CONVERSION OF NATURALGAS TO ULTRACLEAN HYDROCARBONS – A COMPARITIVE STUDY OF AVAILABLE PROCESSES

A Project Report submitted in partial fulfillment of the requirements for the Degree of
MASTER OF TECHNOLOGY
in
GAS ENGINEERING
(Academic Session 2003-05)

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May 2005
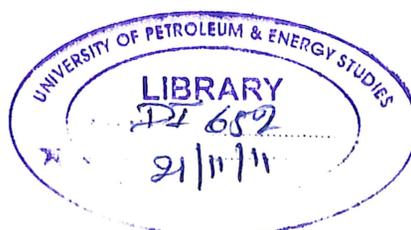
CERTIFICATE

This is to certify that the Project Report on *"Conversion of Natural Gas to Ultraclean Hydrocarbons- A comparative study of available processes"* submitted to University of Petroleum & Energy Studies, Dehradun, by **Mr. Vamshidhar Nagavelli,** in partial fulfillment of the requirement for the award of Degree of Master of Technology in Gas Engineering (Academic Session 2003-05) is a bonafide work carried out by him under my supervision and guidance. This work has not been submitted anywhere else for any other degree or diploma.

Date: 24.5.2005

Dr.Himmat Singh

ACKNOWLEDGEMENT

I would like to express my most sincere gratitude to many people, notably among them are numerous scholars at UPES who have given guidance at various levels and gave me an opportunity to work with them. They provided me necessary impetus with all their zest, zeal and motivation and without their guidance, support and extremely helpful attitude; this project would not have seen the light of the day. They gave valuable suggestions to me and were considerate enough to share their knowledge and experience for the accomplishment of project work.

I express my deep sense of gratitude and indebtedness to my guide Dr.Himmat Singh, (Distinguished Professor, UPES) for his invaluable and efficient guidance.

I am highly grateful to Dr.B.P.Pandey (Dean, College of Engineering, UPES) for his kind cooperation during project.

VAMSHIDHAR NAGAVELLI

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EXECUTIVE SUMMARY

There has been an increased level of activity recently in the conversion of natural gas to liquid fuels as evidenced by a flurry of announcements from such companies as Sasol, Exxon, Shell, Syntroleum, Williams Cos., British Petroleum, Texaco, and ARCO. It would appear that a combination of economic and technological factors has converged to bring natural gas conversion to liquid fuels to the forefront of industry consciousness. The modern history of gas conversion began in the 1920s with the discovery of Fischer-Tropsch (F-T) chemistry in Germany. Synthesis gas could be converted to long chain paraffinic hydrocarbons for use as liquid fuels. The technology generally proved to be uneconomical compared to less expensive crude oil based fuels, but F-T synthesis did find important niche applications.

Because of the oil shocks of the 1970s there was renewed interest in alternative fuel sources. F-T enjoyed a resurgence of research activity, but interest in F-T waned once again due to the collapse of oil prices.

This report focuses on the comparison of the technologies making natural gas conversion to liquid fuels a potentially viable option. The technologies analyzed in this report include the current commercial technology as well as two technologies reportedly close to commercialization: Shell Middle Distillates Synthesis (SMDS) & Exxon Advanced Gas Conversion Process (AGC-21) & Syntroleum Process and compared the economics of these three process technologies

1. **INTRODUCTION**

Conversion of natural gas to synthetic fuels through F-T synthesis is considered to be the technology of the 21st century. It offers potential for monetising heretofore unmarketable stranded gas resources by conversion into valuable and profitable synthetic fuels. And, more importantly, it is a solution that provides ultra clean, high quality transportation fuels and speciality products that meet increasingly stringent environmental regulations and are now the key drivers behind GTL development. The use of crude oil based products for transportation are expected to continue over the next decade or more, though their dominance will face emerging and mounting challenges over time. Recent events in the crude producing regions and their effect on the prices have again pushed the issue of alternate fuels to the forefront. One area that is expected to provide considerable growth is direct fuel substitutes: renewable fuels, gas to liquid synfuel products and ethers. These direct fuel alternatives are projected to increase more than 2.5 times the current levels or about one million bpd by 2015. Other alternatives (compressed natural gas, liquefied petroleum gas, advance vehicle technology, fuel cells etc.) will also contribute to the move away from the crude oil. Numerous government policies and commercial plans are paving the way for this to occur. GTL, of the three alternatives, is moving fastest to reconcile the world's conflicting desires for more energy and cleaner air and water. Compliance with increasingly stringent clean air standards calls for some entirely new, non conventional concepts and approaches. The fuels of the future may be 'designed' rather than refined.

To meet this challenge one needs a technology that:

• Is based on raw materials available in quantities enough to support large-scale production required for the huge worldwide transportation vehicle fleet

• Yields extra clean designer fuels that are compatible with both existing and new engines designs and fit seamlessly into the existing distribution infrastructure

• Is environmentally friendly in the production phase. Remarkably, natural gas refining using gas to liquid (GTL) technology developed by Syntroleum, Shell, Sasol, Rentech, Exxon-Mobil, AGC 21 (Advance Gas Conversion) and others have all these and more. This technology converts, either using slurry bed or fixed processes, natural gas into a

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waxy synthetic crude oil, which can be refined into valuable, virtually contaminant free products like low sulphur distillate fuels, waxes and lubricant base stocks. Sasol is considered to be the most experienced process developer in this field. There is growing awareness that GTL offers strategic solutions to the world's increasingly complex energy supply needs, as focus widens to encompass not only supply side issues but also the demand side of the equation.

What Is GTL

GTL is a process for converting natural gas into synthetic oil, which can then be further processed into fuels and other hydrocarbon-based products. In the simplest of terms, the GTL process tears natural gas molecules apart and reassembles them into longer chain molecules, like those that comprise crude oil. However, with this particular conversion process, the result is an extremely pure, synthetic crude oil that is virtually free of contaminants such as sulfur, aromatics and metals. This synthetic crude can then be refined into products such as diesel fuel, naphtha, wax and other liquid petroleum or specialty products.

WHY GTL?

GTL technology offers a number of significant benefits, including:

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

Eliminating costly and/or environmentally disadvantageous practices - GTL will help eliminate the need for flaring natural gas, associated with oil production, which will permit earlier development and production of oil fields shut in by the inability to dispose of the associated natural gas, and reducing the negative environmental impact of flaring.

Creating environmentally-superior liquid fuels - GTL will yield synthetic hydrocarbons of the highest quality that can be used directly as fuels or blended with lower quality crude oil derived fuels to bring them up to compliance with increasingly stringent environmental and performance specifications. The diesel produced in Conoco's GTL process is crystal clear in color and virtually sulfur free.

BACKGROUND

The recent announcements by many of the major companies involved in the production of gas liquids from stranded gas reserves have made GTL (gas-to-liquids) an increasingly important consideration. Although much has been written about the technologies involved and the finances required (in the multi-billion $US), a strategic assessment of the "landscape" in GTL has yet to be produced.

THE NEED FOR THE STUDY

The current environment for investment in GTL projects is more fertile than it has been for the past 50 years. The reason is actually a confluence of factors that provide a number of drivers from several directions. Some of the most important of these drivers are economic, strategic, market and environmental, as follows:

Economic Drivers
- Crude oil price at historically high levels;
- Peaking of oil production in many regions.

Strategic Drivers

- Gains access to abundant gas reserves;
- Provides a means to monetize stranded and remote gas reserves;
- Need to forge alliances with governments and energy companies in resource rich countries to assure future supply;
- Physical as well as environmental limits on the ability to re- inject associated gas to stimulate oil production;
- A source of clean, synthetic crude oil to blend with heavier/dirtier crudes to gain benefits in both transportation and refining;
- Synthetic crude and fuels can be integrated easily into existing infrastructure.

Market Drivers

- Global growth in demand for clean diesel fuel;
- Markets for energy are remote from abundant, cheap sources of energy reserves, requiring a transportable (liquid) form.

Environmental Drivers

- Legislation mandating low sulfur, lighter, clean-burning fuels;
- Inability to flare associated gas, requiring some way to dispose of gas to allow continued oil production;
- The U.S. Energy Policy Act of 1992, which designates GTL from natural gas to be considered an "alternative fuel." Although the technical, strategic and market drivers are important, the environmental drivers are particularly critical, both from a compliance and public image point of view. Although the strictest regulations originate in certain geographic regions, the protection of the environment and the warding off of climate changes are global problems.

Although a number of these drivers are not new, what is somewhat unique is the fact that they all seem particularly critical at this point in history. Therefore, the circumstances are right for GTL projects to finally begin to realize their long-promised potential.

2. TECHNOLOGY OVERVIEW

The strategy for GTL depends on the location of methane, demand for products, construction costs, the economic and geopolitical stability etc. One should keep in mind that the capital cost involved in any GTL is very high. Where natural gas is extracted along with petroleum crude, there may not be buyers for the purchase of gas along with the crude in which case it becomes a liability, and the gas may be available at cheap cost. There is the other case where the gas extracted is in abundance and the utilization is poor. In such cases transportation through pipeline or conversion to LNG are expensive alternatives. At present in many fields, the excess gas is re-injected into the well and as the oil reserve gets depleted, an increasing amount of gas will be recycled per barrel of oil produced. In a free market economy, the profitability of these facilities will depend on the selling price of the product and the cost of alternative technologies, both of which may fluctuate significantly over a short period. The process of converting natural gas to marketable liquid hydrocarbons comprises three main steps, viz.

i) Synthesis gas, a mixture of CO and H_2 (syngas) production

ii) GTL synthesis and

iii) Product work-up.

The feed gas will typically be treated initially for removal of sulphur compounds which otherwise poison the catalyst, in addition to causing corrosion and environmental problems.

Syngas generation

In GTL technology, FT conversion process is employed which requires a specific molar ratio of hydrogen depending upon the product. One or more of several processes, working in parallel, in a combined mode or with the addition or extraction of hydrogen, can achieve the appropriate syngas composition ratio. Natural gas (primarily methane) is reacted with steam and/or oxygen to produce syngas, which is a mixture of hydrogen and carbon monoxide.

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Three main reactions occur:

Steam reforming:

$$CH_4 + H_2O \text{ ------- } CO + 3H_2$$

Partial oxidation:

$$CH_4 + 3/2\ O_2 \text{ --------- } CO + 2H_2O$$

Water gas shift:

$$CO + H_2O \text{ ----------- } CO_2 + H_2$$
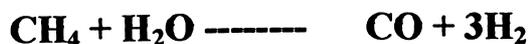
Syngas production is carried out at high temperature (typically above 1800°F or 1000°C). Both catalytic and non-catalytic processes are used. Syngas production is a common process in the petrochemical and petroleum industries to make hydrogen, ammonia and methanol.

History of FTS

The FT process had a lively history of about eight decades since its discovery in Germany by Franz Fischer and Hans Tropsch in the 1920s. During world war-II, two processes for converting coal to liquid transport fuels were tried in Germany. The first, direct liquefaction (Bergius process) involves the direct catalytic hydrogenation of coal to liquids which are further refined. In contrast, indirect liquefaction involves conversion of coal by partial oxidation in the presence of steam to yield syngas, which after purification is reacted catalytically to form liquid hydrocarbon fuels. Both Bergius and FTS were discontinued after war because of easy availability of petroleum. However, FTS was started in a big scale at SASOL in South Africa in the 1950s.

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Fischer Tropsch Synthesis (FTS)

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

The basic reaction is:

$$nCO + (2n+1) H_2 \text{----------} C_nH_{2n+2} + nH_2O \quad \Delta H_R = -39.4 \text{ kcal/mol}$$
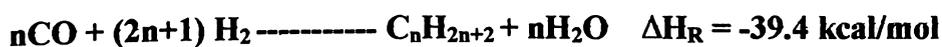
Other reactions also take place in the process, resulting in the formation of olefins and alcohols; besides, there are some side reactions. Much attention is focused on developing catalysts with appropriate selectivity and physical properties. Catalyst selectivity, syngas composition and process conditions (principally temperature) govern the product distribution and the limit of the paraffinic chain length. The mechanisms proposed to explain the chain length with the help of ASF distribution. The exact mechanism is complex and is still a subject of much debate. However, it can be described in a simplified manner in the following steps.

  i) Initiation or C_1 compound formation

  ii) Hydrocarbon chain growth by successive insertion of the C_1 building blocks and

  iii) Chain termination by

      a) Desorption of unsaturated surface species and

      b) Hydrogenation and desorption of saturated species.

The types of catalysts employed in syngas conversion are shown in Table-2.1 below. FT process typically involves the recycle of unconverted gases to the reactor, CO_2 removal from the recycle loop and dehydration of the recycle gas. In some cases, the process separates H_2 for using in the product-upgrading unit. The recycle gas may be used as fuel gas. In addition to distillates, Fischer-Tropsch GTL plants can also produce a range of specialty products, such as normal paraffins (C_{10} to C_{13} range), a feedstock used

in the detergent industry for the production of linear alkyl benzene sulphonate (LAS), one of the world's most widely used surfactants. Some plants however, may not produce paraffins suitable for LAS and suitability will depend on GTL catalyst selection and process conditions. Compared to the traditional route of extracting normal paraffins from kerosene, the GTL route is simpler and has significant capital and operating cost advantages. Normal paraffins made by the Shell GTL plant at Bintulu have been successfully marketed in Asia since the start-up of the plant in 1993. In the future, GTL technology could largely replace traditional technology to meet the growth in demand for normal paraffins.

TABLE 2.1: Potential FT catalysts

Source of carbon	Catalyst	Property
Any Carbon rich (Coal)	Ni Fe	Methanation WGS with CO_2 Production
Hydrogen rich (Natural gas)	Co Ru	Highly active and gives linear hydrocarbons Very active but expensive

ii) Product work-up

The hydrocarbon products from FTS have various chain lengths. They are predominantly paraffins and alpha olefins if the product is aimed at middle distillates. Some oxygenates also may be present. The mixture can be shipped as syncrude, as a feedstock for refineries. Transportation through conventional tankers may not be feasible because of high pour point of syncrude, particularly for plants operated for maximum distillates. Alternatively, the syncrude may be separated and further processed at the production site, producing fuels, fuel blending components or specialty products (like

waxes, lube bases) for local use or export. A mild hydro cracking / hydro isomerization breaks down long chain paraffins into short chain normal and iso paraffins with improved cold properties and boiling range. By this route, high quality jet fuel and diesel fuel blending components can be prepared. Mild hydrotreating can be used to eliminate olefins and alcohols. This type of finishing is not necessarily an integral part of a GTL plant. The decision to include this module is based on economic and market options. The quality of GTL diesel can be seen from the Table 2 below.

TABLE 2.2: GTL diesel quality

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

4. Catalyst Development

The role of the catalyst is

  a) To hasten those CO hydrogenation reactions for the desired products

  b) Avoid wide varieties of competing reactions

  c) To do so at high enough velocity (catalyst activity) to be commercially useful

  d) To do so at relatively low temperature and pressure and

  e) To continue to be active and selective in stable operation for long periods of time.

Although the catalyst development in FTS has been extensive, a review of the data suggests that the choice is limited, and only two types are commercially practiced. These are: **Fe based and Cobalt based catalysts**.

However, due to high capital cost, cheap iron based catalysts are preferred. Cobalt based catalysts gave higher selectivity for any specific product. With high product selectivity, the high cost of the catalyst can be partially compensated. The development on the technology for the catalytic conversion of syngas to hydrocarbons has been periodically reviewed. Initial development was based on cobalt catalyst, which was commercially employed during World War II for producing 10,000 bpd gasoline in Germany. At the same time, Fe catalyst was also developed but was not commercialized. Iron catalyst was commercially used first in the Hydrocol Process at medium pressure (100-150 psig) fixed fluidized bed reactor with syngas produced from natural gas. Several other significant discoveries were also made during this period. It was found that Ru is particularly capable of making high yields of wax. Higher selectivity to desired product should be the primary objective in catalyst improvement. In some cases, in addition to CO hydrogenation, accelerating the water gas reaction is also desired. This makes possible more economical syngas with lower H_2/CO ratio. The catalysts must be able to split the carbon-oxygen bond of carbon monoxide. On Cr, Mo, W etc. CO is dissociatively adsorbed whereas on Pd, Pt and Cu associative adsorption is favoured while metals like Rh favour both. Catalysts such as alkalized iron are good water gas shift (WGS) catalysts and these catalysts deplete the concentration of CO to form H_2 thereby the apparent H_2/CO usage becomes smaller. On the other hand cobalt, which is not a good WGS catalyst, does not affect the feed ratio releasing water as a byproduct.

