

SHELL MIDDLE DISTILLATE SYNTHESIS: THE PROCESS, THE PLANT, THE PRODUCTS

Peter J. A. Tijm
Shell International Gas Ltd.
Shell Centre, Downstream Building
London SE1 7NA, U.K.

Keywords: natural gas conversion, Shell Middle Distillate Synthesis, Fischer-Tropsch

INTRODUCTION

The importance of natural gas as a source of energy has increased substantially in recent years and is expected to continue to increase. As a result of the frantic search for oil set off by the oil shocks of the early and late 1970s, many new gas fields were discovered around the world, leading to a dramatic increase in the proven world gas reserves. This growth in gas reserves is still continuing today and despite the low oil prices, the world proven gas reserves have been growing at a rate which is twice the current world natural gas consumption rate. Proven world gas reserves are now approaching those of oil and, on the basis of the current reserves situation and relative depletion rates, natural gas seems to be set to outlast oil.

Notwithstanding the growing importance of natural gas, its main drawback remains its low energy density, which makes its transportation to the point of use expensive and which, in the case of remote gas, may even prohibit its exploration and for development. Liquefaction is a way to overcome this problem and various liquefied natural gas (LNG) projects have already been realized around the world.

Recognizing the growing importance of natural gas, Shell has been looking at other ways of using natural gas profitably, particularly those reserves which are remote from the market. The key element is in the transportation aspect and so cost improvements to conventional pipeline and LNG schemes are being studied. However, where such schemes will continue to make an important contribution to the natural gas trade, their end products (natural gas) are by nature confined to markets for natural gas. Shell has therefore also been looking at processes that chemically convert natural gas into liquid hydrocarbons. Using such processes not only reduces the transportation costs substantially, but also a much larger market becomes available, especially if these hydrocarbons are transport fuels. Moreover, apart from providing a means to commercialize remote gas reserves, this could also serve to reduce the reliance on oil or oil-product imports and perhaps as important, save on foreign exchange.

The foregoing underlines Shell's strategy in the natural gas business:

1. Bring gas to the market.
2. Bring value to the product.

It has been realized that there are many places in the world where gas is available, without a ready market and where, as a consequence, it would have a much lower intrinsic value compared with transportation fuels. It is this difference in value that would drive a synthetic fuel project and provide opportunities for both government and private enterprises.

The present scene in the field of oil and transportation fuels and the prospects for the near and medium term, however, call for a careful and selective approach to any synfuel development. At current oil prices almost no alternative energy technology can compete with existing refining. On the other hand, the crises of the early seventies and early eighties provided important lessons: emergencies come at relatively short notice, and, because of the lead times usually involved in technological development, in a crisis the answers to problems always come too late.

Next to the synthetic hydrocarbon transportation fuels, a similar role could be perceived for methanol. However, use of methanol as a transport fuel, either as M85 or neat methanol, has considerable drawbacks. These include the required modifications to fuel distribution systems and to car/engine fuel systems. Synthetic hydrocarbons, on the other hand, have the advantage that they can be readily incorporated into existing fuels which can be used in existing equipment. In addition, middle distillates manufactured from natural gas have very environmentally friendly properties, upon which we will elaborate in this paper. The cleanliness of natural gas is, as it were, transferred into its products. The middle distillates from SMDS will therefore be extremely well positioned in the market place.

THE PROCESS

The SMDS process consists of three stages:

1. Syngas manufacturing

2. Heavy Paraffin Synthesis (HPS)
3. Heavy Paraffin Conversion (HPC)

The overall process starts with the conversion of natural gas into synthesis gas, for which there are several commercial processes available. For the production of predominantly saturated hydrocarbons, $-(CH_2)_n-$, the syngas components H_2 and CO, are consumed in a molar ratio of about 2:1, so a production in about that ratio is desirable. This influences the choice of process, as will be explained below.

The next step of the process, the hydrocarbon synthesis, is, in fact, a modernized version of the classical Fischer-Tropsch (FT) process, with the emphasis on high yields of useful products. The Fischer-Tropsch process developed by Shell for SMDS favors the production of long chain waxy molecules which, as such, are unsuitable for transportation fuels. The hydrocarbon synthesis step is therefore followed by a combined hydro-isomerization and hydrocracking step to produce the desired, lighter products. By opting for the production of waxy molecules in the Fischer-Tropsch step, the amount of unwanted smaller hydrocarbons or gaseous products, produced as by-products, is substantially reduced. This means that the process, contrary to the old 1930's Fisher-Tropsch technology, can be fuel balanced and does not make "gas" out of gas. Combined with the high selectivity towards middle distillates in the hydrocracking step this leads to a very high overall yield of product in the desired range.

In the final stage of the process, the products, mainly kerosene, gas oil and some naphtha, are separated by distillation. By judicious selection of the severity of the hydrocracking reaction and the cut-points, the product slate can be biased towards kerosene or towards gas oil.

