"CONVERSION OF NATURAL GAS TO LUBE BASE STOCKS- A STUDY OF PROCESS INVOLVED & PRODUCT PERFORMANCE"

A Project Report submitted in Partial fulfillment of the requirements for the

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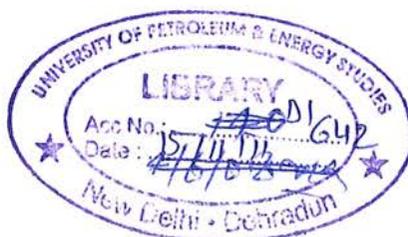## UNIVERSITY OF PETROLEUM & ENERGY STUDIES

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"Success is accomplished through sincere Efforts. Efforts endowed with

appropriate assistance is the key ingredient in bringing out Success"

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Executive Summary

The increasingly important growth in the consumption of Natural gas demonstrates its outstanding position as an Energy source. During its combustion, it produces 40-45% less Carbon dioxide than coal, and 20-30% less than oil based products. The utilization of Natural gas together with going search for efficiency, energy saving and support for profitable development of renewable energy is key to the development of an international strategy for action to deal with climatic change. GTL option allows use, and extends life, of existing oil pipelines. Advanced GTL technologies will allow remote and deep gas to be converted to transportable liquid fuels and petrochemicals. As an energy source, natural gas offers part of the solution to global efforts to reduce greenhouse gas. Some remote natural gas can now be economically converted through a GTL process into an ultra-clean fuel for producing lubricants. 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. Lubricant base oils produced by GTL processing are expected in the market in the 2005/2006 timeframe. They are expected to initially enter the market by competing with Group III and IV in the synthetic and synthetic-blend engine oil market space. To a lesser extent, GTL base oils will also compete with Group II+ as a correction fluid for Group I. Rather than reducing the value of GTL by moving down the quality continuum to Group I and II base oils, GTL base oils are expected to reside in the high-end market space of Group II+, III, and IV and be the beneficiaries of demand being pushed into this market space by more stringent specifications. The projects aims to understand the process details of obtaining Lube base stocks through AGC 21 process of Exxon Mobil, its quality in comparison with conventional basestocks and its economic imperatives.
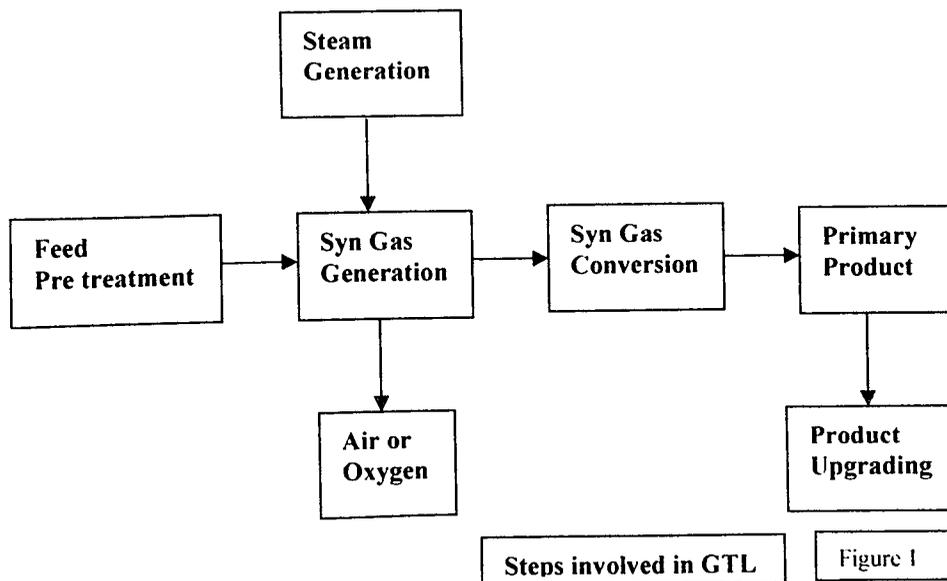
1. AN OVERVIEW OF GAS TO LIQUID TECHNOLOGY

Natural gas is emerging as the new fuel for the 21st century. Its mix in the energy pattern and its usage varies form region to region. Where the developed economies have shown greater interest I using it, its significance is less felt by the developing economies. The estimated proven Natural gas reserve of the world is about 156 trillion cubic metre (tcm). Factoring in the potential reserves, it is 372 tcm. Adding reserves form unconventional sources, this comes to 20000tcm. It has been found that about 80% of the proven and potential reserves are too far from large markets and are not feasible to transport through pipelines. These are stranded reserves and technologies to exploit these resources are in the development phase. A green technology that has emerged over the years, proving commercially viable for converting Natural gas to ultra clean liquid fuels, popularly known to be as Gas to liquid technology, is on the verge of changing the transportation and usage pattern of Natural gas in the global arena. The Process technologies, its major licensors, global scenario, challenges ahead are briefly discussed in the coming sections.

1.1 GTL Process

The basic steps involved in converting Natural gas to ultra clean products are depicted pictorially in the Figure 1.

As a first step, Natural gas which is the feed is cleaned and it is mixed with steam, air/oxygen to produce syngas through a process known as "Reforming". This is then converted to primary products through Fischer Tropsch synthesis. The resulting products are then upgraded according to the requirements. The need for steam, air/oxygen depend on specific processes. The production and conversion steps are those that use catalysts in order to start and maintain chemical reactions.

Steam Generation → Syn Gas Generation

Feed Pre treatment → Syn Gas Generation → Syn Gas Conversion → Primary Product

Syn Gas Generation → Air or Oxygen

Primary Product → Product Upgrading

| Steps involved in GTL | Figure 1 |

1.2 Feed Pre treatment

Natural gas is a combustible mixture of hydrocarbon and non hydrocarbon gases with impurities. The major component would certainly be Methane, gases such as Nitrogen, Carbon dioxide, Hydrogen sulphide; Helium as well as water vapour will also be present. In the production facilities itself, majority of these impurities are removed, even then, it is necessary to ensure that the gas arriving at a conversion plant is absolutely free from sulphur, since its presence can poison the catalysts used.

Two different types of pre treatments are used depending on the amount of gas to be treated. For smaller volumes, the gas is cleaned using either liquid or solid scavengers. Liquid scavengers can be injected into the gas or gas can be passed through a vessel containing liquid or solid scavengers. The used scavengers are then collected and removed. Capital costs are low, but operation costs are relatively high, since the scavengers cannot easily be recycled and must be supplied continuously.

For larger volumes, amine wash systems are used. The gas flows up trough a column fitted with a set of trays and over flow wiers. The liquid amine flows downwards, collecting on each plate and then overflowing downwards through the column. The gas bubbles through the liquid on the trays, ensuring good contact, and the sulphur

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compounds dissolve in the liquid. Once the liquid reaches the bottom of the column, it is removed and then sent to a recovery system where it is recycled to remove impurities. It is then sent back to the top of the column.
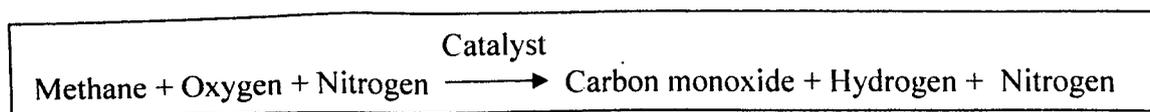
Advantages

System runs in a continuous loop

Amine liquid does not needs to be replaced

Operating cost is low

Disadvantages

Significant capital investment is needed initially in both the column and in the amine regenerator system

1.3 Syngas Production

The reforming process by which syn gas is produced is a chemical reaction in which hydrocarbon molecules in Natural gas are broken down and stripped of their hydrogen atoms. Oxygen, introduced either through stream as air or as pure gas, is substituted, producing a mixture of Carbon monoxide and Hydrogen. Both catalytic process and non catalytic process are developed.

$$\text{Methane} + \text{Oxygen} + \text{Nitrogen} \xrightarrow{\text{Catalyst}} \text{Carbon monoxide} + \text{Hydrogen} + \text{Nitrogen}$$

There are three basic types of reformer and all the industrial plants use either variants or combinations of these. They are

1. Steam Methane reformer

2. Partial Oxidation reformer

3. Auto thermal reformer

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1.3.1 Steam Methane reforming

In Steam Methane reforming, Natural gas and steam are passed over a catalyst, typically nickel dispersed on alumina support contained in tubes located in a fire box. Heat for the reaction is supplied by burning some of the feed stock gas. It is the most widely used technology for syngas production. This is being used in bulk chemical industry for the manufacture of methanol and other chemicals. In combination with a secondary stage, it is also used to manufacture ammonia. But the composition of syngas produced is not suited for producing liquid fuels.

$$CH_4 + H_2O \xrightarrow{\text{Ni/AL}_2O_3} CO + 3H_2 \quad \Delta H = +206 \text{ KJ/Mol}$$
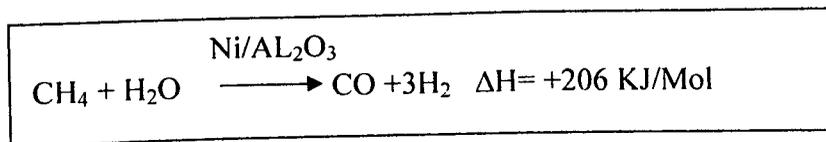
Operating Conditions

Temperature = 850-950 °C

Pressure = 3 MPa

The typical H_2 / CO ratio will be more than 3:1. As discussed earlier, the Natural gas must be de sulphurised to prevent catalyst deactivation. This process is commonly employed for the production of Hydrogen for application in refineries. A steam to carbon ration of 3 to 6 is used and it is an important process variable. A lower steam to carbon ratio will require higher operating temperature and higher fuel consumption. Because of high temperature, hydrocarbons can undergo a complex series of cracking reaction and reaction of carbon with steam may occur.

$$CH_4 \longrightarrow C + 2H_2$$

$$C + H_2O \longrightarrow CO + H_2$$
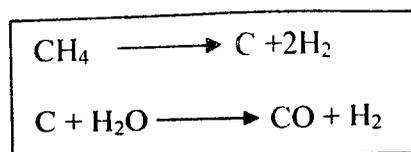
Operating Variables

The operating variables are respectively

- Temperature

- Pressure

- Steam to Hydrocarbon ratio

Picking the operating conditions for a particular plant involves a proper economic trade-off among these parameters. Steam reforming is an equilibrium reaction and conversion of hydrocarbon is favoured at high temperature, which in turn carries a fuel penalty. Because of the increase in volume of fuel, the reaction conversion is also favoured at low pressure. In practise, the temperature and pressure are limited by the tube material. Because of high temperature and heat load in this process, catalyst is used in the furnace. The catalyst is subjected to severe operating conditions. In order to withstand these conditions, the catalyst is usually dispersed in the carries namely alumina. The reforming catalyst is nickel and the reaction is controlled by both diffusion and heat transfer. The catalyst is usually made in rings to provide increased mass and heat transfer at a minimum pressure drop.

Thermal cycling is especially hard on catalyst. When tubes are heated, they will expand and the catalyst tends to settle in tubes. When the tubes expand and contract, the catalyst is crushed. This can cause voids to form in tubes leading to formation of hot spots and it ultimately ruptures. The main catalyst poisons re sulphur, chlorides and heavy metals like arsenic. Chlorides are irreversible poison. The chlorine combines with nickel to form nickel chloride which is volatile. The nickel migrates and evaporates which in turn reduces the activity of the catalyst. Even with high strength carrier catalyst life is limited as much as by physical break down or by de activation.