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

and Ni on a support were shown to generally enhance catalytic activity and suppress methane formation. Also, special porous and amorphous $Ni_{67}Zr_{33}$ alloys have been prepared and tested for catalytic properties. It has been shown that the particle size is important for supported Ru. Small particles (1 nm), produced significant proportions of higher hydrocarbons, and large single crystals, (11 nm), gave mainly methane. The concept of partial poisoning provides a powerful means of improving catalyst selectivity, interpreted in terms of ensemble control. Decreased methane formation by sulphur poisoning of fused magnetite FT catalyst was reported. Fe catalysts treated with a sub-monolayer of chemisorbed sulphur were examined and found that the treated catalysts had a three-fold reduction in methane selectivity relative to the untreated fused iron, when tested with 2:1 H_2/CO syngas at 300oC and atmospheric pressure. The C_2 olefin selectivity approached 100%. McCarty and Wilson demonstrated the improvement in selectivity with Fe, treated with low levels of sulphur. All these developments remained at experimental level and are yet to be tested at higher scale. A variety of catalysts have been tested in the slurry reactor. Fine particles composed of Fe-Co-Ni or pure Fe were found to be more active than precipitated catalysts. A new concept of combining slurry phase followed by upgrading over zeolites is regarded as a significant improvement over classical FT. The potential active catalyst constituents successful in commercial trials are shown in Table 1. It may be noted that most of the formulations are proprietary and very little information regarding preparation or characterization is available.

Company	Typical catalyst Constituents			
	Primary	Reduction Promoter	Activity/Selectivity promoter	Support
Conoco	Co	Re, other	N/A	Alumina, other
Gulf(Shell)	Co	Ru	Oxide promoters	Alumina
Exxon	Co	Re/Ru	Oxide promoters	Titania or TiO_2/silica
IFP	Co			
Intevep	Co	-	Oxide and carbide promoters	Silica
Rentech	Fe	N/A	N/A	-
Shell	Co	With or without a noble metal	ZrO_2	Silica, silica/alumina
Statoil	Co	Re	Oxide promoters	Alumina
SASOL	(Fe)Co	Pt	-	Alumina
Williams	Co	With or without noble metal	With or without oxide promoters	Doped alumina

Table 2.3: Typical Catalyst Constituents

3. PROCESSES FOR SYNTHESIS GAS PRODUCTION

Abstract

Synthetic fuels offer an extremely flexible means of marketing remote sources of natural gas. Different synthesis processes require different synthesis gas specifications. The paper highlights the importance of matching the synthesis gas production process to the needs of the individual synthesis process. Examples discussed cover single-stage and two-stage reforming as well as partial oxidation.

Introduction

It is a truism to observe that the world's hydrocarbon resources are not evenly distributed and in particular that a substantial proportion of known reserves are situated in locations remote from areas of high consumption. Transportation of liquid hydrocarbons from source to consumer is a task for which a large and flexible infrastructure exists. However, where natural gas deposits in remote locations are to be exploited, the transportation task becomes a major challenge - particularly if geography, economics or a combination of both precludes the possibility of a pipeline. This challenge can be met by conversion of natural gas into a transportable and saleable form or product. Historically this has implied LNG, ammonia or methanol as the medium of bringing remote natural gas to the market place. Each of these has its limitations - the heavy investment and, relatively speaking, small number of receiving terminals limits the marketing flexibility for LNG. Neither the ammonia nor the methanol market is large enough to accept the potential volumes available from exploitable natural gas reserves. Current prices for both products would indicate that we are close to these marketing limits - unless of course legislation drives motor fuels in the direction of methanol. An alternative that is gaining increasing attention is the conversion of natural gas to synfuels - ranging from gasoline to middle distillates. This approach avoids the infrastructural limitations of LNG and at the same time provides a market large enough to accept the potential volumes.

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Synthesis Gas Specifications

There are two routes for the production of synthetic fuels,

a) The Fischer-Tropsch route and

b) The Methanol route.

The first step for both routes is the conversion of natural gas into synthesis gas - a mixture of hydrogen, carbon monoxide and carbon dioxide. The proportions of these components in the mixture vary according to the individual synthesis process selected and also according to the product slate desired. Typical values of the principle characteristic, the H_2/CO ratio, for different processes are given in Table 3.1. As can be seen, this covers a wide range from below 1 to nearly 3. In addition varying amounts of pure hydrogen may be required for hydrogenation of the crude product from the synthesis. The wide range of H_2/CO ratios required for the different synthesis processes means that considerable effort is required to match the syngas generation and synthesis process so as to ensure the optimum overall conversion rate.

Table 3.1: Values of H_2/CO ratio

Synthesis	H_2/CO
Dow	0.85
Union Carbide	1
ARGE	1.3-3
Gulf Badger	1.5-2
SMDS	2
Synthol	2.6
Methanol	2.4-3

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Synthesis Gas Production Processes

The number of chemical reactions involved in the manufacture of synthesis gas is very large. The most important of these are listed below. Given the objective of producing CO and H_2 from the methane, the most desirable reactions are those of reforming (reaction 1) and partial oxidation (reaction 3) producing H_2/CO ratios of 3 and 2 respectively. If a source of CO_2 is available (or for a CO_2 rich natural gas) reforming with CO_2 (reaction 2) provides an H_2/CO ratio of 1. The figures for higher hydrocarbons in the natural gas are correspondingly lower. The final H_2/CO ratio is influenced further by the CO shift reaction (5).

Synthesis Gas Production – Principal Reactions

Reforming (strongly endothermic)

$$CH_4 + H_2O \longleftrightarrow CO + 3H_2 \text{ --------(1)}$$

$$CH_4 + CO_2 \longleftrightarrow 2\,CO + 2\,H_2 \text{ --------(2)}$$

Combustion (strongly exothermic)

$$2CH_4 + O_2 \longrightarrow 2CO + 4\,H_2 \text{ ---------(3)}$$

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O \text{ ---------(4)}$$

Shift conversion (mildly exothermic)

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \text{ ---------(5)}$$

Carbon

$$CH_4 \longrightarrow 2H_2 + C \text{ ---------(6)}$$

$$2CO \longrightarrow CO_2 + C \text{ ---------(7)}$$

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The reforming reactions (1 and 2) are strongly endothermic and must be supported by the strongly exothermic reactions of partial oxidation (3) and/or complete combustion (4). The latter reaction is, however, in principle less desirable since neither H_2 nor CO is produced. The three main industrially proven processes of tubular steam reforming, catalytic auto thermal reforming and non-catalytic partial oxidation can be characterized as follows.

In **tubular steam reforming** reaction (1) takes place over a catalyst in a tube which is externally heated. A large steam surplus is required to suppress carbon formation in the catalyst. This tends to drive the shift reaction (5) to the right resulting in a hydrogen rich synthesis gas. The heat is supplied largely by the undesirable complete combustion reaction (4) outside the tubes.

In **catalytic autothermal reforming** oxygen is added to the feed. The heat requirement for reaction (1) is largely met by the partial oxidation reaction (3) thus producing a lower H_2/CO ratio in the syngas product. As in tubular reforming considerable amounts of steam are required to suppress carbon formation. The absence of the metallurgical limitations of the catalyst tubes of a steam reformer allows higher operating temperatures thus reducing methane slip. At these higher temperatures the CO shift equilibrium is also more favourable to CO than in the case of the tubular steam reformer.

In **non-catalytic partial oxidation** reaction (3) is dominant. The absence of any catalyst means that the process is tolerant of a small degree of carbon formation and allows even higher operating temperatures. It is thus possible to operate partial oxidation without any steam addition. The resulting gas is the most CO rich of the three. The art of selecting the right syngas generation process - or combination of processes - consists of ensuring the correct gas specification as required by the selected synthesis while simultaneously minimizing certain inherent inefficiencies of the individual processes. In the case of tubular reforming this inherent inefficiency lies in the use of external complete combustion requiring an expensive heat recovery train and still involving

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substantial losses in the stack gas. In the case of autothermal reforming and partial oxidation the inefficiency lies in the energy requirement and investment for the oxygen plant.

State of the Art Processes

LURGI GMBH is currently involved in the design and supply of synthesis gas production units for two major synfuel projects - one based on SASOL's Synthol process and the other using SHELL's SMDS synthesis. As can be seen from the data in Table 3 there is a substantial difference in the H$_2$/CO ratios required by the two processes and this has led to the selection of different syngas production routes. In the Synthol case LURGI's own Combined Reforming was selected. In the SMDS case SHELL's SGP partial oxidation route is being used. The figures used in the following discussions to illustrate particular features of these two syngas production processes are based on a total hydrocarbon product capacity of 1,000,000 tons/year with a product slate typical for the synthesis process selected. In both cases the same natural gas quality has been assumed.

LURGI's Combined Reforming

LURGI's Combined Reforming process was originally developed for large-scale methanol production and it is with an example from this application that it is described here. In the synfuels context it is suitable as a building block for MOBIL's MTG process. For a Synthol flow sheet some CO$_2$ would need to be purged from the system. The conventional tubular steam reforming process as used for methanol syngas production produces an H$_2$/CO ratio of over 4 and a stoichiometric ratio of 2.6 to 2.9 depending on the natural gas quality, i.e. a hydrogen-rich gas. Autothermal reforming or partial oxidation produce carbon monoxide rich gases with an H2/CO ratio 1.8 to 3.5 and a stoichiometric number of around 1.8. The block flow diagram in Figure 2 shows how a tubular reformer (the primary) and an autothermal reformer (the secondary) are combined to produce an optimum methanol synthesis gas quality. Approximately half the feed is processed in the tubular primary reformer. The other half, together with the primary

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reformer effluent, is autothermally reformed with pure oxygen in the secondary reformer. Besides matching hydrogen-rich and carbon monoxide-rich process steps to produce an optimum stoichiometric ratio, the Combined Reforming process has additional beneficial effects.

- The methane slip of the overall reforming process is governed by the temperature of the secondary reformer which is not subject to the same limitations of tube metallurgy as the tubular reformer. The combined process can thus provide a lower methane slip.

- Less synthesis gas of the optimized quality is required per ton of methanol, reducing both the syngas compressor load and the capital cost of the synthesis unit.

- The operating temperature of the primary reformer need no longer be chosen to minimize methane slip. It can be operated under mild conditions. The higher operating pressure thus possible enables the syngas compressor load to be further reduced.

- The reduced throughput through the primary reformer together with the lower operating temperature combine to reduce the tubular reformer to about 25% of the size of that required for the single stage process. This reduces the stack gas losses referred to earlier by the same amount. Simultaneously a substantial saving in capital cost is achieved.
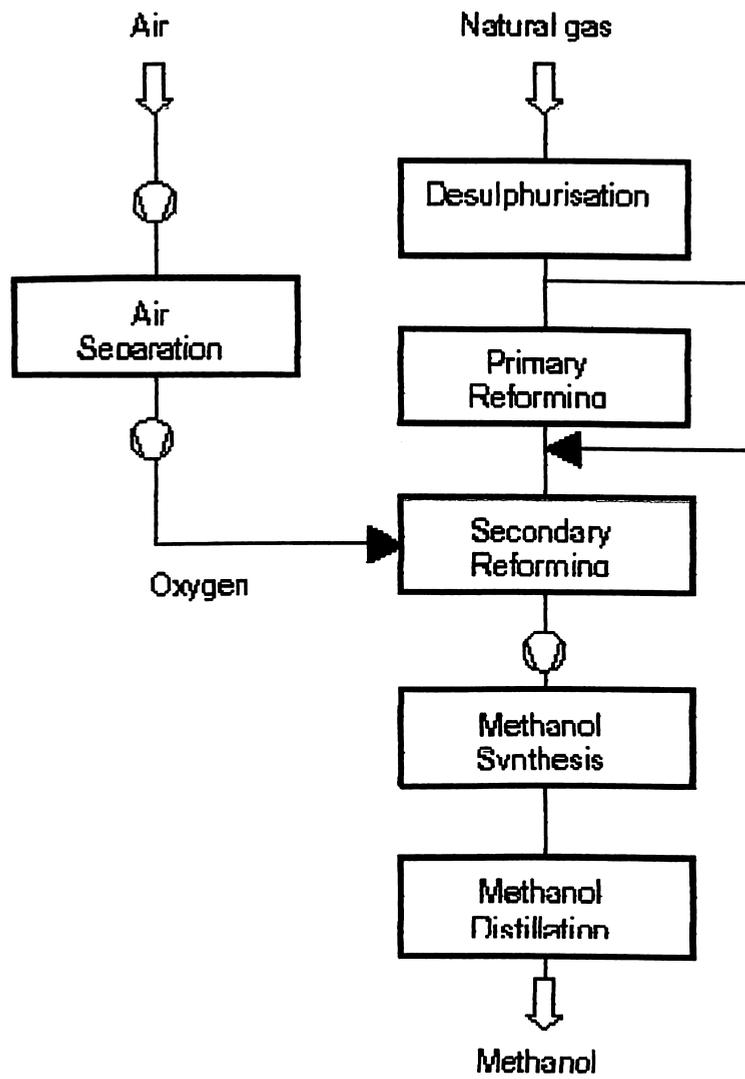
**Fig 3.1: Lurgi Combined Reforming**

SHELL's SGP Process

SHELL's SGP process for which LURGI is the licensing agent is a much older process, the basic development having been made in the 1950's and some 150 units having been built in the meantime. With natural gas feed it produces a synthesis gas with an H_2/CO ratio of typically 1.7 - 1.8 and a CO_2 content of 1.7 - 3 depending on the steam addition rate. A simplified flow diagram of a gas based SGP unit is shown in **Figure**. The gas feed is preheated with the raw gas to a temperature of about 380°C for desulphurization prior to being fed to the SGP reactor with the oxygen. The partial oxidation reaction takes place at about 1300 - 1400°C in the refractory lined reactor. The sensible heat of the hot gas is used to generate high-pressure steam, with or without superheat as required. As mentioned previously the non-catalytic partial oxidation reactor produces small amounts of soot, which are washed out in a scrubber. The carbon is concentrated in the reaction water, which is discharged to the waste water treatment. The gas - now free of soot - is ready for use in the synthesis with an analysis as shown in **table**.

Table 3.2: Analysis of SGP

		SGP
No. of trains		8
Natural gas feed (total)	kmol/h	9 915
Oxygen (total)	kmol/h	5 785
Synthesis gas		
H_2/CO	kmol/h	1.86
CH_4		1.27
Flow (total)		27 861

If we compare the synthesis gas quality with that produced by Combined Reforming we see a considerably lower H_2/CO ratio of 1.86 compared with 3.14 for Combined Reforming making SGP a better match for, for instance, the SMDS process.

Figure 3.2: Shell Gasification Process ('SGP')
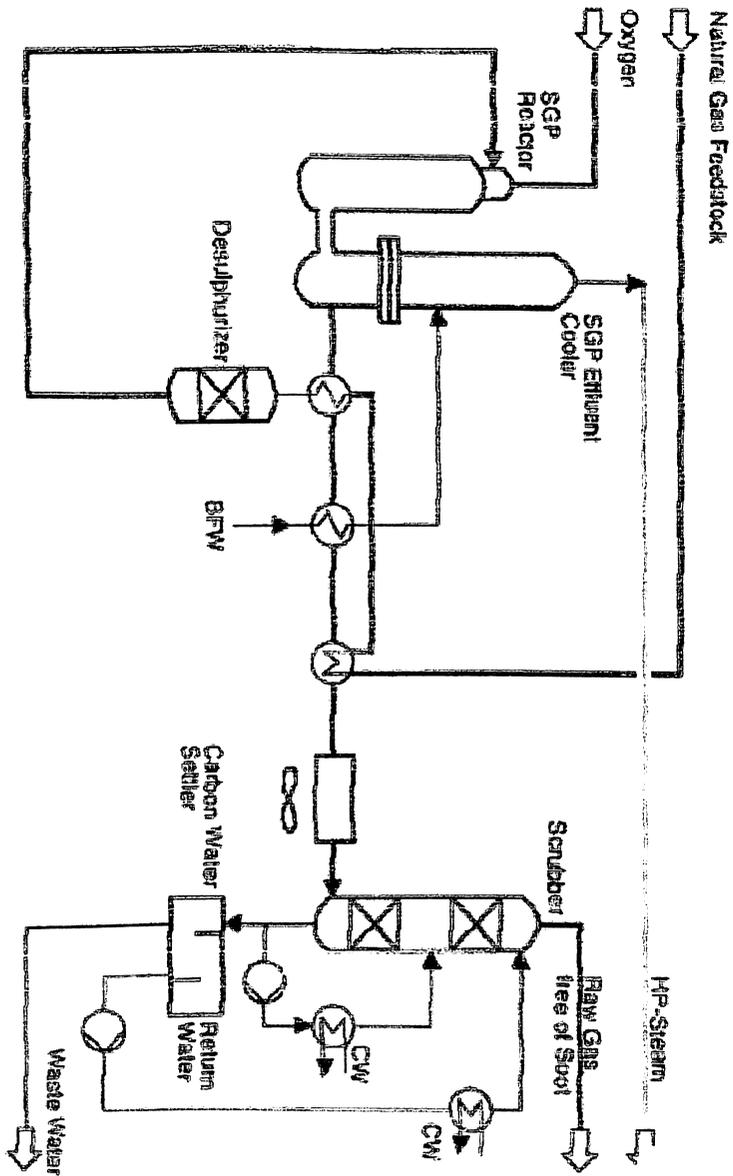
The amount of natural gas required to produce the synthesis gas is some 3.5% lower than for the Combined Reforming case. These advantages are bought at the cost of higher oxygen consumption.

