strong enough to prevent break up which would make the liquid/solid separation more difficult and in the extreme, impossible.

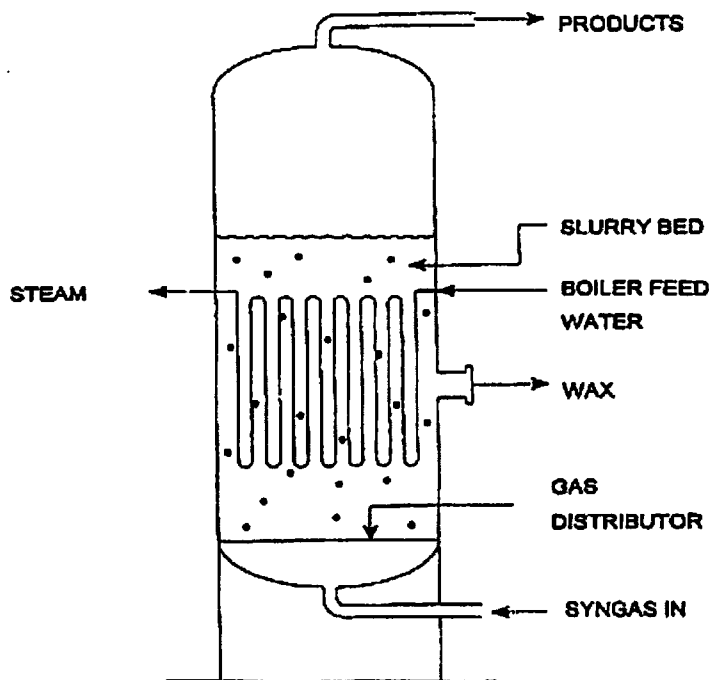


Figure 11 Sasol Slurry Phase Distillate Reactor

A most significant process characteristic of the slurry phase reactor is that it is well mixed and can operate virtually isothermally. The absence of axial and radial temperature gradients as in MTFB reactor, allows for much higher average operating temperatures in the slurry phase reactor and therefore higher reaction rates. As all the catalyst is at more optimal process conditions, the yields per reactor volume are high even though the catalyst concentration in the slurry phase reactor is lower than that for the MTFB reactor. Because the reactor is well mixed, the catalyst tends to see outlet gas concentrations. This has a disadvantage in terms of conversions in a once through system. Through staging inside the reactor and operating reactors in series, the disadvantages of well-mixed reactor behaviour can be reduced to a large extent. The pressure drop across the slurry phase reactor is less than 1 bar.

The slurry phase reactor allows for on-line catalyst withdrawal and addition, which is not feasible with the MTFB reactor. This is especially important for FT reactors that use iron based catalyst that must be replaced periodically. On line catalyst renewal also reduces maintenance costs. Where use is made of cobalt catalyst that has a longer life, this is obviously less important, but in principle the addition and withdrawal features can also be used for reactivation of cobalt catalyst if required.

Because of the isothermal nature of the reactor and the much smaller pressure drops across the reactor, the control of the reactor is much simpler and operating costs are much reduced. The easier control of average catalyst life through regular catalyst renewal, allows for easier control of the process selectivity and hence the quality of the products. This is especially important for processes using iron-based catalyst.

Precautions to be taken for a slurry phase reactors are:

- During normal operating conditions and also during the shutdown of the reactor, no stagnant zones with poor mixing occur which may result in localized hot spots. If the catalyst is exposed to a very high temperature, carbon will be formed, which may damage the structural integrity of the catalyst.
- Another critical design of a slurry reactor is the separation of the catalyst from the wax. Sasol was successful in the development of a very efficient catalyst /wax separation system. By matching the characteristics of the catalyst with

those of the operating system, the loss of catalyst can be restricted in the wax produced by the FT process.

The advantages of slurry over multi-tubular reactors are as follows:

- The cost of reactor train is 45% of that of multi-tubular system.
- The differential pressure over the reactor is about four times lower which results in lower gas compression costs.
- The lower catalyst loading translates to four-fold lower catalyst consumption per tonne of product.
- The slurry bed more isothermal and so can operate at a higher average temperature resulting in higher conversions.
- Online removal / addition of catalyst allows longer runs.

High Temperature Fischer-Tropsch Reactors:

The Sasol Advanced Synthol (SAS) Reactor:

Nineteen Synthol-Circulating Fluidised bed (CFB) reactors were used commercially by Sasol in the period from 1955 to 2000. The reactor system was complex and needed a complex support system to cope with the circulating catalyst loads and temperature differences especially during start up. This made it expensive. The large tonnages of catalyst circulated, caused relatively high pressure drops across the reactor system. At any time only small fraction of the catalyst in the system was used for conversion purposes. The reactor systems were prone to erosion due to the high gas velocities in the reactor which operated in the transport bed mode. These and other disadvantages are eliminated when using a Sasol Advantages Synthol (SAS) reactor that makes use of conventional solid-gas fluidization. For that reason between 1998 and 2000 the 16 Synthol-CFB reactors with capacities of 6500 bbl/day, still in use, were replaced by eight SAS reactors, four 8 m diameter reactors with capacities of 11000 bbl / day each and four 10.5 m diameter reactors with capacities of 20000 bbl / day. Two different capacity reactors were used to fit in with the train configuration used with the then existing CFB reactors. The capital cost of these reactors is about 40% of that of equivalent CFB reactor systems. The SAS reactor shown in figure 2.12, is a vessel containing fluidized bed consisting of reduced, fused iron oxide catalyst. Syngas is bubbled through the bed where it is catalytically converted to hydrocarbons that are in vapor phase at the process

conditions of about 340 °C and 25 bars. The products and unconverted gases leave the reactor through internal cyclones. The SAS reactor is operated in such a way that the cyclones very effectively retain the catalyst. With the CFB reactors, scrubber towers were needed downstream of the cyclones to remove the last traces of catalyst before the product stream is passed to the condensing train. Although these scrubbers have been retained in the plant they can probably be eliminated in future plants using SAS reactors.

