GTL TECHNOLOGY – FRONTIER AREA FOR MEETING FUTURE ENERGY DEMAND

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CERTIFICATE

This is to certify that Ms Garima Shukla and Ms Rupali Chandra of B.Tech (APPLIED PETROLEUM ENGINEERING) have completed their dissertation titled ***``GTL TECHNOLOGY – FRONTIER AREA FOR MEETING FUTURE ENERGY DEMAND"*** under my supervision.

To the best of my knowledge and belief the work is based on the investigation made, data collected and analyzed by them..

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Executive Summary

Great expectations for expanding utilization of natural gas are being held by the world's energy market from the standpoint of addressing the global environmental problems. Since natural gas is in gaseous phase under normal conditions, however, it is difficult for natural gas to directly replace petroleum in the transportation area where energy is utilized primarily in liquid phase. To convert natural gas into energy in liquid state, therefore, is thought to be one of the best ways of having natural gas compete with petroleum

Growing interest is centering on the technology for manufacturing liquid fuel from natural gas and using it as a measures of transporting natural gas and/or utilizing it as a non-petroleum alternative fuel. This technology primarily consists of two stages: convert natural gas to synthesis gas comprising hydrogen and carbon monoxide in the first place and then manufacture liquid fuel from synthesis gas using the Fischer-Tropsch process and the like in the second step.

Liquid fuels such as Fischer-Tropsch synthetic fuel, methanol, DME etc. manufactured by this technology are collectively called GTL (Gas to Liquid) – an environmentally clean fuel, free of sulfur and aromatics, like LNG. Moreover, since a GTL project based on a relatively small-sized gas field producing 1-3 Tcf of natural gas is economically justifiable, it is believed to be one of the best measures of promoting a move to obtain alternative liquid fuel by making use of the most of untapped natural gas resources, and therefore a number of GTL projects have been either placed on-stream or announced one after another at many locations of the world since the latter half of the 1990's.

Each country in the world, has announced plans to further strengthen measures to counter the issue of automotive emissions to prevent environmental pollution. Since sulfur contained in diesel fuel tends to increase the quantity of Particulate Matter in the automotive emissions, plans are under way to strengthen the quality regulation of diesel fuel throughout the world

Diversifying market risks by converting natural gas into something other than LNG coupled with the need to end flaring have also been key drivers behind setting up of GTL plants worldwide.

This report seeks to analyze the process of innovations and strategic business and issues in the GTL technology focusing on all dimensions of this process. The **first part** of the report presents a detailed analysis of the GTL history, the chemical conversion process behind GTL. The **second part** of the report focuses on the innovative effort in the different lines of ongoing research. The **third part** focuses on the various technical and economical issues. Finally, the **fourth part** focuses on a study of GTL technology followed by a case history by taking into consideration various options and economic criteria.

Part - A

1.0 OVERVIEW

The Gas to Liquids technology (GTL) consists of a chemical conversion of natural gas into a stable liquid by means of the Fischer-Tropsch Process. This conversion makes possible to obtain products that can be consumed directly as a fuel (for example, Diesel) or special products such as lubricants. The products that are derived from the GTL technology have two types of economic advantages:

i) Their transport cost is much less than that of the transport of natural gas, which due to its volume, that is 1000 times more than the volume of petroleum, not only presents high transport costs but also requires specific assets (gas pipelines or methane ships);

ii) The products produced by GTL plants present important environmental advantages compared to traditional products, as they are derived from a clean fuel: natural gas.

The decade of the 1990s witnessed the return of the Fischer-Tropsch Process to the centre of attention in the world petroleum and natural gas industry. This technology, developed in the 1920s and put into large-scale operation by Germany, was abandoned due to the low prices of petroleum and the development of abundant markets for natural gas. Nevertheless, a radical transformation in the sphere of the application of this technology has opened the door for the renovation of the GTL technology. The increase of stranded gas reserves and the development of niches in the market for synthetic fuel, due to environmental legislation, prompted the renewal of interest of petroleum companies in this technology. The development of several projects for the construction of GTL plants in the sphere of application can be observed, as part of a truly technological rush to seek the development of more efficient and cheaper processes.

The success of the innovation process in the GTL technology has a very important potential impact on the dynamics of the world markets of oil and gas. The GTL technology represents the maximum limit for the long term petroleum prices in the oil market. In case this price is maintained above the cost of GTL, new companies will be attracted to this business, transforming into cash great gas reserves, which are today stranded because of the limits of traditional transport technologies. The GTL technology represents a minimum level for gas prices in the gas market. GTL is an alternative option for monetizing gas reserves.

1.1 Why GTL ?

According to Dosi (1982), the selection environment can be defined as the economic forces and the social and institutional factors that actuate as selection mechanisms for technologies.

A combination of a series of factors prompted the transformation in the environment of the GTL technology: i) the great increase in the gas reserves (especially associated); ii) the renewed activity of environmental legislation making the creation of niches in the market for clean fuels viable; iii) finally, the impacts of liberalization of the natural gas and electricity industries in the main world markets, creating higher transaction costs for traditional technological options for gas monetisation (LNG and pipelines).

(a) Increase of stranded reserves

The great effort in the search for alternative reserves to Arab petroleum after the petroleum shocks in the decade of the 1970s had a great impact on the increase of tested gas reserves, which jumped from 40 tcm (tera cubic meters) in 1970 to about 140 tcm in 1996. The reserves/production ratio increased from 59 years at the end of 1985 to 65 years at the end of 1996. The Natural Gas Industry is thus experiencing a period of abundant gas reserves. However, this abundance is not a reality in the regions where the markets are concentrated.

One of the most important problems for the gas industry is the higher cost of transportation as compared to liquid fuels. Natural gas has a volume of about 1000 times the volume of oil for the same energy content. Therefore, gas transportation requires specific technological options that are very capital intensive (pipelines or gas liquefaction and cryogenic transportation – LNG). The cost transportation of the same amount of energy in the form of gas is 3 to 10 times more expensive then the cost of oil transportation, depending on the distance. Therefore, when associated gas reserves are far from end-market and when the amount of gas produced is low, investments in the infrastructure necessary for the monetisation of the reserve are not profitable. Gas Flaring and ventilation is then the best economical option.

(b) Increase in environmental restrictions

The World Bank estimates that about 4.3 Tcf of gas are flared and ventilated every year in the World. This represents 12.9% of gross world gas production, or about 70% of the total gas traded via LNG chain. Gas Flaring and ventilation represents a very important environmental problem at the global level (greenhouse gas emissions). Governments are imposing restrictions on gas flaring and ventilation, since the growth of carbon emissions was declared no longer acceptable under the Kyoto protocol of 1998, which aims at mitigating global warming through the reduction of carbon emissions by industrialized countries.

The environmental restrictions to flaring are being introduced by several means. National governments and regulators are creating rules and standards making difficult the development of gas fields that requires substantial flaring. Some governments have signed agreements with oil producers in order to implement “zero burn” programs. GTL can be an interesting option for reducing gas flare. Gas markets are very restricted in poor countries of Latin America and Africa. GTL can transform gas reserves into an international commodity with no market restrictions.

The environmental restrictions imposed on the quality of fuel represents a great incentive for GTL too. First, these demands represent an increase in cost for the traditional refineries. They should confront an increasingly more difficult situation in which they must produce a cleaner product with a worsening raw material (oils which are becoming heavier). This task is even more difficult in a context of growing competition and tighter margins.

(c) Increase of demand for flexibility

Current innovative effort on the GTL technology represents a response to the increase in the requirement for assets flexibility, due to higher uncertainty on the energy markets. These uncertainties are related to the rise in price volatility with the energy market liberalisation.

The selection of the GTL technology corresponds to an attempt of improving the classical trade-off between flexibility and scale. The objective of the innovation effort is to allow a major flexibility to the physical assets, without incurring in the higher costs of the operation in small-scales. GTL allows the reduction of the rigidity of the natural gas chain, escaping from the highly specific assets, and from the contractual difficulties associated with the increasing transaction costs (Williamson, 1993). This technological option has the potential for reducing the amount and the life-cycle of the investments, through equipment compaction. Therefore, GTL can improve the companies' portfolio liquidity and contribute for companies' asset optimisation. Increasing assets' flexibility implies in higher production costs due to the sacrifice of economies of scale. The option between flexibility and scale is marked by specific situations of the countries and companies. R&D programs are influenced by this diversity in situations. Some efforts are focused on the technology versatility and adaptability; others explore the trajectory "standardisation–scale". The outcome of these efforts will depend on the specific characteristics of countries' natural resources and the composition of companies' portfolios.

1.2 Gas-to-Liquids (GTL) Fuel Fact Sheet

Some remote natural gas can now be economically converted through a GTL process into an ultra-clean fuel for diesel engines. At times this fuel can be economically blended with conventional petroleum diesel fuels to: extend California's diesel fuel supplies, and improve refinery capacity of cleaner diesel fuels.

- An opportunity exists to use GTL fuels in California and reduce the emissions from old diesel vehicles especially school buses. One plant in South Africa (Mossgas) and Shell's Indonesia plant both produce GTL fuels suitable for use in heavy-duty diesel applications.
- Discussions are underway to develop a GTL production facility in Alaska to produce 40,000 barrels per day (23% of our current demand) with a goal to produce 300,000 bbl/d. However, with existing technology, oil pipeline capacity and North Slope gas reserves over 1,000,000 bbl/d could be produced.
- Building such a facility would extend the Trans Alaska Pipeline's economic life, which provides 50 percent of California's oil supply.
- Natural gas, is four times more expensive to transport than oil.
- Converting natural gas to a liquid through a Fischer-Tropsch technology provides an opportunity to expand the use of the natural gas and lower the transportation cost from remote sources of low-cost gas.
- Fischer-Tropsch is a gas-to-liquid (GTL) process that can produce a high-quality diesel fuel from natural gas, coal and biomass resources. Shell refers to the GTL process as a middle distillate synthesis (MDS). In all cases the middle distillate produced from this process can be blended with today's diesel fuel.
- GTL diesel has extremely low (0-5-ppm) sulfur, aromatics, and toxics. GTL fuel can be blended with non-complying CARB diesel fuel to make a cleaner diesel fuel complying with stringent diesel fuel standards.
- California's current nearest GTL supplier is the Shell-Malaysia, Bintulu MSD plant. The plant, which began, operation in 1993, and was shutdown between

December 25, 1997, and restarted on May 20, 2000, can produce up to 2400 barrels/day, which is 1.5% of California's diesel demand.

- From November 1993-December 1997 Shell's MSD plant sold over 1 million gallons of middle distillate to four California refiners, which was blended into roughly 4 million gallons of diesel fuel and sold to on-highway fuel consumers.
- Synthetic diesel fuel offers a new opportunity to use alternative fuels in diesel engines without compromising fuel-efficiency, increasing capital outlay, and impacting infrastructure or refueling cost.
- Further commercialization of this fuel improves the prospects of new engines meeting proposed national 2007 heavy-duty diesel engine emission standards. In the near-term, this fuel can play a role reducing existing diesel vehicles exhaust and toxic emissions.
- Since the late-1990s nearly every major oil company including: ARCO, Chevron, Conoco, Exxon, Phillips, Mobile, Statoil, and Texaco announced plans to build pilot plants or commercial plants to produce synthetically derived diesel fuel through the improved GTL process.
- Stringent diesel exhaust emission standards and fuel specifications are compelling the petroleum industry to revisit the new, improved GTL process to competitively produce aromatic and sulfur complying diesel fuel.
- Key to the commercial success of the GTL process lies in increased reactor capacity proven in the mid-1990s. This new process uses a slurry-bed reactor that has 100 times the capacity per reactor over some 1990 reactors and offers lowers cost.
- Synthetic diesel fuel appears to be the most economical fuel product from the GTL process, compared to producing gasoline. Preliminary testing of an unmodified diesel engine, fueled with neat synthetic diesel fuel, shows the following emission reductions compared to typical California diesel:

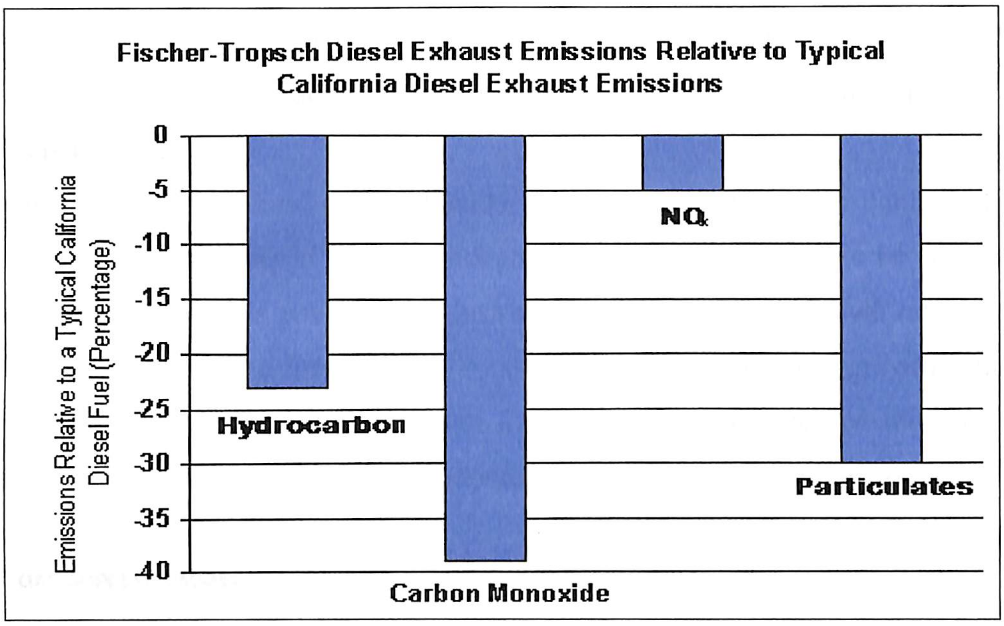


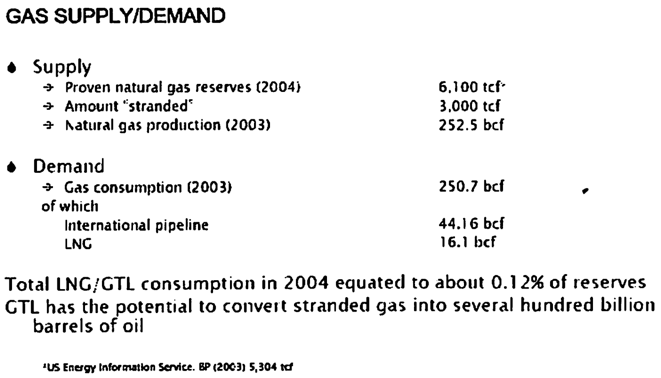
Fig.1.1 F T diesel exhaust

The GTL process needs low-cost natural gas, less than $1 per million BTUs, to compete with traditional diesel fuel. GTL fuels produced from pipeline supplied natural gas would not be competitive due to the higher value of pipeline supplied natural gas.

1.3 GAS RESERVES

Natural gas trails coal as the fastest growing primary energy source in IEO2006. The natural gas share of total world energy consumption increases from 24 percent in 2003 to 26 percent in 2030.

Consumption of natural gas worldwide increases from 95 trillion cubic feet in 2003 to 182 trillion cubic feet in 2030. Although natural gas is expected to be an important fuel source in the electric power and industrial sectors, the annual growth rate for natural gas consumption in the projections is slightly lower than the growth rate for coal consumption. Higher world oil prices in IEO2006 increase the demand for and price of natural gas, making coal a more economical fuel source in the projections.



GAS SUPPLY/DEMAND

♦ Supply	
→ Proven natural gas reserves (2004)	6,100 tcf*
→ Amount "stranded"	3,000 tcf
→ Natural gas production (2003)	252.5 bcf
♦ Demand	
→ Gas consumption (2003)	250.7 bcf
of which	
International pipeline	44.16 bcf
LNG	16.1 bcf

Total LNG/GTL consumption in 2004 equated to about 0.12% of reserves

GTL has the potential to convert stranded gas into several hundred billion barrels of oil

*US Energy Information Service. BP (2003) 5,304 tcf

1.2 Gas supply-demand

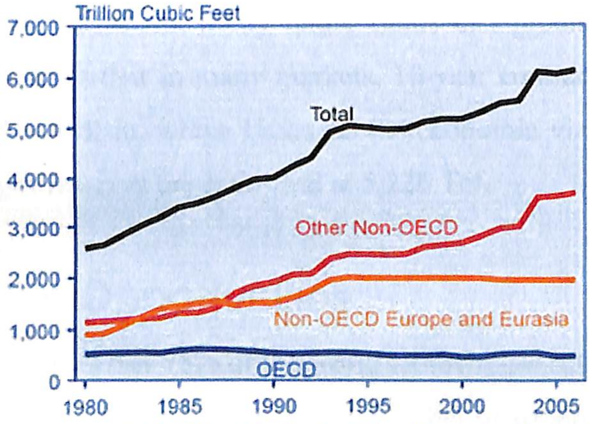
Natural gas consumption worldwide increases at an average rate of 2.4 percent annually from 2003 to 2030, as compared with 2.5 percent per year for coal and 1.4 percent per year for oil. Nevertheless, natural gas remains a more environmentally attractive energy source and burns more efficiently than coal, and it still is expected to be the fuel of choice in many regions of the world. As a result, the natural gas share of total world energy consumption (on a Btu basis) grows from 24 percent in 2003 to 26 percent in 2030.

Historically, world natural gas reserves have, for the most part, trended upward (Figure 2). As of January 1, 2006, proved world natural gas reserves, as reported by Oil & Gas

Journal, 5 were estimated at 6,112 trillion cubic feet—70 trillion cubic feet (about 1 percent) higher than the estimate for 2005.

The largest revision to natural gas reserve estimates was made in Iran. Iran's natural gas reserves increased by 31 trillion cubic feet (3 percent) between 2005 and 2006, from 940 trillion cubic feet to 971 trillion cubic feet. Also in the Middle East, higher reserve estimates were reported by Saudi Arabia, with an increase of 7 trillion cubic feet (3 percent). Other countries with substantial increases in reserves include Norway with a gain of 11 trillion cubic feet (14 percent), Nigeria with an increase of 9 trillion cubic feet (5 percent), and Indonesia with an increase of 7 trillion cubic feet (8 percent). Declining natural gas reserves were reported for Bangladesh (a decrease of 6 trillion cubic feet), and smaller losses were reported for Argentina (3 trillion cubic feet), Taiwan (2 trillion cubic feet), Germany (1 trillion cubic feet), and the United Kingdom (1 trillion cubic feet).

Figure 36. World Natural Gas Reserves by Region, 1980-2006



Sources: **1980-1993:** "Worldwide Oil and Gas at a Glance," *International Petroleum Encyclopedia* (Tulsa, OK: PennWell Publishing, various issues). **1994-2006:** *Oil & Gas Journal* (various issues).

1.3 World natural gas reserves by region

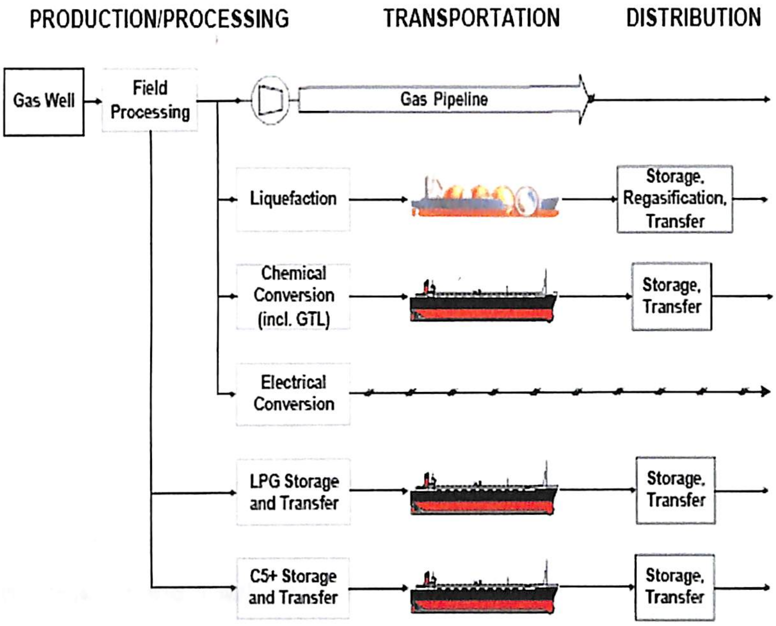
1.4 MONITIZING GAS RESERVES

"Stranded gas" is an all-encompassing term. It can be defined as any hydrocarbon-based gas that is uneconomic to deliver to market. This includes associated and flared/vented gas, and gas that is re-injected purely for regulatory compliance rather than for reservoir-pressure maintenance. Some of the factors that determine when a pipeline is profitable include resource volume, transport route, regulatory environment, market size and demand growth. Sometimes, excess reserves can be considered stranded, since these would require a paltry delivery rate to avoid oversupply of local markets. Negative economics can also be due to technical complexity or expense associated with recovering/gathering the gas. Stranded gas is essentially gas that is wasted or unused. Whenever one thinks of stranded gas, the primary goal is an alternative to pipeline transport.