Process Integration

Having looked at some of the details of two typical gas production processes, it is useful to see how they relate to the rest of an overall synfuels plant, particularly one based on a Fischer- Tropsch synthesis. One feature common to all Fischer-Tropsch processes is their inherent lack of selectivity. The actual selectivity will depend on the desired product slate as well as on the catalyst and the operating conditions. In all cases, however, substantial quantities of gaseous hydrocarbons including methane are produced. In principle it is desirable to recycle these gaseous hydrocarbons to produce more synthesis gas. On the other hand it is necessary to provide a purge of inerts, principally argon and nitrogen from the loop. The other side of the selectivity coin is that a proportion of heavy products including waxes are produced which require some form of hydrotreatment to convert them into a saleable product. As far as the gas production is concerned this means that a side stream must be foreseen for hydrogen production. The block diagram in Figure 4 shows how these considerations can be met in a Combined Reforming-fed Fischer-Tropsch synthesis. The Fischer-Tropsch tail gas is recycled to the secondary reformer. The fuel demand of the primary reformer acts as a sufficient purge to keep the inerts in the loop to an acceptable level. The feed to the pressure swing adsorption unit for hydrogen production is taken off at the outlet of the CO_2 removal unit. The handling of these issues is different in the SGP-based plant (**Figure**). There is no primary reformer. The outlet for the inerts is a separate hydrogen manufacturing unit with its own reformer using tail gas as process feed and fuel. The fuel gas system for steam boilers or refinery heaters is a possible alternative.

Figure 3.3: Lurgi Combined Reforming for F-T Synthesis
 Figure 3.4: SGP for F-T Synthesis
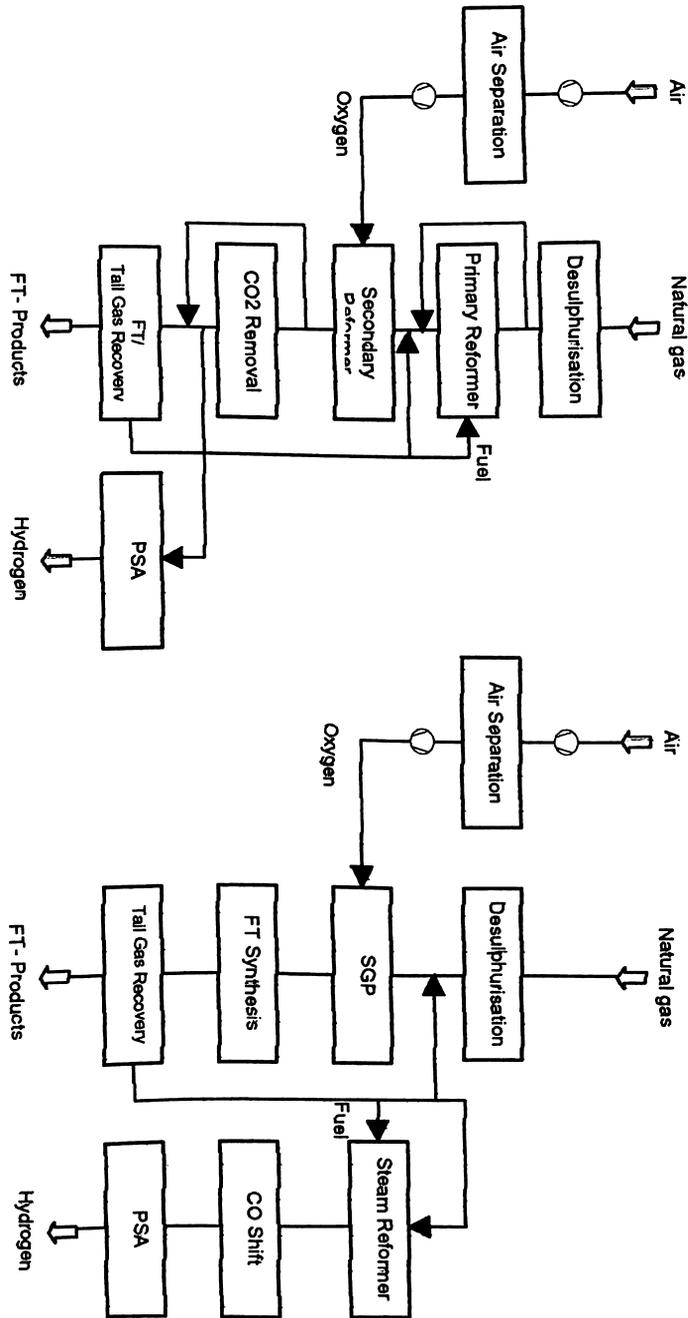
3.1 SYNGAS PRODUCTION TECHNOLOGIES CURRENTLY ADOPTED

3.1.1 Auto Thermal Reforming (ATR)

Background

This process combines partial oxidation and steam reforming in one vessel, where the hydrocarbon conversion is driven by heat released in the POX reaction. Developed in the late 1950's by Haldor Topsøe and Société Belge de l'Azote, the process is used for methanol and ammonia production. Both light and heavy hydrocarbon feedstocks can be converted. In the latter case, an adiabatic pre-reformer is required.

Process description

A preheated mixture of natural gas, steam and oxygen is fed through the top of the reactor. In the upper zone, partial oxidation proceeds at a temperature of around 1200°C. After that, the mixture is passed through a catalyst bed, where final reforming reaction takes place . The catalyst destroys any carbon formed at the top of the reactor. The outlet temperature of the catalyst bed is between 850 and 1050°C. The main advantages of ATR are a favourable H_2/CO ratio (1.6 to 2.6), reduction of emissions due to internal heat supply, a high methane conversion, and the possibility to adjust the syngas composition by changing the temperature of the reaction. However, it requires an oxygen source.

Economic aspects

The capital costs for autothermal reforming are lower than those of the SMR plant by 25%, as reported by Haldor Topsøe. Operational costs, however, are the same or even higher due to the need to produce oxygen. The SINTEF study reported a capital-cost reduction of 35%, but an 8%-increase in operational costs for the ATR technology in comparison to the SMR process.

Development status

ATR technology is commercially available, but still has limited commercial experience. The main licensors are Haldor Topsøe, Lurgi, ICI, Foster Wheeler.
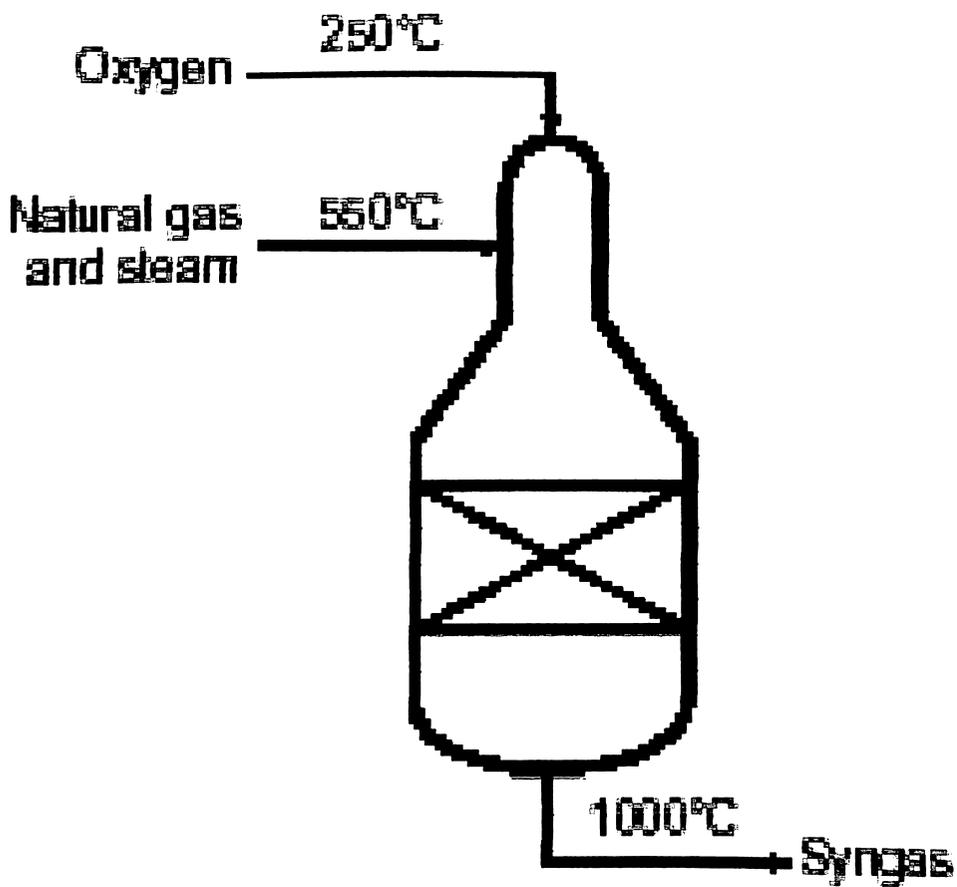

Fig 3.1.1: Autothermal Reforming

3.1.2. Partial oxidation (POX)

Background

In the partial oxidation reaction, which proceeds exothermically according to:

$$CH_4 + \tfrac{1}{2} O_2 \Leftrightarrow CO + 2H_2 \qquad \Delta H_R = -44 \text{ kJ/mol, (3)}$$

Complete conversion of methane is obtained above 750°C, resulting in a H_2/CO ratio of 2. Since the reaction is exothermic, no fuel is required. When applied to heavy hydrocarbons, coal, or vacuum residue this process is commonly referred to as gasification. First papers on this conversion route appeared in the 1930s. In the early experiments, nickel catalyst was used. Temperatures of the reaction varied between 750 and 900°C and the pressure were slightly above atmospheric. From 1946 to 1954 Texaco Laboratory in Montebello performed a series of experiments on their pilot plant to provide syngas by partial oxidation for the Fisher-Tropsch process. In the late 1970's interest in the partial oxidation of methane was resumed. Nowadays, pressures up to 75 bar and temperatures up to 1400°C are employed. In addition to the non-catalytic oxidation, a lower-temperature catalytic process has been developed. The catalytic partial oxidation (CPO) has a higher flexibility and is less susceptible to soot formation.

Process description

A refractory-lined pressure vessel is fed with natural gas and oxygen at a typical pressure of 40 bar (Fig. 3.1.2). Both natural gas and oxygen are preheated before entering the vessel and mixed in a burner. Partial oxidation reaction occurs immediately in a combustion zone below the burner. To avoid carbon deposition the reactants should be thoroughly mixed and the reaction temperature should not be lower than 1200°C. Sometimes steam is added to the mixture to suppress carbon formation. In the case of catalytic partial oxidation steam is not required and the temperature can be below 1000°C. The syngas produced leaves the reactor at temperatures of 1300–1500°C. Since the natural gas is usually supplied from a network at high pressure and oxygen is

delivered in the liquid form, the costs of upstream compression are almost negligible. In this manner, compression work is saved in the downstream synthesis process. In practice, syngas from the POX process has a H_2/CO ratio between 1.6 and 1.8, so a shift converter or steam injection should be employed to increase this ratio, for instance, for methanol synthesis. The non-catalytic process allows the use of a broad range of hydrocarbon fuels from natural gas to coal and oil residue and remains the only viable technology for heavy hydrocarbons. Almost 100% conversion is obtained in the POX reaction, and this is the reason why a POX reactor is used in combined reforming to complete conversion of methane coming from a steam methane reformer . At high temperatures carbon particles are burned completely, so that no steam is required, this simplifies the process operation. However, the need for oxygen results in high operating costs, and also provisions should be made to minimise the risk of explosion. The catalytic process has a reduced size and consumes less oxygen, but runs the risk of catalyst destruction by local thermal stress.

Economic aspects

According to the SINTEF study, the investment costs for a POX-based syngas plant constitute 80% of the reference SMR plant, while a CPO plant would require an investment of just 55% of the reference. Another source indicated that the syngas production costs from a POX plant are 60 to 70% of those of SMR (Norman, 1998). The SINTEF report (Sogge et al, 1993) cites an investment of 116 mln USD for a POX-based syngas plant with an output of 5.5 Nm3/day, resulting in specific costs of 21 USD per Nm3/day. Institut Français du Petrole (IFP) gives a figure of 80 mln USD for a smaller plant of 2 mln Nm3/day, i.e. 40 USD per Nm3/day. The oxygen costs can constitute 50% of operational costs of the syngas production at the POX plant (Sogge et al, 1994).

Development status

Syngas production via the POX route is an established technology. Texaco and Shell technologies have been employed for many years for partial oxidation of petroleum cuts and other heavy hydrocarbons. In the field of coal gasification, along with Texaco and Shell, other companies are active in this field such as Lurgi, Koppers, Foster Wheeler, British Gas, Starchem. In 1992, Texaco had more than 100 licensed commercial

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POX plants on their reference list, of which 28 were using gaseous and 62 were using liquid feedstock.. The POX technology is used at the Shell Middle Distillate plant in Bintulu, Malaysia, where a natural-gas feedstock is processed via Fischer-Tropsch synthesis to produce synthetic fuels and waxes at a scale of 12 000 barrels per day. Exxon has developed a fluid bed in which partial oxidation and steam reforming reactions are carried out simultaneously in a single large reactor containing a bed of catalyst particles.
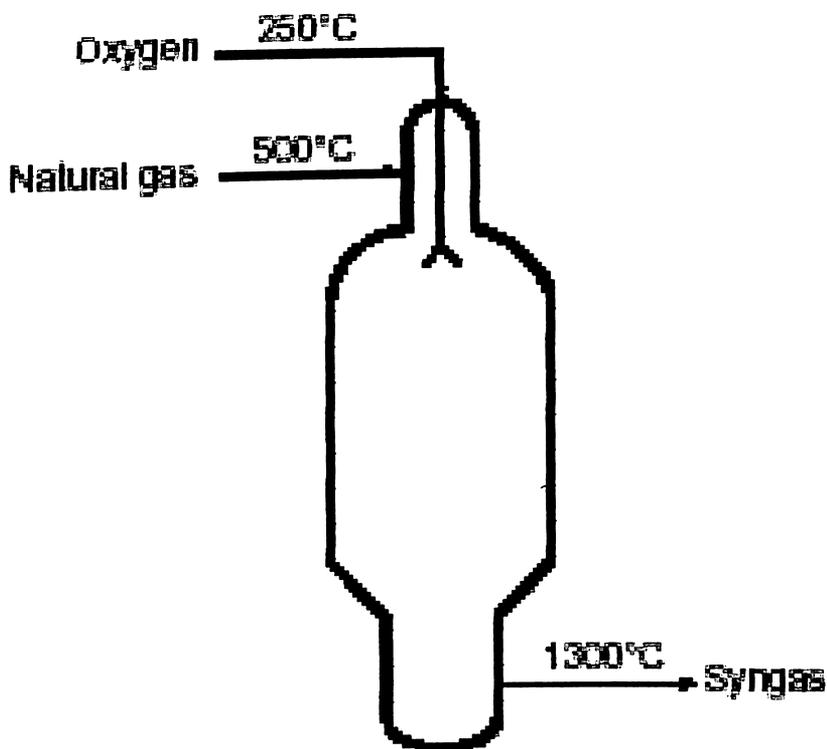
Fig 3.1.2 : Partial oxidation reactor

3.1.3. Combined Reforming

Background

Since less than 100% of methane is converted in the SMR reaction, a secondary reformer behind the SMR unit can be installed to provide complete methane conversion and the possibility to adjust H_2/CO ratio. In addition, the size of the costly SMR plant can be reduced by shifting part of its load to the secondary, oxygen-fired reactor. This is why this process is also called two-step reforming, or oxygen-enhanced reforming.