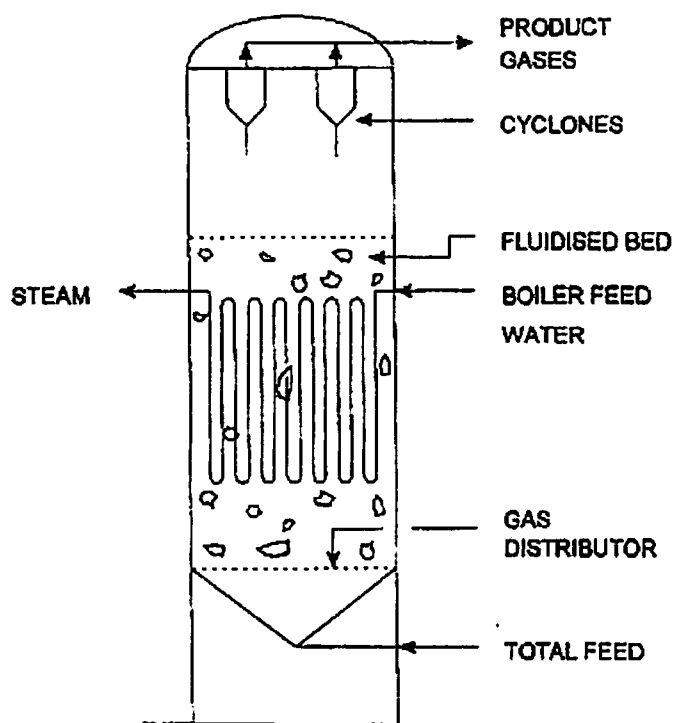


Figure 12, Advanced High Temperature Fischer-Tropsch Synthol Reactor

Advantages of SAS reactor over CFB reactors:

The major advantages of the SAS reactor over the CFB reactor are its simplicity, ease of operation and low operating cost due to elimination of the catalyst recycle. Catalyst consumption is reduced to about 40% and maintenance costs to about 15 % of that of the CFB systems. In general, higher conversions are obtained at higher gas loads. The later together with the fact that more cooling coils can be installed in the SAS reactor and more heat can be removed, allows for larger capacity equipment, which translates into advantages of economy of scale. Capacities are potentially up to 20,000 bbl/day. They also have thermal efficiencies four percentage points higher than CFB reactor systems. The design of the present SAS reactors was geared towards the need to retrofit them into

an existing plant where they had to replace the circulating fluidised bed reactors. Although the catalyst consumption with these reactors is much lower than with the circulating bed reactors, it appears that the catalyst is even now not used with maximum effectiveness. The reactors are operated in parallel mode. In the case of HTFT only iron based catalyst can be used to give reasonable product selectivities. As with the LTFT process, the water which is a product of reaction has an inhibiting effect on the conversion rates. Also here, high conversions per pass can not therefore be obtained and considerable recycle of unconverted gas has to be used to achieve a reasonable overall conversion. Series operation of the SAS reactors with intermediate removal of water allows for lower conversions per pass which reduces the need for gas recycles. Based on these and other considerations, it appears that there is considerable scope to increase the average capacity of the present reactors to well beyond the present capacities of 20,000 bbl/ day. As in the case of LTFT reactors, with higher activity catalyst or in this case with better use of the present catalyst, other mechanisms become limiting with respect to the maximum average capacities that can be achieved of which the most important may be heat removal. Therefore, the optimal design of the FT reactors can not be determined or done in isolation but must be done within the philosophy of the overall plant design.

2.9 State-of-art (International / National):

International Status:

During the past 10 years, there has been a spurt in the activities of many multinationals in establishing GTL on commercial standards through collaborations/ joint ventures/ transfer of technology etc. Innovation in reactor design, introduction of slurry reactors and novel product work-up schemes for value addition have given a boost to GTL. It is now claimed that even at low volumes (say, 5,000-6,000 bpd), the technology can be made viable. For instance Sasol-1 was revamped in 1993 to produce chemicals and wax instead of synfuels, while Sasol-2 and Sasol-3 together produce 5 MTA synfuels and olefins and 1.6 MTA of chemicals.

Shell, Bintulu (Malaysia), a commercial plant started since 1993 using natural gas as feed. The process known as Shell Middle Distillates Synthesis (SMDS) uses a fixed bed reactor using cobalt catalyst and produces superior grade wax, as shown in figure 2.13. This wax is hydroisomerised and cracked to diesel oil. Shell is planning to setup 75,000 bpd GTL plant. A number of companies are working on technology advances that will

lower capital cost. Those are in various stages of development. However, at present only Sasol and Shell have commercially proven technologies. GTL through FT route is a well established process and perhaps sooner than later, the technology will be one of the most sought after.

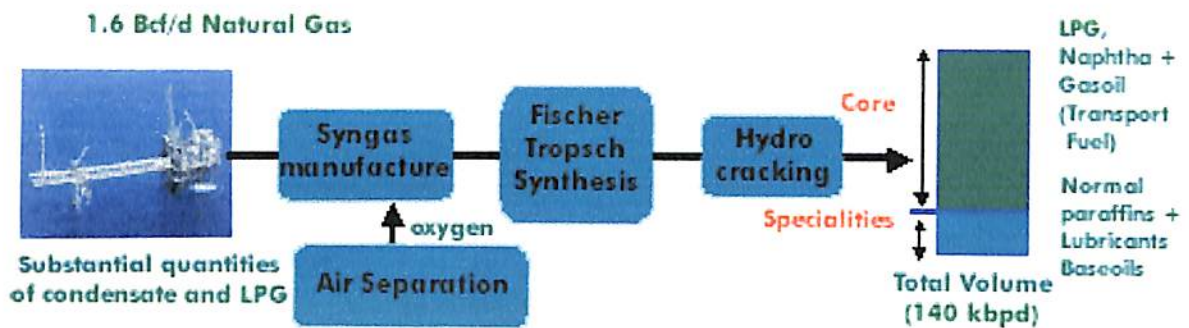


Figure 13, Shell Middle Distillates Synthesis (SMDS) Process

Current Status in India:

Recent years have seen a strong revival of interest for FT synthesis based GTL and DME fuels in India. The process to convert gas to synthetic petroleum has been under development for sometime in the past and several groups in Indian R&D laboratories were active. But only recently new initiatives are being taken as GTL is being seen as commercially viable. In the past a lot of work on Fischer-Tropsch synthesis was carried out at CFRI, (Dhanbad), IIT (Kharagpur), IIT (Chennai), IIT (Mumbai) and IICT (Hyderabad). At present a Task Force has been set up by CSIR with Indian Institute of Technology (IIT), (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, IIT, and NCL have been working on syngas reaction while NCL has done considerable work on conversion of methane to syngas.