A recent study by Zeus Development Corp. and IHS Energy identified some 450 Tcfg stranded in fields greater than 50 Bcf that can be gathered and produced for less than $0.50/MMBtu. Many larger fields can produce gas even cheaper. Recent price spikes suggest that in many markets, 10-year contracts could be secured for more than $3.5 to $4/MMBtu, which broadens the economic viability of smaller fields. Worldwide proved gas reserves are estimated at 5,226 Tcf.

The Opportunities

- Over 75% of the world's known gas reserves are remote and/or stranded.
- About 15.5 trillion cubic feet of stranded gas is flared, vented or re-injected each year.
- The opportunity exists to yield 1.5 billion barrels of fuel per year from this stranded gas. (Over 4 million barrels per day)
- Synfuels GTL Process offers a new solution for a new source of fuel worldwide.



1.4 Various transportation routes

Depending on how one defines "reserves" and "stranded," estimates of stranded gas vary from 900 to 9,000 Tcf. The latter number would convert to about 900 billion bbl of synthetic hydrocarbon liquids. Although such a quantity seems improbable to achieve, any reasonable fraction of this amount is significant and, therefore, worth investigating. The technologies that industry is using to bring this otherwise unused energy to markets include gas conversion to LNG, gas to liquids (GTL), gas to hydrates and gas to electricity.

1.5 **Brief GTL History**

The GTL industry can be viewed as an alternative to oil refining. The basic technology of the industry dates back to 1923 when two German scientists, Franz Fischer and Hans Tropsch (FT), invented a process that could convert natural gas to a hydrocarbon mixture which could then be upgraded into petroleum products. The FT technology provides an alternative to traditional crude oil refining, as liquidpetroleum products, most notably diesel fuel, can be produced from a non-liquid input, natural gas.

The process was used by both Germany and Japan during World War II when their access to adequate oil supplies was disrupted by allied forces. In the 1960s, South Africa used the FT process to produce liquid fuels when the United Nations imposed oil import sanctions on the apartheid government. The South African plant used coal as a primary input rather than natural gas, demonstrating the flexibility of the FT process. GTL production continues in South Africa at the Mossel Bay facility, operated by Petro SA. The plant has a capacity of 22,500 barrels per day of petroleum products. Neither the World War II facilities or the initial South African facilities were commercial, profit making enterprises; rather, the facilities were technological solutions to politically disrupted markets. Under normal market prices they would not have been viable.

From the 1960s through the 1990s, several companies specializing in synthetic fuels, as well as joint ventures between major oil companies and synthetic fuels companies, explored and developed the basic FT technology as well as other technological approaches. Improvements in cost, efficiency, and plant scale were achieved. Today, enhanced catalyst design is developing as a key factor in improving the production process and reducing capital costs per barrel of product. The first fully commercial GTL plant was a 12,500 barrel per day (bpd) plant built in Bintulu, Malaysia in 1993, and owned by Shell. However, an explosion at the plant in 1997 closed it until 2000. Shell, along with other major oil companies has remained interested in developing the GTL technology. ExxonMobil, ChevronTexaco, ConnocoPhillips, and Marathon all either have demonstration plants running, or have committed to investing in GTL investments, mostly in Qatar, but also in Nigeria and Australia.

Few benchmarks:

- **1922**: Franz Fischer and Hans Tropsch used iron based catalyst to convert a CO/H_2 mixture to a mixture of hydrocarbons and oxygenated compounds
- **1925**: they used both iron and cobalt based catalyst to generate hydrocarbons
- **1950-1990**: South Africa SASOL developed FT commercially (in conjunction with coal gasification) to convert coal to hydrocarbons
- **1980-present**: Shell using FT to convert NG to fuels and waxes

1.6 GTL Process and Technology

Gas-to-liquids (GTL) technology generally entails the chemical conversion of natural gas into readily transportable liquids such as methanol or conventional petroleum refinery type distillate fuels. More recently the term GTL has also been more "loosely" applied to physical conversion processes such as that for liquefied natural gas (LNG) as well as for chemical conversion processes that produce products which may not be in a liquid state under ambient conditions, such as dimethylether (DME). In this paper, we focus on GTL technologies based on the production of diesel fuel via Fischer-Tropsch synthesis (FTS). FTS generally involves the synthesis of hydrocarbons and oxygenates from synthesis gas (syngas) consisting primarily of a mixture of CO + H2. The types of hydrocarbons produced can include olefins such as ethylene and propylene, and an extremely wide range of saturated hydrocarbons ranging from methane and ethane to long "straight chain" paraffinic waxes. The oxygenated materials that are produced consist primarily of alcohols such as methanol and ketones such as acetone. When configured to maximize the production of paraffinic hydrocarbons, the resulting intermediate product mix is often described as "synthetic crude oil" (syncrude). Such syncrudes can be readily refined into desirable distillate fuel fractions such as kerosene, naphtha, and heating oil using conventional petroleum refining techniques. The kerosene can be further refined or blended into high quality diesel or jet fuel products while the naphtha can be further refined into gasoline or used as a thermal cracking feedstock for olefins production. Catalysts for FTS were first developed in the early 1900s. Following the discovery by Sabatier and Senderens in 1902 that CO could be hydrogenated over Co, Fe, and Ni catalysts to methane, BASF reported the production of liquids over Co catalysts in 1913. Fischer and Tropsch later reported production of hydrocarbons over alkalized iron in 1923. Much of the early catalyst and process development continued in Germany during the 1930s and 1940s. During World War II, coal based FT production played an important role providing the transportation fuel requirements of the German war effort because of insufficient access to crude oil resources. This production was discontinued when the war ended.

Gas to liquids or GTL is a refinery process to convert natural gas or other gaseous hydrocarbons into longer-chain hydrocarbons. Methane-rich gases are converted into liquid fuels either via direct conversion or via syngas as an intermediate, for example using the Fischer Tropsch process. Using such processes, refineries can convert some of their gaseous waste products into valuable fuel oils, which can be sold as or blended only with Diesel fuel.

The processes of conversion of natural gas into liquid products can be divided into two types: direct conversion and indirect conversion.

The direct conversion processes utilize catalysts and specific synthesis routes to chemically transform the molecules of methane, the main component of natural gas, into more complex chained substances with heavier molecules. The liquid products that can be obtained include the alcohols (mainly methanol), the olefins (ethylene and acetylene) and the aromatics (benzene, toluene and naphthalene). However, the high stability of the methane molecule creates a series of technical problems to make the chemical reactions involved viable. Thus, the research and development efforts of the direct conversion processes are focused on the improvement of the catalysts in the elucidation of the mechanisms of reaction and the development of new equipment.

The indirect route is technically easier than that of the direct conversion processes. The technologies of the processes involved have been better studied and several pilot and commercial plants are already in operation. The processes of indirect conversion are characterized by a preliminary stage of transformation of natural gas into synthesis gas – syngas - (a mixture of carbon monoxide - CO and hydrogen - H2). After being produced, the syngas is converted into liquid hydrocarbon through the Fischer-Tropsch Process (FT). The production of hydrocarbons by this means does not directly result in products of commercial interest. To do so an additional step is needed, the hydro-processing, in which the heavy molecular hydrocarbons are decomposed into smaller molecules according to the products that one wishes to attain (naphtha, Diesel oil, lubricant oil, paraffin and others). Therefore, the conversion of natural gas into hydrocarbons can be better characterized by three distinct types:

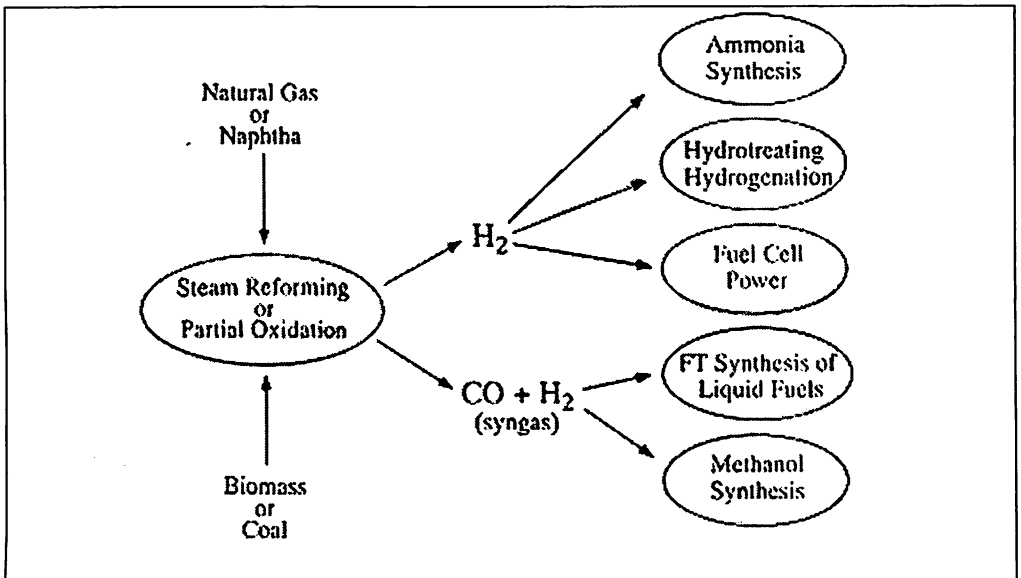
1) Generation of syngas,
2) Conversion of syngas and
3) Hydro-processing

Although the three stages of the GTL process by indirect means have been individually well studied and are available for commercialization, a optimal combination that permits the reductions of costs of the commercial production plants still doesn't exist. In addition to the technical aspects, this optimal combination must consider the size of the plants, the availability of energy and water sources, the volume of natural gas available in the fields to be explored and other factors. Due to its potential, the efforts to innovate carried out by research institutes, universities and mainly by companies in the sector are concentrated in the processes of conversion by indirect route. The search for the reduction of capital costs for the implementation of the processing plants that would permit an improved economic viability of the projects is the main objective of the innovation efforts.

1.6.1 SYNGAS GENERATION

The production of syngas from natural gas is an important process step from the technical as well as economic point of view. More than half of the capital cost of the process relates to the syn gas manufacturing unit.

This step converts natural gas which mainly contains methane into Synthesis Gas, also known as Syn Gas (a mixture of CO and H_2)



Processes based on production of H_2 and synthesis gas

1.5 process based on syngas and hydrogen

Synthesis gas ("syngas") needed for Fischer-Tropsch is produced via a combination of partial oxidation (POX) of methane and steam methane reforming (SMR):

Partial oxidation: $CH_4 + 1/2\ O_2 \rightarrow CO + 2\ H_2$ (exothermic)

Steam reforming: $CH_4 + H_2O \rightarrow CO + 3\ H_2$ (endothermic)

Other possible reactions:

$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$ (combustion)

$CH_4 + CO_2 \rightarrow 2\ CO + 2\ H_2$ (dry reforming)

$CO + H_2O \rightarrow CO_2 + H_2$ (water gas shift)

Table 1: **Reactions occurring in Syn Gas Generator**

REACTION MECHANISM	**REACTION CHEMISTRY**	**HYDROGEN TO CO RATIO, molar**	**HEAT OF REACTION KJ/mol**
Steam Reforming	$CH_4 + H_2O \rightarrow CO + 3 H_2$	3	-206.1
Partial Oxidation	$2 CH_4 + O_2 \rightarrow 2CO + 4 H_2$	2	38.0
Water Gas Shift Reaction	$CO + H_2O \rightarrow CO_2 + H_2$	-	41.15
CO2 Reforming	$CH_4 + CO_2 \rightarrow 2CO + 2 H_2$	1	-247.3
Carbon Deposition	$CH_4 \rightarrow 2 H_2 + C$	-	-74.82
Carbon Conversion	$C + H_2O \rightarrow CO + H_2$	1	-131.3
Carbon Deposition	$2CO \rightarrow CO_2 + C$	-	173.3

SyngasTechnologies

- **Auto thermal Reforming (Haldor Topsoe – Sasol, ExxonMobil)**
  Natural Gas, Steam and Oxygen
  Combines POX and SMR reactions in one reactor
- **Partial Oxidation (Shell SGP)**
  Natural Gas and Oxygen
- **Catalytic Partial Oxidation (ConocoPhillips COPox^{TM})**
  Natural Gas and Oxygen
- **Steam Methane Reforming (various)**
  Natural Gas and Steam
  Primarily used to manufacture Hydrogen

The technologies for Syn Gas generation can be divided into three categories. The first category is where Steam Reforming reactions are carried out predominantly. In the second category, partial oxidation reactions are carried out. In the third category, blends of these reactions are achieved to meet the product characteristics. As can be seen from Fischer Tropsch reaction mechanism, the ratio of hydrogen to CO is in syn gas is an important process criterion. The ideal Hydrogen to CO ratio for Fischer Tropsch synthesis is in the range of 2.0 to 2.3 depending upon required product composition. Each technology option produces inherently different hydrogen to Co ratio.

Thus for competing technologies, H_2 / CO Ratio product ratio is typically the most important process parameter.

STEAM REFORMING

This essentially consists of a fired heater containing catalyst (normally Nickel based) filled tubes. Steam is added to the Natural Gas feedstock. The mixture is preheated to about 550°C and passed through the catalyst tubes. The catalyst converts the gas mixture into Hydrogen, CO and CO2. the reactiopn is endothermic and heat is supplied by external burning of Natural gas. The reaction mixture exits the reformer at about 900°C. Typical operating pressure is 25 bar.

However the process has some inherent limitations:

- Its highly energy intensive
- Poor CO selectivity (< 60%)
- Incomplete C1 Conversion
- High H_2 / CO ratio (> 3)
- High capital cost due to low co productivity

STEAM REFORMING COMBINED WITH OXYGEN SECONDARY REFORMING

This essentially consists of an SMR followed by an oxygen secondary reformer. The Oxygen reformer is a refractory lined vessel containing catalyst and a burner. Products from SMR are fed to the top of oxygen reformer where it is mixed with oxygen fed through the burner. Partial oxidation reactions occur in the combustion zone below the burner. The mixture is then passed through catalyst bed for further reforming.

The limitations are:

- Loss of catalyst component in gas phase
- Conversion/ selectivity per pass limited
- Ethylene yield >40% desired for the reaction to be industrially viable
- Low current interest
- Investment in Oxygen plant

AUTOTHERMAL REFORMING

It is similar to an oxygen secondary reformer except that it does not receive feed from SMR. It is fed directly with steam/ natural gas mixture that is fed directly with oxygen from a burner located near the vessel's top. Partial oxidation reactions occur in a combustion zone just below the burner. The mixture then passes through a catalyst bed where reforming reactions occur. The gas exits at 1000°C which can be integrated to provide heat for the endothermic SMR, resulting in a heat exchanger type SMR unit vis-a vis conventional gas fired unit.

The limitations include:

- High temperature operation
- High thermally stable catalyst required
- Catalyst deactivation by thermal shock and solid Carbon deposition
- Low CO selectivity

PARTIAL OXIDATION

It is similar to autothermal except that it does not contain catalyst. Natural gas is fed directly and is mixed with Oxygen from a burner located near vessel top. Partial oxidation and reforming reactions occur in the combustion zone below the burner. Gas exits at 1400°C.

The following provides the natural gas and Oxygen requirement for production of 100 SM^3 CO product at full CO_2 recycle.

Table 2: natural gas and Oxygen requirement for production

	SMR	**SMR + O2**	**Autothermal**	**POX**
Net natural gas, MMKcal	0.649	0.644	0.473	0.453
Oxygen, kg	0	22.7	22.7	94.0

It can be seen that Autothermal and Partial Oxidation need 27% lower natural gas. This is because most of the oxygen in the feed reacts with Carbon present in Natural gas to produce CO while in SMR; a part of Natural gas is burnt completely to CO2 to meet endothermic heat of reaction. In addition, during Partial oxidation, heat is supplied directly to the feed while in SMR indirect heat transfer requires a temperature difference to be maintained between furnace tubes and furnace box temperature.

1.6.2 FISCHER TROPSCH SYNTHESIS

There has been considerable interest in recent times surrounding gas to liquids conversion technology. This has centred on Fischer-Tropsch technology, but other technologies such as methanol and DME have also seen a renewed interest. The Fischer Tropsch conversion upgrades Synthesis Gas into heavy hydrocarbons by a chain growth process using Hydrogenation route. The reaction was discovered in the year 1923 in Germany and was exploited extensively during World War II. The length of the chain and product characteristics is detemined by catalytic selectivity and the reaction conditions.

The following stoichiometric relationship represents the fundamental aspects

$$(n)\,CO \quad + \quad (2n)H_2 \quad \rightarrow \quad (\text{--}CH2\text{--})n \quad + \quad (n)H_2O \quad \text{(very exothermic)}$$

$$(2n)\,CO \; + \; (n)\,H_2 \; \rightarrow \; (\text{--}CH2\text{--})n \; + \; (n)\,CO_2$$

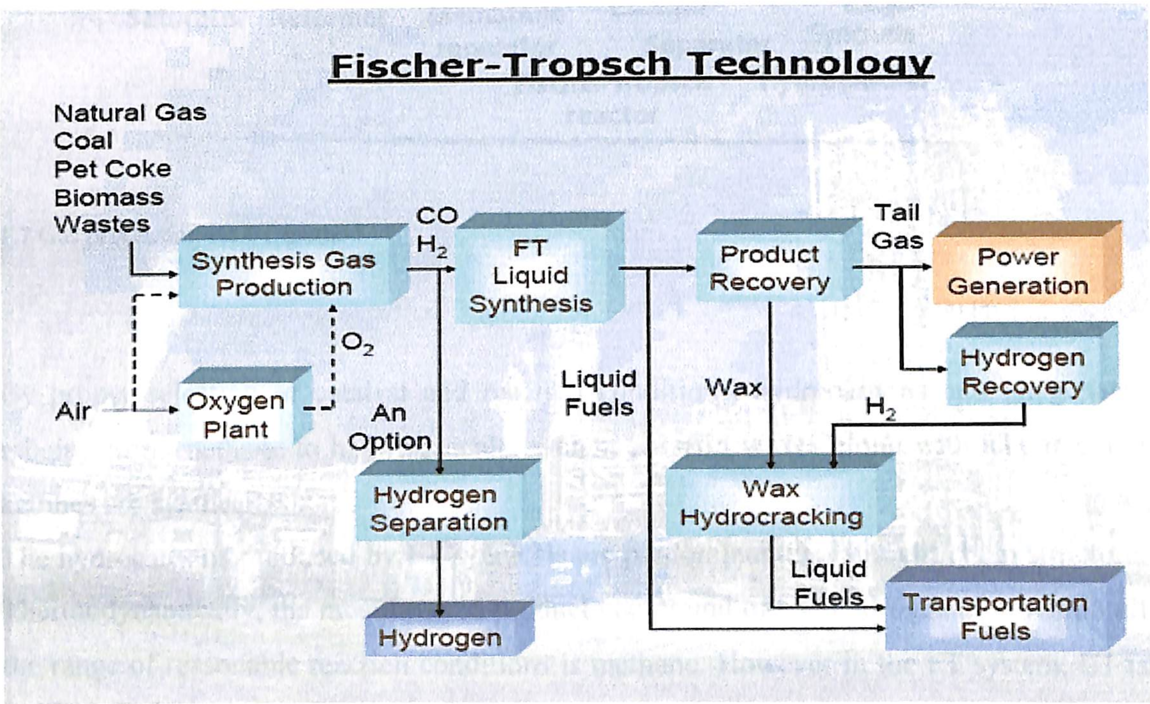
$$(2n-1)\,CO + (n+1)\,H_2 \rightarrow C\,n\;H_2n{+}1OH + (n-1)\,CO_2$$

$$(n)\,CO + (2n)\,H_2 \;\rightarrow H\,(\text{--}CH2\text{--})n\,OH\; + (n-1)\,H_2O$$

Competes with methanation (reverse steam reforming) which is even more exothermic:

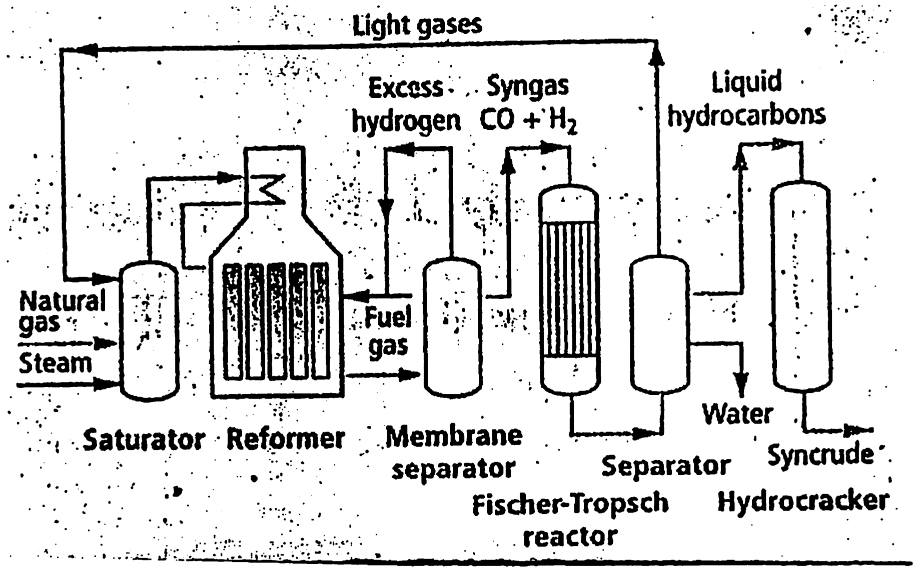
$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

To promote FT over methanation reaction is run at very low temperatures: 220-350 ^{0}C, 2-3 MPa



1.6 F-T process

Byproducts from FT synthesis are methane, Carbon dioxide and alcohol, which are separated in downstream section.