Process description

As the schematic of the process shows (Fig.3.1.3), it consists of a primary SMR unit and a secondary ATR or POX reformer with oxygen supply. A pre-reformer is often installed before the main reformer. Pre-reforming, which proceeds at low temperatures, is usually adiabatic. The pre-reformer widens the range of hydrocarbons suitable for reforming. It also takes over some duty from the primary reformer, in order that it can operate under less severe conditions. This, in turn, allows for less costly materials and a smaller heat transfer surface, which results in reduced costs of the equipment. However, the need for an oxygen plant might overweigh this advantage. Outlet temperatures of up to 1050°C are common. Methane conversion of above 99.6% can be obtained, as reported by Pietrogrande and Bezzeccheri (1993).

Economic aspects

Schneider and LeBlanc (1992) reported that a combined reforming plant would consume about 3% less energy than an SMR plant. Sogge et al (1994) confirm this figure giving a 1-6% decrease in operational costs. The capital costs, however, are lower: these constitute 72–76% of those by SMR. A study undertaken by Haldor Topsøe indicated that the required investment for the combined reforming scheme would be 15% lower, mainly due to the savings in the reformer section.

Development status

This is a technology based on two established processes. Its advancement is directly related to the developments of these processes. Combined reforming technology is being offered by the main contractors in the process industry.
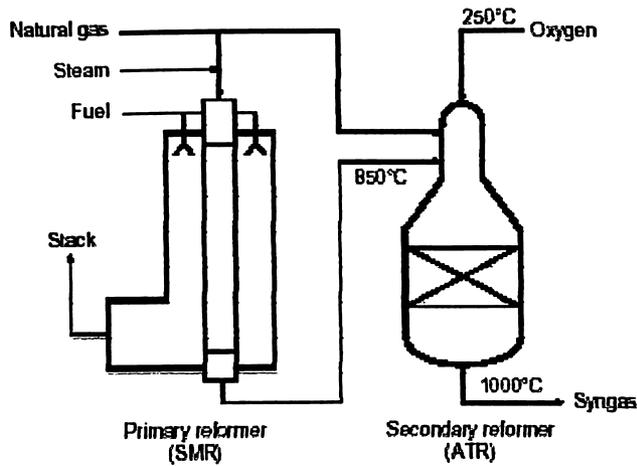

Fig 3.1.3: Combined reforming
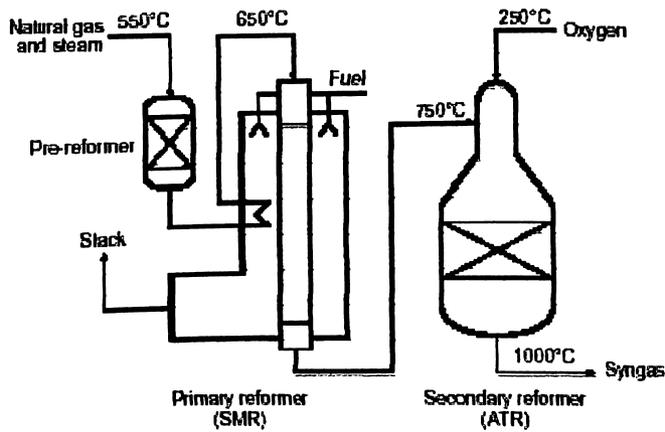
Fig 3.1.3.1:Combined reforming with prereforming

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3.1.4. STEAM METHANE REFORMING (SMR)

Background

The steam methane reforming (SMR) process can be described by two main reactions:

$$CH_4 + H_2O = CO + 3H_2, \Delta H = 198 \text{ kJ/mol} \quad (1)$$

$$CO + H_2O = CO_2 + H_2, \Delta H = -41 \text{ kJ/mol} \quad (2)$$
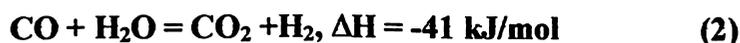
The first reaction is reforming itself, while the second is the water-gas shift reaction. Since the overall reaction is endothermic, some heat input is required. This is accomplished by combustion of natural gas or other fuels in a direct-fired furnace. Reaction (1) favours high temperature and low pressure, and proceeds usually in the presence of a nickel-based catalyst. The first patents on steam methane reforming were awarded to BASF in 1926 and the first reforming plants were built in the 1930s. Large-scale production has began only in the beginning of 1960s following the discovery of large gas fields in Europe and the subsequent change-over from use of coal to natural gas as a feedstock. In the early days, reforming proceeded at atmospheric pressure, later the process parameters were increased to pressures of up to 30 bar and temperatures of up to 1000°C. The increased pressure saves compression energy in the downstream synthesis stage, however, the high temperature necessitates an extensive heat recovery system.

Process description

In a direct-fired furnace a pre-heated mixture of natural gas and steam is passed through catalyst- filled tubes, where it is converted to hydrogen, carbon monoxide and carbon dioxide. It is of a great importance to control the maximum tube temperature and heat flux in the reformer to maintain a reliable and prolonged performance. To obtain this, several burner arrangements are employed: top-fired, bottom-fired, side-fired, terrace-walled, and cylindrical type. Of these, the side-fired and terrace-wall types

provide a better temperature control. Due to the endothermic nature of SMR, 35-50% of total energy input is absorbed by the reforming process, of which half is required for temperature rise and the other half for the reaction itself. The produced syngas leaves the reformer at a temperature of 800–900°C. The heat of the flue gases is usually utilised in the convective part of the reformer by generating steam and preheating the feedstock, thus bringing the overall thermal efficiency to over 85%. Only a portion of the steam generated in the boiler is required for the reforming process, while most of the steam (about 60%) is consumed elsewhere. There are also arrangements to recover the heat of the syngas such as the regenerative burners developed by United Technology Corporation, KTI, and Haldor Topsøe. To avoid catalyst poisoning a de-sulphurisation stage is usually required. In addition to the usual nickel-based catalysts, cobalt and noble metals are often used in SMR processes. Non-metallic catalysts have not proved their feasibility due to their low activity.

Another catalyst problem is carbon deposition, which is especially present when processing higher hydrocarbons. In this case, ruthenium, which can effectively resist carbon formation in steam reforming, can be used.

Typical operating parameters of the SMR process are:

Pressure	20-26 bar
Temperature	850–950°C
H₂/CO ratio	2.9–6.5
Plant capacity	0.4 to 21 mln Nm^3/day

Complete conversion cannot be obtained in the SMR process: typically 65% of methane is converted, at best it is about 98%, so secondary reforming must be used if a higher conversion rate is desired. In view of the high H_2/CO ratio, steam reforming is the most effective means for hydrogen production. The carbon monoxide then is oxidised to CO_2 in the shift reaction (2), thus producing even more hydrogen, which is subsequently purified in a pressure-swing adsorption (PSA) unit.

Summarising the advantages of the SMR process, it should noted that this is the most proven technology with a great deal of industrial experience, it requires no oxygen

and produces syngas with a high H_2/CO ratio. It also has relatively low operating temperatures and pressures in comparison to other technologies. Nevertheless, expensive catalyst tubing and a large heat recovery section make an SMR plant a costly investment that can only be justified for very large-scale production. The large size of the reformer and the potential risk of local overheating leads to a complicated heat management system with a slow response, furthermore, external heating results in relatively high atmospheric emissions from the combustion process. The presence of catalyst imposes other problems: care should be taken to avoid sulfurization and carbon deposition, also the catalyst should be regularly refilled due to its deterioration. These prevent the use of heavy hydrocarbons as a feedstock in the SMR process.
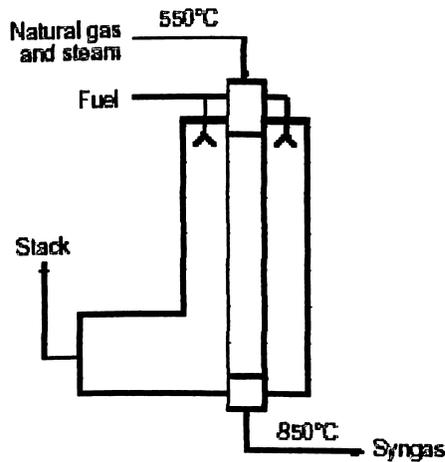

Fig 3.1.4: Steam Methane Reforming

Economic aspects

The large size of an SMR plant results in a higher capital cost than other technologies due to its high-alloy tubes, catalyst, and bulky heat recovery section. An SMR plant of 2 mln Nm3/day syngas capacity would cost 80 mln USD. For each 1000 m^3 of syngas (H_2/CO ratio of 2) about 14 GJ of natural gas will be required. In addition, 7 GJ of fuel, 45 kWh of electricity, and 85 m3 of cooling water will be consumed as utilities. A study by SINTEF gave a figure of 145 mln USD (battery limits) for an 8 mln Nm^3/day syngas plant. Thus, these sources indicate a range of specific investment costs for an SMR-based syngas plant between 20 and 40 USD per Nm^3/day (40–80 USD per kg per day). Unlike other syngas processes, the SMR process does not need oxygen, it is therfore usually the preferable choice when oxygen is expensive.

Development status

Of the syngas production technologies, steam methane reforming is the most developed and commercialized. Lurgi, for example, has built more than 100 plants to date. Many engineering companies design and build SMR plants, among them M.W. Kellogg, Haldor Topsøe, ICI, Howe-Baker, KTI, Foster Wheeler, Kværner.

4. PROCESS DESCRIPTION

4.1 SHELL MIDDLE DISTILLATE SYNTHESIS (SMDS) PROCESS

INTRODUCTION

Gas-to-liquids technology is a method to convert natural gas into liquid hydrocarbons. The Fischer-Tropsch process for synthesis of hydrocarbon fuels using metal catalyst at low pressure was patented in 1926. It was used in Germany during World War II and in South Africa for coal conversion to replace oil imports. For a long time the process was not economically viable. For natural gas conversion this is now changing with the development of new and efficient technology. The potential of GTL technology has resulted in a number of companies searching for opportunities to apply the technology for valorization of remote gas reserves. GTL technology offers a new way to produce middle distillates without coproduction of refinery residuals.

The first commercial SMDS project was approved in 1989; the plant was constructed in Bintulu. Sarawak, Malaysia. Production started in 1993, some 20 years after first research efforts were initiated by Shell.

PROCESS DESCRIPTION

The basic conversions of SMDS involve partial oxidation of methane into synthesis gas and subsequent Fischer-Tropsch conversion to paraffins. The theoretical thermal efficiency of this route is 78 percent on the basis of NG LHV:

$$CH_4 + 1/2O_2 ----- 2H_2 + CO$$

803 MJ/kmol   767 MJ/kmol

100%   96%

$$2H_2 + CO \text{ -------- } -(CH_2)- + H_2O$$

767 MJ/Kmol	621 MJ/Kmol
100%	81%
96%	78%

The three main process stages are shown schematically in **Fig.4.1.1**
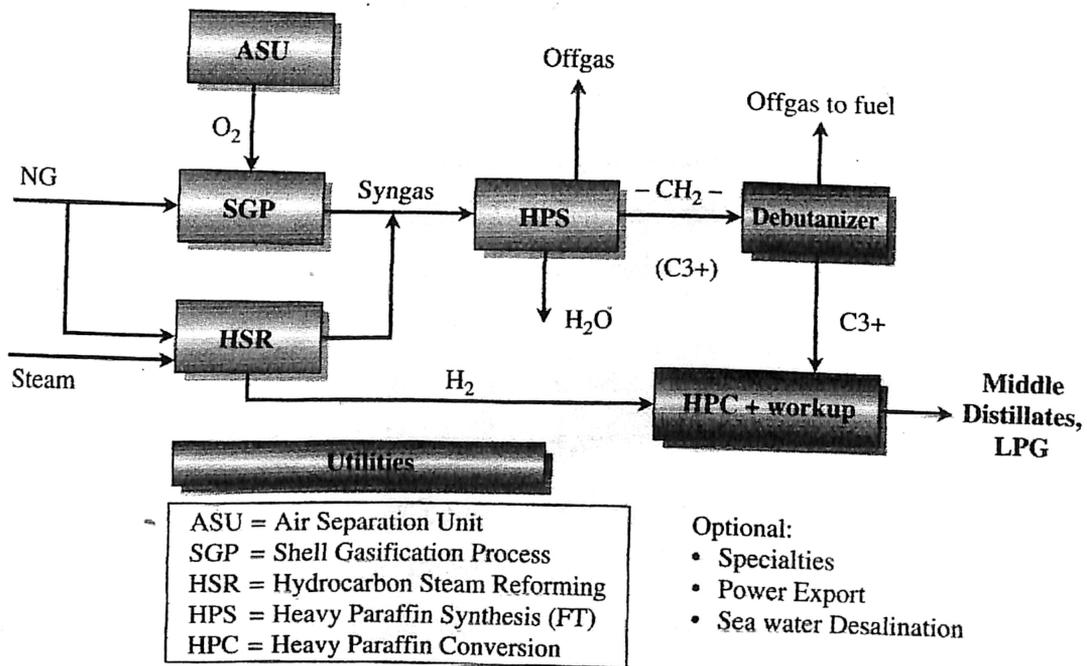
Fig 4.1.1: Shell Middle Distillate Synthesis Process Scheme

In SMDS process, these stages are identified as syngas manufacture, Heavy Paraffin Synthesis (HPS), the Fischer Tropsch synthesis, and heavy paraffin conversion (HPC). These stages will be described here. Several support and utility blocks are added.

Syngas Manufacture (SGP, Shell Gasification Process)

Synthesis gas, a mixture of hydrogen and carbon monoxide, is one of the most versatile, feedstocks for a wide range of (chemical) processes. In GTL technology, the conversion trajectory from methane to liquid hydrocarbons uses syngas as an intermediate. Direct con version of methane to hydrocarbon chains with economic selectivity and conversion is not possible.

SHELL's SGP process for which LURGI is the licensing agent is a much older process, the basic development having been made in the 1950's. With natural gas feed it produces a synthesis gas with an H2/CO ratio of typically 1.7 - 1.8 and a CO_2 content of 1.7 - 3 depending on the steam addition rate. A simplified flow diagram of a gas based SGP unit is shown in Figure. The gas feed is preheated with the raw gas to a temperature of about 380°C for desulphurization prior to being fed to the SGP reactor with the oxygen.

Syngas manufacture in SMDS is relatively expensive; between 50 and 60 percent of total process capital costs related to syngas production. Within the syngas manufacturing section, it is the air separation units (ASUs), which account for a substantial part of the cost of syngas produced.

In developing the SMDS technology it was established that a combination of commercially proven technologies was most suitable:

- Partial oxidation (POX) of natural gas with pure oxygen, using the proprietary Shell Gasification Process (SGP)
- A hydrogen-manufacturing unit (HMU) based on hydrogen steam reforming (HSR), to adjust the syngas H2/CO ratio

Pure oxygen is obtained from an air separation unit. SGP is based on direct partial oxidation without the need for a catalyst (Fig.). The feedstock, natural gas, is converted in an empty, refractory lined vessel. The conversion equilibrium is advantageous due to the high temperature. More than 95 percent of NG carbon is converted to CO. Oxidation heat is recovered on a high temperature level as high-pressure steam. The syngas

effluent cooler (SEC) is a dedicated design, with several features for the operating conditions. Steam superheating can be integrated. Secondary heat recovery is by a boiler feedwater economizer downstream of the SEC. Part of the steam is used for preheat of feed gas and oxygen. The remainder is utilized to drive compressors in the air separation unit(s). Trace components in the cooled raw syngas are removed in a water scrubber and in guard beds prior to transfer to the synthesis section.

Since the 1950s, SGP has been developed into a highly reliable and cost-effective process for syngas production from NG, liquid hydrocarbons, and coal. The process has proved its robustness and reliability in a remote location during the years of operation of SMDS Bintulu. Substantial scale-up from present unit capacities can be done to exploit economies of scale without changes to the process. Scale-up of NG SOP does benefit from developments in oil and coal gasification that have been realized meanwhile.

For Fischer-Tropsch conversion of synthesis gas derived from natural gas, the H_2/CO ratio of the gas leaving the SGP requires some adjustment. SGP produces synthesis gas with an H_2/CO ratio close to 1.7. By nature of the synthesis process, the consumption ratio in the synthesis step is approximately 2.