Existing Commercial Processes:

Currently two GTL plants have commercialized their FT technology by Moss gas, South Africa and Shell Bintulu, Malaysia and several others are under proposal by various

hydrocarbon industries e.g. Sasol, Exxon-Mobil, Statoil, Shell, Syntroleum, etc. which are shown Table 5 and Table 6.

Existing	Country	Capacity b/d	Start Up
Moss Gas	South Africa	22,500	1991
Shell Bintulu	Malaysia	14,700	1993
Under Development			
Sasol/Qatar Petroleum Oryx	Qatar	34,000	2005
Sasol Chevron Oryx Expansion	Qatar	65,000	2009
Sasol Chevron Integrated GTL	Qatar	1,30,000	2010
Conocophillips Qatar	Qatar	1,20,000	2010
Shell/Qatar	Qatar	1,40,000	2009
Sasol chevron Nigeria	Nigeria	34,000	2009
Exxon Mobil Qatar	Qatar	1,54,000	2011
Total		7,14,200	

Table 5, GTL projects- existing or underdevelopment

Company	Country	Capacity, b/d	Company	Country	Capacity, b/d
Marathon	Qatar	1,20,000	Shell Malaysia	Malaysia	75,000
Syntroleum	Chile	10,000	Narkanan GTL	Iran	35,000
Shell/EGPC	Egypt	75,000	Forest Oil	South Africa	10,000
Syntroleum/Repsol	Bolivia	90,000	Ivanhoe Energy	Egypt	45,000
Rentech/Pertamina	Indonesia	15,000	Ivanhoe Energy	Oman	45,000
Australia Power	Australia	50,000	GTL	Bolivia	10,000

Energy			Bolivia		
Sasol Chevron	Australia	30,000	Syntroleum Peru	Peru	5,000
Shell Australia	Australia	75,000	Drake Synergy	Nigeria	20,000
PDVSA	Venezuela	15,000	Syntroleum/ Yakut	Russia	13,000
Shell Iran	Iran	75,000	Sonatrach (Tinhert GTL)	Algeria	36,000
Shell Indonesia	Indonesia	75,000			
Shell Trinidad	Trinidad	75,000			
Shell Argentina	Argentina	75,000			
ANGTL Alaska	USA	60,000	Total		1,134,000

Table 6, Proposed GTL Projects (Units barrels/day)

3. Experimental Work

In this chapter all the experimental methods and techniques used in the work are described. The whole experimental program is to study the activities of iron and cobalt catalysts for Fischer-Tropsch synthesis based Gas to Liquid technology (GTL) and also to convert the synthesis gas (syngas) of specific ratio into middle distillates viz. diesel, gasoline, and kerosene by using above mentioned catalysts at various operating conditions (i.e. temperature, pressure, and space velocity).

The first task for the desired objective was the preparation of different catalysts of varying compositions on different supports. Three different catalysts have been prepared and experimental runs for each were performed. The detailed procedure for the preparation of each catalyst is described separately. The final composite catalysts were characterized by standard characterization techniques such as X-ray diffraction (XRD), thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA), and B.E.T. surface area / pore volume / pore size distribution for each catalyst.

3.1 Catalyst preparation:

Catalyst no. 1: Co/Al₂O₃ catalyst

The alumina supported cobalt catalyst was prepared by incipient wetness impregnation method.

Composition of the catalyst:

Cobalt : Alumina : Palladium
15 : 85 : 0.4

Ingredients of the catalyst:

Co(NO ₃) ₂ .6H ₂ O	:	Cobalt nitrate
Al ₂ O ₃	:	Alumina
Pd NO ₃	:	Palladium nitrate hydrate

Procedure:

- 43.53 gms. of cobalt nitrate was dissolved in 60 ml. of distilled water.
- 50 gms. of alumina (commercial support) was added to cobalt nitrate solution with continuous stirring for 30 minutes.
- The catalyst mass was heated at 110 °C to remove the excess amount of water.
- It was then dried in oven at 110 °C for 16 hrs.
- The dried catalyst mass was grounded into fine particles till it becomes like powder.
- 20 gms. of binder was mixed with catalyst powder.
- 3 % acetic acid solution was added slowly with the catalyst powder till it becomes like semi-solid material. It was then left for peptization overnight.
- Further, 2-3 ml. of acetic acid solution was added and made it into paste.
- It was then extruded and dried at 110 °C for 6 hrs.
- 0.43 gms. of palladium nitrate was dissolved in 25 ml. of distilled water.
- 50 gms. of extrude was added to the palladium nitrate solution and diluted extrudes was heated at 110 °C until the extrudes dried.
- The dried extrudes was kept in oven and maintained at 110 °C for overnight.
- The catalyst was then calcined at 500 °C at the rate of 5°/ min. for three hrs.
- This catalyst was denoted as FT-A.

Catalyst no. 2: Iron catalyst

The iron based catalyst was prepared by precipitation method .

Composition of the catalyst:

Iron	:	Copper	:	Potassium	:	Magnesium
100	:	8.75	:	0.75	:	13.75

Ingredients of the catalyst:

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$:	Ferric nitrate
$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$:	Cupric nitrate
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$:	Magnesium nitrate
K_2CO_3	:	Potassium carbonate

Procedure:

- 13.823 gms. of ferric nitrate, 2.30 gms. of cupric nitrate and 1.30 gms. of magnesium nitrate was dissolved in 30 ml. of distilled water. The solution was heated at 85 °C.
- 125 gms. of sodium carbonate dissolved in 100 ml. of distilled water. The solution was heated upto 85 °C with continuous stirring.
- The hot sodium carbonate solution added with nitrates and heated. The pH was 8-9.
- The solution was then allowed to settle overnight.
- The excess of water over the catalyst was decanted and the settled mass was filtered by using filter cloth. Further washings were made with hot water. The filtration process was continued the next day.
- The residue was washed with the hot water till it was free from nitrates. The freshly prepared FeSO_4 solution was mixed with equal volume of extract in a test tube. Then, concentrated H_2SO_4 solution was poured in a test tube along the wall of the tube. Since if no distinct brown ring was formed at the junction of the above solution, the solution was nitrate free. The residue was further filtered again to remove the last traces of water.