1.7 Gas processing via FT method

By proper selection of catalyst and reaction conditions, hydrocarbons and oxygenates rabging from methane to high molecular weight paraffin waxes along with alcohols and ketones are synthesized.

The hydrocarbons produced by FT synthesis are predominantly a straight chain structure. Thermodynamically, the most favored product compound of CO hydrogenation within all the range of reasonable reaction conditions is methane. However in the FT system, C1 is not easily released from the surface to yield methane but undergo chain prolongation reactions with hydrocarbon species, which are strongly chemisorbed on the surface. The prolongation steps continue until formed hydrocarbon leave the catalyst surface. Thus, the essential principle of the FT system is to slow down the chemi-desorption reactions. The inhibition of chemi-desorption reaction is caused by CO, which is known to be strongly adsorbed on the FT catalyst.

The Reaction Mechanism can be shown thus:

FORMATION

$CO_g \Rightarrow CO_s \Rightarrow C_s + O_s$; S – surface

$C_s + H_s \Rightarrow CH_s \longrightarrow CH2_s \longrightarrow CH3_s \longrightarrow CH4_s$

$CH3_s + CHx_s \longrightarrow CH3\ CHx_s$

Termination and desorption

$CH_3C_nH_{2n}\ CH_x + (3\text{-}X)\ H \longrightarrow CH_3C_nH_{2n}\ CH_3$

$CH_3C_nH_{2n}\ CH_2\ CH_x + (1\text{-}X)\ H \longrightarrow CH_3C_nH_{2n}\ CH{=}\ CH_2$

Reaction mechanism in FT reactor

During the chain growth reaction, water, produced in both partial oxidation and the Fischer Tropsch reaction, inhibits the FT reaction. Thus it may be necessary in certain cases to introduce intermediate separation step to remove process watr, wax and heavy hydrocarbons before a second stage FT reactor. In the first stage Ft reactor, the inhibition of the reaction by steam (5% of the syn gas) is carried out to avoid a thermal runaway. Introduction of inert gases such as Nitrogen or CO2 does not reduce the hydrocarbon production.

FISCHER TROPSCH REACTORS

The high exothermic heat of reaction (40 kcal per gmol of CO reacted) governs the design of the reactor used in the process. The heat removal from the reactor and maintaining the isothermal conditions within the fluid phase are the most important process factors in designof reactor. The other factors are Pressure drop, Residence time, regeneration of catalyst, catalyst behaviour, axial mixing etc.There are essentially four types of reactors available

- Fixed bed reactor
- Circulating Fluidised Bed Reactor

- Fixed Fluidised Bed Reactor
- Slurry Phase Reactor

Table 3: Fischer Tropsch Reactors

CHARACTERISTICS	**FIXED BED**	**CIRCULATING FLUIDISED BED**	**FIXED FLUIDISED BED**	**SLURRY REACTOR**
Heat Removal	Slow	Medium to High	High	High
Pressure Drop	Small	Medium	High	Medium to High
Max reactor Diameter as limited by heat removal	8—10 cm	No limitation	No limitation	No limitation
Regeneration of catalyst	Interruption of Bed required	Continuous regeneration	Possible to carry out continuous regeneration of part of the catalyst	Possible to carry out continuous regeneration of part of the catalyst
Typical Products	Heavy hydrocarbons and paraffin waxes	Low molecular weight gaseous hydrocarbons and gasoline	Low molecular weight gaseous hydrocarbons and gasoline	Middle distillate and high carbon number linear waxes
Commercial Status	Sasol, Shell, Syntroleum	Sasol	Sasol	Sasol, Exxon, Rantech

1.7 FTS Product Distribution

The hydrocarbon synthesis reaction involved in FTS maybe regarded as analogous to a polymerization reaction. An essential characteristic of catalyst applied to FT diesel production therefore is the ability to catalyse chain propagation versus chain termination steps. The specific selectivity for a particular hydrocarbon and the overall product distribution may generally be described by a chain polymerization kinetic model involving the step wise addition of one carbon on another on the growing chain. This model has been ascribed to Anderson, Schultz, and Floryand is commonly refered to as Anderson-schultz-Flory (ASF) model.the ASF product distribution may be mathematically represented as the following equation:

$Wn/n= (1-\alpha)\ 2\ \alpha\ (n-1)$

Where

n = number of carbon atoms in hydrogen molecule

Wn = weight fraction of product containing carbon atoms

α = chain growth propagation probability

Higher value of generally correspond with increasingly heavier hydrocarbon selectivity as desired for FT diesel production, as determined by the choice of reaction condition and catalyst. Value of increase with decrease in reactor tempetarture as would be expected for LTFT. Since value of also increase wid decreasing H2/CO ratio and increasing reactor pressure, such condition would also tend to favor FT diesel production relative to lighter hydrocarbon product distributions.

The following tabulation sumerrizes the FT crude product weight fraction for two different value chain growth probability:

Table 4: FT crude product crude fraction

Description	**Carbon**	**Wt %**	**Wt %**
Gas	$C_1 - C_4$	27.2	2.5
Naptha	$C_1 - C_9$	35.9	6.7
Diesel	$C_{10} - C_{19}$	30.1	18.5
Soft wax	$C_{20} - C_{34}$	6.4	27.3
Hard wax	C_{35}+	0.4	45.0

Table 5: Typical product slate observed for 50,000 B/D GTL unit

-------------------1,000 b/d -------------------

	Without hydro cracking	**With hydro cracking**	**Comments**
LPG	1	2	• Similar to other plant (LNG, refinery) LPG • Can be coprocessed and marketed with them.
Naphtha	9	13	• Straight chain paraffinic • Near Zero sulphur • Preferred use: steam cracker feed
Diesel	25	35	• High cetane • Near Zero sulfur • Low density • Low aromatics
Lubes	15	<1	• High grade • Low volatility • Low pour point • Low viscosity • Low sulphur
Wax	5	<1	• High quality

1.8 Existing Commercial Processes

Several GTL technologies are available for commercial license offer by various hydrocarbon industries e.g Sasol, Exxom-Mobil, Statoil, Shell, Syntorleum, etc. which are shown Table 6.

Table 6: Commercial – scale GTL plants

Company	**Location**	**Size (b/d)**	**Comments**
EXISTING:			
Sasol I	Sasol burg, South Africa	5,600	1955; Sasol technology Feed: coal
Sasol II/III	Secunda, South Africa	124,000	1955/1980; light olefins and gasoline; Sasol technology
Petro S/A (formerly Mossage)	Mossel bay, south Africa	22,500	1991; gasoline and diesel; Sasol technology Feed; coal
Shell MDS	Bintulu, Malaysia	14,000	1993; waxes, chemicals, diesel; re4cently revamped; SMDS technology Feed; natural gas
UNDER CONSTRUCTION:			
Sasol Chevron Texaco	Escravos, Nigeria	34,000	2006; completion; FW; $1.2 billion Feed; natural gas
Sasol Chevron QP	Ras Laffan, Qatar (“Oryx GTL)	33,700	2006: completion; technip-Co flexip; $ 850 million; studying increase to 100,000 b/d by 2009 Feed; natural gas

1.8.1 Sasol

Sasol is a synfuel technology supplier established to provide petroleum products in coal-rich but oil-poor South Africa. The firm has built a series of Fischer-Tropsch coal-to-oil plants, and is one of the world's most experienced synthetic fuels organizations and now marketing a natural-gas-to-oil technology. It has developed the world's largest synthetic fuel project, the Moss gas complex at Mossel Bay in South Africa that was commissioned in 1993 and produces a small volume of 25 000 barrels per day. To increase the proportion of higher molecular weight hydrocarbons, Its products are more olefinic than those from the fixed bed reactors and are hydrogenated to straight chain paraffin's. Its Slurry Phase Distillate converts natural gas into liquid fuels, the resultant diesel is suitable as a premium blending component for standard diesel grades from conventional crude oil refineries. The other technology uses the Sasol Advanced Synthol (SAS) reactor to produce mainly light olefins and gasoline fractions. Sasol has developed high performance cobalt-based and iron based catalysts for these processes.

1.8.2 Statoil

With its large gas reserves, Norway's Statoil has been developing catalysts and process reactors for an F-T process to produce middle distillates from natural gas. The Statoil process employs a three-phase slurry type reactor in which syngas is fed to a suspension of catalyst particles in a hydrocarbon slurry which is a product of the process itself. The process continues to be challenged by catalyst performance and the ability to continuously extract the liquid product.

1.8..3 Shell

Shell has carried out R&D since the late 1940s on the conversion of natural gas, leading to the development of the Shell Middle Distillate Synthesis (SMDS) route, a modified F-T process. But unlike other F-T synthesis routes aimed at gasoline as the principal product, SMDS focuses on maximizing yields of middle distillates, notably kerosene and gas oil. The process consists of three steps: the production of syngas with a H2: CO ratio of 2:1; syngas conversion to high molecular weight hydrocarbons via F-T using a high performance catalyst; and hydrocracking and hydroisomerisation to maximize the middle distillate yield. The products are highly paraffinic and free of nitrogen and sulfur.

1.8.4 Exxon-Mobil

Exxon has developed a commercial F-T system from natural gas feedstock. Exxon claims its slurry design reactor and proprietary catalyst systems result in high productivity and selectivity along with significant economy of scale benefits. Exxon employs a three-step process: fluid bed synthesis gas generation by catalytic partial oxidation; slurry phase F-T synthesis; and fixed bed product upgrade by hydroisomerisation. The process can be adjusted to produce a range of products. More recently, Exxon has developed a new chemical method based on the Fischer-Tropsch process, to synthesize diesel fuel from natural gas. Exxon claims better catalysts and improved oxygen-extraction technologies have reduced the capital cost of the process, and is actively marketing the process internationally.

1.8.5 Syntroleum

The Syntroleum Corporation of the USA is marketing an alternative natural-gas-to-diesel technology based on the F-T process. It is claimed to be competitive as it has a lower capital cost due to the redesign of the reactor; using an air-based autothermal reforming process instead of oxygen for synthesis gas preparation to eliminate the significant capital expense of an air separation plant; and high yields using their catalyst. It claims to be able to produce synthetic crude at around $20 per bbl. The syncrude can be further subjected to hydro-cracking and fractionation to produce a diesel/naphtha/kerosene range at the user's discretion.

The appeal of the liquid products, which would be straight chain hydrocarbons, is that they would be free from sulfur, aromatics and metals, that can help refiners to meet new guidelines for very low sulfur fuels and general environmental standards. The naphtha however would be low in octane and requires isomerising or reforming if used as a fuel but represents a good petrochemical feedstock. The diesel will have a very high cetane number and be a premium blending product.

1.8.6 **Rentech**

Rentech of the Colorado USA, has been developing an F-T process using molten wax slurry reactor and precipitated iron catalyst to convert gases and solid carbon-bearing material into straight chain hydrocarbon liquids. In their process, long straight chain hydrocarbons are drawn off as a liquid heavy wax while the shorter chain hydrocarbons are withdrawn as overhead vapours and condensed to soft wax, diesel fuel and naphtha. It is promoted as suitable for remote and associated gas fields as well as sub-pipeline quality gas.

The integrated GTL technology has a number of features that make it very attractive to oil and gas operating companies and these are:

—High gas utilization and carbon conversion efficiency

—High thermal efficiency and low energy usage

—Simple water balance and low waste water emissions

—Process flexibility for varying gas feed conditions

—Small plant footprint suitable for remote site installation

—Integrated flow sheet including offsite and utility systems, and modular construction with a short project schedule, with lower capital cost and fast payback.

***Part* - B**

Experimental research at IIP

Indian Institute of Petroleum, one of the constituent laboratories of the Council of Scientific & Industrial Research (CSIR), is committed to develop into an internationally reputed R & D centre of excellence for providing globally competitive technologies and services for hydrocarbon and related industries. This is achieved through total quality management and by anticipating and exceeding the expectations of customers through innovation, team work and commitment.

The decade of the 1990s witnessed the return of the Fischer-Tropsch Process to the centre of attention in the world petroleum and natural gas industry. This technology, developed in the 1920s and put into large-scale operation by Germany, was abandoned due to the low prices of petroleum and the development of abundant markets for natural gas. Nevertheless, a radical transformation in the sphere of the application of this technology has opened the door for the renovation of the GTL technology. The increase of stranded gas reserves and the development of niches in the market for synthetic fuel, due to environmental legislation, prompted the renewal of interest of petroleum companies in this technology. The development of several projects for the construction of GTL plants in the sphere of application can be observed, as part of a truly technological rush to seek the development of more efficient and cheaper processes.

One such pilot plant has been set up in the IIP, which basically aims at producing Middle Distillates using CO catalyst in a Fixed Bed Reactor. They have been working to get best possible results from the catalysts available and research is still going on for product enhancement.

The scientists there seek to obtain a slurry bed reactor that will be commissioned in 6 to 10 months.

2.1.1 **Apparatus and reaction procedure**

Experiments carried out and reported in earlier sections were aimed towards the preparation of Co metal promoted ZrO2 by different routes, physico-chemical characterization of these materials and screening of its catalytic activity performance against syngas conversion in micro-flow reactor. The studies were aimed to (i) to check conversion levels (ii) to selectivity to middle distillates (iii) fall in activity of the catalyst with time on stream.

2.1.2 **High-pressure Micro Reactor Unit**

It is a conventional fixed bed, isothermal continuous, down flow, stand-alone, high-pressure micro reactor. The Schematic flow diagram of micro reactor is shown in Fig 1. On–line IR gas analyzer (Fisher Rosemount, Germany) was used to detect the amount of CO, CO_2 produced during in-situ regeneration of coked catalyst and to determine the wt % of coke laid down on the catalyst after reaction.

5.1.2. **Loading of the Catalyst**

About 18 CC volume of FT catalyst (13.2g) in extrudate form of 1.5 to 2mm diameter is loaded in middle zone of the reactor with α - alumina as a diluent. The catalyst to the alumina was in the ratio 1:2.5 by volume. Pre and post heating zone were filled with α - alumina. The loading pattern of the catalyst was showed in Fig 2.

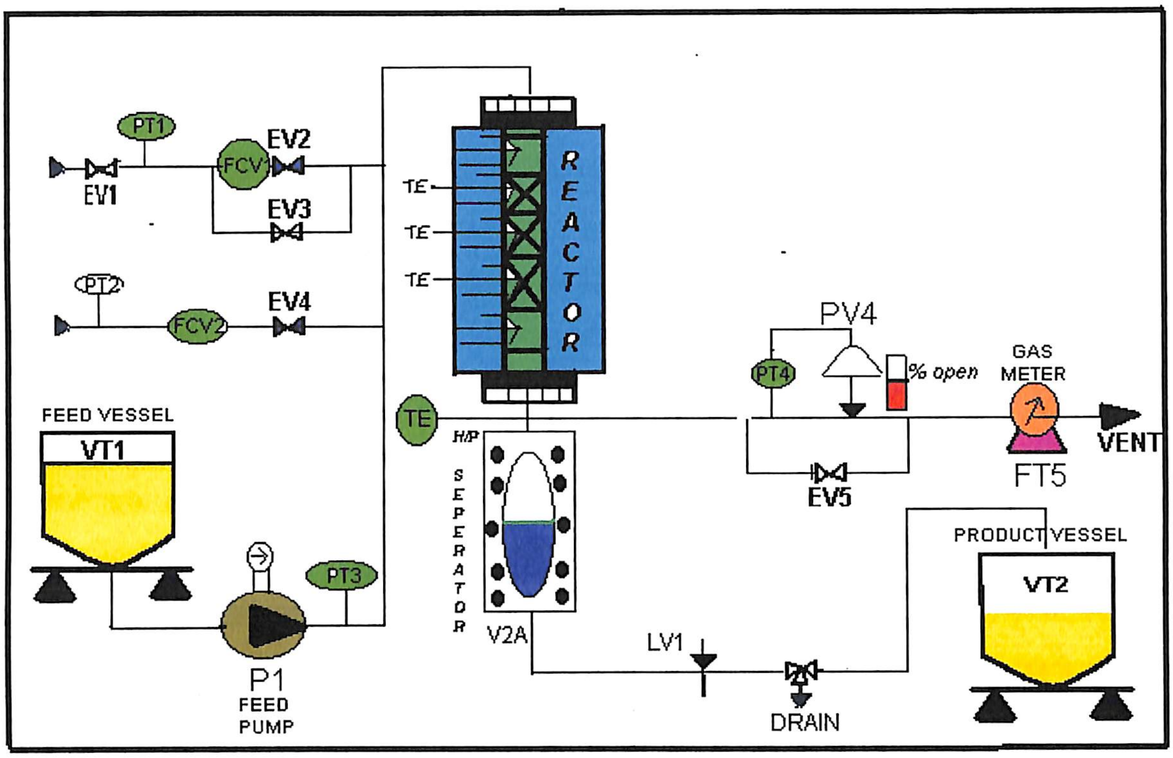


Fig 2.1 Schematic flow diagram of high-pressure microreactor.

2.1.3 **Pressure Testing in Unit**

After loading of the catalyst, the reactor was properly connected to xytel high-pressure micro reactor unit. The entire system was flushed with UHP nitrogen gas and later system was pressurized to 30 kg/cm^2 and was kept for 10 hrs to note fall in the pressure. No pressure fall was observed in this period indicate the leak proofness of the system.

2.1.4 **Start up Procedure**

Initially the system pressure is reduced to desired pressure i.e., 20 Kg/cm^2 then reactor was heated up to desired temperature @60^0C /hr under Hydrogen flow @ 167 CC/min. The temperature of catalyst bed, pre and post-heating zone was measured by mean of thermocouples inserted in the thermo well inside the reactor. Prior to the test runs, FT catalyst is reduced at 450^0 C, 1bar pressure under H_2 gas flow of 150 CC/min for 48 hours. Later it is cooled down to desired reaction temperature in H_2 flow. Three independently regulated temperature controllers controlled the temperature of reaction zone, pre and post-heating zone. The temperature of the furnace was controlled with in range of ± 10^0C. After attaining the desired process conditions, the system was stabilized for 1 hr. To the hydrogen stream CO gas introduced by MFC (mass flow controller) with a rate according to the GHSV (83 CC/min). The effluents from the reactor are cooled in water cooler and separated in high-pressure separator. Liquid products from HP separator are collected in atmospheric product tank and gases separated from HP separator and product tank are vented out through wet gas meter.

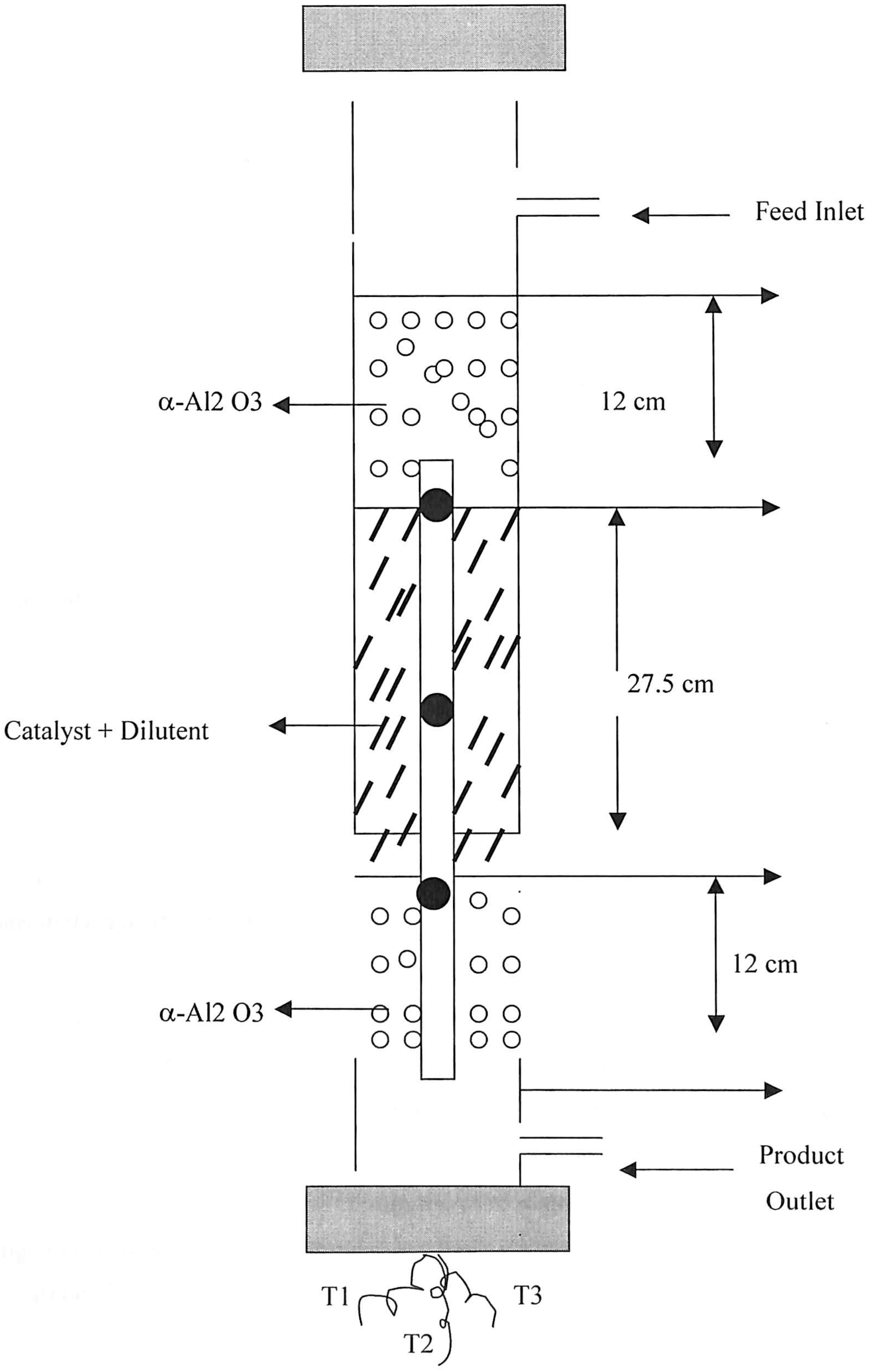


Fig 2. 2 Loading pattern of catalyst in micro-reactor

2.1.5 **Operating Conditions**

The experiments were conducted to investigate the effect of following process parameters:

- Temperature: 220-2000^0 C
- Pressure: 20 kg/Cm^2
- GHSV: 500-300 hr-1
- H_2/CO: 2

In each cycle run after syn gas flow for 50 hours on stream, the coke lay down on catalyst was burnt off in the presence of air under nitrogen atmosphere. The next cycle of reaction has been carried out on this regenerated catalyst.