The hydrogen-manufacturing unit (NMU) provides additional hydrogen

- To adjust the H_2/CO ratio of feed gas supplied to the synthesis section
- As a feed gas for the heavy paraffin cracking unit of the SMDS plant
- For desulfurization of the NG feed

Based on hydrogen steam reforming, the HMU produces raw hydrogen and pure hydrogen (pressure swing unit) depending on the quality required by various consumers.

Alternative syngas manufacturing technologies can be considered, e.g., autothernial reforming (ATR). Studies indicate that ATR could compete with SGP HMU ot SMDS at very low steam/carbon ratio and by recycling CO,. This would require development beyond the industrially proven window for ATR. SGP HSR is still the preferred option for next-generation SMDS plants.

Heavy Paraffin Synthesis

The heavy paraffin synthesis section is the heart of the SMDS process. This section entails the conversion of the synthesis gas with a low-temperature cobalt-based FT catalyst to produce paraffinic hydrocarbons (and an equivalent amount of water). Low-temperature cobalt-based FT synthesis is most suitable for natural gas-derived syngas.

Since the FT synthesis is highly exothermic, temperature control and heat removal are major parameters in design of the reactor. Moreover, the performance of the synthesis step is a key parameter for the economics of a GTL plant. Newer catalysts provide a very high chain growth probability, to promote formation of long paraffinic chains and to minimize production of undesired light products (**Fig.**). The ensuing hydroconversion of the long paraffinic chains provides the SMDS product slate flexibility to fit market conditions.
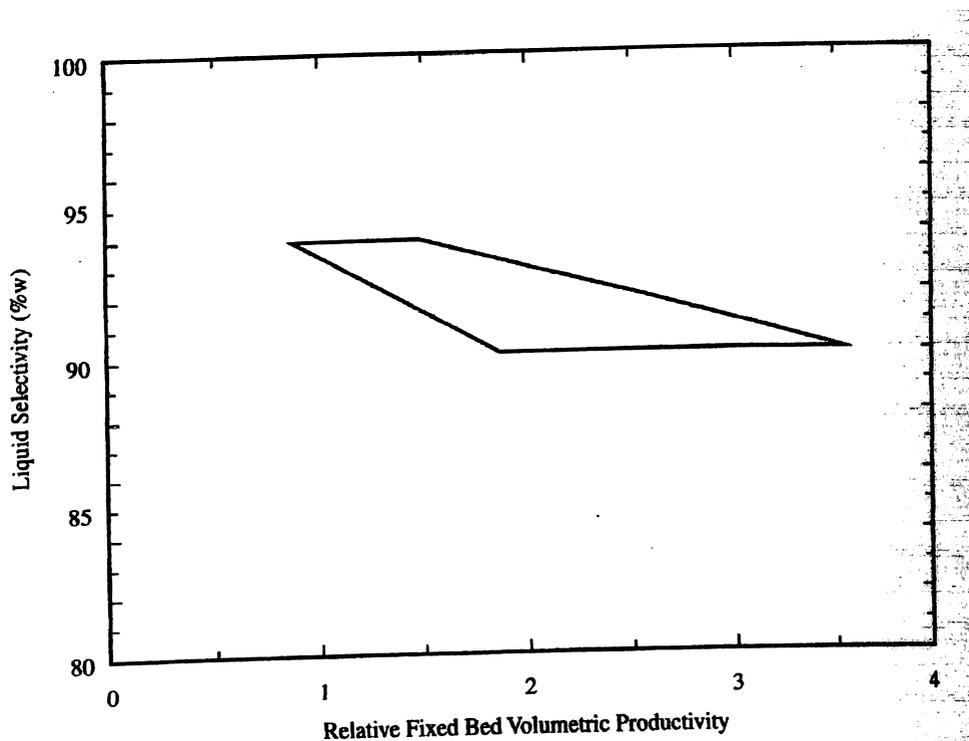

Fig 4.1.2: Potential of Fixed bed heavy paraffin catalyst

The hydrocarbon synthesis process and performance of the FT-catalyst in particular is crucial for commercial viability of a GTL process. Traditional high-temperature FT processes have been used extensively for conversion of syngas from coal. High-temperature FT processes are best suited to production of motor gasoline and other light products.

Obtaining high yields of middle distillates from NG-derived syngas, however, requires a far higher probability of hydrocarbon chain growth than provided by classical Fe and Co catalysts.

The low-temperature Co catalysts developed for SMDS are most suitable for production of long paraffinic hydrocarbon chains from NG-derived syngas with high selectivity. This contributes to high overall thermal and carbon efficiency. Figure 15.3.6 shows the distribution of products, obtained from NC-derived syngas, as a function of chain growth probability. Yield of light fuel components is minimized at high chain growth probability.
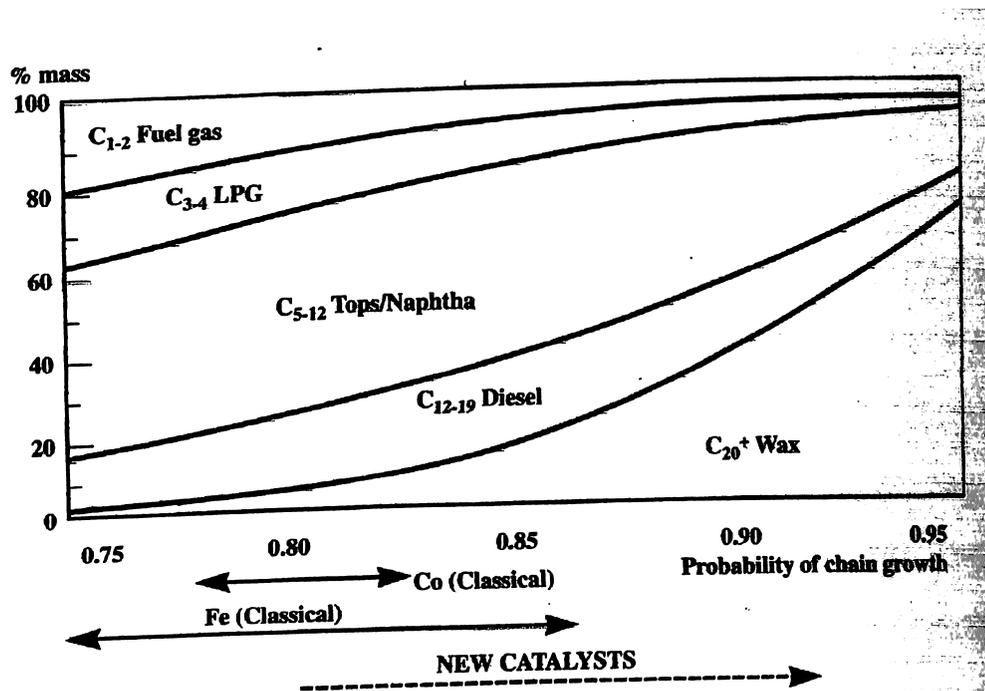

Fig 4.1.3: Fischer Tropsch Product distribution

The desired middle-distillate product slates are obtained in the third stage, the selective cracking and isomerization of the heavy paraffins (wax). The combination of

selective conversion of synthesis gas into heavy paraffins, followed by selective hydrocracking and isomerization into marketable products, is the key to the high thermal/carbon efficiency as well as to the product flexibility of SMDS.

Heavy Paraffin Synthesis Reactor Technology

Various types of reactor technology can be considered for the synthesis stage, in view of the high chain growth probability of the Shell proprietary class of synthesis catalysts, identified as heavy paraffin synthesis:

- Gas-solid fluidized bed
- Three-phase Slurry
- Fixed bed

The Fischer-Tropsch synthesis is a highly exothermic process with an enthalpy change of -146 MJ/kmol CO and operates within a relatively narrow temperature range. Heat removal, thermal stability, and temperature control are key parameters in HPS reactor design.

For the highly exothermic and catalyst pore-diffusion-limited synthesis reaction, gas-solid fluidized-bed reactor technology seems attractive. Heat-transfer coefficients are high, and mass-transfer limitations are avoided with the small catalyst particles.

Operational restrictions apply, however. As long as hydrocarbon product resides within the catalyst pores due to capillary condensation, the particles will behave as dry ones. Once hydrocarbon components start to condense on the external surface of the catalyst particles condition characterized by the hydrocarbon dew point-particle agglomeration and poor fluidization will occur.

The window for troublefree operation of a fluid-bed FT reactor is governed by the (Andersen-Flory-Schulz) chain growth probability a, by syngas conversion, by operating pressure, by operating temperature, and by paraffin vaporization energy depending on chain length. Fluid-bed FT is possible at high temperatures, low operating pressure, and low conversions and will produce relatively light products.

This is confirmed by the operating conditions of the Sasol Synthol reactors and of the Hydrocol plant by Hydrocarbon Research Inc., which was operated in the 1950s. For production of heavy wax, a stationary, nonregenerative fluid-bed FT reactor is not suitable.

The heavy paraffin synthesis aims at producing long, heavy hydrocarbon chains at high selectivity and conversion levels. Thermodynamics dictate that this benefits from low operating temperature and high operating pressure. Hence, gas-solid catalyst fluidized-bed technology has not been considered for SMDS.

Slurry Technology

Slurry technology relies on small catalyst particles, suspended in liquid product hydrocarbons. The synthesis gas is bubbled through the hydrocarbon/catalyst slurry. The catalyst particles are small to enable suspension in the liquid product fraction. With the small catalyst particle size (range of 10 to 200 μm) there is no mass transport limitation within the catalyst particles. Long-chain, heavier hydrocarbons will reside in the liquid phase whereas the lighter products will leave the reactor with the vapor phase. Temperature control and heat removal from the reactor, most conveniently by immersed cooling tubes carrying boiling water, are in principle favorable in comparison to fixed-bed technology. Process side pressure drop is low. Large unit capacities can be realized. Several companies have selected and developed slurry reactor technology for FT synthesis in GTL.

Slurry FT synthesis involves several distinct engineering challenges. The design of large slurry reactors involves three-phase hydrodynamics on a large scale. Too high a catalyst holdup in the liquid phase, in particular with very small particles, increases the apparent slurry viscosity. This affects the favorable mixing, heat removal, gas dispersion, and mass-transfer properties of the three-phase system. Dedicated filtration systems must be installed for separation of liquid product from the catalysts/wax mixture and from the overhead vapor/offgas, after cooling and condensation Slurry catalyst must be mechanically robust to avoid catalyst breakage and fines formation, which might cause losses and product contamination.

Fixed Bed

The SMDS synthesis section (HPS) uses fixed-bed reactor technology (Fig.). The syngas passes through multiple tubes containing the FT catalyst. Reaction heat is removed by boiling water in the reactor shell to produce medium-pressure (MP) steam. This MP steam is the main utility to generate electricity and to drive compressors.

Multitubular reactor technology has matured to a high degree of sophistication with a productivity potential of 10,000 to 15,000 bbl/day per reactor. Today's Shell proprietary fixed-bed FT catalysts provide activity, selectivity, and stability for a unit capacity range of 7000 to 10,000 BPD. HPS syngas conversion can be as high as 96 percent with liquid (C_{5+}) selectivity better than 90 percent.

The catalyst is loaded into a large number of tubes. Specific heat-transfer surface is high. FT fixed-bed reactors are heavier than fluid-bed/slurry reactors for the same unit capacity. Multitubular reactor (MTR) technology has a number of attractive features compared to two- or three-phase fluidized-bed reactors:

- The design of a commercial MTR is straightforward by multiplication of the performance of an individual tube, which can be assessed accurately in a pilot plant.

- Fixed-bed catalyst provides intrinsic and absolute separation of the products, with zero contamination by catalyst. This is important with several of the products or derivatives having FDA approval.

- By nature of the MTR design, axial catalyst distribution is uniform irrespective of operating conditions.

- In situ catalyst (re-) activation, which is done typically once per year, is easy and effective. Conditions are independent of normal operating conditions and are fully controlled.

- A multitubular reactor arrives at the construction site as a fully integrated unit ready for erection and tie-in. This is an advantage for a remote location. Auxiliaries are the thermosyphon cooling system and a shared gas loop utility for catalyst (re-) activation.

The pressure drop over a fixed-bed reactor, operated at a high performance level, is high in comparison to two- or three-phase fluidized systems. Since the FT synthesis

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provides ample steam to provide compressor shaft power, this aspect has little effect on capital expenditure or operating costs.

Selection of fixed-bed FT catalyst size and shape is a balancing act. Heat removal and control of temperature gradients in the fixed bed rely on the effective heat conductivity of the packed catalyst particles, which benefits from high gas velocities and larger particles.

Larger particles also reduce pressure drop. In high-performance FT catalyst particles a few millimeters in size, intraparticle diffusion limitations will prevail. Catalyst utilization imposes an upper limit to particle size. Hence, catalyst size, shape, and reactor tube diameter are carefully optimized with regard to reaction kinetics, heat transfer, pressure drop, catalyst, and hardware costs.

Bintulu SMDS experience has confirmed the easy operation of Fixed-bed MTRs, including start-up, shutdown, and other transient operating modes. Restart of Bintulu FT reactors, after a long standstill, also appeared straightforward: heat up to melt the solidified wax, start up according to standard procedure, and there is no need for inspection or reactivation.

Loading of catalyst is foreseen for every multitubulur HPS reactor typically every 5 years. Experience with the efficiency of automated loading, including preparation and check procedures, is impressive and has turned this into a routine activity. With further development of SMDS technology, and high-performance FT catalysts being available, it was established that fixed-bed technology remains attractive in comparison to alternative reactor technology for a GTL plant on a remote location. The upward potential of MTR technology will be further utilized with new generations of catalyst becoming available.

Heavy Paraffin Cracking

Fischer-Tropsch synthesis alone cannot produce high yields of paraffins of specitied carbon number, with adequate cold flow properties. SMDS consists of separate steps: selective production of heavy paraffins (HPS) with subsequent selective cracking and isomerization (HPC) into the desired middle distillates.

In the third stage of the SMDS process, the raw synthesized hydrocarbons consisting mainly of high-molecular-weight paraffins are hydro cracked. A dedicated hydrocracking process using a proprietary catalyst under relatively mild conditions, typically 30- to 50-bar total pressure and at a temperature of about 300 to 350°C, has been developed to achieve this.

The layout of the HPC section is very similar to that of a conventional gas oil hydrotreater. The Output is subsequently fractionated. HPC removes any oxygenated components; long paraffin chains are broken and isomerized to produce middle distillates.

The HPC stage has four functions:

- Preferential hydrocracking of heavy paraffins into fragments in it specified length/boiling range
- Sufficient hydroisomerization of the resulting cracked components to meet cold flow specifications
- Hydrogenation of olefins in the HPS product
- Removal of small amounts of oxygenates, mainly primary alcohols
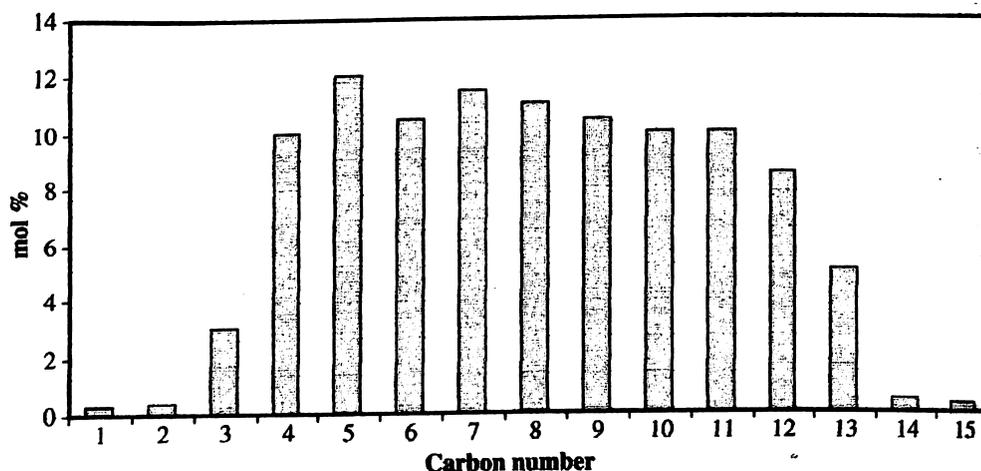
Fig 4.1.4: Selectivity of heavy paraffin cracking

The example of **Fig 4.1.4** shows that very little methane and ethane are formed, and propane is at a very low level. The small fraction of light hydrocarbons is rerouted as feedstock and fuel for the hydrogen-manufacturing unit. The middle-distillate yield is better than 85 percent. Products with an intermediate carbon number are formed in significant quantities; the boundaries of the distribution are remarkably sharp. Indicative for primary cracking; scission of internally located C-C bonds of the paraffin chains is favored above terminal (α) or near-terminal ((β, γ) positions. Another factor contributing to preferential cracking of the heavy paraffin chains is the vaporization of the lighter hydrocarbons, reducing residence time and the probability of further cracking.