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1.3.2 Partial Oxidation

In this method, Natural gas reacts with oxygen at high temperature to produce a mixture of carbon monoxide and Hydrogen. This process does not involve the use of catalyst since the operating conditions are extreme. Heavy feed stock can be used and the capital cost is high. In the past, this method was considered for Hydrogen production because of the expected shortage of light feed stock. It can also be used as a disposal method for heavy high sulphur streams like heavy residue. In this process the syngas is produced whose Hydrogen to Carbon monoxide ratio is approximately to 2:1.This also requires expensive cryogenic air separator plant for the production of oxygen.

$$CH_4 + 0.5\ O_2 \longrightarrow CO + 2H_2 \quad \Delta H = -36\ KJ/Mol$$
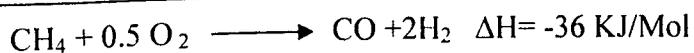
Operating Temperature = 1200 – 1500 °C

The main competing reaction is the decomposition of methane to carbon black. There are three process sections.

1. Burner Section: Here combustion occurs. This happens with pure oxygen and the presence of Nitrogen is undesired.

2. Heat Recovery Section

3. Carbon black removal Section: This is done first by water scrubbing, then extraction by naphtha from sludge

Partial oxidation is a weak exothermic reaction and the reaction rate is one to two orders of magnitude faster than Steam Methane reforming. Traditionally, oxygen separated form air at low temperature increases the investment in energy supply and plant. Recently coupling the mixed-conducting membranes with partial oxidation reaction could use air as a source for pure oxygen.

This merged the separation of oxygen and catalytic oxidation in one process. Such coupling of separation and reaction in one reactor, simplified process operation reduced GTL production cost by 20-30%. Mixed-Conducting oxygen permeable membranes exhibit both oxygen ion and electronic conductivity. At high temperatures, oxygen ions transport through membranes from high to low oxygen pressure side, forming oxygen lattice vacancies. At the same time, electrons move in a reverse direction due to changes of valence state of metals in the membranes. So the permeated selectivity of Oxygen is 100%. Although many mixed conducting materials have been developed, few of them have been successfully applied as membrane reactors for partial oxidation process. Mixed conducting membranes used in partial oxidation process should meet the following requirements.
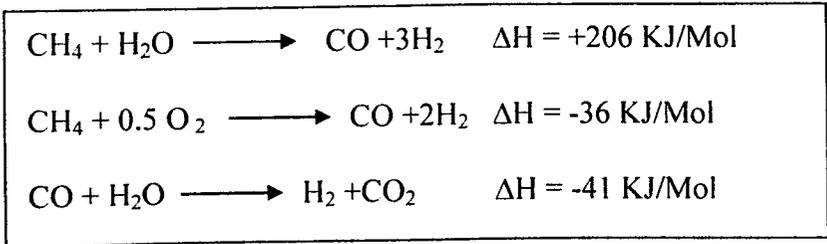
High Oxygen permeation and stable chemical structure under reducing atmosphere

Recently, a novel mixed conducting membrane $Ba_{0.5}Sr_{0.5}CO_{0.8}Fe_{0.2}O_{3-\delta}$ was developed which shows extremely high Oxygen permeability and stability. Furthermore, the membrane was successfully applied to partial oxidation of Methane using air as Oxygen source. Oxygen transported from other side of membrane reacts with Methane and produces syngas.

1.3.3 Auto Thermal Reforming

This process combines steam reforming with partial oxidation. This uses the heat produced from partial oxidation to provide heat for steam reforming resulting combination is auto-thermal the benefits are lower reaction temperature, lower Oxygen consumption and the Hydrogen to Carbon monoxide ratio is exactly 2:1 on molar basis, which is ideally suited for Fischer Tropsch Synthesis. In a normal auto-thermal reactor, the gas is burned with Oxygen and steam and then passed through a bed of nickel, located in the same vessel.

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The combustion reaction is very fast and produces very high temperatures. No additional heat source is required, hence the name auto-thermal. It produces syngas suitable for most conversion processes. Air blown reactors, which utilise air rather than Oxygen, have also been developed and these avoid the use of air separation plant. However, they produce a Nitrogen diluted syngas that requires special processing for conversion as well as meaning that large equipment is needed.

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \quad \Delta H = +206 \ KJ/Mol$$

$$CH_4 + 0.5 \ O_2 \longrightarrow CO + 2H_2 \quad \Delta H = -36 \ KJ/Mol$$

$$CO + H_2O \longrightarrow H_2 + CO_2 \quad \Delta H = -41 \ KJ/Mol$$

The system is in heat balance, no heat transfer system is required. The syngas at the reactor outlet is in equilibrium with respect to the reactions and it is soot free.

1.4 Syngas Technology Comparisons

Technology	Principal Advantages	Principal Disadvantages	Capital Cost	Exported Power(1)	Carbon Efficiency(2)	Applications that are well suited:
Steam Methane Reforming	No oxygen plant needed, mature technology	Single unit size limitation to about 10,000 bbl/day. Net water consumption	lowest	~6	~60	Remote sites with power market and that are capex sensitive.
Partial Oxidation	Good control over H2:CO, ease of waste stream disposal, mature technology	Large exported power, large O2 requirement	highest	~9	~55	Low gas cost and market for power

Autothermal Reforming	Can have very large single-unit train.	Large O2 requirement	middle	~5	~60 Very	Very large single train plants
Steam Methane Reforming +Autothermal Reforming	Uses about 1/2 the O2 of stand alone ATR, much larger single-unit train than standalone SMR, net water excess.	ASU is still needed	middle	~6	~60	Where larger single train than SMR and better efficiency than ATR are desired, and where water is scarce.
Gas-Heated Reforming + Autothermal Reforming	Uses less oxygen than stand-alone ATR, good heat balance	Not yet commercial at large scale	high	~0	~65	Sites with no power market, high gas cost
Compact Reformer	No oxygen plant needed, compact, modular, good heat balance	Not yet commercial (presently in large demo), net water consumption.	low	~0	~65	FPSO, sites with no power market, high gas cost

Table 1

1. Power is generated from excess steam
2. Carbon efficiency is defined as carbon in collected C5+ crude product divided by carbon in all natural gas supplied to the plant

1.5 Syngas Conversion

Once syngas has been produced, the next step is to convert Carbon monoxide and Hydrogen into the required products. All of the current processes commercially available are based on Fischer-Tropsch catalytic conversion. The product generally depends on the catalyst used, the reactor type and operating conditions. Typical catalysts include Iron, Cobalt and Nickel. The reaction proceeds through growth of
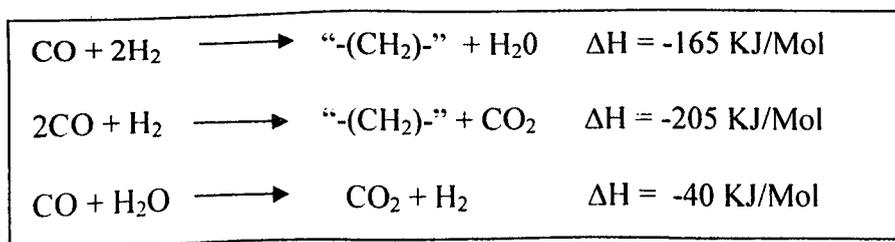
chain of hydrocarbons. If the chain growth is limited, then lighter hydrocarbons will predominate. If the chain growth is high, then heavier wax hydrocarbons will be formed. Typically the chain growth is related to reaction time.

Fischer-Tropsch process was discovered by Franz Fischer and Hans Tropsch in the year 1923 at the Kaiser Wilhelm Institute for coal research in Mullheim, Germany. Coal and Natural gas are utilized as the feed stock to produce several chemicals and transportation fuels. This technology is currently used by companies like Beyond Petroleum, Exxon Mobil, and Shell which together hold almost two hundred patents on this process. They proved that hydrogenation of Carbon monoxide over Iron, Cobalt or Nickel as catalysts at 180-250 °C and atmospheric pressure results in a product mixture of several hydrocarbons. This method has been refined to the use of Iron and Cobalt at 200-300 °C, 10-60 bar pressure.
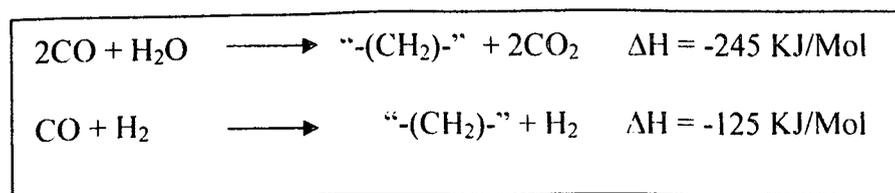
1.5.1 Reactions

There are three main reactions in Fischer-Tropsch synthesis. The two main products are paraffins which are saturated hydrocarbons and olefins which are unsaturated hydrocarbons. The water-gas shift reaction is important to regulate the Hydrogen to Carbon monoxide ratio, so that the reaction will take place.

Main Reactions 1-3(shown below)

$$CO + 2H_2 \longrightarrow \text{``-}(CH_2)\text{-''} + H_2O \quad \Delta H = -165 \text{ KJ/Mol}$$

$$2CO + H_2 \longrightarrow \text{``-}(CH_2)\text{-''} + CO_2 \quad \Delta H = -205 \text{ KJ/Mol}$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \quad \Delta H = -40 \text{ KJ/Mol}$$

Combining the above three equations, we get reactions 4, 5 as shown below

$$2CO + H_2O \longrightarrow \text{``-}(CH_2)\text{-''} + 2CO_2 \quad \Delta H = -245 \text{ KJ/Mol}$$

$$CO + H_2 \longrightarrow \text{``-}(CH_2)\text{-''} + H_2 \quad \Delta H = -125 \text{ KJ/Mol}$$

Side Reactions 6-7 (shown below)

$$2CO \longrightarrow C + CO_2 \qquad \Delta H = -134 \text{ KJ/Mol}$$

$$CO + 3H_2 \longrightarrow CH_4 + H_2O \qquad \Delta H = -215 \text{ KJ/Mol}$$
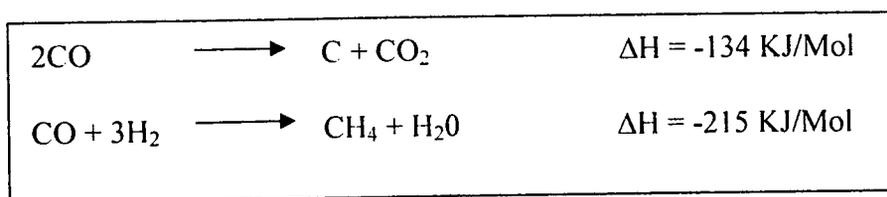
Water-Gas Shift reaction is used to create equilibrium when non-stoichiometric amount of Hydrogen is used. This uses the product water from Fischer Tropsch reaction or a separate source of water, reacts it with Carbon monoxide to increase the Hydrogen to Carbon monoxide ratio. This reaction is useful when Iron is used as a catalyst and negligible when Cobalt and Ruthenium is used. The Fischer Tropsch Synthesis consists of Fischer Tropsch reactors, recycling and compression of unconverted syngas and steam and removal of excess Hydrogen and Carbon dioxide. The most important aspects of commercial Fischer Tropsch reactions is the high reaction heats and varying vapour pressures.

1.5.2 Catalysts

Iron is the most commonly used catalyst due to relative inexpensiveness. This produces reasonable results and it is very stable when syngas with high Hydrogen to Carbon monoxide ratio is converted. This is active in the water gas shift process, high activity, and very selectivity to olefins.

Cobalt has the highest yield of products, predominantly linear alkanes. It has the longest life span. The disadvantage is that it is expensive and its low water gas shift activity.