2.1.6 **Regeneration Procedure**

With increasing time on stream, the FT catalyst was deactivated due to coke laid down. To regains its original activity, the catalyst was regenerated in situ by the following procedure. After completing the material balance (MB) experiments, the unit pressure was kept at 5.0 bar with a nitrogen flow @36 lit/hr. The temperature was increased to 250^{0}C @ 60^{0}C/hr. Then the air was introduced and increased in steps to control the exothermicity during the coke burn. Initially it was 5.0 lit/hr then 10 lit/hr and finally 25 lit/hr. At each air dose, half an hour stay was kept to watch the reducing trend of CO, CO_2 in IR analyzer. During the incremental injection of air, if there is any temperature rise, airflow was stopped and N_2 flow was increased. Then the temperature was increased upto 350^{0}C @ 50^{0}C/hr under the same flow of air and nitrogen. When the decreasing trend of CO, CO_2 was monitored by the IR analyzer, the temperature was increased upto 400^{0}C @300C/hr and the following conditions were maintained for 3 hrs till the complete burning coke took place.

Temperature	:	400^{0}C
Pressure	:	5.0 kg/cm^2
Nitrogen Flow	:	36.0 lit/hr
Air flow	:	25.0 lit/hr

After complete removal of coke, as confirmed by negative to Ba (OH) $_4$ test, the reactor temperature was cool down up to 250^{0}C then nitrogen flow was increased to 50 lit/hr. At 400^{0}C the air injection was stopped and the unit pressure was reduced to 0.5 kg/cm^2 and again increased to 5.0 bars. This was repeated 3 times to remove all concentration of air from unit. Unit was pressurized to 20 kg/cm^2 with nitrogen and it is kept ready for another cycle of reaction.

2.1.7. **Product Analysis**

The products obtained as C_5+ in liquid and C_1-C_5 hydrocarbons in gas product were analyzed by gas chromatography. The ex-reactor yields of the products were calculated based on weight of feed. The gas products were analyzed by using Hewlett Packard gas chromato graph model 5730A fitted with a squalene column. For liquids, as separation of all the components of such a long boiling range was not possible using a single column, simulative distillation Gas chromatograph is used for the quantitative analysis of the liquid product. In addition to the above diesel characteristics of liquid product is also carried out as per BIS standards.

2.1.8. **Results and Discussions**

At higher temperatures and higher space velocities no liquid product was observed for 40 hours. Later process conditions were optimized in order to get liquid product. Preliminary catalyst evaluation studies indicated encouraging results, which are shown in Table 7. About 33 ml C_5+ liquid hydrocarbon product is obtained along with 97 ml water as by-product on 13-hour process time at particular operating conditions.

Simulated distillation results show that 97.5% is liquid boiling up to 370^{0}C and exhibits 0.7266 density at 150C. Further more the estimated Cetane Index of C_5+ liquid is 71 and it contains 99 wt% non-aromatic hydrocarbons as revealed by SFC analysis. The above typical product characteristics indicated that the obtained C_5+ liquid hydrocarbon product is much better than the middle distillates available in the market due to zero sulfur and high cetane of FT fuels

Table 7: Product pattern obtained over Co based Alumina supported catalyst

Temp (^{0}C)	220	210	200
GHSV	500	350	350
TOS in hrs	13	35	13
CO	0.6	1.2	3.3
CH_4	75.8	80.5	41.4
C_5+ (CC)	-	-	33
H_2O	-	-	57
Density15^{0}C			0.7266
IBP^{0}C			53.5^{0}C
97.7%			370^{0}C
FBP			434^{0}C
Cetane No.			70.98

***Part* - C**

3.0 ECONOMIC ISSUES

The Gas-to-Liquid (GTL) industry is witnessing a monotonic growth that is expected to increase the liquid fuel production from currently 51,000 bbl/day to approximately 1.3 millions bbl/day by year 2015. GTL appears to be a viable and promising solution for the future of alternative and cleaner energy technologies. Recent advances in GTL technology have lowered the cost to the level where GTL plants are profitable at crude oil prices of $23/bbl, for a 10% rate of return, and an annual operating expenditure (OPEX) that is 7% of a $40,000 per-barrel-a-day capital expenditure (CAPEX). Technology advancements, reflected mainly in the reduction of the capital costs are likely to lower this price to about $11.5 for a 10% rate of return and a 7% OPEX of a $20,000 PBD CAPEX. At a current CAPEX value of approximately $35,714 BPD for a number of oil companies, crude oil price lower than $20/bbl would place this particular GTL venture in an area of economic uncertainty. The expansion of the GTL industry is likely to place the GTL industry in direct competition with the liquefied natural gas (LNG) industry for access to natural gas supply. By year 2015, GTL units are likely to consume about 4.75 tcf/year and LNG units will consume approximately 7.25 tcf/year. Together, this represents a fifty-year consumption of 600 tcf from the world natural gas reserves. This fifty-year consumption of both GTL and LNG plants represents only 20% of the proven stranded gas reserves that currently stand at about 3006 tcf. The global GTL industry will consume about 8% of the world stranded natural gas reserves, or 4% of the world proven natural gas reserves, for the same 50-year production-period. These statistics indicate that there are plenty of gas resources for the continuity of both the GTL and the LNG industries in the long term future.

The GTL technology involves the conversion of natural gas into liquids, via Fischer-Tropsch synthesis. These liquids may consist of petroleum distillate fuels and oxygenates like methanol. Fischer-Tropsch synthesis (FTS) entails the synthesis of hydrocarbons and oxygenates from synthesis gas (syngas) consisting primarily of a mixture of CO + H2. The hydrocarbons produced may include olefins such as ethylene and propylene, and an extremely wide range of saturated hydrocarbons that may even include long "straight-chain" paraffinic waxes. The resulting intermediate product mix of paraffinic hydrocarbons is often described as "synthetic crude oil" (syncrude). Syncrudes can be readily refined into desirable distillate fuel fractions such as kerosene, naphtha, and heating oil using conventional petroleum refining techniques. The kerosene can be further refined or blended into high quality diesel or jet fuel products while the naphtha can be further refined into gasoline or used as a thermal cracking feedstock for olefins production. The oxygenated materials that are produced consist primarily of alcohols such as methanol, and ketones such as acetone. Methanol is another GTL derivative. Methanol can be used directly or blended with other petroleum products for use as a clean burning transportation fuel. It is also an intermediate chemical used to produce formaldehyde, dimethyl ether (DME), methyl tertbutyl ether (MTBE), acetic acid, and olefins. Currently, the majority of methanol is synthesized from syngas. Hydrogen, used in the production of fertilizers (ammonia), is another product from Syngas. Several factors have resulted in an increased interest in GTL. These include: the need to develop and exploit additional energy resources, the existence of large reserves of stranded natural gas, and the environmental drivers consisting of f a movement to reduce flaring, and the commitment of a number of countries to auto-emission regulations. Natural gas is supplied from a market of large gas reservoirs geographically spread but linked to consumers by options as gas pipelines, LNG, and by large tankers carrying liquid or solid products manufactured from natural gas, as well as through gas-by-wire conversion. The GTL technology provides another option to monetize gas, and creates new markets for GTL diesel. Diesel oil consists of hydrocarbons having carbon numbers predominantly in the range of C9-C20, and boiling in the range of approximately 163-357 oC. Diesel fuels are classified as middle distillates and are more dense than gasoline; thus, providing more energy per unit volume than gasoline. Diesel fuel is intended for compression ignition engines. Diesel engines are more expensive to build than gasoline-fueled engines. Their advantage lies in their use of a relatively inexpensive fuel, and in their long life and low maintenance costs. The major current uses of diesel engines are in commercial trucks, private automobiles, ships and boats, railroad locomotives, and industrial engines. Diesel engines used to be largely stigmatized because motorists regarded this fuel as too dirty, odorous and inferior. Diesel-fuelled compression-ignition engines in passenger cars were also noisier and less potent than their gasoline-fuelled, spark ignition counterparts.

Today's new-generation passenger car compression ignition engines are much more improved than those built twenty years ago. Diesel-powered cars are quieter, smoother, cleaner, and feature an engine's superior fuel efficiency. A typical diesel-fuelled car built today can travel up to 60 per cent further than its gasoline fuelled counterpart with the same size fuel tank and driving under the same conditions.4 GTL diesel produced through FTS process has virtually no sulfur (less than five parts per million; 5ppm), a high cetane number (greater than 70) and a notably low aromatic content (less than 1%). These properties enable significant reductions in tailpipe emissions generated by vehicles powered by compression-ignition engines. GTL diesel has a significant combustion performance advantage because its cetane value is much higher than that of conventional diesel fuels. The higher cetane number not only decreases tailpipe emissions, but also allows for easier engine starting in cold conditions. GTL diesel is also significantly more efficient when comparing its use in a compression ignition car with that of gasoline in a spark ignition counterpart. Besides reduced tailpipe emissions, the ultra-low sulfur content of GTL diesel also offers better engine wear, causes lubricants to have greater longevity, causes fewer deposits to form inside the engine and reduces the exhaust odor,, and reduces engine noise.

3.1 Status of the World Natural Gas Reserves

The proven world natural gas reserves are abundant, and are growing at a faster rate than proven oil reserves. The world natural gas reserves are estimated at about 6012 tcf. Russia, Iran, and Qatar combined hold natural gas reserves representing about 54% percent of the world total (Figure 3.1). The current world natural gas reserves represent approximately 60% of the energy equivalence of proven oil reserves. About 3,006 tcf of these natural gas reserves are considered stranded. Stranded natural gas is accessible by drilling; however, it is located in regions distant from consuming markets. It is noted that about 65% of the world's crude, but only 25% of its natural gas reserves, are located in Arab countries (Figure 3.2). About 31% of the world's natural gas is located in the Russian Federation, with the rest in Iran, Asia Pacific, Europe, the Americas, and Africa (Figure 3.3). By year 2020 the world natural gas reserves are expected to exceed 8000 tcf (Figure 3.4). That is an increase of approximately 33% over the current reserves. Worldwide consumption of natural gas stood at 89.4 tcf/year in 2002, equivalent to about 24.5 million bbl/day of crude. Worldwide consumption of natural gas has been steadily increasing for the past decades. The global consumption stood at 100 tcf/year in 2005, which is equivalent to about 27.4 million bbl/day of crude. The global consumption is expected to increase to about 110 tcf in 2010, with approximately 75% of the world natural gas resources being used by the industrialized nations, Eastern-Europe countries and the Former Soviet Union. By year 2020, the world natural gas consumption is projected to reach approximately 130 tcf for that particular year.4-6 This is about 30% increase compared to the current consumption. The natural gas supplies by 2020 are expected to grow by approximately 3% more than the global consumption.

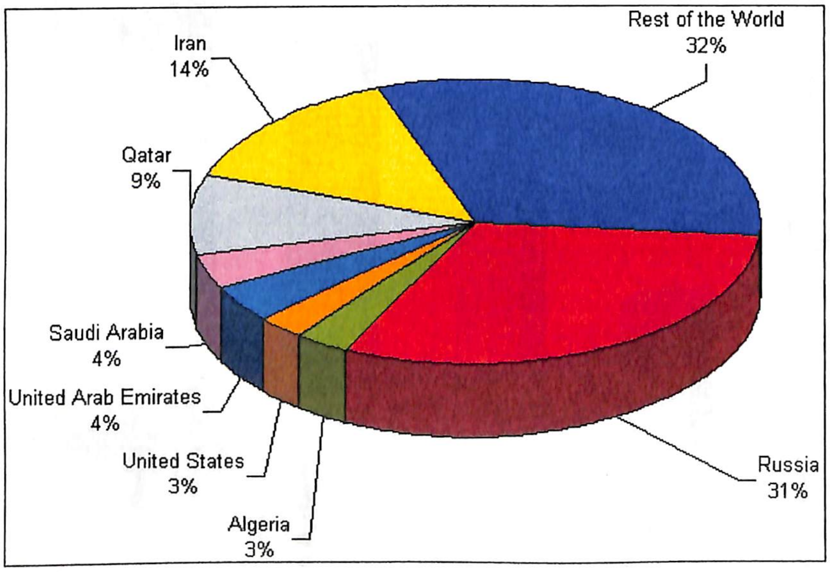


Figure 3.1: Proved world natural gas reserves as of January 2007.

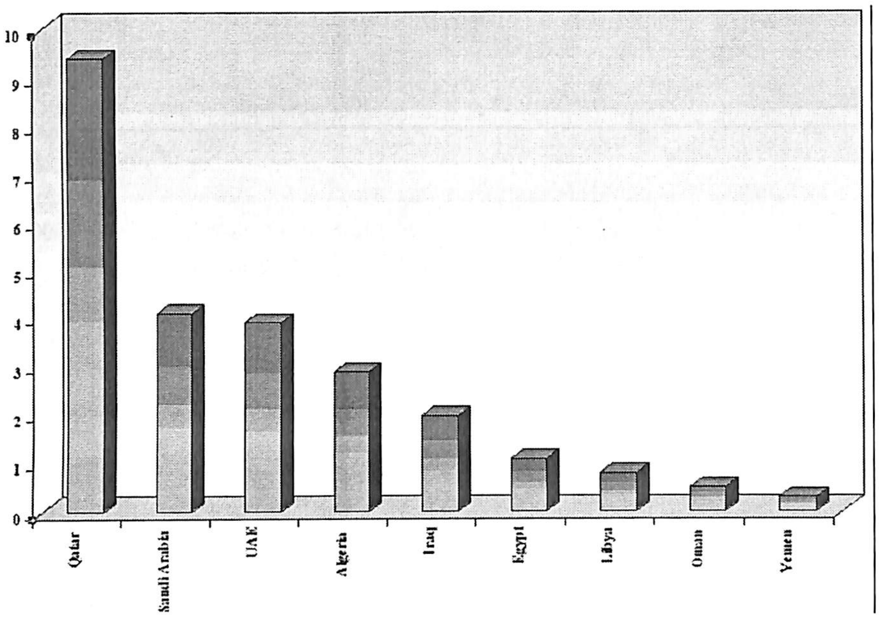


Figure 3. 2: Percentage distribution of Arab countries natural gas reserves (January 2007).

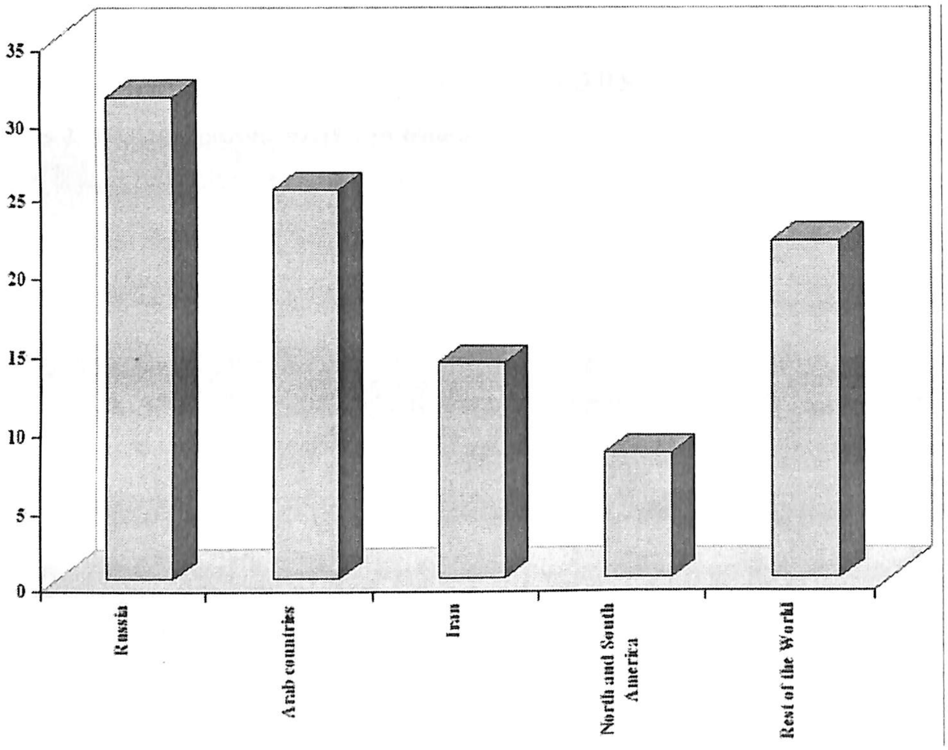


Figure 3.3: Percentage distribution of natural gas reserves in the world (January 2007).

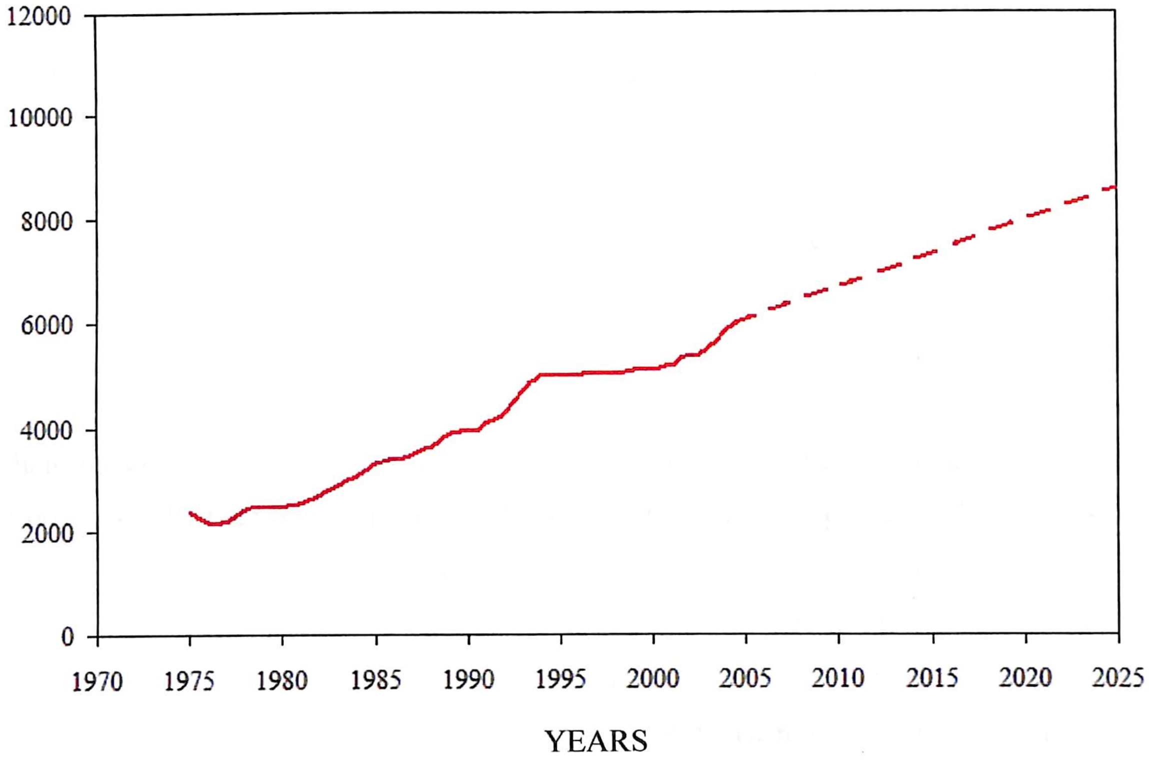


Figure 3. 4: Global proven reserves of natural gas.