Varying the hydrocracking severity provides SMDS product slate flexibility, to vary the distribution over gas oil, kerosene, and naphtha, as shown in **Fig 4.1.5** and **Fig4.1.6**; 60 to 75 percent gas oil yield can he achieved.
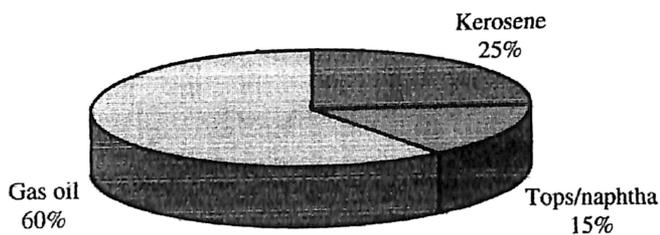

Fig 4.1.5 : Product Distribution in Gas oil mode

Gas oil
25%

Kerosene
50%

Tops/naphtha
25%
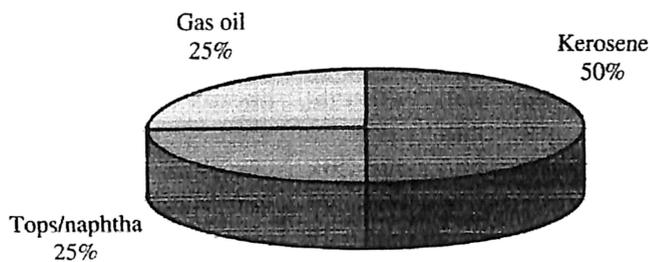
Fig 4.1.6: Product Distribution in Kerosene mode

Selectivity toward the desired product range can be achieved by HPC severity. The HPC effluent is separated by conventional distillation. In the kerosene mode, kerosene yield is some 50 percent of total liquid product whereas a gas oil mode yields some 60 percent gas oil. The theoretical maximum thermal efficiency of the basic SMDS scheme

$$CH_4 + 1/2 O_2 \,\text{----}\, 2H_2 + CO \,\text{---}\, -(CH_2)- + H_2O$$
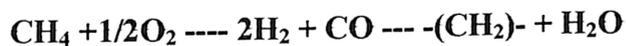
is 78 percent based on LHV. The thermal efficiency of SMDS, which can be actually achieved, is typically 63 percent, that is, 80 percent of the thermodynamic maximum. The carbon efficiency is 78 to 82 percent. Considering the number of process steps and trims, this is a remarkable achievement. It should be realized that the efficiency number is affected by the quality of the feed gas, by the environmental conditions, as well as by investment optimization considerations.

Thermal efficiency will be raised further with new generations of HPS and HPC catalyst becoming available, which offer better activity and selectivity of synthesis, and by more favorable operating conditions.

QUALITY OF THE PRODUCTS

By their nature, products synthesized from carbon monoxide and hydrogen are extremely clean. They contain no sulfur, no nitrogen, and no aromatics. The SMDS products have impurities that are several orders of magnitude lower than highly refined crude oil-derived products. The highly paraffinic nature of SMDS products makes them stand apart from crude oil-derived distillates in terms of density, Combustion characteristics, and chemical composition.

Although the first SMDS plant at Bintulu, Malaysia, produces several hydrocarbon products, an interesting and profitable group of products is the FDA-approved, food-grade waxes. The waxes are ultimately used in chewing cosmetics, medicines, cup coatings, and a host of other products. Prices obtained for these products are high and contribute substantially to plant economics.

Here, we focus on the middle-distillate fuel qualities.

Naphtha

The naphtha fraction is completely paraffinic and therefore makes an excellent ethylene cracker feedstock, giving a higher yield of ethylene and propylene in comparison to petroleum-derived naphtha feedstock.

Kerosene

SMDS kerosene is a clean-burning fuel for domestic heating. It can also be used to upgrade kerosene fractions that have a low smoke point and high aromatics. It may offer possibilities as a jet fuel component. However, it has not yet been approved.

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TABLE 4.1.1 : Middle Distillate Properties

Property	Unit	Naphtha	Kerosene	Method
		Typical Middle Distillate Properties		
Density (a) 15°C	kg/m	690	738	ASTM D1298
Saybolt color		+29	+30	ASTMD156
Distillation range				ASTM D86
IBP	°C	43	155	
FBP	°C	166	191	
Sulfur	ppm	<3	<10	ASTM D1266
Cetane index		n/a	58	ASTM D976
Smoke point	mm	n/a	>50	ASTM D1322
Flash point	°C	n/a	42	ASTM D93
Aromatics	%v	0	<0.1	ASTM DS186

Moreover there are attractive solvent/chemical applications for SMDS kerosene. It can be tailored to n solvent of high purity, which together with its low odor and water-clear appearance makes it particularly attractive in applications Such as dry cleaning and other "speciality solvent" applications.

SMDS kerosene is also suitable as a trimming agent for heavy gas oils that need to he upgraded to specification diesel, for example, winter diesel for automotive use in cold climates.

SMDS Diesel/Gas Oil

The GTL product with the brightest future seems diesel for use as transportation fuel. SMDS produces an exceptional quality of synthetic fuel that can be used directly (after including a lubricity additive) in diesel engines or as a blendstock to upgrade refinery diesel.

Independent studies with SMDS gas oil have shown the significant reduction in emissions (NO, SO, HC, CO, and particulates). SMDS diesel has a cetane index (CI) of 76, no detectable sulfur even on the ppm level. It is virtually paraffinic (with a high proportion of straight-chain paraffins) and contains almost no aromatic, cycloparaffinic, or polar species. The SMDS diesel responds well to commercial lubricity additives,

allowing it to meet the given lubricity specification. Compatibility of the fuel with elastomeric seals in fuel injection equipment (FIE) may need some consideration.

Table details the properties of SMDS and comparable automotive gas oil (AGO) - samples, i.e., an EU reference CEN (Comite Europeen de Normalisation) fuel (typical 1998 quality) and a Swedish Class 1(a very low sulfur content fuel). The forthcoming EU specifications for diesel fuel, which require a maximum sulfur content of 50 ppm mass, could ideally use SMDS gas oil as a blending component.

Table 4.1.2: Typical SMDS and AGO Sample Analyses

Property	CEN(1998)	Swedish Class	SMDS
Density*(a)15°C g/m³	837	814	776
Distillation. °C			
IBP	201	197	184
10%	219	213	-
50%	269	231	275
90%	326	269	340
FBP	368	293	357
Cetane number	50	58	81
Cetane index	52.2	50 .4	76
Viscosity @ 40°C Cst	2.823	1.903	2.702
Sulfur. %mol	0.05	0.001	<0.0002
Aromatics. %mol	25	9.7	<0.05
Mono			
Di	2.1	0.1	<0.05
Tri	1.2	<0.05	<0.05
Total	28	10	<0.05

IPI60/ASTMD1298IP123/ASTM D86.

IP380/94. IP71/ASTMD445 HPLC, IP391.

Alternatively the products could do well on a market where premium specifications are desired to meet local requirements, for example, the California Air Resources Board (CARB) specifications, a maximum of 500 ppm sulfur and maximum 10 vol % aromatics. SMDS gas oil with zero aromatics, zero sulphur, and cetane index of 76 can be used in blends to meet these severe CARB regulations. Since 1995, SMDS diesel has been sold to refiners and blenders who used it to upgrade its mineral diesel to CARB specification to Californian market.

Another attractive characteristic of SMDS gas oil is that the material is fully biodegradable. For certain applications this is of prime importance (e.g., where spills into environment could occur); this feature is expected to gain momentum in the near future.

COMPLEX INTEGRATION

GTL involves large energy streams. Partial oxidation of NG (SGP) and Fischer-Tropsch synthesis are highly exothermic processes. Plant utilities are integrated such that all requirements, including these of the air separation units, are generated from the complex energy streams.

Produced steam is utilized for direct or indirect drive (via electricity generation) of compressors, including those needed for air separation. Light hydrocarbons are recycled for utility generation or as fuel for hydrogen manufacturing.

If commercially attractive outlets are available, export of nitrogen, steam, and/or electricity is an option as shifting the internal balance of the SMDS complex could produce these.

The SMDS system offers major gains in air quality compared to the refinery system, thanks to its significantly lower emissions of hydrocarbons, nitrogen oxides, sulfur oxides, and waste. Nor do these gains in air quality result in a greenhouse gas penalty, since its carbon emissions are in the same range as those of a conventional refinery system.

Process water and condensate can be reused in the plant. Most of the oxygen feed to the plant ends as water. Note that the Fischer-Tropsch synthesis alone produces some 1.3 tons of water per ton of hydrocarbons. Wastewater is biotreated to the extent that it

can be discharged as surface water. In areas of water scarcity, production of clean water is an option.

Light hydrocarbon gaseous by-products, which are produced in small quantities by different process units, are recycled or used for utility generation. Flue gases emitted to air are almost free from sulfur, meeting most stringent specifications worldwide.

Catalysts used in several process units (synthesis, cracking, hydrogen manufacture) have a lifetime of several years. Spent catalyst, the only solid waste of the process, is returned to the manufacturer for metals recovery.

FUTURE PROSPECTS

The economic viability of gas-to-liquids projects today and in the near future depends on several key economic factors: the availability of low-cost gas, crude prices, capital and operating costs, site-specific factors, and the fiscal regime of the host country. Low-cost gas as well as fiscal friendly regimes are of the utmost importance to make a gas-to-liquids project viable.

If natural gas is priced at 0.50 U.S. $/millionBtu, then the feedstock cost element in the product is about U.S.$5/bbl. The total selling price further includes a capital charge which depends on numerous factors, including fiscal regimes, local incentives, debt/equity ratio, type of loans, and corporate return requirements.

Another important factor is whether the products are for domestic use or export. For countries with Sufficient gas but needing to import oil or oil products to meet local demand, SMDS products manufactured in that country should realize at least import parity values. For such countries, therefore, the national benefit of the SMDS process can be substantial. In addition to these factors, the capacity of the plant is of great importance. Especially for remote locations, where self-sufficiency of the plant is essential, larger plants in the range of 75,000 bbl/day benefit from the economy of scale.

SMDS (Malaysia) Sdn Bhd has demonstrated the commercial viability of the SMDS process. Further developments have reduced the specific capital cost, such as

- Equipment scale-up, notably in the synthesis gas manufacturing plant, which accounts for more than 50 percent of the total process capital cost.
- Further catalyst improvements. A second-generation catalyst, which yields significantly more liquid', than the catalyst originally implemented in Bintulu, has been developed and is ready for application in the next plant.
- General process integration within the project.

Operational experience, coupled with technological improvements, has resulted in specific capital costs of around U.S. $20,000/bbl, as shown in **Fig 4.1.7.**

The successful application of GTL technology at SMDS Bintulu represents an important advance in the commercialization of that technology and is an asset in Shell's portfolio of technologies for making natural gas transportable. It provides exciting opportunities in terms of marketing hydrocarbon products of a quality ideally suited for a business environment requiring increasingly high-performance standards.
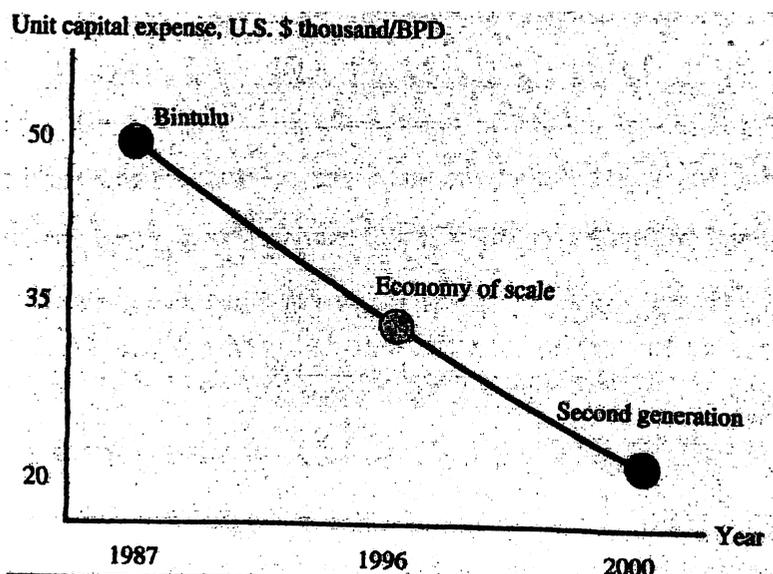

**Fig 4.1.7: Reduction of specific costs of SMDS**

4.2. THE SYNTROLEUM PROCESS OF CONVERTING NATURAL GAS INTO ULTRACLEAN HYDROCARBONS

HISTORY OF THE SYNTROLEUM PROCESS

Syntroleum's history began in 1984 when the founder, Ken Agee, began experimenting with the use of air as a source of oxygen for the GTL process. After several years of experimenting, the first series of patents were filed in 1988 that were later issued in 1989. In 1990, Syntroleum began the operation of its first pilot plant, which still operates today. The pilot plant has a production rate of 2 barrels per day (BPD) and is used to test a variety operating conditions for various catalysts. In 1998, Syntroleum's research and development facilities quadrupled with the purchase of a new building and the surroundi acres. During the following year, Syntroleum, along with Arco (now BP), began th ation of a 70-BPD facility using slurry reactor designs. After approximately one operation, the demonstration plant was relocated to Tulsa. The demonstration plant began operation in 2003 as part of the U.S. Department of Energy's ultraclean fuels program. Fuel demonstrations are planned in the bus fleets of Washington, D.C., Metri Area Transit Authority and Denali National Park. As of 2001, Syntroleum had lice technology to several companies, including Texaco, Marathon, Arco, YPF, Enron McGee, Ivanhoe, and the Commonwealth of Australia. Syntroleum has also formed many alliances related to fuel production, testing, and certification; catalyst testing and production; and the design of both onshore and floating GTL plants.

PROCESS DESCRIPTION:

The Syntroleum Process consists of the following steps for converting natural gas to finished fuel products: (1) gas pre treating, (2) air compression, (3) synthesis gas generation (4) Fischer-Tropsch synthesis, and (5) product upgrading. The process converts approximately 10,000 standard cubic feet (SCE) of gas into 1 barrel (bbl) of synthetic hydrocarbons. The maximum capacity of each GTL train is about 11,500 BPD. The process produces several by-products, tail gas, water, and heat, which can be used to

generate other products from the plant, such as exportable electricity and steam for desalination. The Syntroleum Process can be adapted for either offshore or onshore applications and can be designed small gas fields. Figure below is a process flow diagram of the inside-battery-limits (ISBL) portion of the Syntroleum Process.
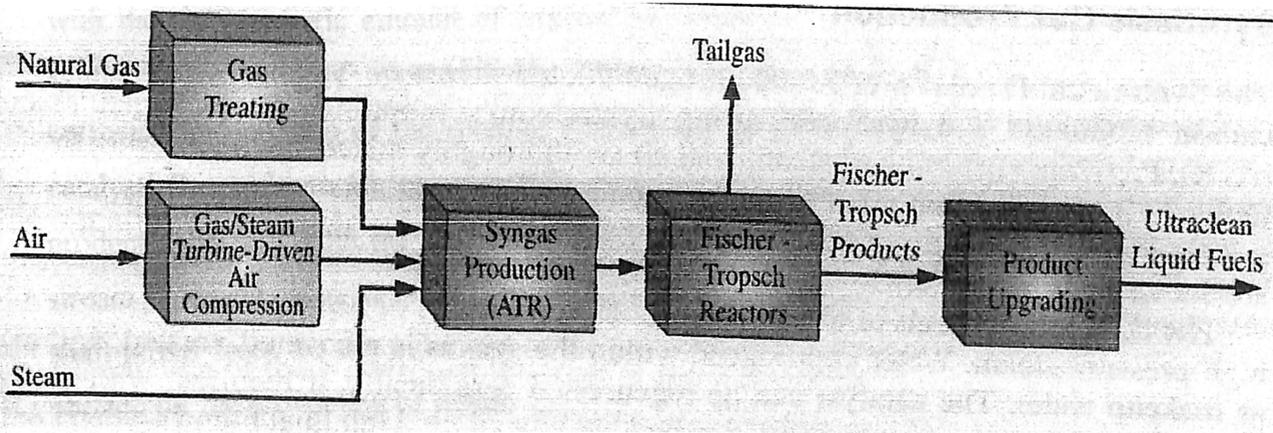
Fig 4.2.1: Process flow diagram for Syntroleum Process

Feed Gas Pre-treating

The feed gas pre-treating section is determined by the gas composition and Syntroleum's feed gas specifications, which are based upon those components that are detrimental to the catalytic reactor systems. The gas feed specifications are summarized in Table

For example, for a gas composition that does not exceed the limitations in Table, minimal gas pre-treating is required. In this case, sulfur removal is the only gas treatment needed. Cobalt/Molybdenum (Co/Mo) and Zinc Oxide (ZnO) guard beds are used to reduce the sulfur concentration to 100 ppb for the catalytic processes. When the limitations of CO_2, and/or sulfur are exceeded, the cost of treatment determines whether the gas is feasible for use. Finally, gas that exceeds the specification for ethane and heavier molecules either can be processed to recover and sell natural gas liquids (NGLs) for additional revenue or can be processed to reform the C_{2+} components into methane for use as feedstock. The choice will depend on the amount of recoverable NGLs and market conditions. Overall, the robust gas specifications of the Syntroleum Process enable many gas fields that are considered marginal to be monetized.