Ruthenium is very rarely used. It is the most expensive catalyst and it has low activity. It produces higher molecular weight waxes when used at low temperature and high pressure.

1.5.3 Stochiometry and Thermodynamics

The Catalytic hydrogenation of Carbon monoxide in presence of Cobalt, Iron or Ruthenium produces

- alkanes and alkenes, predominantly of linear structure ranging from Methane to Poly- methylenes, as long chain hydrocarbons

- oxygenates such as alcohol, aldehydes, ketones, acids and esters as by-products

- at high synthesis temperatures, aromatic hydrocarbons are formed in small amounts

On the basis of above seven reactions the formation of long chain hydrocarbons form the synthesis may be summarized as follows

- Long chain compounds are formed depending on the reaction conditions and properties of catalysts.

- Maximum yield of components are formed when Carbon monoxide and Hydrogen are introduced in the same ratio as they are converted (Feed ratio =Consumption ratio).

- For each type of synthesis or catalyst an optimum fed ratio can be chosen which may either be reaction in presence of Carbon monoxide of Hydrogen

The maximum attainable yields of hydrocarbon for different feed and consumption are linked as follows

Maximum attainable yield (gram/m^3)			
Consumption Ratio		Feed Ratio	
H$_2$: CO	1:2	1:1	2:1
1:2	208.5	156.3	104.3
1:1	138.7	208.5	138.7
2:1	104.3	156.3	208.5

Table 2

The main reactions and side reactions of Fischer Tropsch synthesis possesses negative reaction conditions. The enthalpy of total reaction increases with increasing concentration of Carbon monoxide in feed gas and Carbon dioxide in the tail gas. With increasing chain length of the resultant products, the enthalpy per mole products nears a limiting value. The temperature dependency of the reaction enthalpy is minor. The standard free reaction enthalpies (ΔG^0_R) are listed in the table below. Additionally the inversion temperature (T_i), when $\Delta G^0_R = 0$ are given. These two data allow the temperature range in which the single reaction may contribute thermodynamically to product formation.

Reaction Number	ΔG^0_R (KJ/Mol)	T_i (°C)
Primary Reactions (1-3)	-26	346
	-83	393
	-20	740
Side Reactions (4-7)	-66	427
	-8	330
	-80	700
	-91	636

Table 3

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1.5.4 Kinetics and Mechanism

The components of the reaction products of Fischer Tropsch synthesis, namely alkane to alkene ratio, chain length distribution, formation of water of Carbon dioxide is kinetically controlled and does not correspond to completion predicted by thermodynamics. Thermodynamic products consist of Methane and Carbon dioxide. The hydrogenation of Carbon monoxide through a complex system of consecutive and parallel reactions paves the way to final products.

The first step is the simultaneous chemisorptions of Hydrogen and Carbon monoxide on metallic surface of catalyst. Hydrogen is not likely to be chemisorbed dissociatively whereas Carbon monoxide is bound to catalyst metal by carbon bond facilitating with Hydrogen. The products formed are assumed to have either alcoholic or aldehyde structure capable of inter of intra molecular obstruction of water, followed by additional interaction with Hydrogen and Carbon monoxide. The primary complex so formed may stabilise by disorption or by hydrogenation after passing through series of consecutive reactions. As a consequence of complex reaction (the parameters namely the temperature, pressure, syngas composition, catalyst, mass and heat transfer), no valid equation for rate of reaction was possible to establish. However, for certain defined catalyst and reaction conditions reaction rates conditions have been evaluated.

- In the presence of Cobalt as a catalyst, the reaction rate is proportional to ratio of partial pressure of Hydrogen to Partial pressure of Carbon monoxide.

- In the presence of Iron as a catalyst the rate of the reaction nears first order with respect to partial pressure of hydrogen and nears to zero order wit respect to partial pressure of Carbon monoxide.

- Water vapour or Carbon dioxide tend to decrease the rate of the reaction

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- For Cobalt, Iron or Ruthenium, the apparent activation energy cover the range of between 85-110 KJ/Mol, there by indicating that transport reactions to and from catalyst surface are likely to be the rate determining step.

1.5.5 Process Variables

Temperature, Pressure and syngas composition are the main factors that influence the reaction path way by thermodynamics and kinetics. Temperature of syngas varies with the nature of catalyst and with the type of heat source of the system as applied to process. The common range is likely to be

Temperature (°C)	Catalyst
180 °C-210 °C	Cobalt
220 °C-350 °C	Iron
100 °C-120 °C	Ruthenium

Table 4

The high temperature limit, results from increase in side reactions. Boundary equilibrium and methanation result in loss of yield, catalyst activity. Operating temperature comprises of many factors

Increase in temperature results in the following

1. Reaction rate of main reaction and side reaction increases.

2. Average molecular weight of the products decreases

3. Formation of branched chain hydrocarbon increases

4. Formation of Oxygen containing compounds increases

At a fixed temperature, the increase in the pressure is limited mainly by technical or economic aspects and tendency of catalyst metals to form carbonyls, which are soluble and volatile products.

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Increase in pressure will result in the following

1. Average molecular weight of products increases

2. Formation of Methane decreases

3. Specific conversion of catalyst, on-stream factors of catalyst is increased.

4. Cobalt catalyst is more sensitive to pressure than Iron

The composition of the syngas which must be adapted to consumption ratio influences reaction rates as well as product components increased the partial pressure result in the following reaction

1. Formation of Methane increases

2. Average molecular weight of products decreases

3. Formation of alkenes decreases

4. Reaction rate increases

As increase in space velocity or reduction in retention time causes a decrease in conversion and in some reactions, as a consequence average molecular weight of product decreases together with increase in formation of alkenes and Oxygen containing by products.

As such the combination of temperature, pressure, syngas composition and space velocity has to be arranged process where with the limits set by made reaction and properties of catalyst used.

1.6 Reactor Types

The main reactor types which have been proposed and developed after 1950 are

a. Three phase fluidized bed reactors or Slurry bubble column reactors with internal cooling tubes

b. Multitubular fixed bed reactor with internal cooling

c. Fluidized bed reactors with internal cooling

1.6.1 Slurry Bed Reactor

The slurry bubble reactor contains slurry of liquid wax with catalyst dispersed through it. The syngas is bubbled through this mixture where it is converted. Heat is recovered form the slurry via cooling coils while generates steam. The slurry is will mixed, which means tat the reactor operates at approximately constant temperature. This allows higher average operation temperatures and reaction rates and this process is easier to control. This relies on the small catalyst particles, suspended in liquid product hydrocarbons. The syngas is bubbled through the hydrocarbon or catalyst slurry. The catalyst particles are small to enable suspension in liquid product fraction. The catalyst particle size is of the order of 10 to 200 micrometres. In this small dimension, there is no mass transfer limitation within the catalyst particles. Long chain heavier hydrocarbons will reside in the liquid phase whereas the lighter products will leave the reactor with vapour phase. Temperature control and heat removal by immersed cooling tubes carrying boiling water are merits. Process side pressure drop is low. Large unit capacities can be realized.

Challenges

a. Design of large slurry reactors involves three phase hydrodynamics on a large scale

b. Catalyst hold up is high in liquid phase which increases the viscosity

c. Hence favourable mixing is affected, along with heat removal gas dispersion and mass transfer properties.

d. Dedicated filtration system is to be installed for separation of liquid product from catalyst and overhead vapour off gas

e. Catalyst must be mechanically robust.

1.6.2 Multitubular Fixed bed Reactor

Multitubular fixed bed reactor technology has matured to an extent were the productivity potential is about 10000 to 15000 barrels per day. This provides activity, selectivity and stability for a unit capacity range of 7000 to 10000 barrels per day. The catalyst is loaded into a large number of tubes. Specific heat transfer surface is high. Fischer Tropsch fixed be reactors are heaver than fluid bed for the same capacity.

Features

a. The design of a commercial multitubular reactor is the product of the performance of an individual tube

b. Fixed bed catalysts provide intrinsic and absolute separation of products with zero contamination of catalyst.

c. Axial catalyst distribution is uniform irrespective of operating conditions

d. In-situ catalyst re-activation is easy and effective and operating conditions can be controlled easily

e. A multitubular reactor arrives at the construction site as a fully integrated unit

f. The pressure drop over a fixed bed reactor operated at a high performance level is high in comparison to fluidized bed system

g. Selection of fixed bed Fischer Tropsch catalyst size and shape is a balancing act

h. Heat removal and control of temperature gradients in this technology rely on the effective heat conductivity of the paced catalyst particles.

Catalyst size, shape and reactor tube diameter are carefully optimized with regard to reaction Kinetics, heat transfer, pressure drop and hardware costs.

1.6.3 Fluidized bed Reactor

This is similar to slurry bubble reactor except that it contains no liquid. The gas is blown up through the solid catalyst particles, causing them to lift and separate, for improved mixing. Once this has happened to all of the particles, they are said to be fluidized. Again, the operating temperature is nearly constant and the process is readily controlled. In this case, liquids do not need to be removed form the raw product stream. This is suited for highly exothermic and catalyst pore-diffusion-limited synthesis reaction. Heat transfer coefficients are high and mass transfer limitations are avoided with small catalyst particles. As long as hydrocarbon product resides within the catalyst pores, due to capillary condensation the particles will behave like dry ones. Once hydrocarbon components start to condense on the external surface of the catalyst particles, a condition characterised by the hydrocarbon dew point is achieved which results in particle agglomeration and poor fluidization.

The trouble free operation of the reactor is governed by

- Chain growth probability 'α'

- Syngas conversion

- Operating pressure

- Operating temperature

- Paraffin vaporization energy

Fluidized bed Fischer Tropsch reaction is possible at high temperature, low operating pressure and low conversions and will produce relatively light products.

1.7 Products of Fischer Tropsch Synthesis

The subsequent Fischer Tropsch chain-growth process is comparable with a polymerisation process resulting in a distribution of chain-lengths of the products. In general the product range includes the light hydrocarbons Methane (CH_4) and Ethane (C_2), LPG (C_3-C_4), gasoline (C_5-C_{12}), diesel (C_{13}-C_{22}), and light and waxes (C_{23}-C_{32} and >C_{33}, respectively). The distribution of the products depends on the catalyst and the process operation conditions (temperature, pressure, and residence time). The theoretical chain length distribution can be described by means of the Anderson-Schulz-Flory (ASF) equation, which is represented as:

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

where W_n is the mass fraction of a product consisting of n carbon atoms and the chain growth probability factor (α). A plot of the relative mass fractions of products formed as function of the chain growth factor α is given in figure below. It can be seen from this plot that higher values of α give higher molecular weight products.
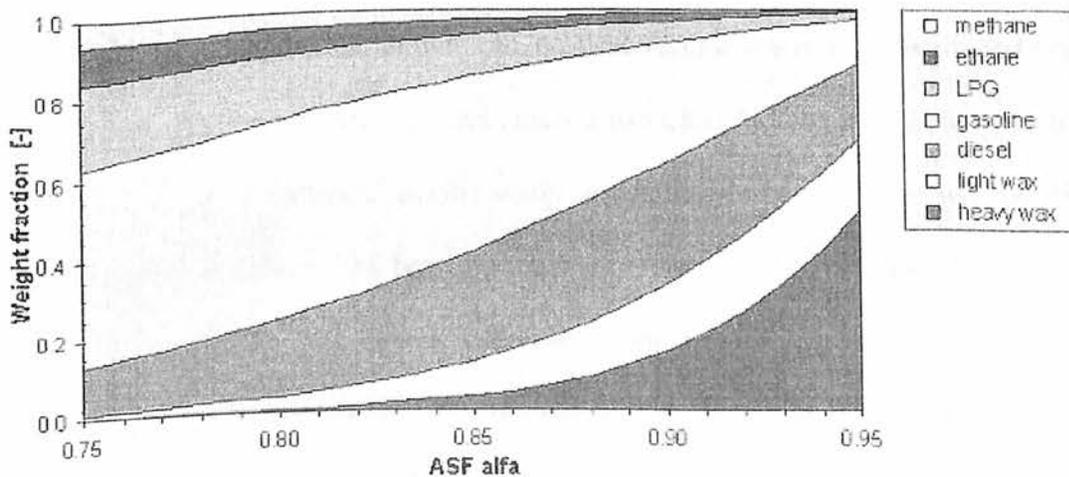
| F-T Product Distribution | Figure 2 |