- 0.212 gms. of K_2CO_3 mixed with distilled water and the solution was added with catalyst mass till it becomes like paste (i.e. semi-solid material). It was then allowed to dry overnight at $110^\circ C$.
- 3 % acetic acid solution was added slowly-slowly with the dried cake. It was then left for peptization overnight.
- Further, 2-3 ml. of acetic acid solution was added and made it into paste.
- It was then extruded and dried at $110^\circ C$ for 6 hrs.
- The extruded catalyst was then calcined at $500^\circ C$ for three hrs.
- This catalyst was denoted as FT-B.

Catalyst no. 3: Monolith

- Monolith cube that has cell size of 14 per cm is considered for the experiment.
- Monolith cube is treated with dry air to remove unwanted materials present in the cube cells.
- Before leaching, weight of the cube was found to be 4.828 gms. Then, this cube is leached with HNO_3 at $100^\circ C$ for 3 hrs. Leaching enables to increase the pore volume of the cells in this cube.
- Cube is kept immersed in HNO_3 for next 24 hrs.
- Then weight of the cube is found to be 5.659 gms. Cube is kept in the oven at $110^\circ C$ for drying.
- Weight of the cube after drying is measured to be 4.745 gm.
- Monolith cube is wash coated with alumina and kept for drying at $110^\circ C$ for drying.
- Then weight of cube is measured to be 6.153 gm.
- This sample is calcined at $500^\circ C$ at the rate of $5^\circ C$ for about 3hrs.
- Weight of the sample after calcination is reduced to 5.929 gms.
- Then this sample is wash coated with cobalt nitrate solution and dried at $110^\circ C$.
- After drying sample weight is found to be 7.849 gm.

- Finally, the catalyst sample is calcined at $500\text{ }^{\circ}\text{C}$ at the rate of $5\text{ }^{\circ}\text{C}$ for about 3hrs.

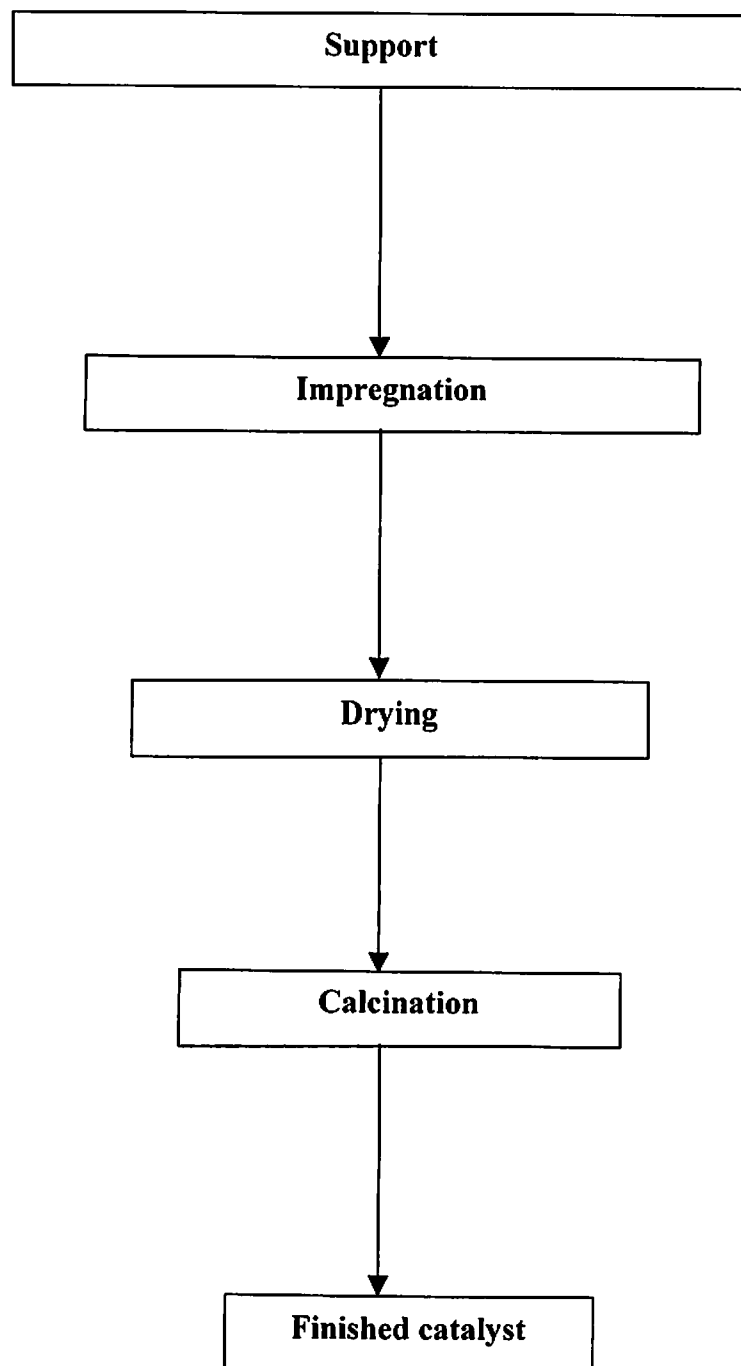


Figure 14, General Schematic Representation of Preparation of FT Catalysts

3.2 Characterization Of Catalysts:

The finished catalysts were characterised by following characterization techniques.

- Thermogravimetry (TG)
- Derivative Thermogravimetry (DTG)
- Differential Thermal Analysis (DTA)
- B.E.T. surface area
- X-Ray Diffraction (XRD)

Thermogravimetry (TG):

Principle:

It is a technique whereby the weight of a substance, in an environment heated or cooled at a controlled rate, is recorded as a function of time or temperature. In this analysis, the mass of a sample in a controlled atmosphere is recorded continuously as a function of temperature or time as the temperature of the sample is increased (usually linearly with time). A plot of mass or mass percent as a function of time is called a thermogram or a thermal decomposition curve.