Air Compression

Unique to the Syntroleum Process is its use of air as an oxygen source. A process air compressor driven by a steam or gas turbine supplies the synthesis gas generation section with the stochiometric amount of oxygen (as contained in air) required to generate a synthesis gas ratio of approximately 2:1(H_2:CO). The inlet air is filtered to avoid corrosion and erosion of the rotating components and deactivation of the downstream catalyst. Gas turbines ire commercially available that will burn low-Btu tailgas, a by-product generated from the FT reactors. In addition to providing fuel value, this tailgas stream represents a large mass flow of high-pressure gas that aids in the generation of shaft power from the expander end of the gas turbine. For a steam turbine, the tailgas is utilized for the production of steam.

Synthesis Gas Production

The Syntroleum Process produces a nitrogen-diluted stream of synthesis gas, a mixture of carbon monoxide and hydrogen, using Syntroleum's proprietary autothermal reactor (ATR). Pretreated natural gas, steam, and air are thoroughly mixed before entering the in the ATR. The reaction proceeds over a commercially available catalyst and yields syn gas having a H_2: CO ratio of approximately 2 : 1. The reactions that take place in the ATR are shown below.

The net thermal result of all three reactions is a surplus of heat, which is used to raise high-pressure steam. Water co-produced within the syn gas is recovered, treated, and used as makeup water. The catalyst can be regenerated periodically, if required, with air hydrogen to remove any coke formation and has an expected minimal life of 4 years. After exiting the vessel, the synthesis gas is cooled and compressed prior to entering the Fischer- Tropsch reactors.

Fischer-Tropsch Synthesis

Nitrogen-diluted synthesis gas from the ATR is compressed and enters the Fischer-Tropsch reactors to predominantly produce paraffinic, synthetic hydrocarbons. The compressed synthesis gas flows into the bottom of the FT reactor and is bubbled through a slurry Fischer-Tropsch liquid and suspended solid particles of a proprietary and commercially available Cobalt catalyst. On the active surface of the catalyst, carbon monoxide is hydrogenated into paraffinic hydrocarbons of various molecular weights. The balanced reaction is shown below. Excess heat produced from the Fischer-Tropsch reactions is removed by raising low-pressure steam. Syntroleum catalysts yield a Shultz-Flory-Anderson distribution corresponding to an alpha ranging from 0.88 to 0.94, depending the formulation. Unreacted synthesis gas exits the top of the reactor and may become feedstream for the subsequent stage or a fuel for the gas turbine. The cobalt catalyst has expected minimal life of 4 years and is continuously regenerated to sustain high levels activity. Each reactor produces two streams of hydrocarbons:Light Fischer-Tropsch (LFTL) and Heavy Fischer-Tropsch liquid (HFTL); and three by-products-water, tailgas and heat. The unrefined heavy and light Fischer-Tropsch streams are sent to the product upgrading section for processing into fuels. Syntroleum has also developed and licenced the Fischer-Tropsch reaction of a fixed bed design.

Synthesis gas generation

Reaction 1: $CH_4 + 1.5O_2 \longrightarrow CO + 2H_2O$

Reaction 2: $CH_4 + H_2O \longrightarrow 3H_2 + CO$

Reaction 3: $CO + H_2O \longrightarrow H_2 + CO_2$
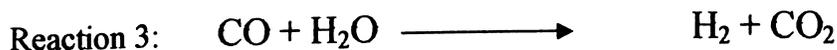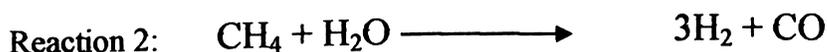
Fig 4.2.2: Syntroleum Process
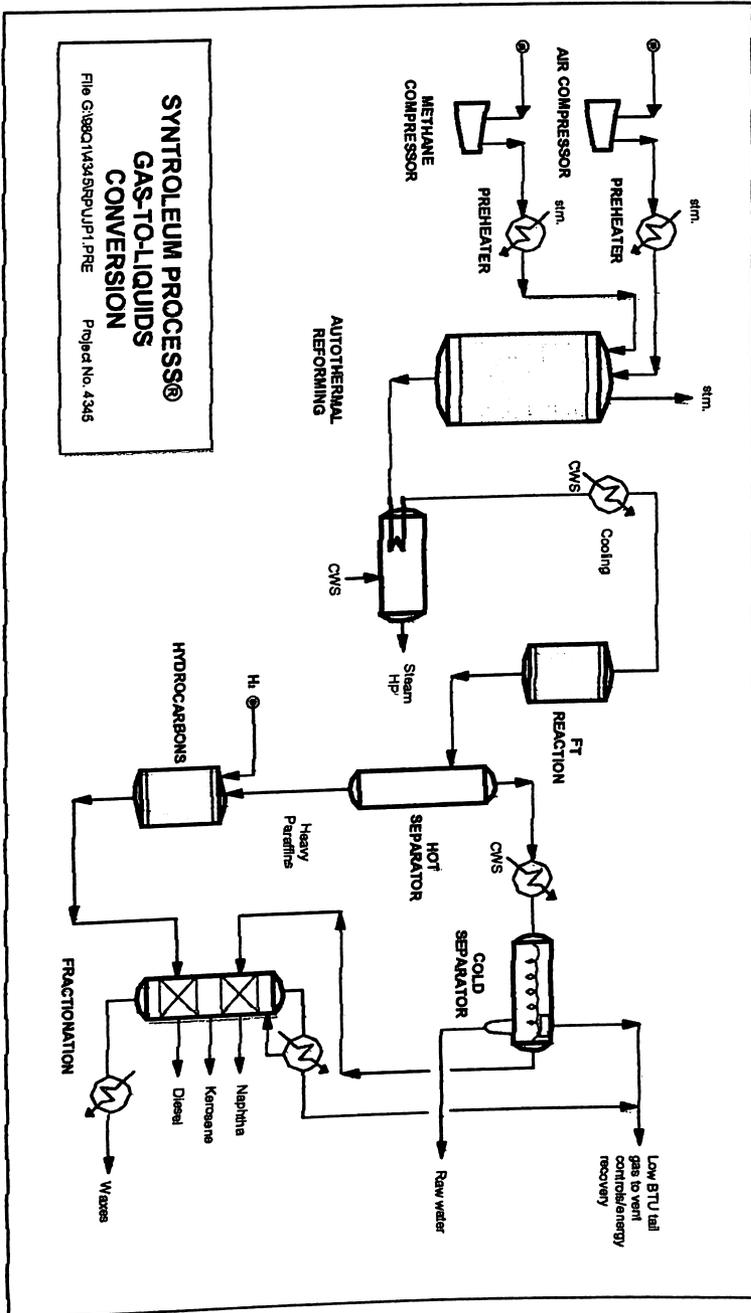
Fisher-Tropsch reaction.

Synthesis gas (diluted with nitrogen)   Catalyst   Hydrocarbons   Water   Nitrogen

$$n(2H_2 + CO) + N_2 \longrightarrow -(CH_2)_n- + nH_2O + N_z$$

Product Upgrading

The final step in a Syntroleum GTL fuels plant is product upgrading (upgrader), which converts the waxy effluent from the FT reactions into useful fuels. The upgrader consists of distillation and hydroprocessing units that are of similar configurations found in conventional petroleum-based refineries. As in petroleum-based refineries, the upgrader's exact configuration and processing scheme will depend upon the facility's particular product slate and associated specifications. Although the processing schemes may be varied, several general processing requirements are needed and can be broken down into the following major areas:

1. Distillation of the F'T effluent into two or more fractions.
2. Hydroprocessing of one or more of the fractions to improve low-temperature

   properties.
3. Distillation of the hydroprocessed effluent streams into finished products

Due to the high purity and low variability of the FT stream, the Syntroleum upgrader will have a lower capital and operating cost than that of an equivalent petroleum-based system. Specific areas of cost savings include these:

- Since there is no sulfur in the feed, the metallurgical requirements of the hydroprocessing unit are reduced, resulting in a lower cost (e.g., no stainless overlay is required for the reactor). Also, sulfur recovery requirements are completely eliminated.
- Hydrogen consumption is lower (<50 percent of a typical sour feedstock), which

reduces not only the operating costs associated with producing hydrogen, but also compression requirements on both the makeup and reactor recycle gas loop.

- Hydroprocessing conditions are milder (i.e., lower pressures and temperatures) and bear more resemblance to a fuels hydrotreating unit than to a fuels hydrocracker.

- The need for an independent residual cracker or coking unit is eliminated due to the ability of high-molecular-weight normal paraffins to crack into lower-molecular-weight paraffins in the fuels hydroprocessing unit itself. Contaminants, such as polynuclear aromatics and heavy metals (e.g., nickel and vanadium), are not present in the feed, and therefore the unconverted bottoms can be recycled to extinction.

Syntroleum uses commercially available hydroprocessing catalysts in its licensed hydrocracker and hydrotreating units. Overall, these attributes reduce the complexity and cost of producing ultraclean fuels compared to a conventional crude oil refinery.

ADVANTAGES OF THE SYNTROLEUM PROCESS

The Syntroleum Process has several advantages over competing processes. The process utilizes air instead of pure oxygen to generate FT liquids. This reduces the cost of the plant and increases the safety of plant personnel. Additionally, the process produces several recoverable by-products-tailgas, heat, and water. These by-products are used to reduce the operating costs of the plant and to provide additional revenue. The process has the advantage of being flexible in terms of operating configuration and feedstock quality, allowing the process to be adapted to a range of environments. Finally, as detailed earlier, the lack of contaminants, sulfur, aromatics, and heavy metals simplifies the refining section of the plant.

Oxygen versus Air

The use of ambient air as the source of oxygen in the ATR is a unique characteristic of the Syntroleum Process that has several advantages over competing

processes, which utilize air separation units to obtain a pure stream of oxygen. First, ambient air utilization has significantly lower capital and operating costs, because no refrigeration, which requires costly metallurgy and a considerable amount of electricity (often not included in efficiency Calculations), is avoided. The Syntroleum Process uses off-the-shelf turbines and comprises to supply air to the reactors. These turbines and compressors are commonly used in plant projects and oil and gas operations. Second, liquid oxygen is extremely explosive requires highly trained and experienced personnel and a rigorous maintenance schedule reduce the risk of accidents. To the contrary, the use of air reduces increases safety of plant, because the presence of inert nitrogen in the Syntroleum Process provides additional thermal control of the energy released from the ATR and FTR reactions. The resulting thermal control benefits of nitrogen from the use of air are (1) a fairly uniform temperature profile, (2) moderation of the temperature rise in the ATR, (3) more efficient heat removal in the FT reactor, and (4) minimal coke formation.

Even though the Syntroleum Process uses air instead of pure oxygen, the Syntroleum FT reactors are not twice as big and therefore not more expensive than oxygen-blown FT reactors. The Syntroleum Process operates on a single-pass basis; the oxygen-blown processes operate with a recycle loop. Due to recycle, inerts (CO_2, C_1, C_2, etc.) accumulate, dilute the synthesis gas, and act in much the same manner as nitrogen in Syntroleum Process. The net effect is that the combined air feed system and the FT reactor system of the Syntroleum Process will in most cases cost less than the air separation and FT reactor system of an oxygen-blown system.

By-products

All three by-products---water, tailgas, and heat---are recovered and utilized in the for makeup water, plant fuel, steam generation, and/or producing additional ex products to nearby markets. Approximately 1.1 bbl of water is produced for every of unrefined hydrocarbon. The water contains contaminants including suspended and small amounts of dissolved oxygenates, such as alcohols, and inorganic ions, such as ammonia. The water is fed to a wastewater stripper, where volatiles are removed and

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to a pre-reformer for recovery of hydrocarbon value. The stripped water is routed, wastewater treatment plant for conditioning as makeup water for cooling towers, process boilers. The second by-product, tail gas, is a clean-burning and abundant energy that fuels low-Btu heaters, gas turbines, and any additional power generation., tailgas displaces the use of natural gas and therefore reduces operating costs and increases plant efficiency. The tailgas can also be sold to nearby refineries for steam or power generation. The final by-product is high-pressure and medium-pressure steam, raised the ATR and FT reactor, respectively. The steam is used in a variety of applications, from steam turbine operations for power generation and/or compression to water reclamation, such as water stripping and desalination.

Process Flexibility and Simplicity

The Syntroleum Process has a tremendous amount of flexibility. Under appropriate conditions, the process can be economically designed to produce as little as 6000 BPD synthetic fuels. Reserves of less than 500 BCF recoverable gas would be required to 6000 BPD of synthetic fuels for 20 years. The process can also be configured to surplus electricity for sale. For example, the tailgas and steam can be used as fuel for generation in gas turbine(s), and flue gas from the gas turbines can be routed to heat recovery steam generators (HRSGs) to raise additional steam for additional power. Also, the can be designed for marine applications with the use of floating production, storage and Off-loading systems (FPSOs) and barges. Offshore infrastructure for processing and transporting gas to markets is typically designed around a collection of gas and oil discoveries. In many cases, the cost of transporting the gas onshore is prohibitive, and therefore the gas is re-injected, flared, and/or vented after condensate and/or LPG has been removed. Floating plants of the Syntroleum Process would enable gas in such isolated fields to be produced and converted to higher-valued products. Finally, perhaps someday, surplus team and tailgas generated from the process will be used to produce gas from the largest known source of natural gas-methane hydrates. Conceptually, the tailgas and steam from the plant would be used to heat seawater to produce a heated brine solution,

which would be used to melt the hydrates and free the gas for conversion into synthetic hydrocarbons.

QUALITY OF FUELS PRODUCED FROM SYNTROLEUM PROCESS

The attributes of the synthetic fuels are discussed in the following sections. The synthetic fuel data reflect a 2001 analysis conducted by Syntroleum at its laboratories, national laboratories, including Southwest Research Institute, and car manufacturers, including Volkswagen and Daimler Chrysler.

Synthetic Diesel (S-2)

Synthetic diesel produced from the Syntroleum Process, also known as S-2, is a highly paraffinic, high-cetane distillate product suitable for conventional and advanced compression ignition diesel engines and fuel cells. S-2 is physically similar to petroleum-based diesel engines and fuel cells, but with superior combustion emission characteristics. At ambient temperature and pressure, S-2 is a colorless, stable, environmentally safe liquid that can be shipped, stored, and dispensed using the same fuel distribution and handling procedures as petroleum diesel. A comparison of the S-2 to other conventional diesel fuels is shown in Table below. Due to its attributes, S-2 outperforms diesel fuel produced from crude oil. First, due to high paraffin content (99 percent) and absence of aromatics, S-2 has a cetane number of 74. As a comparison, the minimum cetane number in the United States is 40 and in Europe is 50. With its inherent high cetane number, S-2 will reduce the ignition delay periods, especially for cold starts, and increase power and performance without the need of cetane additive. Also S-2 contains no detectable amounts of sulfur, aromatics, or heavy metals. Because of this attribute, tests by Southwest Research Institute have confirmed that S-2 has reduced emissions in every category of criteria pollutant compared to EPA no. 2 diesel, CARB diesel, and Swedish City diesel. The results of these tests are summarized in Table below. Furthermore, since S-2 contains no measurable olefins or aromatics, the fuel does exhibit stability problems, such as gum formation and insoluble organics associated with

conventional diesel fuels. Another advantage due to the absence of contaminants is S-2's compatibility with emission after-treatment devices and fuel cells, which are sensitive to

TABLE 4.2.1: Specifications of Diesel Fuels Tested by SWRI

Specificatio	S-2	EPA no.	CARB	Swedish
Specific	0.77	0.85	0.83	0.82
Sulfur, ppm	0	350	*155*	< 10
Aromatics,	0	31	8	4
Cetane	74	47	51	52

TABLE 4.2.2: Criteria Pollutant Emissions from S-2

Fuel	Measured	emission,	g	
	HC	C	NO	P
EPA no. 2 diesel	0.12	1.2	4.0	0.1
CARB diesel	0.09	1.1	3.7	0.0
SwedishCity	0.09	1.2	3.6	0.0
S-2	0.07	0.8	3.2	0.0

the sulfur levels in diesel fuel. Since S-2 contains no sulfur or heavy metals, these after-treatment devices are not susceptible to deactivation caused by contaminants normally found in conventional fuels. Finally, S-2 has excellent low-temperature properties due to a high percentage of isoparaffins. Testing has demonstrated that the cloud point and the cold filter plugging can be as low as -30 and -34°C, respectively. This implies that S-2 will not require additives to improve the low-temperature properties and that engines using S-2 in cold environments will not be as susceptible to clogged fuel lines and filters as engines using conventional diesel.