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1.8 Product Upgrading

This consists of the following steps

- Distillation of Fischer Tropsch effluent into two or more fractions

- Hydro processing of one or more of the fractions to improve low temperature properties

- Distillation of hydro processed effluent streams to finished products

1.9 Major Licensors

Sasol Chevron

Sasol is a synfuel technology supplier established to provide petroleum products in South Africa. These plants have used Lurgi coal gasfiers to produce syngas. Haldor Topsoe autothermal reformer is used for syngas manufacturing. An air separation plant is necessary to produce Oxygen. It uses multitubular fixed bed and fluidized bed reactors for Fischer Tropsch synthesis. They had developed a Slurry-phase distillate process with Cobalt based catalyst in 1990. In the Sasol Slurry Phase reactor, preheated synthesis gas is fed to the bottom of the reactor where it is distributed into the slurry consisting of liquid wax and catalyst particles. As the gas bubbles upward through the slurry, it diffuses into the slurry and is converted into more wax by the Fischer-Tropsch reaction. The heat generated from this reaction is removed through the reactor's cooling coils, which generate steam and the lighter, more volatile fractions leave in a gas stream from the top of the reactor. It was combined with Chevron product upgrading technology and partial oxidation syngas. The Fischer Tropsch designs tested and commercially available include circulating fluid bed (Synthol), multitubular fixed-bed wit internal cooling (Arge), non-circulating fluid bed reactors (Sasol Advanced Synthol). The company claims a single module or the

Sasol Slurry Phase Distillate plant, which converts 100 mmscfd of natural gas into 10000 barrels a day of liquid transport fuels. They have contracts for Nigeria and Qatar.

Statoil

Norway's Statoil has been developing catalysts and process reactors for an Fischer Tropsch 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.

Shell

Shell has developed the Shell Middle Distillate Synthesis (SMDS) route, a modified Fischer Tropsch process. 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. Shell has built a 12000 bbl/day plant in 1993 in Bintulu, Malaysia. The products are highly paraffinic and free of nitrogen and sulfur.The process consists of three steps:

1. Production of syngas with a H_2:CO ratio of 2:1;

2. Syngas conversion to high molecular weight hydrocarbons via F-T using a high performance catalyst; and

3. Hydro cracking and Hydro isomerisation to maximise the middle distillate yield.

Exxon Mobil

They have developed a process known as Advanced Gas Conversion 21st Century (AGC 21). This includes fluidized syngas production by catalytic Partial oxidation coupled with slurry phase bubble column Fischer Tropsch synthesis and Hydro isomerization of waxy product. The primary catalysts used are Cobalt or Ruthenium. They have 200 barrels per day pilot plant operating in Baton Rouge since 1996. In future, they plan to go for 100000 Million barrels per day plant in Qatar.

Conoco Phillips

They had developed a process which uses partial oxidation for syngas manufacture. It has a proprietary Fischer Tropsch Catalyzed "high efficiency" reactor design. It uses feedstock oxygen and natural gas to produce premium diesel and naphtha. They have a demonstration plant in Ponco City which commenced on 2003. They have Qatar joint contract with Sasol.

Syntroleum Corporation

The Syntroleum Corporation of the USA is marketing an alternative natural-gas-to-diesel technology based on the fixed bed or fluid bed F-T process. It uses nitrogen in air to remove heat from syngas production. It uses 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.

Beyond Petroleum

They have a compact steam reformer design. The process uses fixed bed Fischer Tropsch reactor wit more efficient catalyst. This is followed by wax hydrocracking for upgrading. They have a demonstration plant in Alaska.

Rentech

This is a small Colorado company which formerly ad strong working agreement with Texaco. They use combined partial oxidation and Steam methane reforming for internal heat balance. Iron based catalyst is used in syngas production and in Fischer Tropsch synthesis Slurry phase reactor is used.

2. AN INSIGHT INTO LUBRICATING OIL AND BASE-STOCKS (LOBS)

Modern lubricants are formulated from a range of base-stocks and chemical additives. Base-stocks are the base fluids, usually a refined petroleum fraction or a selected synthetic material into which additives are blended to produce the finished lubricants. The basic functions of lubricant are friction & wear reduction, heat removal and contaminant suspension. Designing a lubricant to perform functions involves careful balance of properties, both in the lube base-stocks and the performance enhancing additives. Lubricants are classified into two major groups

- Automotive lubricants

- Industrial lubricants

Industrial lubricants can be subdivided into industrial oils and specialties. Specialties are principally greases, metal working lubricants and solid lubricant films. On the global market automotive lubricants account for more than 60% of the volume sold. Lubricating oil is formulated by blending appropriate quality lube base stock and additives. Lubricating oil consists of about 93% Base-stocks, 7% chemical additives and other components. The performance of a finished lubricant depends upon the type and quality of Base-stocks and on the additives used. Lube base-stocks are complex mixtures of paraffinic, aromatics and naphthenic hydrocarbon type molecules ranging in carbon number from 14 to 40+. Hydro processing, de aromatisation, dewaxing and hydro finishing, hydro cracking/hydro isomerisation are the routes for processing of lube base-stocks. Different processing configurations involving replacement of de aromatisation dewaxing, hydro finishing have been developed.

Paraffinic base-stocks are comparable in performance to synthetic base-stocks. They have better oxidation stability, higher viscosity index and lower volatility. Hence they are preferred to formulate world's automotive and industrial lubricants. Naphthenic base oils have lower pour point and better solvency characteristics which makes them suitable for formulating low temperature hydraulic oils, refrigeration oils, rubber process oils, metal working oils and cylindrical lubes.

2.1 Market Scenario

2.1.1 The North American and European Markets

The base oil market, especially in North America, is going through unprecedented change today. The switch to fast-changing base oil product specifications, which started in the early 1990s, was initially met with modest changes in existing hardware and introduction of specialty supplemental products, especially in Europe. But as the specifications transitioned from upgrades in physical properties, such as volatility, to chemical performance upgrades, such as oxidation stability, fundamental changes in the way producers met the challenge were seen. Recognizing the inherent inflexibility of solvent technology, the substantial investment in that technology and the need to make better cost position of the newer technologies, producers started building Group II/II+/III plants in North America. Europe introduced stringent volatility requirements in the early 1990s that could be met cost-effectively by bringing fuels from hydrocracker bottom streams into an existing solvent plant for processing to Group III base oil. With some notable exceptions, these oils were designed mostly to address volatility. In North America, the drive to improve volatility was slower in coming and coincided with development of

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engine tests. The higher saturates content also brings better oxidative and thermal stability that brings many other desired benefits described earlier. Simultaneously, in the mid 1990s base oil processing technology advancements, mostly led by Chevron, offered a solution to these and other problems by offering:

- Better volatility through higher VI

- Better oxidative/thermal stability through higher saturates

- Better low temperature performance through catalytic dewaxing technology

- More flexibility to meet the changing needs of the base oil market through modern plant design and the capability to move from Group II to III

- Greater crude source flexibility

- Much lower operating cost to run a Group II plant – critical in a mature market with flat growth.

Thus, the concomitant availability of technology for licensing, the need for flexibility to manufacture Group II and Group III base oils, and the development of specifications that demanded such oils drove North American suppliers to build new Group II/III plants rather than follow the European solution of just a few years earlier.

In addition to these events, three other factors made this move to Group II/III plants gain momentum in North America:

- The prior existence of Chevron's, Petro Canada's, and Sun's Group II plants in North America meant that many formulators were already familiar with how to work with these types of base-stocks.

- Group II technology licensing became practical and competitive, with more than one supplier.

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As a result, Group II/III capacity expanded so rapidly that now, after only a few short years, these base-stocks are approaching half of the paraffinic base oil capacity in North America. With such a critical mass of these stocks now here, movement of specifications to take advantage of these higher quality base-stocks has accelerated. It would have been inconceivable just a few years earlier that a 15% Noack volatility specification would have survived the various industry committees that develop and approve these specifications. Industry's rapid and cost-effective commercialization of Group II+ base-stocks made this possible. While the extensive availability of Group II stocks facilitates rapid change in lubricant specifications, there are also supply chain drivers that slow them down in North America:

- Incumbent Group I suppliers find themselves falling farther and farther behind, with little opportunity to upgrade due to low industry margins and high capital costs, and the promise of very high remediation costs preventing them from exiting the business.

- Independent lubricant manufacturers, who are dependent on purchased base oils, see specifications that would require higher-priced Group III base oils as an unfair advantage to the majors who are basic in those stocks.

Fortunately, North America is capable of creating new base oil products to meet the changing needs of formulators largely because of the inherent flexibility of the new generation of hydroprocessing-based plants. The creation of Group II+ base oils in North America is a good illustration of this adaptability. The new breed of base oil suppliers independently worked with additive suppliers and lubricant customers to develop products to address the volatility challenge.

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The results were in every case 110-119 Viscosity index Group II base oil, now commonly called Group II+. These products are the most cost-effective solution for the industry, bringing maximum value to the consumer. With future specifications it can be seen that base oil industry in North America respond to technical challenges by offering custom designed base oils to meet an industry need, and do so quickly. The North American base oil industry has woken up and became dynamic in responding to ever-tightening specifications.

European base oil market is also dynamic and responsive to specification challenges. However, due to the relative inflexibility of the dominant Group I facilities and even much of the first generation Group III facilities, the options available to European producers are more limited at the moment. The fact that most of the Group III facilities have limited capacities and cannot makes Group II or Group II+ stocks limits the rapid upgrading of mainstream motor oils. Whatever can be achieved with additives in combination with existing Group I stocks, supplemented with modest Group III volumes, determines mainstream performance. The current mainstream specifications can be met through this combination.

In North America, key majors stepped out and made the plunge to manufacture Group II stocks. Now, this seems to be on the verge of happening in Europe, with Petrola planning to offer Group II, II+ and III base-stocks in the near future. Until now, the dominant producers have appeared to be content with their current Group I plants, despite the movement of their North American counterparts to Group II production.

With the expected introduction of hydroprocessed Group II by a new supplier in Europe, the pressure to move to modern Group II/III capability may soon begin. The globalization of motor oil specifications in recent years, though slow and far from complete, has brought North American bench and engine tests to Europe and vice versa. With substantial Group II/III capacity to address these new tests that often prefer Group II/III base oils, many North American suppliers are well positioned to take advantage of these stocks, resulting in lower additive mixing rates for those who have access to these components. In Europe, since there is minimal Group II capacity, the playing field is even, with all blenders using higher additive treats and/or Group III or IV base-stocks to meet the most stringent specifications. Two situations promise to disrupt this equilibrium:

1) A new Group II supplier offers these products at competitive prices to the European market, and

2) Top tier OEM specifications become so demanding that Group I base-stocks are effectively excluded from that segment of the market.