3.2 **Economic Viability**

The economic viability of GTL plants is affected primarily by three main variables. These are the crude oil price, the capital cost and the operating costs including the cost of gas feed. This is different from the economics of LNG, which are related not to the crude oil price, but to the gas market dynamics. The operating costs of an LNG plant are much lower since the process does not involve expensive catalysts. Furthermore, the number of processing units in an LNG facility are fewer than those required for a GTL \ facility. In terms of capital investment, both GTL and LNG involve high up-front investment costs. Although the LNG facility is less capital intensive than GTL (about 50 per cent of a GTL facility), the overall costs are essentially similar, if we take into consideration full value chain (costs of LNG ships and re-gasification facilities). Another important factor is the product yield or carbon efficiency. The LNG plant being a physical change process exhibits high carbon efficiencies in excess of 92 per cent, whereas the GTL chemical change process results in lower product yields reflected in carbon efficiencies of around 78 per cent range. A higher efficiency means lower feed costs. The capital cost repayment for a GTL plant represents the majority of the cash outflow. Consequently, the capital costs of a GTL venture play an important role in the plant economics, and this high capital cost has been one of the main factors that delayed the industry expansion. The capital expenditures (CAPEX) are based on per-barrela-_day (PBD), that is the total capital expenditure divided by the daily-expected production rate. The annual operating expenditures (OPEX) are expressed as percentages of CAPEX. The capital cost of an integrated GTL facility (including the upstream gas plant) ranges from $20,000 to about 40,000 PBD of liquid capacity. The capital cost trend of some of the GTL projects since year 1983 is illustrated in Figure 5. A number of companies asserted that the capital expenditures for GTL facilities may decline to $20,000 PBD as a result of scale economies and technology improvement. These low capital costs translate into $2 billion for a plant with a capacity of 100,000 bbl/day. Product type governs the design basis and, therefore, the cost of a plant. For example, a plant designed for the production of distillates (about 80% diesel and 20% naphtha) is less costly than one designed for the production of specialty waxes. The non-feed stock annual operating expenditures ("OPEX") for large projects have been estimated at 5 to 7% of CAPEX.1 Therefore, factors of 5%, 6%, and 7% are used to estimate annual OPEX for GTL plants. These operating expenditures for a GTL plant excluding the cost of feedstock range from US$3.00-8.00/bbl of liquid product. The major part of this cost is associated with the cost of the FT catalysts. These expenditures include operation and maintenance of facilities, overhead costs, environmental compliance, and payroll. They do not, however, include feedstock cost. The economic viability and profitability of GTL plants is also evaluated using the pay-out time (POT) and the rate of return (ROR). The un-discounted POT is the time required in years to pay back the un-discounted initial investment. The ROR is the discount rate at which the net present value (NPV) is equal to zero. For a 60% overall thermal efficiency, implying approximately 10,000 scf of gas are required to produce 1 bbl of GTL products, the following rate of return to un-discounted pay-out time equivalencies have been deduced1:

1. ROR of 10% is equivalent to a POT of about 8 years,
2. ROR of 15% is equivalent to a POT of about 6 years, and
3. ROR of 20% is equivalent to a POT of about 4 years.

Although CAPEX is a significant factor in determining the viability of the GTL venture, the swing in netback value is also influenced by the crude oil price. Consequently, the decision to invest in GTL is largely dependent on the prediction of future oil prices. The overall profitability of a GTL plant can, therefore, be benchmarked against crude oil prices. For a GTL plant with an overall thermal efficiency of 60%, for a natural gas price of 1.00 USD/Mscf, the break-even price of crude oil for a profitable GTL venture varies between $10.3/bbl to $37.8/bbl.1 This minimum crude oil price is sensitive to the CAPEX, OPEX, and the ROR values. For a CAPEX value of $40,000 PBD, a 10% ROR, and an annual OPEX that is 7% of CAPEX, the break-even crude price is about $23.0. Technology advancements, causing a reduction of the capital costs are likely to lower this break-even price to about $11.5 for a 10% rate of return and a 7% OPEX of a $20,000 PBD CAPEX. At a current CAPEX value of approximately $35,714 PBD for some operating companies, crude oil price lower than $20/bbl would place this particular GTL venture in an area of economic uncertainty. The cost of the natural gas feedstock also represents a significant share. It varies between $6 to $10/bbl. A typical production cost comparison based on a barrel of GTL product, and a crude oil refined product is shown in Table 8. For the projected crude prices between $30- 55/bbl, the cost of a refinery barrel may range from $36 to $64; whereas, the cost of a GTL barrel may range from $18 to $32. The GTL barrel costs significantly less than the refined crude barrel, even with the current state of technology.

Table 8: Comparing cost of production of an integrated GTL plant with a conventional refinery.

GTL	Refinery	
Natural Gas	$6-10	-
Crude Oil	-	$30-55
Operating costs	$3-8	$2-3
Capital costs	$9-14	$4-8
Cost of Product	$18-32	$36-64

GTL plant and refinery have both a 100,000 bbl/day capacity Cost per barrel. Strong growth in the demand for oil worldwide, particularly in China and other developing countries, and the tight crudeoil supply situation are generally cited as the driving forces behind maintaining sharp crude prices for a long time to come. The current and predicted future crude prices reinforce the economic viability of a strong GTL industry. However, the need to constantly lower the capital and operating costs of GTL plants remains the main challenge facing the GTL industry. The focus is on reducing the per-barrel-a day installation cost from currently as high as $40,000 to $20,000 and even less. Continuous research and technology improvement is the main drive of many major companies investing in GTL to focus on the improvement of the process integration, catalyst efficiency, reformer carbon efficiency, and the overall thermal efficiency of the process. These advancements are likely to make the GTL industry even more sustainable in the future. The diesel-range material is among the GTL products that warrant focus.

Currently, the global middle-distillates market is at about 31 million bbl/day.4 This is a significant portion of the worldwide fuels market with a history of about 3% per year average growth during the past decade. About 14 million bbl/day of this consumed volume is automotive diesel. Asia- Pacific has the largest diesel market, with a demand of 10 million bbl/day. This is followed by North America with a demand of 7 million bbl/day and Europe, with a demand of 7 million bbl/day. These numbers are expected to continue to grow, largely driven by increased diesel-powered auto sales. It is estimated that the sale of such vehicles in Europe will grow from approximately 6 million units in 2002 to over 8 million by 2008, constituting over 60% of sales in countries such as France and Austria.8 The increase of diesel-powered car sales in Europe is mediated by a combination of emission mandates, jurisdictional tariff strategies, improved auto designs, and increased availability of low-emission fuels. Based on overall economic growth and regional trends, observers anticipate demand for middle distillates (incorporating automotive diesel) to continue growing from 30 million bbl/day currently to approximately 44 million bbl/day by 2020. Of the year 2020 demand level, 22.5 million bbl/day is projected to be automotive diesel.2

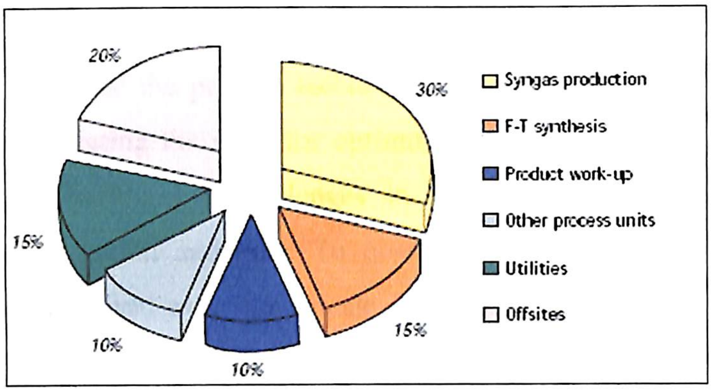
As world demand for ultra clean fuels increases, it is likely that the GTL clean fuels produced will influence premium prices, making GTL investments more profitable. The projected numbers for GTL liquid product volume are subject to some uncertainty, though. All GTL projects existing or under various stages of consideration represent a total maximum liquid product capacity of approximately 1.3 million bbl/day by 2015. Nearly 70% of this projected flow rate is likely premium diesel stock suitable for use as automotive diesel-blend material. This is expected to be less than 3% of the total worldwide automotive diesel market. The introduction of GTL diesel is, therefore, not likely to cause any oversupply in the diesel market.

GTL offers nations seeking to develop natural gas resources an alternative to diversify their resources beyond natural gas markets. The benefits of diversification are enhanced because the products of the GTL industry do not compete with LNG in the natural gas product market. A number of countries are currently involved in GTL operations. For instance, the Malaysian GTL operation is small, and is directed to local and regional supply needs. Qatar has large reserves of natural gas and may become the world capital for the GTL industry. There is plenty of gas reserves for operating both LNG and GTL facilities for a long time to come. By year 2015, GTL units are likely to consume about 4.75 tcf/year and LNG units 7.25 tcf/year, which together represent a fifty-year consumption of 600 tcf. This fifty-year consumption of natural gas by both GTL and LNG plants represents approximately 20% of the proven stranded natural gas reserves that currently stand at about 3006 tcf. A fifty-year consumption of GTL plants alone stands at approximately 8% of the proven stranded gas reserves.[1]

3.3 **Challenges**

Attention has been focused on catalyst developments or improvements, the undoubted outstanding quality of the product fuels, and the challenges facing us as engineers. Most people are aware of the basic economics behind GTL and the fact they are not clear-cut for most regions of the world, even though, on paper, typical reported gas prices correspond to feedstock prices of around $4–6/bbl. However, we must now realise that the time for these type of debates is over. GTL projects have come of age and the engineering challenges that have been debated at length over recent years have been resolved. Possibly, the economic arguments have also been overcome for certain regions of the world, and we are seeing projects in these regions on the verge of construction.

The three main process technologies in a GTL process are well known: syngas preparation; Fischer- Tropsch (FT) synthesis; and hydrocarbon upgrading (mild hydrocracking / hydrotreating). Much has been written about the advantages and disadvantages of a variety of proprietary technologies for each of these steps. Debates have raged over partial oxidation, catalytic partial oxidation, autothermal reforming, slurry beds, fixed beds and so on. However, all of these debates still tackle the area which accounts for 40–50% of the cost: the utility and offsite support systems.



3.5 :Distribution of cost

Virtually all the technologies in a GTL plant have a common utility thread. This includes: the need for large quantities of high grade energy to drive the air separation processes; the preheat needs for the syngas generation step; waste heat recovery from syngas and its effective utilisation; medium/low grade heat generation by the FT process; hydrogen provision for the hydrocracker; and optimum product recovery to maximise yield. And finally, as GTL projects are around 60% thermal efficiency, resulting in around 40% heat rejection to the surroundings, ways to economically reject ~40% of the feed natural gas heat have to be found. In addition to this, the offsite systems are also significant, especially when dealing with greenfield remote locations. Such offsite systems may include water treatment to reliably support the large steam systems and effluent treatment of oxygenated hydrocarbon contaminated water (and utility system blowdowns).

Flare systems to deal with high heat flows from the hydrocarbon processing units and high hydraulic flows from the gas processing units, and firefighting systems to deal with potentially large volumes of hydrocarbons at their boiling points and streams containing hydrogen, are also important. Tankage and product-loading facilities are a significant factor; compared to a refinery they may require similar volumes, but their utilisation can be low (when considering projects of around 34,000 barrels per day (bpd)). It may be necessary to employ systems that require virtually 100% sulphur quarantine to protect sulphur sensitive FT catalyst (for tankage, flare and vent systems), as well as large-scale, reliable electrical systems, often internally generated derived from waste heat.

So whilst the process technology has generated the most interest, and rightly so when considering the need for optimum catalyst and reactor design, we must not forget that there are equal challenges in the support systems when considering engineering, construction and cost. To give an idea of what is involved, a GTL facility can be summarised as a world-scale gas processing and syngas generation facility at the front, together with at least two of the largest singletrain air-separation plants ever built, with a large-scale chemical conversion process in the middle and a refinery on the 'back end', all supported by 'power station'-sized steam and electrical systems, a wastewater treatment facility, and associated infrastructure.

3.4 **Process Engineering Opportunities**

A GTL facility of around 34,000 bpd has a considerable steam system that, depending on the technology selected for each of the processes, will have to handle a total steam rate of around 1500 tonnes per hour. This level of steam handling will no doubt surprise the refiners, but will also surprise those used to dealing with syngas complexes, as this is approximately double what you would expect from the syngas capacity. For GTL, this steam will normally be of two discrete pressure levels; one associated with the syngas generation, and one associated with the Fischer- Tropsch synthesis. The steam generated by the syngas processes is available at a variety of conditions, and is largely limited by what you feel able to generate with the syngas waste-heat boiler (levels are normally limited by metal-dusting concerns). However, the steam generated by the FT process is limited by the FT reaction conditions, and is normally limited to less than 200°C for liquid-phase processes. This steam should be viewed as an opportunity, as it gives unprecedented flexibility in configuring the utility systems. High-pressure (HP) steam pressure and the degree of superheat can be optimised for a particular cycle and steam turbine set. Medium-pressure (MP) steam can be superheated, and due to the pressure level, this could be done easily using waste heat from another fired heater. The HP steam can be used for compressor drives, preheat or power generation. Used within the air separation unit (ASU), it is possible to have the main and booster air compressors on the same shaft with a single large turbine. The MP steam can be used for preheats or for power generation. This may be considered for smaller compressor drives, if economically viable. To reduce equipment, simply view the MP steam as a FT cooling medium and condense it. The MP steam has been a problem area with FT plants in the past, but considerably larger turbines are now available for using this valuable utility cost-effectively, again shifting the basis for what a GTL plant can achieve. This, coupled with more recent advances in mechanical design of gearboxes and complex shaft arrangements, gives the engineer even more flexibility in using this grade heat.

3.5 **The fuel system**

FT plants unfortunately do not convert the synthesis gas into 100% C5+ hydrocarbons. The combined FT reactor effluent is a cocktail of hydrogen, nitrogen, CO, CO2, water, water-soluble oxygenated hydrocarbons, methane and C2+ olefinic and paraffinic hydrocarbons. This stream exits the FT reactor in the vapour phase and is usually condensed, at which point a hydrocarbon-rich and a water-rich phase are removed. This leaves a vapour stream for which the engineer has several options – to burn as fuel, to recycle into the process, to remove 'useful' molecules such as hydrogen, or any combination of these. Each of the different GTL processes has different methods of handling this stream, including some once-through processes that propose simply combusting the entire stream in a specially designed gas turbine. However, all of these processes have two factors in common. The vapour stream represents the single largest quantity of high-grade heat within the process (ignoring, for now, small vents and light ends productions in other units). Also, the stream is of low heating value, due to the CO2 and nitrogen it contains (typically <350 Btu/SCF), which represents challenges in designing a stable fuel system and combustors. GTL facilities, whilst exothermic overall, do have needs for high-grade heat, as this can be exploited more cheaply in general than, say, the FT steam. Users include preheat requirements for chemical conversion (in syngas generation and hydrocracking), steam superheating, large rotating equipment within the

ASU (the fuel could be used for gas turbines), and power generation. The challenge is to have a good database of costs and ensure that you are targeting the highest value energy at the right user.

3.6 **Capital Cost vs. Process Efficiency**

Firstly, the process rejects ~40% of the feed energy as waste heat. Due to the significant investment in air or water cooling facilities, efficiency is a key issue in capital cost reduction.

Secondly, the plants are very equipment intensive, so unfortunately opportunities are limited for reducing the cost of a large item (such as a single turbine), but savings in utility cycles chip away at all equipment items in the system and so reduce cost. Lastly, the plants are capital intensive, so a large portion (>50%) of the cash flow is capital repayment. This results in the usual capital versus operating expenditure balance being tipped towards capital costs. The requirement to check life-cycle costs is therefore more important than normal, but it is essential that any optimisation of this type is done against hard economic data and decision-making indicators (net present value, NPV, rather than payback), which reflect reality and not some project quirk.

3.7 Technological Strategies

The strategies of the companies involved in the GTL technologies must be examined inside the context of renovation of a mature technology, the development of which was interrupted more than 50 years ago with the petrochemical advances and dominance. The technology has been restricted in the last decades, from the operational point of view, to the activities of Sasol, which installed and operated syngas production plants using coal as raw material, in South Africa; and the activities of Shell, which built a plant in Malaysia at a cost of US$ 600 million with a capacity of 12,500 bpd.

The return to the GTL conversion can be seen today as a definition of a new trend that would thus have characteristics assimilated to the fluid phase of the life cycle of the technologies. The essential characteristic of the fluid phase is the existence of numerous competing options, seeking definitions to be validated by the market in order to constitute the dominant project. This search for convergence among the several possible conceptions of technology makes the competitive scenario particularly complex as well as uncertain for the participants who must make their bets, confronting the risk of making options that could become losers as there is a natural reduction of the number of technological options utilized. It must be therefore emphasized that the case in question essentially relies on the process innovations. The products to be obtained are in the best hypothesis superior versions of established products of which the markets are well known.

The strategic positioning of the actors is thus characterized by the search for positions in a still open environment, in which a certain number of options are competing.

3.8 The Scales of the Plants

The scales of the GTL plants currently present an important dimension for strategic positioning in the GTL market. On the one hand, some actors are positioning themselves in search of greater scale, part of the natural trajectory of chemical processes industries, aiming to reduce the cost of production and increase profitability on the large investments demanded. The large petroleum companies which possess great reserves of stranded natural gas (for example, Shell and ExxonMobil) are the most interested in large-scale plants. On the other hand, some companies seek efficient plants on a smaller scale (fewer than 10,000 barrels per day), capable of exploring a large number of small stranded natural gas fields. The barge-mounted plants proposed by Syntroleum expressively represent the concept of small scale (from 2000 to 10,000 bpd), whereas the petroleum companies' projects, which would produce about 80,000 or more bpd, give priority to the reduction of cost as well as the competitiveness of the GTL technologies compared to the established technologies of natural gas exploration.

Direct conversion versus conversion via synthetic gas

Parallel to the positioning on the question of the size of the plants, there is also a lot of space for strategic positioning on the research effort as to the different technological routes of gas conversion. This positioning is not taking place independently of the objectives in terms of the scale of plants, but rather extrapolates this question. The strategic game is related to the choice of a route to be given priority. The concentration of research efforts of one route can result in great competitive advantages in case the effort is successful. Nevertheless, the selection of a route presents risks at the same time, since other routes are no longer given priority.

Efforts of maximization of the traditional route compete to the research, although at a beginning stage, that are attempting to develop catalysts capable of eliminating the step of producing syngas, thus drastically reducing the investment in the plants. Research and development efforts are, at the same time, seeking new options for the production of syngas, trying to make it more efficient by means of radically new processes, as, for example, the reform by catalytic membrane.

3.9 The Product Lines

One line of motivation of the GTL technologies sets as a target market the ultra-clean fuels, without sulphur, aromatics and heavy metals. In this case, the products would receive a prize compared to the traditional fuels. However, if other solutions make the production of ultra-clean fuels viable, the GTL technologies would directly compete with the refineries and the prize would be reduced or even disappear. In this case, a considerable reduction in the cost of production would be demanded so that the plants become competitive, and thus give priority to scale economies.

Another option also mentioned refers to the markets of chemical specialities that offer much higher prices than those of the fuels, but demand small volumes of products, limited to niches of applications. The dilemma of the lines of products is less restrictive than the previous ones, although they are related to them, especially the question of the scale of production.

3.10 Economics of GTL Plants

Introduction

The conversion of natural GTL using the Fischer-Tropsch (F-T) process was first effected in 1923 with the conversion of synthesis gas (syngas) (CO+H2) into synthesis fuels (synfuels). The conversion is based on a three-step process: syngas generation, F-T synthesis, and product upgrading. The liquid products are stable at atmospheric temperature and pressure and may be transported with pipelines and/or standard tankers.

Syngas Generation: The syngas-generation step involves a chemical reaction, reforming, wherein the hydrocarbon molecules of natural gas are broken down and stripped of their hydrogen atoms. Oxygen, introduced either in steam, in air, or as a pure gas, produces a mixture of hydrogen and carbon monoxide. The production of the ideal syngas calls for an H_2/CO ratio of approximately 2, and both catalytic and noncatalytic processes have been developed. If necessary, the reforming step may be preceded by a feed pretreatment step to remove sulfur compounds such as hydrogen sulfide (H2S). In addition, other secondary/side reactions may proceed simultaneously during the syngas-generation step, yielding undesirable products, and thereby must be controlled (Gaffney, Cline & Assocs. 2001). These reactions may include:

- $CO+CO \rightarrow 2C+O_2$ (carbon formation reaction).
- $CO+H_2 \rightarrow C+H_2O$ (carbon formation reaction).
- $CO+H_2O \rightarrow H_2+CO_2$ (water/gas shift).