Derivative Thermogravimetry (DTG):

Principle:

In DTG, the mass of a sample (m), is continuously recorded as a function of temperature (T) or time (t), i.e.

$$m = f(T \text{ or } t)$$

The quantitative measurements of the mass changes are possible by determination of the distance, on the curve mass axis, between the two points of interest or between two horizontal mass levels. In derivative thermogravimetry, the derivative of mass change with respect to time, i.e. dm/dt , is recorded as a function of temperature or time. In other words,

$$dm / dt = f(T \text{ or } t).$$

The derivative curve may be obtained either from TG curve by manual differentiation methods or by electronic differentiation of the TG signal. Accessory equipment is available for most thermobalances so that the DTG curve can be easily recorded along with the TG curve. It should be noted that the DTG curve whether derived

mathematically or recorded directly gives no more information than does an integral TG curve obtained under similar experimental conditions.

Differential Thermal Analysis (DTA):

Principle:

DTA is a technique in which the difference in temperature between a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program. Usually, the temperature program involves heating the sample and reference material in such a way that the temperature of the sample T_s increases linearly with time. The difference in temperature ΔT between the sample temperature and the reference temperature T_r ($\Delta T = T_r - T_s$) is then monitored and plotted against sample temperature to give a differential thermogram.

Procedure:

Thermal analyses were performed on Perkin-Elmer Thermogravimetric/Differential thermal analyzer using a Pyris Diamond TG-DTA instrument. All measurements were carried out at a heating rate of 10 °C/minute under a flow of nitrogen (99.999 %) of 100 ml/minute in the temperature range of 50-1000 °C. α -Alumina was used as reference for the differential thermal analyses measurements.

X-Ray Diffraction (XRD):

Principle:

X-ray diffraction is one of the most widely used technique for probing the nature of solid catalysts. The phenomena of diffraction arise from the interaction of X-ray with a periodic structure of polycrystalline material. In X-ray diffraction technique, a fixed wavelength is chosen for the incident radiation and Bragg Peaks are measured by observing the intensity of the scattered radiation as a function of scattering angle 2θ . The 'd' spacing is calculated from the values of the peaks observed from the Bragg's equation:

$$n\lambda = 2d \sin\theta.$$

Where, $n = 1, 2, 3...$

In powder diffraction analysis, information relating to the structure of the substance, its allotropic transformation, transition to different phases and purity of the substance can be obtained.

Procedure:

The samples were recorded on a Rigaku Dmax $\square\square$ X-ray diffractometer using $\text{CuK}\alpha$ radiation generated at 40 kv & 30 mA conditions. The X-ray diffraction patterns were recorded in the range 2θ range of $5\text{-}75^\circ$ at a rate of $1^\circ/\text{minute}$. The system was fitted with a divergent slip of 1° and a receiving slit of 0.15 mm. The X-rays were monochromatized using a graphite crystal monochromator. The intensities of the diffracted were measured using a scintillation counter detector.

3.3 Catalyst Evaluation:

The FT catalysts were evaluated in high pressure fixed bed micro reactor unit. The unit is operated by PC-PLC based control system with necessary control, Trip points, safety alarms, Data logging and interlocks.

Plant Description:

The high pressure fixed bed micro reactor unit is comprised of following modules:

- Gas feed module
- Liquid feed module
- Reactor module
- Product collection module

Gas feed module:

Five gases namely syngas, CO, hydrogen, and nitrogen and air is to be used in this module. Syngas or CO & hydrogen are process gases required for FT synthesis reaction. Nitrogen gas is used for initial pressurization and purging. Carbon monoxide and H_2 (i.e. syngas) lines are used at time of process run. Air is to be used for catalyst regeneration. The flow rates of syngas, CO, H_2 , N_2 and air to be controlled using thermal mass flow controllers (MFC).

Liquid feed module:

The liquid to feed is hydrocarbons e.g. methanol, naphtha (C₅-C₁₆). The feed is to be stored in 10 liter capacity vessel. The vessel is to be mounted on single pan balance of least count 0.1 gm. The vessel vapor space is purged with nitrogen for handling of highly volatile petroleum feeds. The liquid is to be fed with the help of reciprocating metering pump. The liquid feed is dried in a twin dryer assembly. The feed flow rate and the weight of the vessel are to be monitored by PC-PLC. The liquid and gas feeds are to be mixed and preheated in a pre-heater before entering into the reactor up to 300 °C. The heating of the mixture is also to be monitored and controlled through PLC.

Reactor module:

The Fixed Bed Reactor is a tubular reactor having 60 cc catalyst volume and 180 cc overall volume of reactor. This reactor can be operated in down flow as well as in up flow arrangement. The reactor can be heated by using furnace and using temperature controllers can control the temperature of reactor.

The reactor has the maximum operating conditions:

- Temperature : 550° C
- Pressure : 75 bar

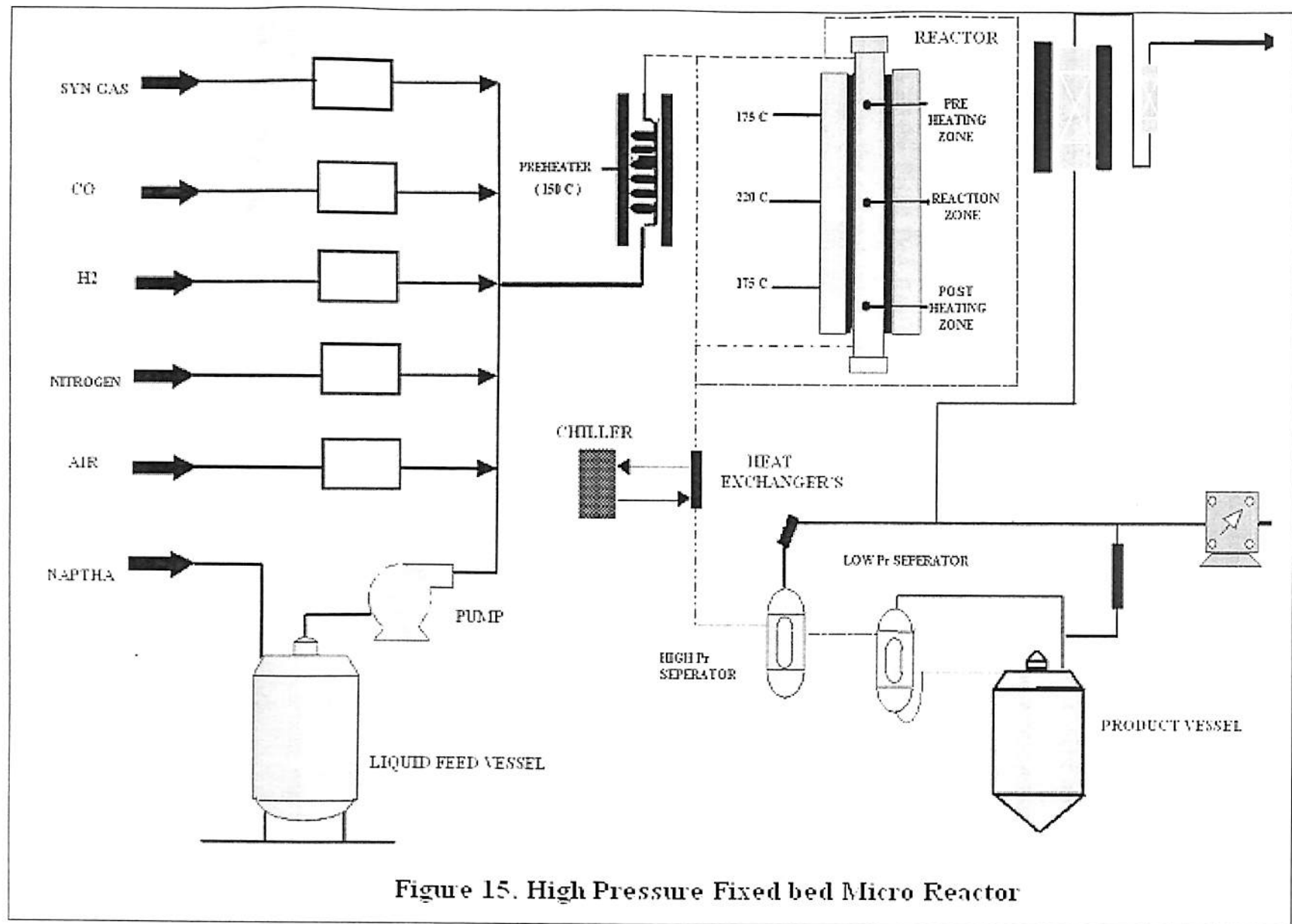
The reactor has to be heated with a split type electric furnace with three zones (i.e. Pre heating, Reaction & Post heating) with isothermal conditions at reaction zone. The temperature control and monitoring as and when desired has to be done at the heart and at skin of reactor with separate thermocouples for all the three zones. The temperature control and monitoring is to be done with PC-PLC.

Product Collection module:

Since the FT synthesis is a gas to liquid (GTL) process, outlet of reactor is gas & liquid. These two phase stream is condensed in a condenser. The condenser is a double pipe typed; Chilled water is used as utility from chiller. The liquid is collected and separated from an unreacted gas in HPS (high pressure separator). Due to possibility of formation of waxy liquid, line is heat traced and temperature of heat-traced line is kept around 100° C to avoid solidification of wax. The liquid from HP separator should go to LP separator to separate out the dissolved gases. The liquid from low-pressure separator

(LPS) goes to product collection vessel having around 3-liter capacity. The product receiver should be mounted on a weigh scale of least count 0.1 gm. The unreacted gases are then passed through wet gas meter for flow measurements. Also, this module has a regeneration module it can be used for catalyst regeneration purpose. The deposit carbon on the catalyst is removed by passing air. The gas from reactor outlet is passed through a regeneration section. The gases are passed through catalyst converter where oxidation of the CO is carried out. The gases are passed through dryer for moisture removal. The flow rates of these dried gases are measured using mass flow meter. Finally, the percentage of the CO₂ in regenerated gases can be analyzed in a CO₂ analyzer.

The process flow diagram of the above process description is shown in figure 15.



Run Procedure:

Experiment was carried out in a Fixed Bed Reactor (FBR) having volume of 180 cc. The reactor was equipped with a preheater, temperature control device, mass flow controllers and control panel. A CO₂ analyzer was connected to the outline. Synthesis gas in the specific ratio and at pressure of 20 bars is fed from the cylinders to the preheater. In the preheater, syngas is preheated to a temperature 150 °C. The temperature of the preheater is controlled from the control panel attached to the whole assembly i.e. reactor assembly.

The synthesis gas which is coming out from the preheater bottom is then fed to the top of the Fixed Bed Reactor (FBR). In the FBR, temperature of syngas is further increased to the desired value. The Fixed Bed Reactor is filled with known volume of catalyst such that a desired Gas Hourly Space Velocity (GHSV) can be maintained. As the preheated syngas goes to the reactor, the FT reaction takes place while it passes through the catalyst bed. The tail gas analysis of the gases coming out of the reactor was done by using Gas Chromatograph.

The reaction products along with the unconverted syngas are then passed through a condenser (Shell & Tube type). Cold water is used in the shell side of the condenser while the reaction products along with unconverted syngas pass through the tube side of the condenser. The condensed liquid product is then collected in product vessel and uncondensed gases are flared.

Performance Evaluation of F-T Catalysts:

1. FT- A (Co/Al₂O₃) catalyst:

The experimental work on the conversion of syngas to liquid hydrocarbons was initiated with Co/Al₂O₃ catalyst. Co/Al₂O₃ catalyst (FT-A) with noble metal promoter was charged in the Fixed Bed Reactor unit. The catalyst was reduced in the reactor under hydrogen flow before the start of the experimental run under the following reduction conditions.

- Catalyst volume : 30 cc
- H₂ GHSV : 500 hr⁻¹
- Reduction temperature : 10 hours at 325 °C and 40 hours at 450 °C
- Pressure : Atmospheric

During reduction, hydrogen gas was passed through the catalyst at above mentioned conditions. Hydrogen gas was first made to pass through preheater, which was maintained at 300 °C (Preheating of the gas was done so that there is not much temperature fluctuation when it comes in contact with the catalyst). After the first ten hours, the temperature of the reactor was increased to 450 °C. Accordingly, the temperature of the preheater was also adjusted upward. The long reduction time was chosen to ensure the reduction of cobalt metal as Co/Al₂O₃ have tendency of metal support interaction to form cobalt aluminate phase which is very difficult to reduce.