It is no surprise that the transition to hydroprocessing in Europe is starting. Fortum (formerly Neste) has successfully built a Chevron–licensed Group III plant in Finland, and are marketing their stocks effectively. Petrola Hellas, as mentioned before, has recently announced plans to build a Chevron-licensed Group II/III base oil plant in Greece by 2003. Although their product slate could change, plans are to offer a 5cSt Group III product, and two grades of Group II, likely 150N and 500N, all of which will be marketed by Chevron. Thus, the tide in Europe seems poised to shift toward Group II/III stocks.

2.1.2 Asian Base Oil Product Trends

Product trends in the Asian base oil market are substantially different than those in Europe and North America. The two mature economies discussed above are driven to upgrade based to a significant extent, though not entirely, on ever increasing product performance hurdles, the Asian base oil product trends are minimally driven by performance needs. In Asia the current mainstream motor oils are API SE, SF, SG and/or CC, CD quality where almost any Group I base oil meets the need, and where Group II/III are completely unnecessary. Transportation lubricants dominate the total lubricant market, though industrial oils and marine oils are growing. In addition, approximately 75% of the motor oil market is reported to be single grade motor oils, which is about opposite of the multigrade or monograde ratio found in North America and Europe. This bias towards single grades, inspired by warmer climates and widespread perceptions that "thicker is better", results in base oil products heavily emphasizing heavy neutral grades, mostly 500N. Bright stocks and 150N typically fill out the product slate but are smaller percentages.

There is a trend to higher performance multigrade driven by OEM warranty requirements and by the multinational oil companies' desire to grow their top tier product offerings for better margins. These products do find a need for Group II/III, but their market share is still small and they are not a major driver for base oil product upgrades. Despite minimal need for higher performance base oils, Asia has seen a number of new base oil plants come on stream in recent years (two in Thailand, one each in Singapore, Korea and China), and more are slated to start up in the next few years.

While the region had a base oil deficit, the new supply has more than made up for this, to the extent that Asia now has excess base oil capacity. These new plants have been a mixture of Group I and Group II/III, with the latter plants all using the newer hydroprocessing technologies. The robust Asian economies of the mid-1990s and the base oil deficit made it easy to justify construction of these plants, and the more common choice of adopting Group II/III capability was driven mostly by the lower cost of operating such plants. However, the recent Asian economic slowdown coupled with weak base oil prices due to excess capacity should temporarily slow or stop construction of additional new or upgraded base oil plants in the region. But it is not anticipated that this expansion will stop entirely. There are a number of reasons why there will still be upgrades and new plants in the near future:

- The lowering of trade barriers has intensified competition, and forced many national oil companies to compete on a global scale through improved operations.

- Large automotive and heavy-duty OEMs, particularly common now due to consolidation, mergers and joint ventures, are pushing for uniform, high-quality lubricants that meet the same specifications throughout the world.

These drivers will spur investment despite the reality that low base oil prices and a slow economic recovery would suggest that these plants often should be marginal investments. When a new plant is being contemplated, low operational cost and crude flexibility are the biggest drivers; which in turn favors Group II/III facilities. The flexibility to upgrade from Group II to Group III, important in the future is also a consideration, though not the most important factor.

The Asian base oil market will continue to be dominated by Group I facilities, though Group II/III plants will play a significant role in the market. Many of the older inefficient and poorer quality Group I plants will continue to operate into the future, often driven by local governmental pressure to maintain operations for full employment. As a result there are possibilities of continuing base oil capacity overhang for some time for this region, though the extent and length depend on the rate of economic recovery. In fact, if the economy accelerates significantly, the current regional supply excess could diminish fairly rapidly. Nevertheless, any new start-ups in the region will not have the luxury of backing out imports as did some recent plants, and therefore will have to battle it out with local producers for market share. The continued availability of the lower tier base oils will also sustain the strong position of the corresponding lower tier lubricants that now dominate large parts of Asia. Group II/III plants still will be built, though at a slower pace than in the 1990s. There may even be some upgrades of existing Group I plants to Group II/III. These volumes will be more than sufficient to meet the performance needs of lubricants well into the future. In fact, the more immediate product need for the near future in Asia is flexibility to shift to lighter viscosity grades as the market moves from single grade to multi-grade motor oils. Again, modern Group II/III plants have greater flexibility in this dimension than older Group I plants. Only in the medium term will the need for flexibility to transition from Group II to Group III be needed as Asia moves to low volatility, fuel conserving and high performance motor oils as currently being asked for in the mature economies of Western Europe, North America and Japan.

Though relatively complacent for decades, the base oil industry has seen remarkable change in the last ten years, a process likely to continue into the future. In the more developed regions of the world, particularly North America and Western Europe, changes have been spurred in large part by increasingly more stringent performance requirements for passenger car and heavy duty motor oils. In the past, advances in chemical additive technology have provided the majority of performance improvements in such lubricants. However, the combination of advances in base oil manufacturing technology, particularly hydroprocessing technology and the advent of performance requirements which respond strongly to base oil quality has changed this paradigm. Base stock suppliers, seeing this demand, are responding by moving more and more to offer these newer hydroprocessed base oils. In North America, where the timing of new requirements and the availability of competitive processing technology coincided, a large-scale shift from Group I to Group II, II+ and III base-stocks has occurred, so that these stocks now represent approximately 40% of the total paraffinic base oil market in the region. In Europe, where higher performance requirements slightly preceded those on the other side of the Atlantic, specialty Group III products sprang up instead, postponing somewhat a more widespread conversion to hydroprocessed Group II/II+/III capacity. However, with one such new plant already offering Group III and another planning to come on line with Group II, II+ and III in the near future, migration away from Group I stocks may begin to occur in Western Europe, also. As a result, motor oil products which benefit from higher quality base-stocks are becoming widespread in these two regions. By using Group II, Group II+ or Group III stocks, more alternatives exist for meeting the latest and highest quality specifications, and/or achieving high quality at lower additive treat rates.

In Asia, the base oil landscape is changing rapidly also, although for much less performance-driven reasons. There, the combination of a former regional supply shortfall, plus the desire of manufacturers to run plants that offer the lowest possible operating cost along with feed source flexibility have driven the construction of new plants, more commonly of the hydroprocessing variety. Although this recent capacity, in combination with the current economic downturn in the region have led to a supply surplus, economic recovery will erode this overhang and return the region closer to balance. Further, with much of the new capacity in the Group II/II+/III category, the ability of this region to jump to higher performance levels is significant, and with equipment OEM's desires to employ the same high-quality lubricants in all regions of the world, taking advantage of these better base-stocks is just a matter of time. With all of this change in base oils throughout the world, particularly the addition of new hydroprocessing plants, the downside has been an increase in supply that has outstripped growth and demand in this industry. However, with clear advantages for the newer hydroprocessed stocks, the consolidation that has taken place in the base oil industry has seen in the Group I category, a trend which is expected to continue. Although worldwide excess base oil supply is likely to continue for some time, stocks in the Group II, Group II+ and Group III category should nevertheless be preferred for their advantages in engine oils, the biggest of all lubricant segments. This together with the operating cost benefits of hydroprocessing plants should position these stocks relatively well in an industry where worldwide future growth is expected to be modest.

2.2 Properties of Lubricants

Though the ability to minimize friction is the number one function of a lubricant, there are other major functions that must be considered. Here are some of the basics without getting to technical. A lubricant is likely to be also required to

Clean- A lubricant must maintain internal cleanliness by suspending contaminants from adhering to components

Cool Moving Elements- Reducing friction will reduce the amount of heat that is generated and lower the operating temperature of the components. A lubricant must also absorb heat from components and transfer it to a location where it can be safely dissipated.

Prevent Contamination- The lubricant should act as a dynamic seal in locations such as the piston, piston ring and cylinder contact areas. This minimizes contamination by combustion byproducts (for example) in the lubricating system. Lubricants are also relied upon to support mechanical seals found elsewhere and to minimize external contamination and fluid loss.

Dampen Shock- The lubricant may be required to cushion the blows of mechanical shock. A lubricant film can absorb and dispense energy spikes over a broader contact area.

Transfer Energy- A lubricant may be required to act as an energy transfer median as in the case of hydraulic equipment or lifters in an automotive engine.

Prevent Corrosion- A lubricant must also have the ability to prevent or minimize internal component corrosion. This can be accomplished either by chemically neutralizing the corrosive products or by setting up a barrier between the components and the corrosive material.

The ASTM (American Society for Testing and Materials), founded in 1898, is a scientific and technical organization formed for the development of standards on characteristics and performance of materials and services. ASTM is the world's largest source of voluntary consensus standards. ASTM operates through a system of committees and subcommittees. Its committees function in prescribed fields under regulations that ensure balanced representation among producers, users and general interest and consumer participants. ASTM standards govern the majority of testing performed on motor oils in North America.

a. Kinematic Viscosity

Test Number & Name: ASTM D-445 Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids

Significance & Use: The proper operation of equipment depends on the proper Kinematic viscosity at operating temperature of the oil used for its lubrication.

What it means: Kinematic viscosity is a measure of a liquid's flow under the influence of gravity. It's handy to think of a lubricant's Kinematic viscosity as its "I.D. card." AMSOIL formulates its synthetic lubricants to tighter viscosity limits than other manufacturers do, so AMSOIL synthetic lubricants' Kinematic viscosities are midrange, close to neither the high or the low limit. That helps components work their best and helps the lubricants stay in grade. *Viscosity Index*

Test Number and Name: ASTM D-2270 Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 deg. C. and 100 deg. C.

Significance & Use: Viscosity index indicates how much of a lubricant's viscosity will change according to changes in temperature between 40 deg. C (104 deg. F) and 100 deg. C (212 deg. F), which roughly define the normal temperature range of most operations.

What it means: The smaller a lubricant's viscosity as a result of temperature change, the higher that lubricant's viscosity index. High viscosity index lubricants, such as AMSOIL products, protect better in operations with temperature variations.

b. Cold Crank Simulator Apparent Viscosity

Test Number & Name: ASTM D-2602 Standard Test Method for Apparent Viscosity of Engine Oils at Low Temperature Using the Cold-Cranking Simulator

Significance & Use: Apparent viscosity has been established as a valid predictor of engine-cranking viscosities at specified low temperatures. Apparent viscosity depends on temperature and shear rate.

What it means: Cold cranking viscosity affects the start ability of engines and other equipment in cold temperatures. Low cold cranking viscosities, such as those of AMSOIL synthetic lubricants, make for easier cold cranking and more dependable cold temperature starting.

c. Borderline Pumping Temperature

Test Number & Name: ASTM D-3829 Standard Test Method for Predicting the Borderline Pumping Temperature of Engine Oil.

Significance & Use: Borderline pumping temperature is a measure of the lowest temperature at which engine oil can be continuously and adequately supplied to the components of an automotive engine.

What it means: The lower the borderline pumping temperature, the lower the temperature at which the engine is protected by circulating oil. AMSOIL synthetic motor oils' extremely low borderline pumping temperatures assure excellent low temperature protection.

d. Pour Point

Test Number & Name: ASTM D-97 Standard Test Method for Pour Point of Petroleum Oils

Significance and Use: The test determines the lowest temperature at which an oil flows as the jar is tilted for a prescribed period. The pour point of an oil indicates the lowest temperature at which an oil may be used in some applications.

What it means: The lower the pour point, the more useful the lubricant is in cold temperatures. AMSOIL synthetic lubricants offer exceptionally low pour points.

e. Flash and Fire Points

Test Number & Name: ASTM D-92 Standard Test Method for Flash and Fire Points by Cleveland Open Cup.

Significance & Use: Flash point is the lowest temperature at which application of a flame causes specimen vapors to ignite. Flash point is used to assess the overall hazard of a material and is used in shipping and safety regulations to define "flammable" and "combustible" materials.