There are three basic types of reformers: the steam methane reformer (SMR), the partial oxidation reformer (POX), and the autothermal reformer (ATR) (Doshi 2002). A new plasma reformer also has been developed for the production of syngas from natural gas whereby electricity provides the reaction energy for the endothermic process (Blutke et al. 1999). In the SMR, natural gas feedstock and steam at 20 atm and 500°C (with an exit temperature of approximately 800°C) pass over a nickel catalyst contained in tubes within a firebox. The heat of reaction is supplied by burning some of the feedstock. The SMR produces a syngas with an H_2/CO ratio much higher than 2.0 and is thereby not ideally suited for producing synfuels. The theoretical H2/CO ratio is 3.0 ($CH_4+H_2O \rightarrow CO+3H_2$), but the actual H_2/CO ratio is 5.0 (75% H_2, 15% CO, and 10% CO_2) (Gaffney, Cline & Assocs. 2001).

In the POX, natural gas and oxygen are directly reacted without a catalyst. The POX produces a syngas with an H_2/CO ratio much lower than 2.0 and is thereby not ideally suited for producing liquid fuels. It operates at an existing temperature of approximately 1400°C (Robertson 1999). The theoretical H_2/CO ratio is 2.0 ($2CH_4+O_2 \rightarrow 2CO+4H_2$), but the actual H_2/CO ratio is 1.8 (62% H_2, 35% CO, and 3% CO_2) (Gaffney, Cline & Assocs. 2001).

In the ATR, natural gas, steam, and oxygen at 1200 to 1500°C (with an exit temperature of approximately 800 to 1000°C) pass over a bed of nickel in the reaction vessel. The combustion reaction is rapid and exothermic and, therefore, autothermal.
Because the ATR results in an H2/CO ratio of approximately 2.0, the process is best suited for the production of synfuels. To provide oxygen, an air-separation plant or other special provision may be required to resolve nitrogen-related problems. The theoretical H_2/CO ratio is 2.3 ($3CH_4+H_2O+O_2 \rightarrow 3CO+7H_2$), but the actual H_2/CO ratio is 2.0 (64% H_2, 32% CO, and 4% CO_2) (Gaffney, Cline & Assocs. 2001).

F-T Synthesis: The conversion of syngas into synfuel is based on F-T catalytic synthesis, which ideally calls for an H2/CO ratio of approximately 2.0. The reaction is strongly exothermic, and thereby significant heat must be removed. It may be represented by the following reaction (Gaffney, Cline & Assocs. 2001).

$nCO\ 2nH_2 \rightarrow n\ \_{-}CH2{-}\_\ nH_2O$.

There are three basic types of reactors: the tubular fixed-bed, the fluidized-bed, and the slurry-bubble.

In the tubular fixed-bed reactor, also called the Arge-type reactor, syngas flows downward through vertical tubes packed with catalyst. The heat of reaction produces steam by removal through the tubes' walls. Iron, which is relatively cheap and works well with a wide range of syngas compositions, is one of the first catalysts used and produces light hydrocarbons. Cobalt, which is more expensive and must be supported on an inert material such as alumina or silica, produces a heavier, waxier hydrocarbon that requires less eventual upgrading.

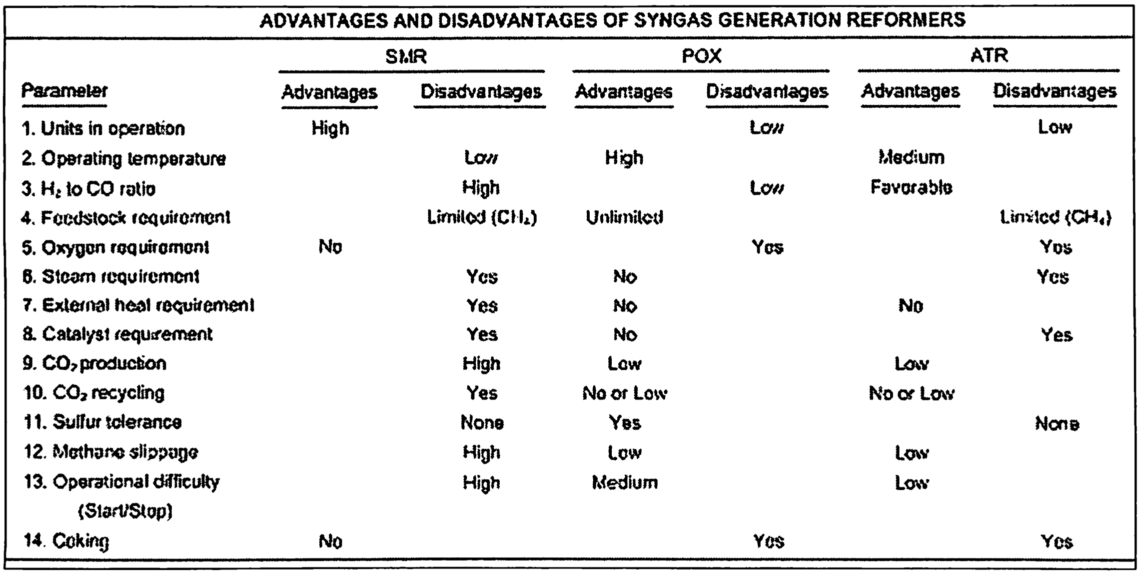
In the fluidized-bed reactor, the syngas is blown upward through solid catalyst particles, causing the particles to become fluidized. The heat of reaction produces steam by means of cooling coils.

In the slurry-bubble reactor, syngas is bubbled through slurry of liquid wax and dispersed catalyst, typically cobalt. Heat is also removed from the slurry by means of cooling coils to produce steam. The effluent products are sent to a condenser for the recycling of unconverted syngas.

Product Upgrading: The raw products are treated further to maximize their sales value or to meet particular market needs. The treatment may entail thermal or hydro cracking of the waxes to produce only naphtha and diesel; vacuum separation of the waxes into distinct, highly specialized products; and distillation of the combined naphtha/diesel stream into multiple separation products including mineral spirits, white oils, kerosene, and jet fuels.

Some of the companies involved in the development and licensing of GTL process technology include Rentech Inc., Shell, Exxon, Sasol Ltd., Syntroleum Corp., British Petroleum/Davy Process Technology, Conoco, and Reema Intl.

Table 9: Advantages and Disadvantages OF syngas generation reformers



ADVANTAGES AND DISADVANTAGES OF SYNGAS GENERATION REFORMERS

	SMR		POX		ATR	
Parameter	Advantages	Disadvantages	Advantages	Disadvantages	Advantages	Disadvantages
1. Units in operation	High			Low		Low
2. Operating temperature		Low	High		Medium	
3. H_2 to CO ratio		High		Low	Favorable	
4. Feedstock requirement		Limited (CH_4)	Unlimited			Limited (CH_4)
5. Oxygen requirement	No			Yes		Yes
6. Steam requirement		Yes	No			Yes
7. External heat requirement		Yes	No		No	
8. Catalyst requirement		Yes	No			Yes
9. CO_2 production		High	Low		Low	
10. CO_2 recycling		Yes	No or Low		No or Low	
11. Sulfur tolerance		None	Yes			None
12. Methane slippage		High	Low		Low	
13. Operational difficulty (Start/Stop)		High	Medium		Low	
14. Coking	No			Yes		Yes

Economics

Capital Expenditures. The capex of GTL plants is estimated to be $20,000 to $40,000 per BLPD. The capex depends on many factors, including type of technology used, geographical location of the facility, product workup/slate, economies of scale, learningcurve cost improvement, and local infrastructure availability. Distribution of capex among the three GTL processes is estimated as follows: 60% for syngas generation, 30% for F-T synthesis, and 10% for product upgrading. Oxygen generation is a significant portion of syngas generation, and thereby of capex, and is important to explore for purposes of cost reduction.

Economies of scale relate capex to plant capacity and may be
expressed as follows:

Cost Ratio □_Capacity Ratio_Y,

Cost □Base Cost * _Capacity/Base Capacity_Y,

□Constant * _Capacity_Y,

wherein Y reflects the degree to which a particular process facility benefits from economies of scale. A value of 1.0 implies that the facility does not benefit from economies of scale. For example, the construction of parallel trains (instead of larger trains) would yield Y values approaching 1.0. Y values for refining and petrochemical plants are typically 0.5 to 0.8, with 0.60 as a common value leading to the relationship known as the sixth-tenths rule (Turton et al. 2003). A U.S. Dept. of Energy (DOE) study (1995) showed that quadrupling a GTL plant capacity would result in an estimated savings of approximately 33%. This is equivalent to a Y value of 0.7.

Table 10: GTL technology used by five major competing companies

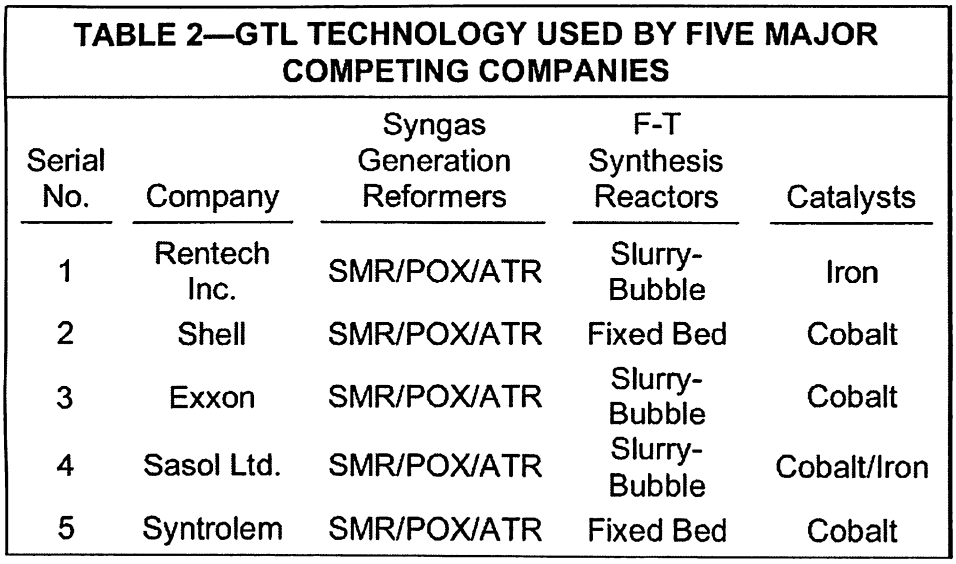


TABLE 2—GTL TECHNOLOGY USED BY FIVE MAJOR COMPETING COMPANIES

Serial No.	Company	Syngas Generation Reformers	F-T Synthesis Reactors	Catalysts
1	Rentech Inc.	SMR/POX/ATR	Slurry-Bubble	Iron
2	Shell	SMR/POX/ATR	Fixed Bed	Cobalt
3	Exxon	SMR/POX/ATR	Slurry-Bubble	Cobalt
4	Sasol Ltd.	SMR/POX/ATR	Slurry-Bubble	Cobalt/Iron
5	Syntrolem	SMR/POX/ATR	Fixed Bed	Cobalt

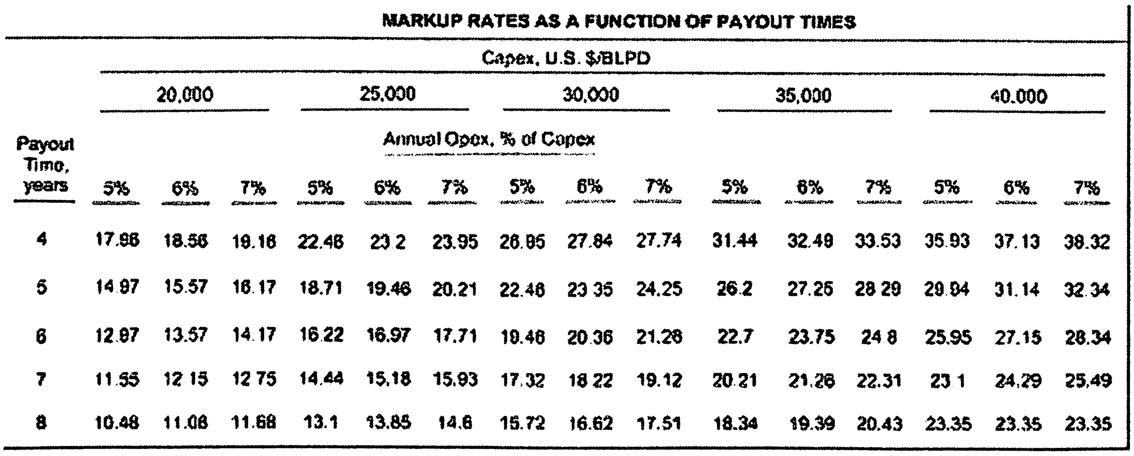
Product workup governs the design basis and, therefore, the cost of a plant. For example, a plant designed for the production of distillates (approximately 80% diesel and 20% naphtha) is less costly than one designed for the production of specialty waxes. Robertson (1999) cited several references that estimated the capex of generic GTL plants to be in the range of $12,000 to $35,000 per BLPD. He has elected to use a capital cost for the U.S. Gulf Coast of $24,000 per BLPD (i.e., equal to the capital cost for Exxon's 50,000 BLPD Qatar project). Vosloo (2001) also cited a capex of $24,000 per BLPD. The capex amounts used in this analysis will be $20,000 to $40,000 per BLPD, evaluated in $5,000 per BLPD increments (i.e., capex amounts to be analyzed are $20,000, $25,000, $30,000, $35,000, and $40,000 per BLPD).

Annual Opex. The nonfeed stock annual opex amounts for large projects have been estimated at 5 to 7% of capex. Accordingly, factors of 5, 6, and 7% are used to estimate annual opex for GTL plants. These expenditures, amounting to $3.03 to $8.48 per BLPD, include operation and maintenance of facilities, overhead costs, environmental compliance, and payroll. They do not, however, include feedstock cost. This range of opex encompasses other estimates of $4.00 to $5.50 per bbl.

Net Cash Flow Analysis of GTL Plants

The two measures used to assess the economic viability and profitability of GTL plants are POT and ROR. The undiscounted POT is the time required in years, as of the startup date of the plant, to pay back the undiscounted initial investment, before income tax. The ROR is the discount rate at which the net present value is equal to zero. Undiscounted POTs of 4, 5, 6, 7, and 8 years and RORs of 10, 15, and 20% are used in this analysis. To assess the profitability of GTL plants, a simple mathematical approach using the concept of profit markup, profit margin, or tariff rate per bbl of GTL products is introduced. The markup rate is defined as follows: Markup rate per bbl of GTL product_sale price of 1 bbl of GTL product–cost of feedstock required to produce 1 bbl of GTL product.

Table 11: markup rates as a function of payout times



MARKUP RATES AS A FUNCTION OF PAYOUT TIMES

	Capex, U.S. $/BLPD														
	20,000			25,000			30,000			35,000			40.000		
	Annual Opex, % of Capex														
Payout Time, years	5%	6%	7%	5%	6%	7%	5%	6%	7%	5%	6%	7%	5%	6%	7%
4	17.96	18.56	19.16	22.46	23 2	23.95	26.95	27.84	27.74	31.44	32.49	33.53	35.93	37.13	38.32
5	14 97	15.57	16.17	18.71	19.46	20.21	22.46	23 35	24.25	26.2	27.26	28 29	29.94	31.14	32.34
6	12.97	13.57	14.17	16.22	16.97	17.71	19.46	20.36	21.28	22.7	23.75	24 8	25.95	27.15	28.34
7	11.55	12 15	12 75	14.44	15.18	15.93	17.32	18 22	19.12	20.21	21.26	22.31	23 1	24.29	25.49
8	10.48	11.08	11.68	13.1	13.85	14.6	15.72	16.62	17.51	18.34	19.39	20.43	23.35	23.35	23.35

The following assumptions and parameters are also used in the analysis:

- 25 years for plant life.
- 3 years for plant construction.
- \$20,000, \$25,000, \$30,000, \$35,000, and \$40,000 per BLPD

for capex, divided equally over the 3-year construction period.

- 5, 6, and 7% of capex for annual opex.
- 100% for owner's equity.
- 0% for rate of inflation.
- 91.5% for on-stream factor.
- 4, 5, 6, 7, and 8 years for payout periods.
- 10, 15, and 20% for ROR with midyear compounding.
- 60% for overall thermal efficiency.

The assumption that overall thermal efficiency is 60% implies that 10 Mscf of 1000 Btu/scf gas are required to produce 1 bbl of GTL products. The parameters used for the base case are: \$30,000 per BLPD for capex, 6% of capex for annual opex, payout time of 6 years, and ROR of 15%. For the base case, markup is \$20.36 per BLPD at a payout time of 6 years and \$21.47 per BLPD at an ROR of 15%. The following rate of return to undiscounted payout time equivalencies can be deduced from Tables 11 and 12:

- ROR of 10% is equivalent to a POT of 8.2 years.
- ROR of 15% is equivalent to a POT of 5.6 years.
- ROR of 20% is equivalent to a POT of 4.1 years.

For a 4-year construction period, the markup rates as a function of undiscounted POT are unchanged and thereby remain exactly as shown in Table 11. The markup rates as a function of rates of return, however, are higher than those shown in Table 12. Table 13 presents the incremental increase in markup rates resulting from the 1-year increase in the construction period. The increase in markup rates amounts to 3.45, 5.9, and 8.5% at discount rates of 10, 15, and 20%, respectively.

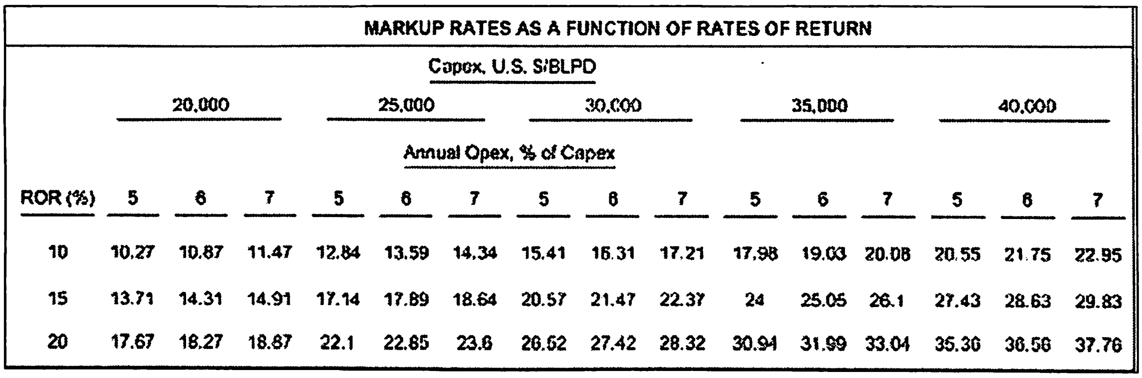
GTL Product Value

The wholesale prices of gasoline and No. 2 fuel oil average approximately $8/bbl and $6/bbl higher, respectively, than crude oil. In addition, GTL products are more valuable than those derived from crude oil because of their higher quality. GTL products are ideally suited to meet low-emission regulations for diesel. This superiority equates to more than a $2/bbl premium over oil-derived distillates. Overall, the premium for GTL products over crude oil is approximately $10/bbl or more. For a GTL plant with an overall thermal efficiency of 60%, 10 Mscf of 1000 Btu/scf natural gas is required to produce 1 bbl of GTL products. Thus, to ensure GTL plant profitability, the minimum or break-even crude oil price in $/bbl is equal to (Markup rate−10)+(10)*(natural gas price, $/Mscf). Thus, for the base case: Crude oil price, $/bbl_(21.47−10) +(10)*(natural gas price, $/MMBtu)_(11.47)+(10)*(natural gas price, $/MMBtu).

Accordingly, for a natural gas price of $1.00/Mscf (i.e., $1/MMBtu), the minimum or break-even price of crude oil for the base case must equal or exceed $21.47 bbl for the GTL plant to be profitable. Table 6 summarizes the minimum crude oil prices needed for GTL plant profitability at a natural gas price of $1/MMBtu. It should be noted that all tabulated values are identical to those in Table 4. Thus, for the worst-case scenario ($40,000 per bbl for capex, 7% for opex, and 20% for ROR), the minimum crude oil price is $37.76/bbl. A detailed net cash flow (NCF) analysis for the base case (with $1/MMBtu) is shown in Table 7 to illustrate the reliability of the simplified approaches used in Tables 3 and 4.

It should be noted that when feedstock (natural gas) cost increases by $1/MMBtu, the minimum (break-even) price of crude oil must increase by $10/bbl, as shown below.