Synthetic Naphtha (FC-2)

FC-2 is an ultraclean, synthetic naphtha that is saturated with hydrogen and has many applications in the petrochemical and fuels industry. FC-2 is free of aromatics, metals and sulfur and is composed of >99.99 percent naphtha. With these qualities, FC-2

can be for feedstocks in ethylene crackers, fuel cells, and low-compression engines (4 : 1 or less) undergo further processing into upgraded products, such as high-octane gasoline liquefied petroleum gas.

Ethylene Feedstock Applications.

FC-2 is an excellent ethylene cracker feedstock. Naphtha feedstocks with high paraffin content are preferred, because they produce much higher yields of light olefins. As stated earlier, FC-2 has paraffin content 99.99 percent, content higher than that of any naphtha isolated from a conventional crude oil, such as Saudi Arabia's A-180 natural gasoline, which has paraffin content in the range of 90 to 95 percent.

Combustion Engine/Heating Applications.

Due to its high paraffin content, FC-2 has a low octane rating of approximately 30, making it an ideal straight-run fuel compression (4:1) engines. However, the octane level of FC-2 can be upgraded vehicular use with the addition of an akylation unit. Alternatively, FC-2 cracked into liquefied petroleum gas (LPG). This would provide a sulfur-free fuel for residential and commercial heating needs. Finally, FC-2 is an excellent fuel substitute that is currently being used in industrial turbines. A significant reduction of emissions would result, eliminating the need for expensive scrubbing of the exhaust.

Fuel Cell Applications.

As a fuel-cell fuel, FC-2 is very attractive fuel for generating hydrogen. The paraffinic nature of FC-2, more specifically the lack of unsaturated and aromatic hydrocarbons, favors minimal coking in the reforming of the fuel cell. Additionally, the lack of sulfur and heavy metals in FC-2 prevents the need for sulfur removal beds or guard beds to protect the reforming catalyst. In comparison to other fuels, tests conducted by Ida Tech showed that the hydrogen yield per unit volume is nearly double that of CNG or methanol. These attributes are expected to contribute significantly toward minimal operating costs and favorable overall economics of a FC-2 fuel cell.

Synthetic LPG

Snthetic LPG is used for domestic heating, cooking, and transportation and has outstanding qualities when compared to conventional LPG. Synthetic LPG contains no contaminants such as hydrogen sulfide, carbon dioxide, oxygen compounds, and moisture that are commonly found in conventional LPG. Because of these attributes, synthetic LPG does not require any gas conditioning, such as dehydration or amine processing. The lack of contaminants also implies that synthetic LPG can be handled more safely and will have a higher performance for end-use markets, especially in terms of emissions.

CAPITAL INVESTMENT REQUIREMENTS

Several key variables affect the profitability of a GTL plant; these variables include the capacity of the plant, capital cost of the plant, gas price, operating and maintenance costs, and transportation costs. Only a detailed front-end engineering design for a site-specific project can provide a definitive cost estimate. The cost information provided here is based on generic studies, which typically have an accuracy of ±30 percent. The cost estimate is based upon the following:

Capital cost estimate is based on U.S. Gulf Coast pricing in 2001 U.S. dollars.

Capital cost estimate includes home office/EPC costs of 15 percent.

Capital cost estimate has an accuracy of ±30 percent.

Operating cost estimate excludes cost of natural gas.

The following exclusions apply: gas pipeline and other gas transportation costs outside plant fence, cost of recovering NGLs from feed gas, unusual water acquisition costs, cost of land, taxes, licenses, permits, duties, start-up costs, insurance, and cost of front end engineering design.

CAPITAL COST ESTIMATE

Capital cost of plant	$25,000/bbl of daily capacity
Operating cost	$5.00/bbl

4.3. EXXON MOBIL'S ADVANCED GAS-TO-LIQUIDS TECHNOLOGY

AGC- Process Technology

The AGC-21 process connects three key steps, as shown in **Figure 4.3.1**. In the first step, syngas is generated by contacting methane with steam and limited oxygen in a high capacity catalytic reactor. Hydrocarbons are synthesised in the second step at high alpha as described by a Shulz-Flory distribution in a novel slurry reactor using new, high productivity catalysts operating at high levels of syngas conversion.
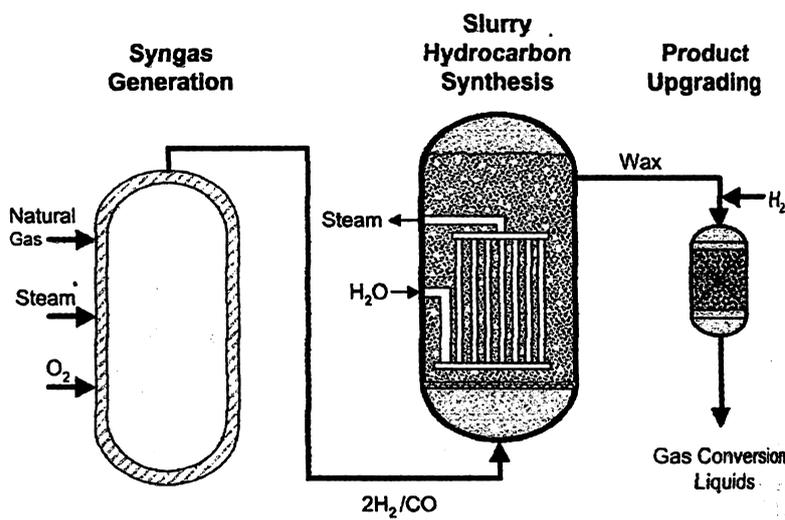

Fig 4.3.1: AGC 21 Process

The full-range, primarily normal paraffin product contains significant 650°F+ waxy material which is a solid at room temperature and melts above 250°F, unsuitable for pipelining or transporting in conventional crude carriers. The final step, accomplished with proprietary catalysts in a packed bed reactor, converts wax to high quality liquids that make excellent feeds for refineries and chemical plants and directly marketable products in some instances, such as lube basestocks or speciality solvents. As shown in **Figure 4.3.2**, chemistries inside these steps are straightforward yet become more complex as processes go to high yields and selectivities. Oxygen, methane and steam ratios are carefully controlled to produce syngas (carbon monoxide and hydrogen) at stoichiometric proportions of about 2.1 to 1 H_2 to CO.
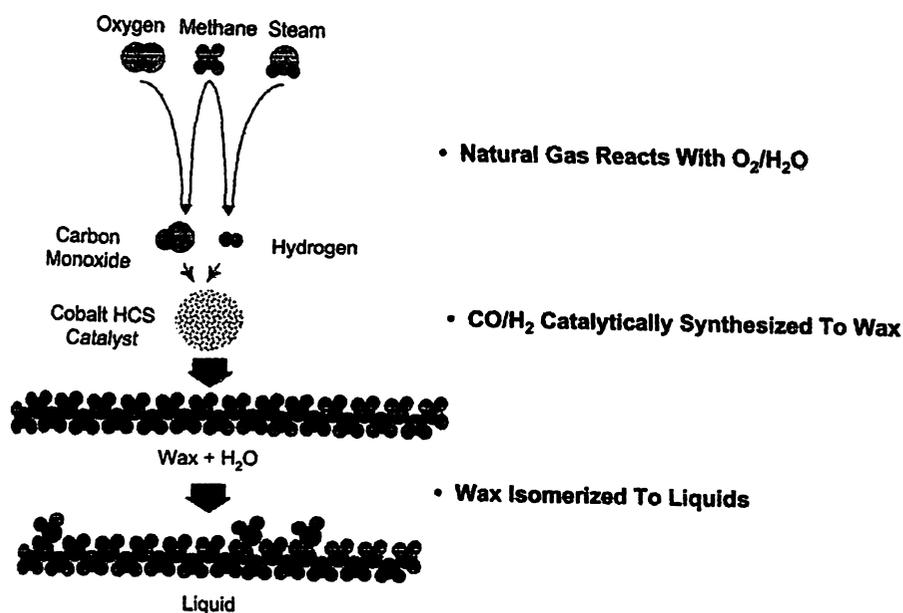
Fig 4.3.2: AGC 21 liquids ultraclean

A high productivity cobalt-based HCS catalyst converts syngas with focus on $C_{10}+$ yield to improve plant efficiency and to optimise preferred products. These product molecules are predominantly normal paraffins that define the waxy character of this material. Mild isomerisation improves cold flow properties of these molecules to acceptable levels for a variety of products. This isomerisation mainly rearranges the structure to produce short side chains that significantly lower melting points.

ExxonMobil's industry leading hydrocarbon-conversion and wax-upgrading catalyst technologies are important elements of AGC 21. The upgrading process has been fully integrated into the overall AGC21 scheme, allowing naphtha, diesel and lubes to be generated in high efficiency. The relative yield of various products can be tailored to meet project needs. Fischer-Tropsch PDU studies, and recent experience with our upgrading technology, have confirmed yield and quality improvements over competing alternatives. The lube basestocks are zero-sulphur, highly biodegradable materials that are well suited for next generation motor oils. Wax upgrading studies are continuing to quantify other benefits of GTL product streams.

The products of Fischer-Tropsch synthesis are clear, colourless liquids that are biodegradable, have low odour and are very clean burning. They are free of sulphur, nitrogen, aromatics and other contaminants, and are ideal feeds for petrochemical and refining applications. AGC21 fuels are ultra-clean, and offer emissions and environmental henetits relative to conventional analogues. In addition, we have found them to he particularly useful as blendstocks for upgrading various refinery streams. Other studies have shown that F-T hydrocarbons are useful as fuel cell fuels. This is a result of their ultra low sulphur content and the relative ease with which they can be converted to hydrogen.

AGC-21 Fuels

Diesel will be a major portion of the overall GTL product, and key properties are outstanding, as shown in Figure 4.3.3. Sulphur content is well below the standard measurable range of 10 parts per million, and the measured cetane of 74+ is consistent with its high concentration of paraffinic molecules which are known to be excellent diesel components.

- **Qualities Well Beyond Conventional Diesel**

	Conventional	AGC-21™
Cetane No.	45	74
Sulfur, ppm	330	<10
Specific Gravity	0.84	0.78
Flash Pt, °C	71	81
Cloud Pt, °C	-17	-12

- **Excellent Blendstock For Gravity Correction**

Fig 4.3.3: AGC 21 produces high quality diesel

The absence of high density aromatics along with an abundance of paraffins leads to a somewhat lighter diesel with a specific gravity below that of the conventional sample. Flash point can he controlled through distillation without interfering with other key properties. Properties related to performance in cold environments merit special attention because the same paraffinic nature that provides high cetane can also impact drivability-related tests such as cloud point or wax appearance point. Of course, undercutting diesel provides one path for altering low temperature performance but at the expense of diesel yield. We have found that the same flexibility that allows significant control over product slate also applies to key product qualities. In other words, cold flow properties can be adjusted with catalytic processing if needed for local markets.

It is shown that a 280-700°F GTL diesel burns more cleanly than conventional US or European diesels, where AGC-21 diesel is shown to provide significantly lower PM and NOx emissions that conventional US or UK low sulphur diesel samples.

On the other hand, it is known that raising the T, point of conventional diesel fuels can negatively impact vehicle emissions. But these data show that higher boiling GTL components can be added to diesel while still maintaining substantial emissions improvement, even with end points as high as 800-900°F. The hydro-isomerisation process facilitates production of low cloud point diesel fuels even when the boiling range is extended, by converting high-boiling normal paraffins into iso-paraffins. The cetane values remain high, ~70+, and the densities are low when compared to those of petroleum diesel fuels. The cloud point remains low even when T_{95} is extended beyond the range of normal diesel fuels. These heavier components may also offset inclusion of some light components from GTL that also have high cetane values. In fact GTL naphtha performs well in diesel engines but, of course, it does not meet flash specifications.

Exxon Mobil and others have found that F-T fuels provide reductions in emissions when compared to conventional fuels such as a CARB diesel. The unique properties of F-T fuels also make them attractive for blending into conventional petroleum diesel fuels and diesel fuel blending stocks.

'Blend X', made of the F-T fuel and a cracked stock in equal proportion, compares favourably with CARB diesel. The blend produces similar levels of NOx emissions, and slightly more PM emissions. However, this blend achieves these emission levels with

much higher aromatics (27.2 vs. 8.7%,) and poly-aromatics (12.7 vs. 0.3%) content at identical sulphur content. The high cetane and low density of F-T fuel make it possible to blend a fuel with good emissions performance from distressed refinery streams, even though the blended fuel contains high levels of aromatics and poly-aromatics.

AGC Lubes

The lube basestocks are zero-sulphur, have a high viscosity index and are highly biodegradable, making them well suited for next generation motor oils. AGC21 technology allows us to produce these basestocks in higher yield and better quality than competing GTL processes. Lubes are another potential product from GTL, and an outlook for lube basestock demand shows that over the next 10 years or so, Group II, Group II+ and Group III basestocks will make up the fastest growing segment of the basestock market. Current global basestock demand is about 640 kBD today, with over 85 % of the total demand being met by conventional Group I basestocks.

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

For GTL, the high productivity and selectivity of ExxonMobil's HCS technology along with high selectivity MSDW upgrading technology provides ExxonMobil with industry leading capability for manufacture of GTL basestocks.

The future of AGC-21 technology

Finally, a large-scale commercial GTL plant will likely have small impact on fuel markets, but could have a significant impact on lube basestock markets. For example, a commercial-scale GTL plant having a total capacity of 80kBD product might be designed to produce at least 16kB/D lube basestock along with 50kBD of diesel fuel. The impact of such a volume of diesel product on the global diesel market is relatively inconsequential, while the lubes volume from this single plant will equate to 2%, of the world's basestock market, or almost 10% of today's global high-quality basestock market.

CONCLUSION:

The available processes for the conversion of gas to liquids have been studied with respect to its process conditions, reactors used, operating cost and the purity of products obtained from it. Shell Middle Distillate Synthesis is preffered over other process.

Reactor:

Syngas conversion can be as high as 96 percent with liquid (C_{5+}) selectivity better than 90 percent. Design of a commercial MTR is straightforward by multiplication of the performance of an individual tube.Fixed-bed catalyst provides intrinsic and absolute separation of the products, with zero contamination by catalyst. Axial catalyst distribution is uniform irrespective of operating conditions.

Products:

Table 5.1: Comparison of SMDS and Syntroleum Diesel.

Specifications	SMDS	S-2
Specific gravity	0.776	0.770
Sulphur, ppm	0	0
Aromatics, vol%	0	0
Cetane number	81	74

Table 5.2: Comparison of Synthetic Diesel with Normal Diesel

Property	CEN(1998)	Swedish Class	SMDS
Density*(a)15°C g/m^3	837	814	776
Distillation. °C IBP	201	197	184
10%	219	213	-
50%	269	231	275
90%	326	269	340
FBP	368	293	357
Cetane number	50	58	81
Cetane index	52.2	50 .4	76
Viscosity @ 40°C Cst	2.823	1.903	2.702
Sulfur. %mol	0.05	0.001	<0.0002
Aromatics. %mol Mono	25	9.7	<0.05
Di	2.1	0.1	<0.05
Tri	1.2	<0.05	<0.05
Total	28	10	<0.05

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