Fire point is the lowest temperature at which a specimen sustains burning for five seconds.

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What it means: Lubricants with high flash and fire points, such as AMSOIL synthetic lubricants, are safer to use and transport than lubricants with lower ones and have a greater high temperature operating range.

f. NOACK Volatility

Test Number & Name: ASTM D-5800 Determining the Evaporation Loss of Lubricating Oils (Noack's Method)

Significance & Use: Test determines the evaporation loss of lubricating oils at high temperature. Evaporation loss is particularly important to motor and cylinder lubrication, due to the high temperature of these operations and the tendency of evaporative loss to increase in high temperatures. Significant evaporative loss of oil leads to excessive oil consumption and destructive changes in oil properties.

What it means: Lubricants with low Noack scores, such as AMSOIL synthetic lubricants, lose less to volatility than lubricants with higher scores. Low-loss oil keep their original protective and performance qualities longer than high-loss oils do, which keeps oil consumption low and fuel economy and equipment protection high.

g. High Temperature/High Shear Viscosity

Test Number & Name: ASTM D-4683 Standard Test Method for Measuring Viscosity at High Temperature and High Shear Rate by Tapered Bearing Simulator

Significance & Use: Viscosity at the shear rate and temperature of this test is considered representative of the condition encountered in the bearings of automotive engines in severe service. Lubricant viscosity in the bearings of automotive engines in severe service is a critical factor in bearing wear.

What it means: Lubricants with high scores, such as AMSOIL synthetic lubricants, maintain their viscosity in high temperatures after exposure to high shear. That means they continue to protect engine bearings even after exposure to severe service conditions.

h. Four Ball Wear Test

Test Number & Name: ASTM D-4172B Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four-Ball Method)

Significance & Use: Test method determines the relative wear preventive properties of lubricants in sliding contact under the test conditions. Lubricant comparisons are made by comparing the average wear scars on three fixed balls made by one ball in rotating contact with them in baths of the test lubricants.

What it means: The smaller the average wear scar, the better the protection. AMSOIL synthetic lubricants deliver much smaller wear scars- and much better protection- than other lubricants do.

The Four Ball Wear Test may be conducted at various levels of severity. Independent laboratory testing shows AMSOIL Series 2000 and Series 3000 motor oils' wear scars are significantly smaller than those of popular competitor oils in extremely severe test conditions, making these oils ideal for extreme service operations.

2.3 Classifications of Lube Base-Stocks

Base-stocks differ widely in molecular composition, physical and chemical properties due to the crude sources and processing steps used in their manufacturing process. In 1990, API established a base oil classification system which provided an easy way for the lubricant blenders to interchange one base-stock for the other. The system uses physical and chemical parameters to divide all Base-stocks to the following categories.

Group	Sulphur (wt %)	Saturates	Viscosity Index
I	>0.03 and/or	<90	80-119
II	<=0.03 and	>=90	80-119
III	<=0.03 and	>=90	>120
IV	All Poly alpha olefins (PAO)		
V	All stocks excluded in Groups I-IV (Pale Oils and Non-PAO synthetics)		

Source: Petroleum Trends International, Inc. Nov 2001

Table 5

Base oils produced by solvent refining and solvent de-waxing technology fall into Group I. Those manufactured using hydro-processing technology fall into Group II and Group III. Poly alpha olefins are Group IV and everything else is Group V. Group V includes low quality Base-stocks like naphthenic base oils as well as very high quality Base-stocks like esters. In Europe, a new group has recently been established known as Group VI oils. They are poly internal olefins. These oils are not readily available anywhere outside of Italy.

Group I Base oils

Solvent refined base oils are commonly called Group I base oils. They have less than 90% saturates, greater than 10% aromatics, more than 300 ppm sulphur and viscosity index is greater than 90 and less than 120.

Group II Base oils

Group II base oils are differentiated from Group I base oils because they contain significantly lower levels of impurities, less than 10% aromatics, less than 300 ppm sulphur. They are manufactured through modern hydro isomerisation technology and are so pure that they have almost no colour at all. Improved purity means that base oils and additives in the finished product can last much longer, i.e. it is very inert and forms less oxidation by products. They have greater than or equal to 90% saturates, with a viscosity index greater than or equal to 80 but less tan 120.

Group III Base oils

Group II and III base oils differ only in terms of viscosity index. Group III base oils have greater oxidation stability and excellent low temperature performance. They are manufactured by the same processing route as modern Group II base oils. Higher viscosity index is achieved by increasing the temperature or time in the hydro cracker. This is referred to as "severity". The product viscosity index could be increased by increasing the viscosity index of the feed by selecting appropriate crude. Modern Group III base oils have properties which allow them to perform at a higher level than conventional Group I and Group II base oils. The match exists in levels of performance of finished lube applications. The demand for Group III has been driven by the need for better performance in automotive lubes primarily in Europe, North America and Japan.

Higher quality oils also possess better cold temperature characteristics and help to reduce emissions because of lower sulphur, nitrogen and aromatics content. Asia-Pacific is the largest source of Group III. It produces about as much as Western Europe and North America. Theoretically North America has most of the world's Group III capacity. They import a steady volume of Group III form Asia-Pacific and Europe.

Worldwide Group III production in the year 2000

Region	Barrels per day
Asia-Pacific	7300
Western Europe	5400
North America	1800
Rest of World	Minor amount
Total	16600

Table 6

Source: Lubes n Greases, Sep 2003

Group IV Base oils

Polymerised base oils popularly known as Poly Alpha Olefins (PAO) are manufactured from small molecules. The term "synthetic" was due to the fact that there types of oils were considered as high performance lubes. The first commercially viable process for manufacturing PAO was unveiled by Gulf Oil in 1951 using $AlCl_3$ Catalyst. In 1960, Mobil patented an improved process using a BF_3 / $AlCl_3$ catalyst. In 1970, Mobil oil commercially marketed Mobil1™ engine oil. Following fifteen years PAO faced a steady, slow growth I the last decade PAO market significantly increased in Europe and North America. PAO have superior lubricating performance characteristics like Viscosity index, pour point, volatility ad oxidation stability than conventional mineral oils.

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Formulating a lubricant wit proper additives and base oils can create a chemical balance that provides low temperature fluidity, heavy load protection, high levels of detergency ad solves other industry specific challenges.

Poly Alpha Olefins are generally straight-chain synthetic hydro carbon molecules designed t the proper chain length for the appropriate viscosity.

$$CH_2=CH_2 \longrightarrow CH_2=CH-[CH_2-CH_2]_3-CH_2-CH_2-CH_3$$
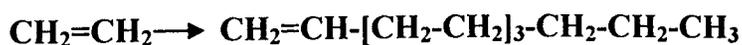
Ethylene   *Decene 1*

There are wax molecules to hinder fluidity at low temperature. This ensures that critical machinery components consistently get the lubrication needed for stable processing. Due to their excellent low-temperature properties, hydrolytic stability, PAOs have long been the synthetic ingredient of choice for many applications. PAO's narrow molecular weight distribution also offers much lower volatility, compared to a mineral oil of the equivalent ISO viscosity grade. Moreover, being polymerised olefins, their non-interruptive transition when replacing with a synthetic. As a result of these varied benefits, PAOs are important to providing proper lubrication in applications conducted at well below ' freezing temperatures.

In recent years these categories have been informally subdivided into Group I+, Group II+ and Group III+.

Group I+ base oil

Exxon Mobil has launched a Group I base stock with a viscosity index of 105. This was given the name Group I+. This will extend the useful life of conventional base-stocks. This is manufactured by solvent extraction and solvent dewaxing in France and Italy, is trade marked as CORE 145. By carefully choosing the feed stocks and tightly controlling the fractionation, extraction and dewaxing steps, the refineries can select for specific high viscosity index molecules.

Specifications

Viscosity @ 40 °C (mm2/s)	26.5 -29.0
Viscosity index	105
Volatility NOACK, mass % loss	15
Pour point	-15 °C
Viscosity ccs @ -20°C mPa sec	1650

Table 7   Source: Lubes n Greases, April 2003

Group II+ base oils

Chevron Texaco produced the first Group II+ base oil commercially in 1998. It is the most cost effective base oil. Group II+ has higher VI, which translates to improved (low-temperature) cold cranking performance and lower volatility. At the Richmond, California refinery, they make high-purity Group II+ base oil with optimized viscometric properties Adjusting processing conditions, several refineries can make these oils with 110-120 viscosity index This enables significantly improved CCS and volatility, making it possible to blend 5W-20 and 5W-30 GF-3 and GF-4 engine oils using these oils without any correction fluids.

Group III+ base oils

Exxon Mobil will soon roll-out its Group III+ base stock. This product is trademarked as **visom** aims to meet one of Europe's most difficult engine oil specifications. The name visom is derived by combining "viscosity index" and 'isomerisation". This has a viscosity index of 140. Basically it upgrades slack wax to very pure base-stocks with high viscosity index, low volatility, excellent cold cranking properties, and superior blending properties.

Thus Lubricants play a very vital role in the smooth and trouble free operation of any automobiles. The engine technology development is currently driven by the emission standards and fuel economy. Newer versions of engines are being introduced from time to time, for use in the vehicles to comply with the emission standards. As the engine technology improves, the demand of the lubricant quality is also becoming more and more stringent. Hence new high performance oils are continuously being introduced by major organizations to keep the pace through.

3. LUBRICATING OIL AND BASE-STOCKS (LOBS) THROUGH GAS TO LIQUID TECHNOLOGY (GTL)

In recent years, the process of converting Natural gas to high value products has gained momentum. It is expected that large volumes of this products will flow in the coming decade. GTL products includes kerosene, ATF, diesel and also they can produce lube base-stocks. The significant shift in the interest to developing this technology hails from the following facts.

- Huge reserves of stranded Natural gas

- Theoretically these reserves can be converted into 250 billion barrels of synfuels, which is equivalent to the estimated oil reserves of Saudi Arabia.

- Growing environmental regulations

- Fluctuation in international crude oil prices

- Increased tensions in Middle East

- Strategic maneuvering by oil giants

Major oil companies already own immense gas reserves. They are now looking for stranded gas reserves as a way of increasing profits. Two significant things related with GTL are

- Fuel, which is the primary driver

- Global Competition

Through GTL a waxy feed stock is manufactured. This is then hydroprocessed and isomerized to yield high quality baseoil. They show

    a. No level of aromatics, Sulphur or Nitrogen

    b. Excellent oxidation stability, low temperature performance

    c. Have a viscosity index of about 140 to 155

    d. Lower NOACK volatility

These base-stocks are competing against high performance end of market against Group II+, III and IV. Based on some of the performance data currently being developed, it is believed that GTL base oils would likely be handled in one of the three ways

1. Another API group will be established to accommodate it

2. It will simply fall into Group III because it meets the criteria for Group III

3. GTL base oils will follow Group II+. This is likely to result in a market place designation of Group III+.

The fact being, its performance is considered nearly equal to Group III, it could also enjoy significantly lower manufacturing costs.

3.1 GTL BASE OIL MARKET SPACE DEVELOPMENT

GTL base oils are positioned to track the footsteps already established by Group II and II+. They are the workhorse in some multigrade engine oils and as a correction fluid in others. The challenge for GTL base oils in the US, however, will be the relatively sluggish market penetration of 5W-30.

In addition, Group II and II+ base oils have already established themselves as the solution for 5W- and 10W-30 engine oils. This means that additives are well on their way to being optimized, blenders are comfortable working with these stocks, and product development costs have been invested. Rather than potentially giving away value by competing with Groups I and II base oil in the 10W-30 PCMO market and others, a more likely scenario is one that allows GTL to maintain its value by waiting for the direction of specifications to mature the market into the market space currently occupied by Group III and IV, and to a lesser extent Group II+.