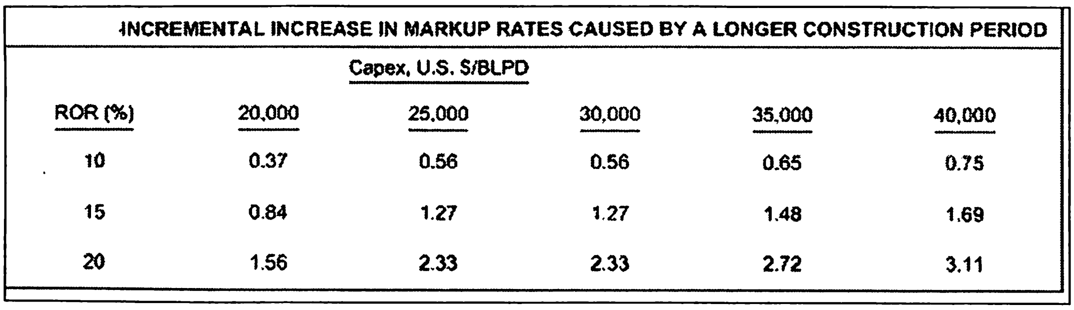
Table 12



MARKUP RATES AS A FUNCTION OF RATES OF RETURN

	Capex, U.S. $/BLPD														
	20,000			25,000			30,000			35,000			40,000		
	Annual Opex, % of Capex														
ROR (%)	5	6	7	5	6	7	5	6	7	5	6	7	5	6	7
10	10.27	10.87	11.47	12.84	13.59	14.34	15.41	16.31	17.21	17.98	19.03	20.08	20.55	21.75	22.95
15	13.71	14.31	14.91	17.14	17.89	18.64	20.57	21.47	22.37	24	25.05	26.1	27.43	28.63	29.83
20	17.67	18.27	18.87	22.1	22.85	23.6	26.62	27.42	28.32	30.94	31.99	33.04	35.36	36.56	37.76

Table13



INCREMENTAL INCREASE IN MARKUP RATES CAUSED BY A LONGER CONSTRUCTION PERIOD

	Capex, U.S. $/BLPD				
ROR (%)	20,000	25,000	30,000	35,000	40,000
10	0.37	0.56	0.56	0.65	0.75
15	0.84	1.27	1.27	1.48	1.69
20	1.56	2.33	2.33	2.72	3.11

Feedstock (Natural Gas)	**Break-Even Crude Oil Price,**
Cost, $/MMBtu	**$/bbl**
1.00	21.47
2.50	36.47
5.00	61.47
7.50	86.47

The economic viability of converting natural gas to liquids depends on four major factors: capex, opex, natural gas (feedstock) prices, and crude oil prices. The markup rate (i.e., the markup required to cover both capex and opex) ranges between $10.48 and

$38.32 per BLPD for payout times of 8 to 4 years, respectively, and between $10.27 and $37.76 per BLPD for rates of return of 10 to 20%. Low natural gas prices coupled with high crude oil prices will ensure the economic viability of GTL plants. For a natural gas price of $1/MMBtu, crude oil prices must range, at least, between $10.48 and $38.32/bbl for payout times of 8 to 4 years, respectively, and between $10.27 and $37.76/bbl for rates of return of 10 to 20%. Stranded natural gas, especially associated gas in regions with a zero flare policy, is an ideal feed stock for GTL plants. With current crude oil prices hovering around $60/bbl (first quarter 2007), GTL plants are a viable alternative to crude oilderived fuels.

Part - D

4.0 **Advance Gas To Liquid Technology- AGC-21**

Conversion of natural gas to liquids (GTL) utilizing Fischer-Tropsch hydrocarbon synthesis technology is available option to bring gas resources to market. Over the past two decades, ExxonMobil has invested in the development of proprietary technology, Advanced Gas Conversion for the 21st Century (AGC-21) 1. This state-of-the-art GTL technology provides an important option for commercialization of natural gas resources. ExxonMobil is continuing to pursue technology enhancements to further reduce the cost of producing fuels, lube basestocks and other specialty products from natural gas. This paper discusses advances in ExxonMobil's AGC-21 technology achieved over the years as a result of a comprehensive research, development and engineering program.

Current day gas-to-liquids options involve multiple processing steps. These options are being advanced in development efforts at a number of locations worldwide.2 The effort at ExxonMobil is culminating in a complete, integrated processing scheme, Advanced Gas Conversion for the 21st Century, or AGC-21. This is part of a wider ranging activity on natural gas, an increasingly important resource in meeting future world energy demand. We are continuing efforts to develop a wide range of technology options such as GTL, while simultaneously working on other gas utilization activities such as the development of high strength steel to improve the economics of long distance pipelines, and our continuing activities to develop and market LNG. ExxonMobil is spending considerable time and effort in understanding how best to use energy resources, and we continue work to develop new technologies for more efficient and cost effective utilization of them.

4.1 AGC-21 Process Technology

The AGC-21 process connects three key steps, as shown in Figure 4.1.1. In the first step, syngas is generated by contacting methane with steam and limited oxygen in a high capacity catalytic reactor.

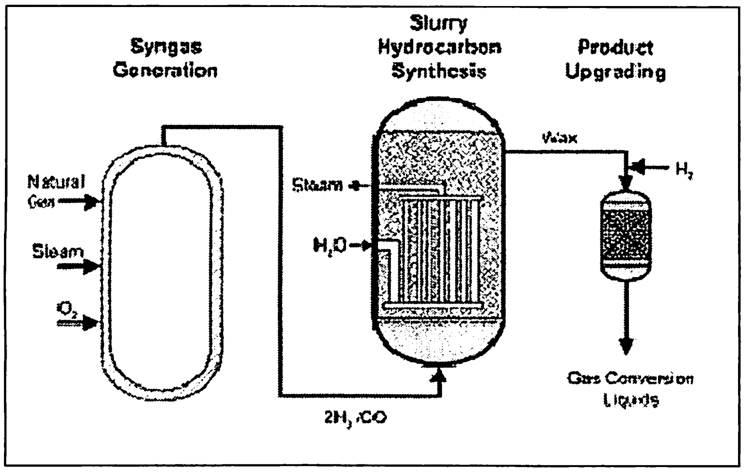


Fig 4.1.1 Advance gas conversion process

Hydrocarbons are synthesized in the second step at high alpha as described by a Schulz-Flory distribution in a novel slurry reactor using new, high productivity catalysts operating at high levels of syngas conversion. The fullrange, primarily normal paraffin product contains significant 650°F+ waxy material which is a solid at room temperature and melts above 250°F, unsuitable for pipelining or transporting in conventional crude carriers. The final step, accomplished with proprietary catalysts in a packed bed reactor, converts wax to high quality liquids that make excellent feeds for refineries and chemical plants and directly marketable products in some instances, such as lube basestocks or specialty solvents. As shown in Figure 4.1.2, chemistries inside these steps are straightforward yet become more complex as processes go to high yields and selectivities. Oxygen, methane, and steam ratios are carefully controlled to produce syngas (carbon monoxide and hydrogen) at stoichiometric proportions of about 2.1 to 1 H2 to CO.

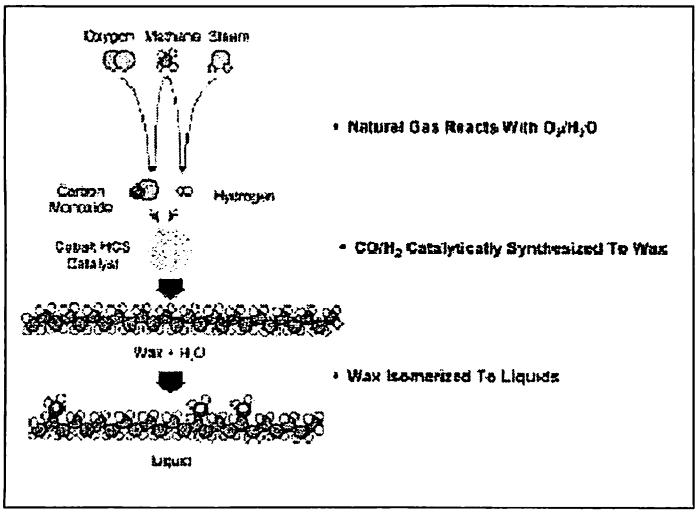
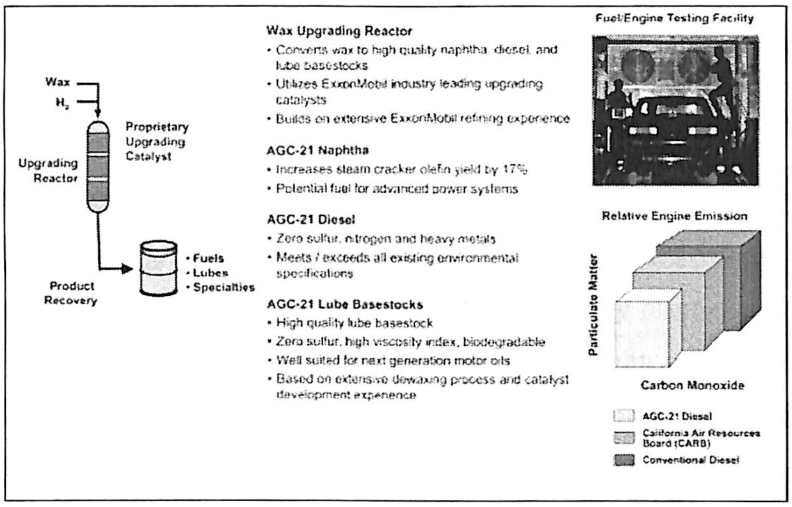


FIG 4.1.2 Liquid ultra clean fuel

A high productivity cobalt-based HCS catalyst converts syngas with focus on C10+ yield to improve plant efficiency and to optimize preferred products. These product molecules are predominantly normal paraffins that define the waxy character of this material.9-12 Mild isomerization improves cold flow properties of these molecules to acceptable levels for a variety of products. This isomerization mainly rearranges the structure to produce short side chains that significantly lower melting points.

Exxon Mobil's industry leading hydrocarbon conversion and wax-upgrading catalyst technologies are important elements of AGC-21, as noted in Figure 4.1.3. The upgrading process has been fully integrated into the overall AGC-21 scheme, allowing naphtha, diesel and lubes to be generated in high efficiency. The relative yield of various products can be tailored to meet project needs. Fischer-Tropsch PDU studies, and recent experience with our upgrading technology, have confirmed yield and quality improvements over competing alternatives. The lube basestocks are zerosulfur, highly biodegradable materials that are well suited for next generation motor oils. Wax upgrading studies are continuing to quantify other benefits of GTL product streams.

Fig 4.1.3 upgrades wax into ultra clean product



Wax Upgrading Reactor
- Converts wax to high quality naphtha, diesel, and lube basestocks
- Utilizes ExxonMobil industry leading upgrading catalysts
- Builds on extensive ExxonMobil refining experience

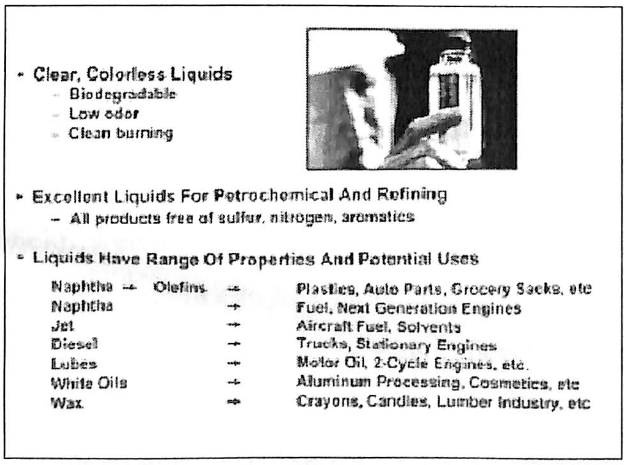
AGC-21 Naphtha
- Increases steam cracker olefin yield by 17%
- Potential fuel for advanced power systems

AGC-21 Diesel
- Zero sulfur, nitrogen and heavy metals
- Meets / exceeds all existing environmental specifications

AGC-21 Lube Basestocks
- High quality lube basestock
- Zero sulfur, high viscosity index, biodegradable
- Well suited for next generation motor oils
- Based on extensive dewaxing process and catalyst development experience

As noted in Figure 4.1.4, these The products of Fischer- Tropsch synthesis are clear, colorless liquids that are biodegradable, have low odor and are very clean burning. They are free of sulfur, nitrogen, aromatics and other contaminants, and are ideal feeds for petrochemical and refining applications. AGC-21 fuels are ultra-clean, and offer emissions and environmental benefits relative to conventional analogs. In addition, we have found them to be particularly useful as blendstocks for upgrading various refinery streams.Other studies have shown that FT hydrocarbons are useful as fuel cell fuels. This is a result of their ultra low sulfur content and the relative ease with which they can be converted to hydrogen.

Fig 4.1.4: Ultra clean fuels



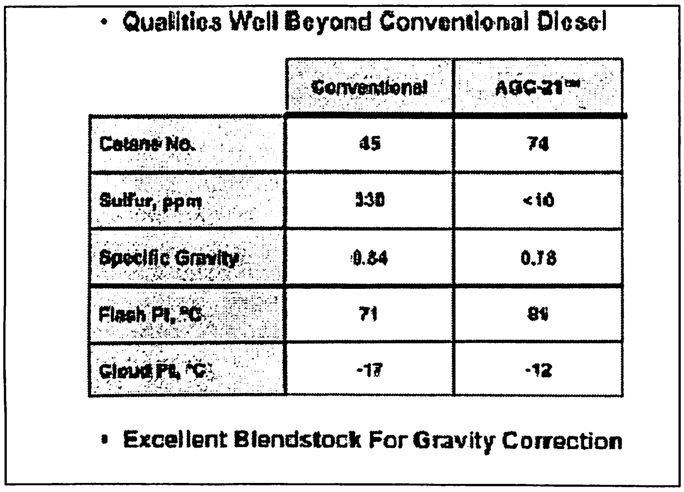
- **Clear, Colorless Liquids**
  - Biodegradable
  - Low odor
  - Clean burning
- **Excellent Liquids For Petrochemical And Refining**
  - All products free of sulfur, nitrogen, aromatics
- **Liquids Have Range Of Properties And Potential Uses**

Naphtha → Olefins → Plastics, Auto Parts, Grocery Sacks, etc
Naphtha → Fuel, Next Generation Engines
Jet → Aircraft Fuel, Solvents
Diesel → Trucks, Stationary Engines
Lubes → Motor Oil, 2-Cycle Engines, etc.
White Oils → Aluminum Processing, Cosmetics, etc
Wax → Crayons, Candles, Lumber Industry, etc

4.1.1 **AGC-21 Fuels**

Diesel will be a major portion of the overall GTL product, and key properties are outstanding, as shown in Figure 4.1.5. Sulfur content is well below the standard measurable range of 10 parts per million, and the measured cetane of 74+ is consistent with its high concentration of paraffinic molecules which are known to be excellent diesel components. The absence of high density aromatics along with an abundance of paraffins leads to a somewhat lighter diesel with a specific gravity below that of the conventional sample. Flash point can be controlled through distillation without interfering with other key properties.

Fig 4.1.5: AGC-21 Product high quality diesel



- Qualities Well Beyond Conventional Diesel

	Conventional	AGC-21™
Cetane No.	45	74
Sulfur, ppm	330	<10
Specific Gravity	0.84	0.78
Flash Pt, °C	71	84
Cloud Pt, °C	-17	-12

- Excellent Blendstock For Gravity Correction

Properties related to performance in cold environments merit special attention because the same paraffinic nature that provides high cetane can also impact drivability-related tests such as cloud point or wax appearance point. Of course, undercutting diesel provides one path for altering low temperature performance but at the expense of diesel yield. Weíve found that the same flexibility that allows significant control over product slate also applies to key product qualities. In other words, cold flow properties can be adjusted with catalytic processing if needed for local markets. We have shown that a 280-700°F GTL diesel burns more cleanly than conventional US or European diesels. This is illustrated in Fig 4.1.6,where AGC-21 diesel is shown to provide significantly lower PM and NOx emissions that conventional US or UK low sulfur diesel samples. On the other hand, it is known that raising the T95 point of conventional diesel fuels can negatively impact vehicle emissions. But these data show that higher boiling GTL components can be added to diesel while still maintaining substantial emissions improvement, even with end points as high as 800-900°F. The hydroisomerization process facilitates production of low cloud point diesel fuels even when the boiling range is extended, by converting high-boiling normal paraffins into iso-paraffins. The cetane values remain high, ~70+, and the densities are low when compared to those of petroleum diesel fuels. The cloud point remains low even when T95 is extended beyond the range of normal diesel fuels. These heavier components may also offset inclusion of some light components from GTL that also have high cetane values. In fact GTL naphtha performs well in diesel engines but, of course, it does not meet flash specifications. 3 SPE 93653

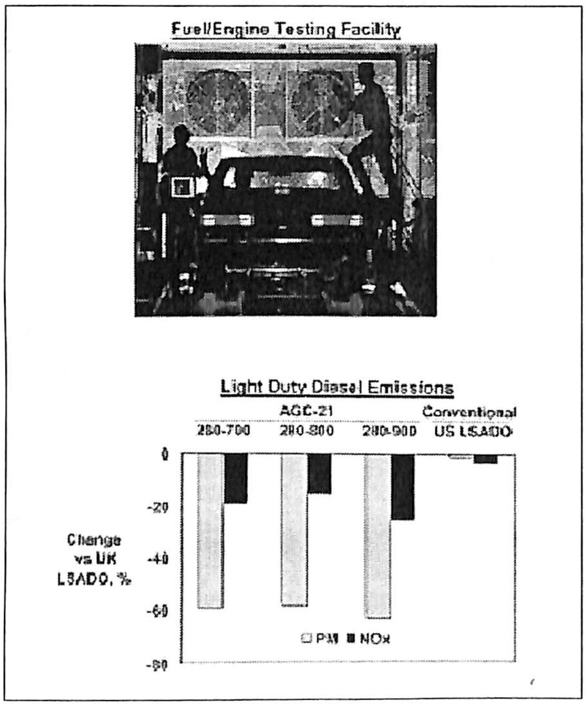
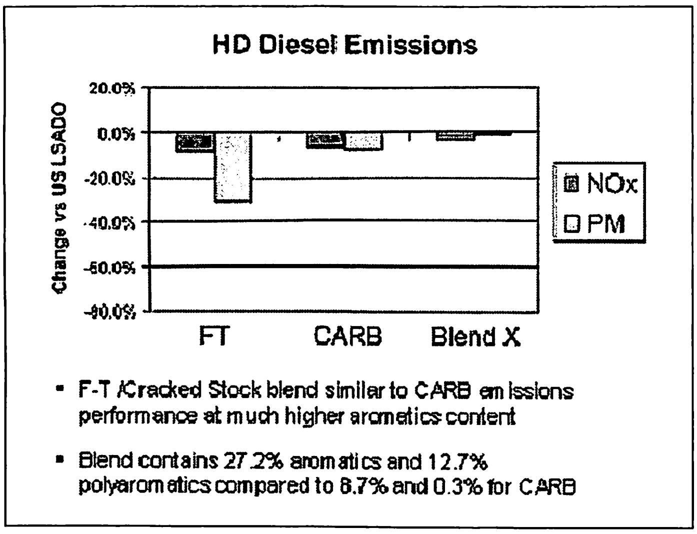


Fig 4.1.6: diesel cleaner in engine test

We and others have found that F-T fuels provide reductions in emissions when compared to conventional fuels such as a CARB diesel. As shown in Figure 4.1.7, we have found that the unique properties of F-T fuels also make them attractive for blending into conventional petroleum diesel fuels and diesel fuel blending stocks.



- F-T /Cracked Stock blend similar to CARB emissions performance at much higher aromatics content
- Blend contains 27.2% aromatics and 12.7% polyaromatics compared to 8.7% and 0.3% for CARB

Fig 4.1.7:Emission performance by FT/Cracked stock blend

Blend Xî, made of the F-T fuel and a cracked stock in equal proportion, compares favorably with CARB diesel. The blend produces similar levels of NOx emissions, and slightly more PM emissions. However, this blend achieves these emission levels with much higher aromatics (27.2 vs. 8.7%) and polyaromatics (12.7 vs. 0.3%) content at identical sulfur content. The high cetane and low density of F-T fuel make it possible to blend a fuel with good emissions performance from distressed refinery streams, even though the blended fuel contains high levels of aromatics and polyaromatics.

4.1.2 **AGC-21 Lubes**

The lube basestocks are zero-sulfur, have a high viscosity index, and are highly biodegradable making them well suited for next generation motor oils. AGC-21 technology allows us to produce these basestocks in higher yield and better quality than competing GTL processes.

Lubes are another potential product from GTL, and an outlook for lube basestock demand shows that over the next 10 years or so, Group II, Group II+, and Group III basestocks will make up the fastest growing segment of the basestock market. As shown in Fig 4.1.8, basestock production is evolving from conventional routes involving acid/clay treating and solvent dewaxing to more advanced forms of hydroprocessing and GTL. This has been accompanied by an increase in unit capacity and economy of scale, and the ability to produce higher Group III+ basestocks at lower cost.