Synthesis Run:

After reduction, the synthesis run of the syngas was then performed. The reaction conditions are as follows:

- Catalyst Volume : 30 cc
- Temperature : 220 °C
- Pressure : 20 bar
- GHSV : 500-300 h⁻¹
- H₂/ CO Ratio : 2:1

For the synthesis Run, carbon-monoxide and hydrogen gases were mixed as per the above ratio and passed first through the preheater and then through the reactor. The temperature of the preheater was maintained at 150 °C below the reactor temperature. The whole synthesis run was performed for almost 110 hrs.

The tail gas analysis of the gases coming out of the reactor was done using Gas Chromatograph (GC). Also, the collected liquid product was discharged time to time. The liquid product separation was done by ASTM distillation.

2. FT- B (Iron) catalyst :

Iron catalyst (FT-B) was charged in the Fixed Bed Reactor unit. The catalyst was reduced in the reactor under hydrogen flow. The reduction conditions for FT-B catalyst are as follows:

- Catalyst volume : 30 cc
- H₂ GHSV : 500 hr⁻¹
- Reduction temperature : 4 hours at 150 °C and next 4 hours at 450 °C

- Pressure : Atmospheric

Synthesis Run:

After reduction of the catalyst was over, the reaction run was performed by passing syngas through the catalyst. The reaction conditions are as follows:

- Catalyst Volume : 30 cc
- Temperature : 200 °C-220 °C
- Pressure : 20 bar
- GHSV : 300 h⁻¹-500 h⁻¹
- H₂/ CO Ratio : 2

The whole synthesis run was performed for almost 110 hrs at different temperature. The feed and gaseous products were analyzed by Gas Chromatograph (GC). The liquid product (water& hydrocarbon) was collected and separated. The liquid product separation was done by ASTM distillation. The GC results and the distillation result are discussed in the next chapter.

4. Results & Discussion

In the second part of this chapter, the results of experimental FT runs for the following catalysts are described.

1. Co/Al₂O₃ catalyst (FT-A catalyst)
2. Iron catalyst (FT-B catalyst)

1. Co/Al₂O₃ (FT-A) catalyst:

The Co/Al₂O₃ (FT-A) catalyst was charged in high pressure fixed bed reactor for synthesis run at two different space velocities. The tail gas analyses of the synthesis run using FT-A catalyst are shown in tables 7 and 8.

From the Gas Chromatograph (GC) analysis, as shown in table 7, it has been observed that at space velocity 500 h⁻¹, pressure 20 kg/cm² and for H₂/CO ratio of 2, the maximum favorable temperature for the FT reaction seems to be 210 °C. At this temperature, much of the carbon monoxide is being converted to the liquid products. Further, reduction of temperature to 200 °C leads to lower conversion of carbon monoxide.

In the next run, Gas Hourly Space Velocity (GHSV) was reduced to 350 °C (as shown in table 4.4) and other parameters remain constant and the FT reaction was carried out at different temperatures from 200 °C to 220 °C. It is again observed that the conversion of Carbon monoxide is more at 210 °C.

Sr. no.	Operating Conditions					Catalyst FT - A
	Temperature (°C)	Pressure (kg/cm ²)	GHSV (h ⁻¹)	H ₂ /CO Ratio	Time on stream (hrs.)	GC Analysis of tail gas (%)
1.	220	20	500	2:1	12	H ₂ = 2.7 CO = 89.2 CH ₄ = 3.5 CO ₂ = 4.6
2.	210	20	500	2:1	22	H ₂ = 65.2 CO = 29.2 CH ₄ = 2.1 CO ₂ = 3.5
3.	200	20	500	2:1	26	H ₂ = 62.48 CO = 32.7 CH ₄ = 2.02 CO ₂ = 2.8

Table 7, Effect of temperature on carbon monoxide conversion

Sr. no.	Operating Conditions					Catalyst FT - A
	Temperature (°C)	Pressure (kg/cm ²)	GHSV (h ⁻¹)	H ₂ /CO Ratio	Time on stream (hrs.)	GC Analysis of tail gas (%)
1.	220	20	350	2:1	10	H ₂ = 2.8 CO = 88.7 CH ₄ = 4.6 CO ₂ = 3.9
2.	210	20	350	2:1	22	H ₂ = 66.6 CO = 27.6 CH ₄ = 3.2 CO ₂ = 2.6
3.	200	20	350	2:1	35	H ₂ = 63.6 CO = 31.3 CH ₄ = 2.8 CO ₂ = 2.3

Table 8: Effect of temperature on hydrocarbon formation:

The material balance for the best runs so far in respect of FT- A catalyst at different space velocities are shown in tables 9 and 10.

Feed, g	
Hydrogen	92.85
Carbon monoxide	650.0
Total	742.85
Product, g	
Water	215.42
Liquid Hydrocarbon	104.00
Carbon monoxide	148.57
Hydrogen	222.85
Methane	37.14
Carbon dioxide	14.85
Total	742.85
% Conversion (CO basis)	77.14

Table 9, Material Balance Run, FT – A Catalyst; GHSV = 500 h⁻¹

Feed, g	
Hydrogen	65
Carbon monoxide	454.97
Total	519.97
Product, g	
Water	156.0
Liquid Hydrocarbon	67.59
Carbon monoxide	103.86
Hydrogen	155.96
Methane	25.98
Carbon dioxide	10.39
Total	519.79
% Conversion (CO basis)	77.17

Table 10, Material Balance Run, FT – A Catalyst; GHSV = 350 h⁻¹

The liquid product collected from the run-1 using Co/Al₂O₃ catalyst (as per the operating conditions mentioned in chapter-3) was distilled. The ASTM distillation report is given in table 11.