The direction of specification has already moved a significant volume of base oil demand out of the Group I space and into the Group II and II+ space in the US market. Future specifications will continue to push demand through the Group II and II+ space into the space occupied by Group III, Group IV and GTL, as shown in the figure below.

Market Space Development For GTL Base Oils

Figure 3

Source PetroTrends, Inc.
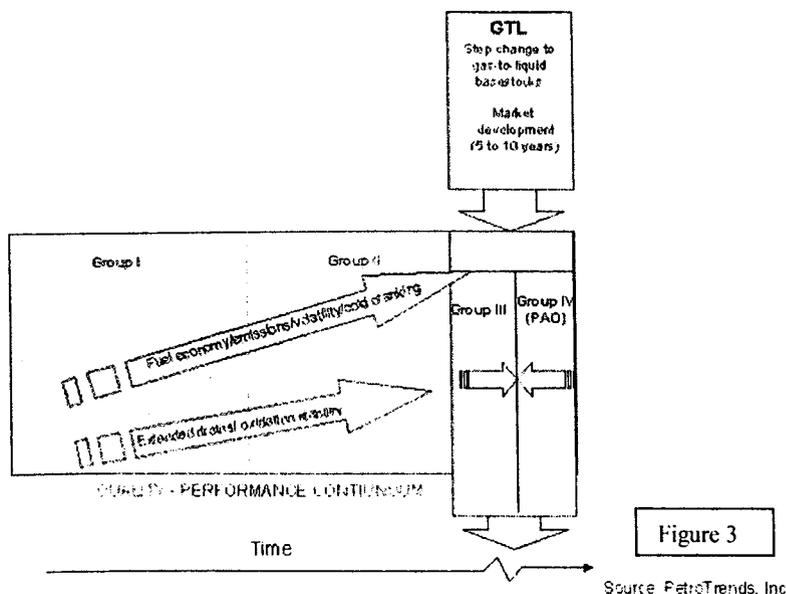
3.1.1 GTL Challenges

a. Successful implementation of GTL base-stocks can be achieved by ensuring supply reliability and quality control.

b. Ability of the formulators to blend GTL base-stocks to competitive lubricants is a key parameter in its usage.

c. Strong technology and proven expertise in plant operation will establish confidence in the reliability of GTL plants.

Base Oil Product Life Cycle, US
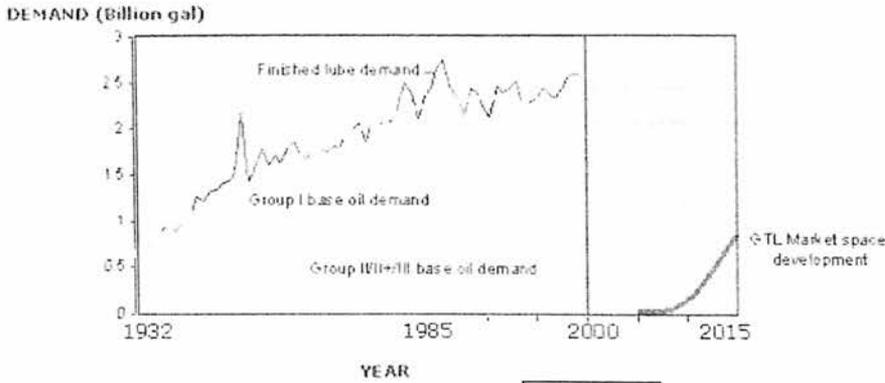
Figure 4   Source: PetroTrends, Inc.

If one uses the GTL plant completion schedules currently tabled, the supply build model of Group II/II+ and III, the introduction phase of the GTL life cycle will likely begin in 2005 and take about five years before it advances into the growth phase, as shown in figure below. Initially it will do so at the expense of Group III and IV base oils by capturing market share in the synthetic and synthetic-blend automotive lubricant market space. It will also penetrate the ATF and automotive driveline market space at the same time. Market acceptance of GTL is, however, expected to be modest during this introductory phase of its life cycle due to a limited number of suppliers. GTL base-stocks performance may approach that of chemically derived PAO
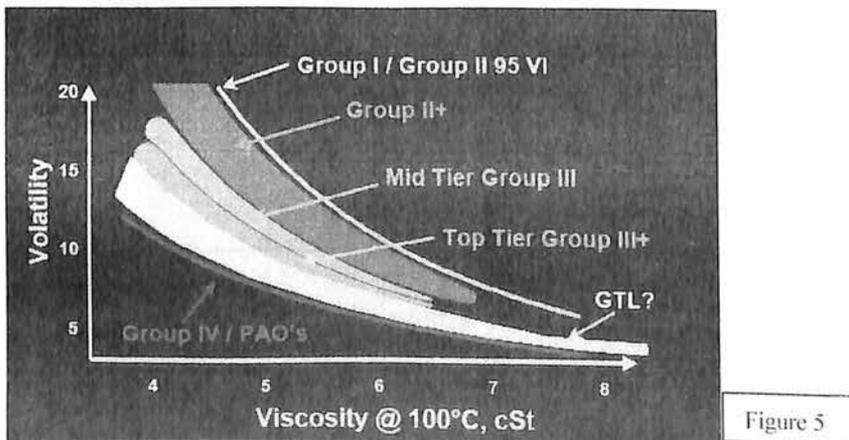
Figure 5

Source: Outlook for the East of Suez Lubricants and Baseoils Conference April 6 - 7, 2005, Dubai, UAE.

The kind of base-stocks used will have an impact on lubricant oxidation stability.

Highly paraffinic GTL base-stocks show improved performance in formulated oils.
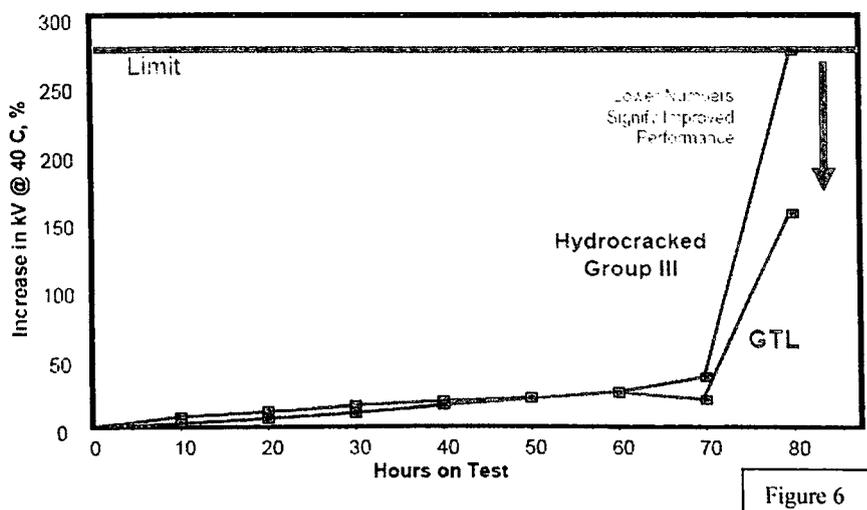
Figure 6

Source: Outlook for the East of Suez Lubricants and Baseoils
Conference April 6 - 7, 2005, Dubai, UAE.

A comparison of the typical product through conventional refining of Brent crude and

that of GTL-FT is provided below

Typical Products	Refined Brent (vol %)	GTL-FT (vol %)
LPG	3	
Naphtha and Gasoline	37	15-25
Distillates	40	50-80
Fuel Oils	40	
Lubes + Waxes		0-30

Table 8   Source: After BP study (Euroforum, Feb 2003)

3.2 Economic Perspective

This depends on the size of the GTL plants which is going to be installed. Three scenarios have bee identified and each one has its own critical parameters and assumptions.

- **Mega fuel Plants**

  This plant is fuel driven, located near gas fields that are far from usual markets. They will have fuels and a waxy bottom as its principal output. Shipping the waxy bottom to an existing lube plant could be costly. Adding a lube basestock plant to its configuration could be done simply and at comparatively low cost.

- **Small fuel Plants**

  This plant is designed to make fuels and specialties and it is closer to markets. It is used for tapping the Natural gas from a field or refinery that is now being flared. This is also fuel driven.

- **Small Specialties Plant**

  Paraffins and waxy residue would be the intended products of this plant. This plant will further process them or sell them on merchant market.

  In all the three scenarios, the lube plant will have to carry some portion of the capital cost burden. When the lube portion is a by-product then the capital cost burden should be limited.

In the specialties plant the cost and risk would have to be borne by the lubes and wax segments. It is sure that, GTL base stocks produced in mega fuel plants will be in a position to not only compete with Group IV and III, but Group I and Group II refiners because other things being equal, formulators will choose high performance GTL base oil.
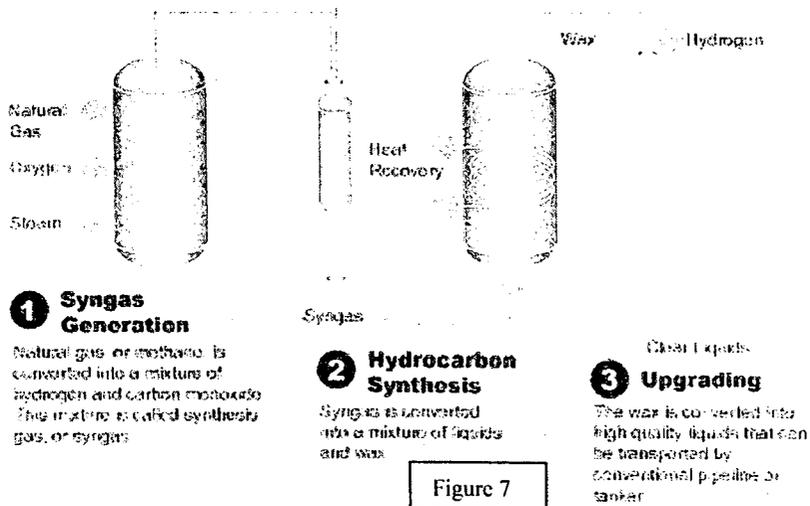
3.2.1 Potential GTL Plants by the year 2010

Company	Location	FT liquids (BPD)	FT base-stocks (BPD)	Comments
Shell	Bintulu, Malaysia	12,500	100	Refines waxy feed into Group III base oil.
Exxon Mobil	Qatar	100,000	Upto 20000	Fuel plants will have lube as a by-product
Sasol Chevron	Nigeria	34,000	?	Lubes could be added

Source: Lubes n Greases (January 2003)   Table 9

3.3 The AGC 21 Process

AGC 21 is the acronym of Advanced Gas Conversion for the 21st century. Exxon has been involved in Synthetic fuel research for the past five decades. They had developed a three step process based on proprietary in-house technology for syngas production, Fischer-Tropsch synthesis and product upgrading. It operates a demonstration plant at Baton Rouge, Louisiana. The Schematic representation of the process is provided below in Figure 7.

1 **Syngas Generation**

Natural gas or methane is converted into a mixture of hydrogen and carbon monoxide. This mixture is called synthesis gas, or syngas.

Syngas

2 **Hydrocarbon Synthesis**

Syngas is converted into a mixture of liquids and wax.

Clean Liquids

3 **Upgrading**

The wax is converted into high quality liquids that can be transported by conventional pipeline or tanker.