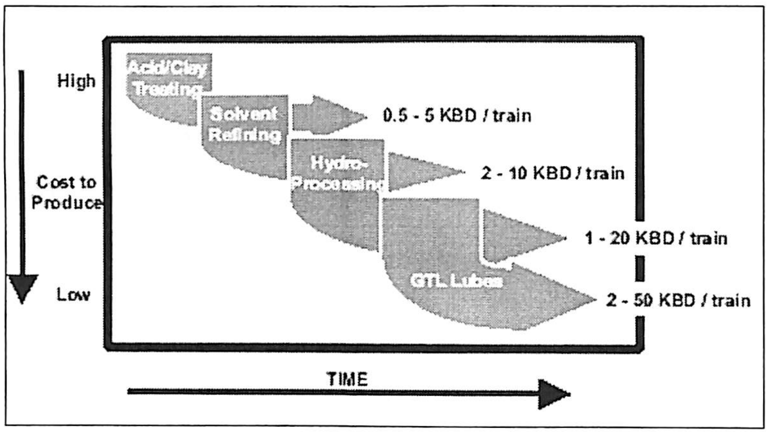


Fig 4.1.8: Basestock quality evolution

Demand for Group II, Group II+, and Group III basestocks is projected to grow between 30 and 50%, to almost 20% of the total basestock pool by 2010. Significant hydroprocessed basestock manufacturing capacity is available to meet these demands and new capacity is being added by conversion of existing Group I capacity and low-cost debottlenecks. Proposed capacity additions will keep the supply of hydroprocessed basestocks well ahead of demand. All-in-all, we project the hydroprocessed basestock capacity around the world to be over 250 KBD by 2010, well exceeding the projected technical demand for these types of basestocks. ExxonMobil has been a leader for decades in developing a family of dewaxing process technologies. The ZSM-5 based catalyst for distillate dewaxing rapidly evolved with innovation to industry leading MSDW-2 selective dewaxing technology. A proprietary bifunctional catalyst provides excellent performance over a range of applications and viscosity grades. And we are not resting on this achievement, we are anticipating further enhancements in this class of catalytic processing. For GTL, the high productivity and selectivity of ExxonMobil's HCS technology along with high

selectivity MSDW upgrading technology provides ExxonMobil with industry leading capability for manufacture of GTL basestocks.

4.1.3 The Future Of AGC-21 Technology

Finally, as shown in Fig 4.1.9, a large-scale commercial GTL plant, such as the 154KBD ExxonMobil project in Qatar, will likely have small impact on fuel markets, but could have a significant impact on lube basestock markets.

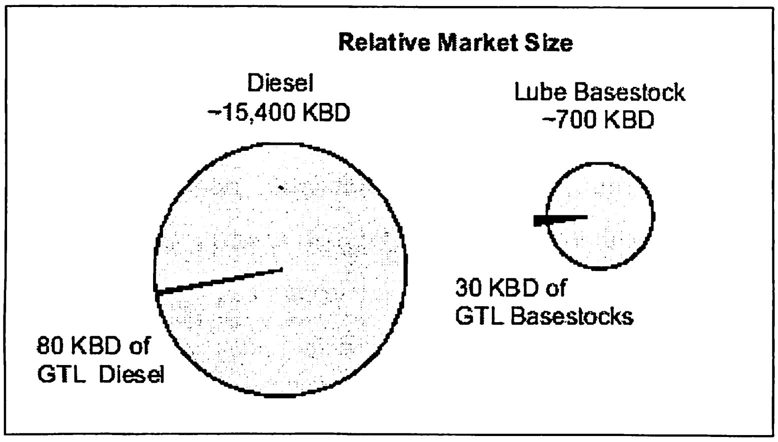


Fig 4.1.9:impact of GTL on fuel and lube market

For example, a commercial-scale GTL plant having a total capacity of ~150KBD product might be designed to produce at least 30KBD lube basestock along with 80KBD of diesel fuel. The impact of such a volume of diesel product on the global diesel market is relatively inconsequential, while the lubes volume from this single plant will equate to 4% of the world's basestock market, or almost 20% of today's global high-quality basestock market. These considerations clearly indicate that development of a large-scale global GTL industry will require a technology that can be tailored to market needs, and AGC-21 is well suited to this task. We are enthused about Gas Conversion technology and products. It will bring both commercial and technical challenges that play to our strengths. Exxon Mobil capabilities span the entire commercial and technical ranges that will be needed to establish large, efficient Gas Conversion plants. They cover the full range of upstream and downstream activities needed for bringing on a plant, operating it, and gaining best value for its products. And the technical base and special expertise underpinning those activities are solid and well developed for commercializing Gas Conversion.

4.2 CASE HISTORY

In the fields of energy production and use, there is a serious and increasing need to preserve our natural environment on a global scale. Trends point to the fact that there will also be a continued increase in the demand for natural gas. Natural gas has less of a negative impact on our natural environment than that of other sources of energy, namely coal or petroleum. Furthermore, natural gas is a relatively evenly distributed resource. However, pipelines must be constructed, and there is a need for an LNG infrastructure (manufacturing, shipping/ receiving, transport). Therefore, there are small reserves and many undeveloped gas fields that include impurities such as carbon dioxide gas that do not meet the criteria for large investments for their development. GTL technology converts natural gas into clean naphtha, kerosene and light oils thereby making it possible to ensure the same distribution routes as petroleum. Thus, this technology also contributes to preserving our environment and to the diversification of our resources. **At the center of this technology are global corporations such as Shell, Sasol and Exxon Mobil.** They are making efforts into the commercializing of this energy source. However, Nippon Steel Corporation has also promoted research into the practical application of this important technology with the features described below in the GTL technical development project known as JOGMEC (Japan Oil, Gas and Metals National Corporation). Nippon Steel Corporation is an active participant in the planning of this project.

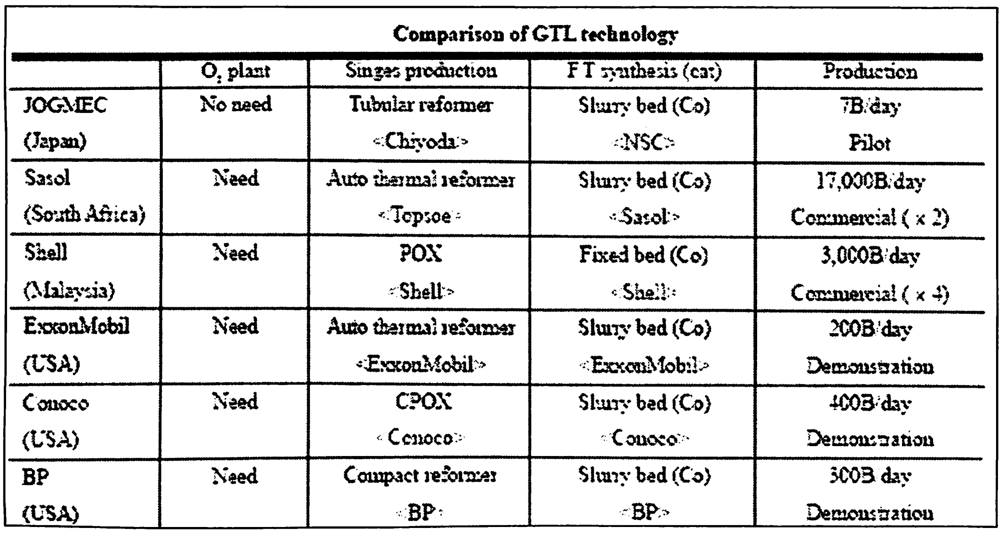
It is important to promote the development of technologies that have characteristics and superiority over overseas technologies, in the development of new energy technologies of the future. This GTL technical development should be advanced as a national project with links to the main players of each industry and country from the viewpoint of measures for the degree of further dependence on Middle Eastern oil, the atmospheric environment that is linked to the diffusion of diesel vehicles and to measures against carbon dioxide issues. Currently, progress is being made toward the next step of commercialization, in view of the results obtained.

A GTL (Gas to Liquid) technology was developed under the JOGMEC (Japan Oil, Gas and Metals National Corporation) project. This technology is anticipated to contribute to clean energy production processes in future. Nippon Steel was responsible for the development of FT synthetic technology. In the process of this development project a **cobalt basis catalyst** was developed. Its high performance and high strength were confirmed as being superior to other existing competitors, such as a catalyst at the Yufutsu pilot plant test (7BPD). s for the process development, a simulation model was developed as well as a scale up design method. A feasibility study of this developed technology was also developed to confirm the feasibility in its application to actual gas fields.

COMPARISON OF GTL TECHNOLOGY

Table 15 shows the syngas manufacturing technologies, FT synthesis technologies and the developmental stages at each company developing GTL technology.

Table 15: Comparison of GTL technology



Comparison of GTL technology

	O_2 plant	Singas production	F T synthesis (cat)	Production
JOGMEC (Japan)	No need	Tubular reformer <Chiyoda>	Slurry bed (Co) <NSC>	7B/day Pilot
Sasol (South Africa)	Need	Auto thermal reformer <Topsoe>	Slurry bed (Co) <Sasol>	17,000B/day Commercial (x 2)
Shell (Malaysia)	Need	POX <Shell>	Fixed bed (Co) <Shell>	3,000B/day Commercial (x 4)
ExxonMobil (USA)	Need	Auto thermal reformer <ExxonMobil>	Slurry bed (Co) <ExxonMobil>	200B/day Demonstration
Conoco (USA)	Need	CPOX <Conoco>	Slurry bed (Co) <Conoco>	400B/day Demonstration
BP (USA)	Need	Compact reformer <BP>	Slurry bed (Co) <BP>	300B/day Demonstration

(1) Syngas manufacturing technology

While there are a variety of methods undertaken in the development of syngas, many methods vary according to each company's developmental concepts and objective applications. As a general flow, there is a move toward ATR (Auto Thermal Reforming) that uses oxygen. However, because it requires an oxygen plant, thus incurring enormous costs, the issue of excess equipment costs becomes a problem.

(2) FT synthesis technology

Both BP and Shell employ a multi tubular fixed bed, but that method is considered to be better suited for a slurry bed because it is more efficient in removing the heat of the reaction in the FT synthesis, and because the equipment can be more compact. However, this method still has many unanswered technical issues, such as establishing a method for designing scaled-up systems.

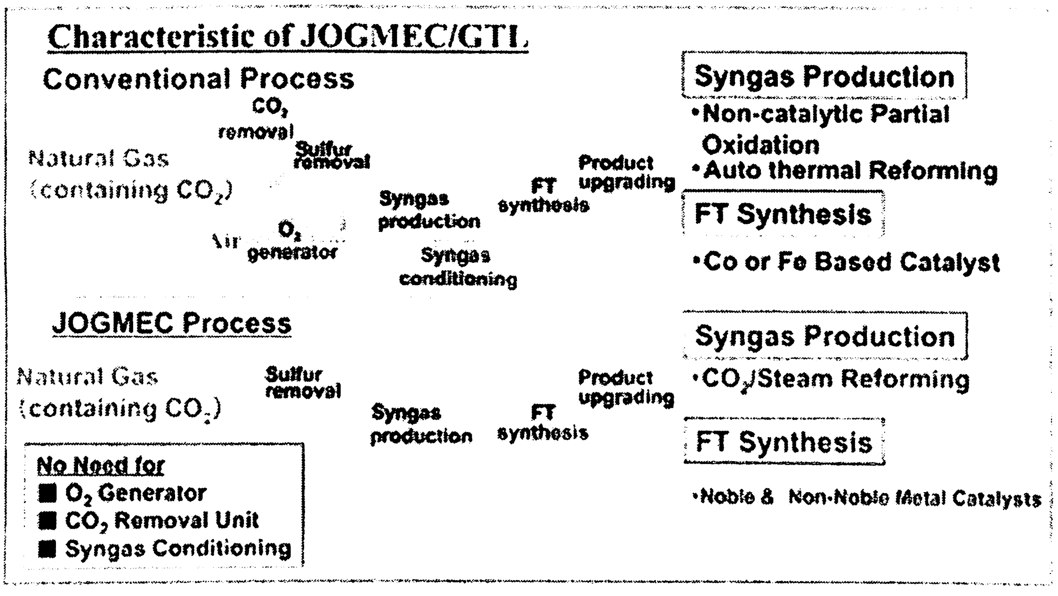


Fig 4.2.1 Characteristic of JOGMEC/GTL

The JOGMEC-GTL processes are compared in **Fig. 4.2.1** to the latest representative model of conventional GTL processes (ATR). The conventional process requires an oxygen plant and equipment for the removal of carbon dioxide gas in order to manufacture syngas. To derive syngas having an optimum mole ratio of 2:1 (hydrogen to carbon monoxide) in the FT synthesis, equipment that adjusts the hydrogen concentration in the synthesized gas is necessary. On the other hand, by employing carbon dioxide gas reforming, natural gas that includes carbon dioxide gas in the crude material can be utilized as it is. This makes it possible to obtain syngas having an optimum composition in the FT synthesis in one step. That capacity translates into lower construction and operating costs. This was achieved through the development of a **stable catalyst** that is operable even under the conditions where continued operations were impossible because of the precipitation of oxygen in the conventional technologies.

Using the FT synthesis developed by Nippon Steel, the following were possible.

(1) Developed a catalyst (patent pending) that has high durability to wear, and high performance based on control of the boundary surface to an optimum structure;

(2) Continuing from laboratory tests, verified performance that exceeds the prior technical level at a pilot plant in Yufutsu, Hokkaido;

(3) Advanced development for a simple slurry bed reaction model that has superior heat transfer transmission characteristics and that is compact, studied the reactor structure that has heat transmission characteristics and that allows for uniform flow of catalyst slurry, and verified stable slurry circulation and processing capabilities even in the pilot tests.

FT synthesis catalyst development, and testing evaluations Nippon Steel Corporation optimized the properties of a silicatype carrier and cobalt holding method for the FT synthesis catalyst, and evaluated them in a laboratory to test at the pilot plant. In the development, the technologies of 1) Metal structure control; 2) Ceramic (carrier) control and 3) Analysis and control of the boundary, were applied. By optimizing the structural controls, it was possible to link highly active, and strong catalysts to the development.

Pilot plant FT synthesis reactor

The pilot plant FT synthesis reactor is a slurry-bed type. **Fig. 3** shows the flow in the FT reactor at the pilot prototype. The raw material of syngas is supplied from the spersier on the bottom of the reactor as air bubbles. It passes through the slurry composed of catalyst and catalyst oil and reacts in suspended state. The FT synthesis reaction generates heat so it is important for the reaction temperature to be efficiently controlled. For that reason, the heat removal tube inside the reactor is a heat exchanger type. As a cooling agent, BFW (or Boiler Feed Water) is supplied. Thus, steam is let off because of the exchange of heat. The heavy reaction generated product and catalyst exist in a slurry form in this slurry bed type reactor, so these elements must be separated. To that end, a sediment separation vessel is established outside of the reactor to separate these elements using the different gravity between the catalyst and the reaction generated product. Separated catalyst is returned to the reactor bottom.

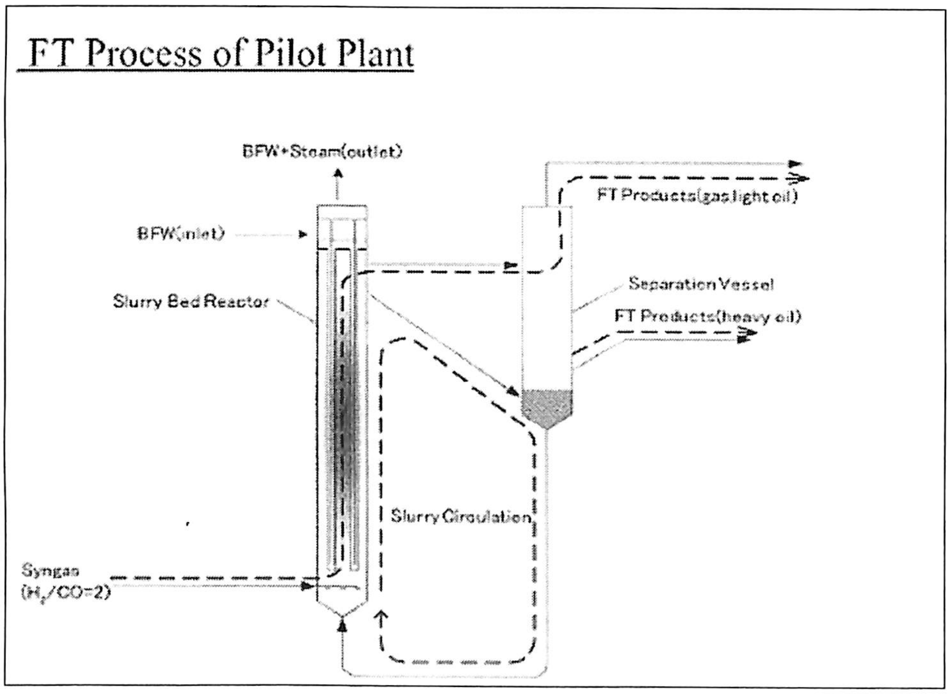


Fig 4.2.2: Flowsheet of FT reactor

Economic evaluation

A commercial prototype plant was designed in view of Southeast Asia, based on the data attained in the development stage.Under calculations of the JOGMECGTL process based on crude natural gas conditions of actual gas fields in Southeast Asia, a **plant of the scale of 15,000 bbl/day can produce approximately 440,000 Nm3/h of syngas from approximately 200,000 Nm3/h of crude natural gas (H2 and CO (H2/CO = 2.0).** This syngas can be converted to approximately 74 t/h of FT synthetic oil.

Based on that, calculations were done on FT oil prices, assuming a cost of .1.00/MMBTU of natural gas. Adding the costs for refining and transport ($5 US/BBL) for the price of the FT oil, it should be compared to the environmental premium depending on products such as naphtha.

GAS CONVERSION IN INDIA

Applicability Of Gas Conversion In India

1. Gas reserves of NE region - Tripura
2. Gas hydrates in deep sea
3. Gas reserves in deepwater

Gas Conversion At Tripura

Gas production scenario:

1. Production potential - 4.03 MMSCMD
2. Gas sales - 1.11 MMSCMD
3. Surplus gas - 2.92 MMSCMD
4. Future discovery prospects very optimistic

Field potential, remoteness and product evacuation options favors gas conversion

Of the three gas conversion processes F-T scores over others, due to:

- Ready market
- Reduction in crude import
- Premium grade crude/fuels

Thus We Can Conclude That:

1. Gas conversion into Syn Fuels /Syn Crude holds promise at Tripura
2. GTL plant at Tripura
    - Regional development
    - Meets local demand
    - Reduced import burden
    - Eco friendly products
    - Improves refinery product quality
3. Substantial govt. subsidies essential for project viability
4. Involvement of oil companies for product transfer & marketing
5. SynFuel option more favorable
6. SynFuel transport by tanker more economical
7. Post tax IRR range from 8.5% to 11.5% based on option chosen
8. Effective utilization of India's dormant natural resource to nation's advantage

The Significance and Scope of GTL Technical Developments

2.1 The significance of developments

The significance of developments can be described as falling into the following three Es categories. (Energy security, Ecology, and Economy)

(1) Energy security

A. This is the effective use of untapped natural gas resources, and diversification of fuel resources by ensuring substitutes for crude oil.

B. This is reduced dependence of resources from the Middle East by effectively utilizing untapped gas fields including carbon dioxide gas from Southeast Asia and Western Australia.

C. This is the suppression of future GTL enterprise monopolization and cost controls by major international oil company overseas.

(2) Ecology

A. This is to provide clean resources of flue gases (NOX, PM) from the characteristics of the Sulfur component and aromatic sweet-free fuels in petroleum based fuels.

B. This is to promote the diffusion of highly efficient diesel powered vehicles (with low carbon dioxide gas discharge) linked to GTL light oil introduction.

C. This is the reduction and effective use of associated (flaring) in oil and gas producing countries.

(3) Economy

A. This is the participation in the planning of a development project and contribution to technologies through independent and superior, domestic technologies.

B. This is the promotion of development of domestic company's gas fields and linking to gas producing countries that have superior technologies.

CONCLUSION

Technological improvements and investment commitments from the world's largest oil companies suggest the gas to liquids (GTL) industry is likely to expand rapidly over the next decade. GTL uses large quantities of natural gas to produceliquid petroleum products like diesel fuel and home heating fuel. The GTL industrymight become an important competitor to the liquefied natural gas industry (LNG)in the effort to secure natural gas supplies.

It appears likely that the GTL industry will begin to develop into a commercial factor in world energy markets over the next few years. Technological improvements coupled with favorable economics are responsible for the increased investment activity. Developing the industry is in the interest of producing nations with economically stranded natural gas resources, because it gives those nations the opportunity to choose the best use for their resources consistent with available rates of return and risk.

The major oil companies are committing to multi-billion dollar investments in GTL, as well as LNG facilities, at a time when their investment in oil refining capacity expansion in the U.S. is low. The reason for this investment strategy is likely based on forecast relative rates of return. The combination of a receptive business environment from the producing countries, especially Qatar, and the investment commitments of the major oil companies suggest that rapid growth is likely to be made by the GTL industry over the next decade.

The implications of the growth of the GTL industry for the consuming nations is mixed. While the availability of ultra clean diesel fuel is a benefit, promising to relieve supply worries and moderate price increases due to the increased supply, the beneficial effects on the natural gas side of the market are less clear. More GTL means that less LNG will be available on the world market, slowing the development of competition and resulting in higher prices and less available supply of natural gas.

These developments suggest that consuming countries might also consider the benefits as well as the costs of developing other sources of natural gas. Beyond LNG, available natural gas supply options include an Alaskan pipeline, increased exploration and production on protected land and water areas, and more intense development of existing known fields. No one source is likely to provide the supply and price stability that consumers desire.

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