Sr. No	% Volume of distillate	True boiling point (°C)
1.	IBP	276
2.	25	294
3.	45	302
4.	70	336
5.	85	356
6.	95	377.5
7.	FBP	405

Table 11, ASTM DISTILLATION:

2. Iron catalyst (FT-B catalyst):

The iron (FT-B) catalyst was also charged in the reactor for synthesis run at two different space velocities. The tail gas analyses of the synthesis run using FT-B catalyst are shown in tables 12 and 13.

Sr. no.	Operating Conditions					Catalyst FT - B
	Temperature (°C)	Pressure (kg/cm ²)	GHSV (h ⁻¹)	H ₂ /CO Ratio	Time on stream (hrs.)	GC Analysis of tail gas (%)
1.	220	20	500	2:1	10	H ₂ = 4.5 CO = 81.2 CH ₄ = 8.2 CO ₂ = 6.1
2.	210	20	500	2:1	25	H ₂ = 46.3 CO = 41.7 CH ₄ = 7.4 CO ₂ = 4.6
3.	200	20	500	2:1	35	H ₂ = 44.6 CO = 46.8 CH ₄ = 5.2 CO ₂ = 3.4

Table 12, Effect of temperature on hydrocarbon formation

Sr. no.	Operating Conditions					Catalyst FT - B
	Temperature (°C)	Pressure (kg/cm ²)	GHSV (h ⁻¹)	H ₂ /CO Ratio	Time on stream (hrs.)	GC Analysis of tail gas (%)
1.	220	20	300	2:1	11	H ₂ = 12.2 CO = 74.6 CH ₄ = 7.4 CO ₂ = 5.8
2.	210	20	300	2:1	25	H ₂ = 54.6 CO = 34.8 CH ₄ = 6.5 CO ₂ = 4.1
3.	200	20	300	2:1	27	H ₂ = 54.2 CO = 38.3 CH ₄ = 4.7 CO ₂ = 2.8

Table 13, Effect of temperature on hydrocarbon formation

The material balance for the best runs so far in respect of iron (FT-B) catalyst at different space velocities are shown in tables 14 and 15.

Feed, g	
Hydrogen	98.21
Carbon monoxide	687.47
Total	785.68
Product, g	
Water	141.42
Liquid Hydrocarbon	62.85
Carbon monoxide	235.70
Hydrogen	54.96
Methane	274.98
Carbon dioxide	15.71
Total	785.62
% Conversion (CO basis)	65.7

Table 14, Material Balance Run, FT – B Catalyst; GHSV = 500 h⁻¹

Feed, g	
Hydrogen	58.93
Carbon monoxide	412.50
Total	471.43
Product, g	
Water	103.71
Liquid Hydrocarbon	51.82
Carbon monoxide	132.12
Hydrogen	23.50
Methane	150.85
Carbon dioxide	9.40
Total	471.40
% Conversion (CO basis)	67.97

Table 15, Material Balance Run, FT – B Catalyst; GHSV = 300 h⁻¹

The liquid product collected from the run-2 using iron catalyst (as per the operating conditions mentioned in chapter-3) was distilled. The ASTM distillation report is given in table 16.

Sr. No	% Volume of Distillate	True boiling point (°C)
1.	IBP	285
2.	15	302
3.	30	308
4.	40	338
5.	60	360
6.	75	384
7.	FBP	410

. Table 16, ASTM Distillation

5. Conclusion

The concern for Global warming and environmental pollution is increasing day by day. Many international Environmental Societies have been active in preparing policies which recommend stringent specifications on fossil fuels such as sulfur level, aromatics content in transportation fuels (gasoline, diesel, etc). With such a global concern on the environment the demand for cleaner fuels has been gaining significance.

With price volatility in global oil prices and concern over 'Peak production' of oil from major Oil reserves, the dependence on the oil is gradually loosing ground to the Natural gas. Natural gas, with gradual increase in global reserves, is being declared as a fuel for 21st century. Natural gas can be used to produce Synthesis gas, which has huge applications in manufacturing of Synthetic chemicals.

Another concern is the monetizing of stranded gas reserves. Natural gas, which is not commercially viable for transporting through pipelines, is being flared unnecessarily. Such natural gas reserves can be utilized to produce synthesis gas and further into synthetic fuels by Fischer-Tropsch method.

Experiments have been conducted on different catalysts with varying composition. Cobalt and iron based catalysts have been prepared in the laboratory and further characterized and evaluated for their selectivity for Fischer- Tropsch synthesis of middle distillates from synthesis gas.

It is concluded that, Cobalt based catalysts are highly selective for the production of middle distillates from the synthesis gas through Fischer-Tropsch synthesis. The conversion of synthesis gas to diesel on cobalt-based catalysts is found to be 80%. Monolith catalyst could not be characterized and evaluated due to lack of time.

References:

1. C. Song, in: C. Song, C.S. Hsu, I. Mochida (Eds), Chemistry of Diesel Fuels, Taylor & Francis, London, 2001
2. P.C.H. Mitchell, F. Trifiro, J. Catal. 33 (1974) 350
3. M.S. Rana, B.N. Srinivas, S.K. Maity, G. Murali Dhar, T.S.R. Prasada Rao, J. Catal. 195 (2000) 31.
4. T. Chiranjeevi, P. Kumar, M. S. Rana, G. Murali Dhar, T. S. R. Prasada Rao, J. Mol. Catal. A: Chem. 181 (2002) 109.
5. Alexander A. Khassin, Tamara M. Yuviera, Anatolii G. Sipatrov, Valeri A. Kirillov, Galina K. Chermashentseva, Valentin N. Parmon, Catalysis Today 79-80 (2003) 465-470
6. Hans Schulz, Applied Catalysis A: General 186 (1999) 3-12
7. Nimir O. Elbashir, Christopher B. Roberts, Dept. Of Chem. Engg, Auburn university.
8. Tapan k. Das, Whitney Conner, Gary Jacobs, Xiaodong Zhan, Jinlin Li, Mark E. Dry and Burton H. Davis, University of Kentucky, Centre for Applied Energy Research
9. Y. Liu, J. Patzlaff, J. Gaube, The Selectivity of FTS on Fe and Co Catalysts-a comparison.
10. T. Klimova, M. Calderon, J. Ramirez, Appl. Catal. A: Gen 240 (2003) 29.

Web Sites:

1. www.sciencedirect.com
2. www.springerlink.com
3. www.fwc.com