Figure 7

Source: Exxon Mobil's advanced gas-to-liquids technology,
Hydrocarbon Asia, July/Aug 2003

3.3.1 Syngas Generation

In the fluidized bed syngas generation step of the process, syngas is produced by simultaneous partial oxidation and steam methane reforming in a single circulating fluidized bed reactor that requires both Oxygen and steam. The use of a single combination process replaces a number of small vessels, thus giving economies of scale. Oxygen, Methane and steam ratios are controlled to produce syngas at a stoichiometric proportion of 2:1 (H_2: CO).
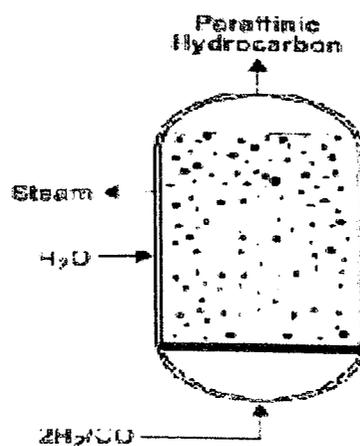
Figure 8

Source: Exxon Mobil's advanced gas-to-liquids technology,
Hydrocarbon Asia, July/Aug 2003

3.3.2 Hydrocarbon Synthesis
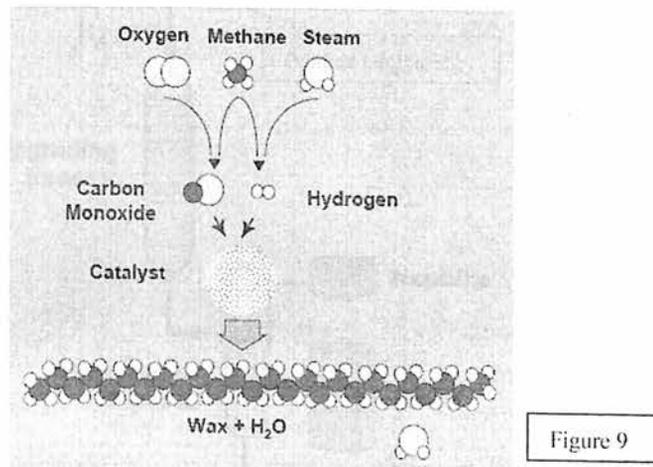
Figure 9

Source: Outlook for the East of Suez Lubricants and Baseoils Conference April 6 - 7, 2005, Dubai, UAE.

This follows Shulz-Flory distribution in a novel slurry reactor using a new and high productivity catalyst. The product primarily consists of normal paraffin (waxy at temperature of 650 °F). A high productivity Cobalt based catalyst converts syngas to waxy crude with focus on C10+ yield to improve plant efficiency and to optimise the products.

3.3.3 Product Upgrading

This is done with proprietary catalyst in a packed bed reactor as shown in figure 10. Through this the waxy crude is converted to high quality liquids that make excellent feeds for refineries and chemical plants and directly marketable products.

Mild isomerization improves cold flow properties of these molecules to acceptable levels for a variety of products. Through this the short side chains are produced which significantly lower melting point. The upgrading process is 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 need.
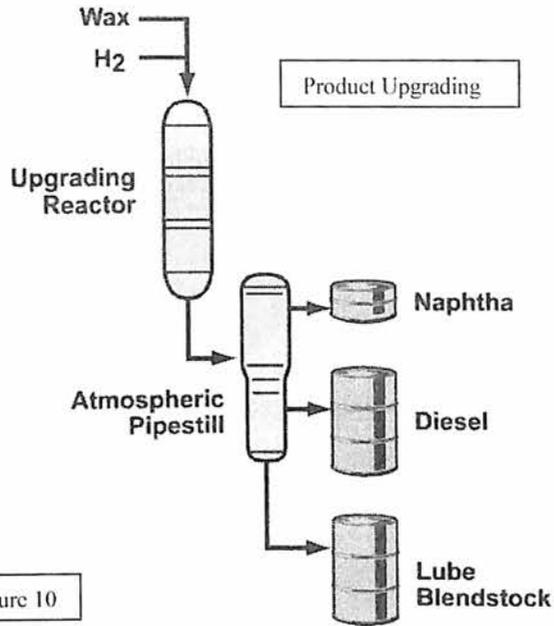
56

Figure 10

Source: Exxon Mobil's advanced gas-to-liquids technology. Hydrocarbon Asia, July/Aug 2003

For lubes upgrading, isomerization is preferred

– Maintains viscosity

– Higher viscosity index molecules

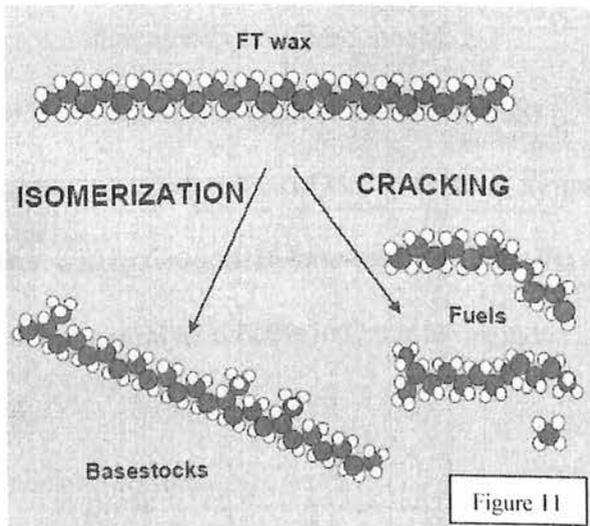– More selective (less diesel or methane make)

Figure 11

Source: Outlook for the East of Suez Lubricants and Baseoils Conference April 6 - 7, 2005. Dubai, UAE.

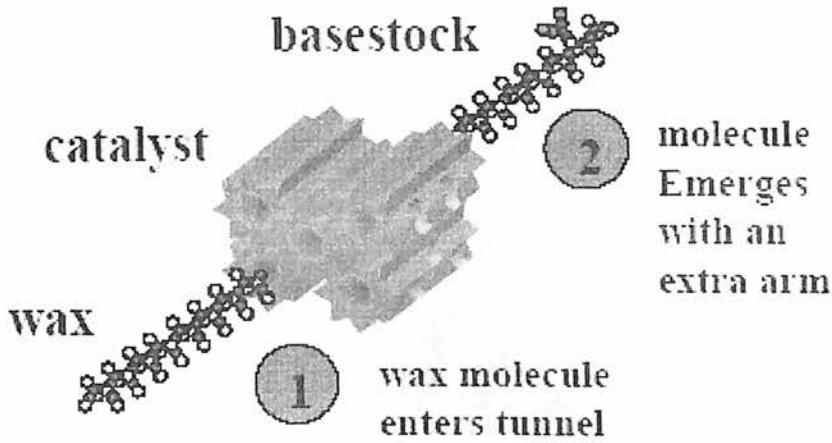MSDW Catalyst Converts Wax to Base-stocks

basestock

catalyst

2 molecule
Emerges
with an
extra arm

wax

1 wax molecule
enters tunnel

Figure 12

Source: Outlook for the East of Suez Lubricants and Baseoils
Conference April 6 - 7, 2005, Dubai, UAE.

Exxon Mobil proprietary catalyst efficiently converts wax to base-stocks

- Isomerization process reduces pour point, improves low temp performance

- Hydrotreating process removes olefins and other impurities

- Final product is a high quality lube base-stocks

Excellent performance for both dewaxing and wax conversion

- Improvement low temp properties of Group II/II+ at Singapore, Wakayama

- Converts slack wax to Group III+ base-stocks (Visom™) in the U.K.

- Expect to use same catalyst process in Qatar to upgrade GTL wax

3.3.4 Product Quality

GTL Base-stocks Expected to Be Highly Paraffinic
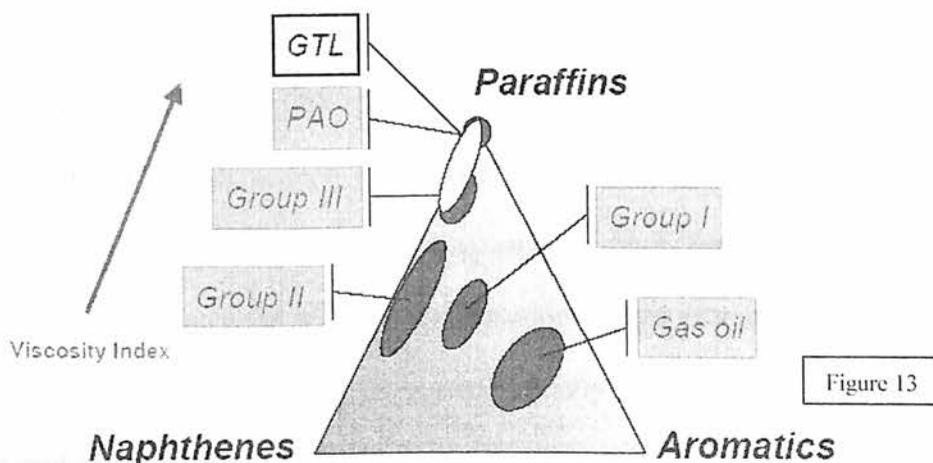
Figure 13

Source: Outlook for the East of Suez Lubricants and Baseoils Conference April 6 - 7, 2005, Dubai, UAE.

a. Have zero sulphur

b. Almost nil Nitrogen and aromatics

c. Highly bio-degradable

d. Have high viscosity index (because they are 100% iso-paraffins)

e. Process yields base-stocks with higher yields

f. Are clear colorless liquids, low odour

g. Very clean burning

4. CONCLUDING REMARKS

The estimated demand of high performance end basestocks is about 20,000 to 25,000 barrels per day. If 20% of a GTL plant's output is diverted to make lube basestock, then one large scale GTL plant of the order of 1, 00,000 barrels per day capacity could sustain this. In the meanwhile more GTL plants are going to be put-up throughout the world which certainly adds value to the existing capacity this is supplemented by the growing stringent environmental regulations, technological and economic pressure. It is estimated tat the lube demand may grow exponentially in the forthcoming decade with an amount of about 75 to 83 KBPD.

The following factors will accelerate the growth of GTL basestocks in the future.

1. Level of capital investment required.

   Lower the level of the capital, the more interest will be towards GTL

2. Gas disposition alternatives

   There are a couple of other routes to monetize stranded gas, including building the infrastructure. Pipelines to carry gas liquefy the natural gas; conversion of Natural gas to methanol or ammonia. The higher the hurdles for these alternatives more will be interest in GTL.

3. Natural Gas prices

   Lower the price of gas, there will be an inclination towards interest for GTL

4. Markets for products

   As the market demand for premium products grows, the possibilities of GTL will be improving.

5. Innovative and efficient technology will certainly make a difference in commercializing GTL.

6. Manufacturing cost considerations.

This include the cost of capital and how it is allocated; raw material costs; utility costs; labour costs; operating costs and others

7. Alternative disposition costs

Can the waxy feedstock created by the Fischer Tropsch process be used to make lube base oil or another product? The alternative usage will create more value to the GTL technology.

Lube basestock manufacturing has continued to evolve

- High quality basestocks

- Lower manufacturing costs

GTL is the next logical extension of basestock manufacturing technology. It builds off of existing catalytic hydroprocessing and isomerization technology. GTL continues the migration to more paraffinic basestocks with very low impurities, high viscosity index and performance approaching PAO is possible. But the actual quality depends on wax upgrading process and technology.

Though they are of high quality, GTL basestocks may face formulation challenges. The high viscosity index, good low temp properties is currently struggling to meet fuel economy. Also it may want to change classifications to take advantage of basestock quality. In addition, very highly paraffinic stocks have very limited solvency for polars, additives which requires substantial work in additive technology, formulation will be required.

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