Synthesis Gas Manufacture

For the production of synthesis gas in principle two technologies are available, viz., steam reforming and partial oxidation.

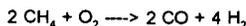
Steam Reforming (SMR)

Starting from pure methane, SMR is the most commonly used conversion process, and could theoretically produce a synthesis gas with an H_2/CO ratio of about 3. However, as a result of the occurring CO - shift, more H_2 is produced and this ratio will be in the range of 5-7 rather than 3.

Because the H_2/CO ratio in the synthesis gas is greater than 2, in the subsequent hydrocarbon synthesis step less hydrogen will be consumed than is produced in the syngas step. This means that steam reforming always results in the production of excess H_2 . An often practiced solution is to burn the surplus hydrogen in the reforming furnace. This means, however, that part of the synthesis gas is used as fuel. Another disadvantage is that the maximum SMR pressure is about 30 bar, while the Fischer-Tropsch reaction is preferably carried out at somewhat higher pressures.

Partial Oxidation

A synthesis gas suitable for the production of middle distillates, with a H_2/CO ratio of about 2, can be produced by partial oxidation:



For partial oxidation with pure oxygen, an excellent eligible process is the Shell Gasification Process (SGP). The question, whether the costs involved with the production of a gas with the wrong H_2/CO ratio, as in the case of steam reforming, are not substantially smaller than the cost required for the production of pure oxygen, has been answered in favor of the SGP process combined with modern oxygen technology.

For the Fischer-Tropsch type of catalysts, the synthesis gas must be completely free of sulphur. For this requirement, it has been found to be economical to remove all sulphur components upstream of the partial oxidation step for which, in principle, a number of well-known treating processes are available. In practice, zinc oxide beds are employed, to remove the last traces of sulphur and to act as an absolute safeguard.

The Hydrocarbon Synthesis Step

In the next step, the synthesis gas is converted into long chain, heavy paraffins, and this step is therefore called the Heavy Paraffin Synthesis (HPS) step, the heart of the SMDS process. In this step the reaction mechanism follows the well-known Schultz-Flory polymerization kinetics, which are characterized by the probability of chain growth (α) vs. chain termination ($1-\alpha$). There is always a regular molecular mass distribution in the total product and a high

alpha, corresponds with a high average molecular mass of the paraffinic product. The paraffinic hydrocarbons produced via the FT reaction are highly linear. This implies that the synthesis reaction can be regarded as a stepwise addition of a C1 segment to the end of an existing chain. Since atoms of the alkyl chain remote from the end will hardly be capable of influencing this reaction, it is plausible that the relative probabilities of chain growth and chain termination will be independent of the length of the alkyl chain. The carbon number distribution of the FT product can therefore be described fairly accurately by a simple statistical model with as a single parameter (the Anderson Flory-Schultz [AFS] distribution, the value of being dependent upon the catalyst and reaction conditions. In a few hundred formulations under different operating conditions it was confirmed that the carbon number distributions were in close agreement with the AFS chain growth kinetics discussed above, with values varying between 0.70 and 0.95

The above feature implies, however, that the FT process will yield either large amounts of gaseous hydrocarbons such as methane, or products which have a very wide carbon number distribution. Theoretically, only methane can be produced with 100% selectivity. All other products including fractions boiling in specific ranges, such as gasoline, kerosene and gas oil, can be produced only with relatively low selectivities. The only product fraction, beside light gases, which can be produced with high selectivity is heavy paraffin wax. It is for this reason that the synthesis part of the SMDS process has been designed to produce a long-chain hydrocarbon wax.

During the reaction: $2 \text{H}_2 + \text{CO} \rightarrow \text{H}_2\text{O} + \text{-(CH}_2\text{)-}$ an appreciable amount of heat is released. For the classical catalyst system, this requires a considerable control of the temperature in view of the following constraints:

- The temperature window of stable operation is rather small
- A high space-time yield demands a high temperature
- At only moderately higher temperature a side reaction leading to methane formation becomes more dominant, reducing selectivity and, eventually, stability.

Because of these shortcomings, Shell has developed a new and proprietary catalyst system, which establishes substantial improvements in all these areas. Its robustness allows the use of a fixed bed pipe reactor system at a temperature level where heat recovery, via production of steam, leads to an efficient energy recovery. The catalyst, which is regenerable (cycle > 1 year) has an expected useful life of well over five years.

Heavy Paraffin Conversion (HCP)

One of the prerequisites for attaining a high selectivity towards middle distillates is a sufficiently high average molecular weight of the raw product. This product, which is predominantly waxy but contains small amounts of olefins and oxygenates, has to be isomerized and cleaned up, while little hydrocracking should take place concurrently. A commercial Shell catalyst is used in a trickle-flow reactor as is employed in refinery hydrocracking operations, but under rather mild conditions of pressure and temperature.

An important observation in this respect is the carbon number distribution of the total product obtained after hydro-cracking of a Fischer-Tropsch fraction containing normal paraffins. As an example the product distribution after cracking n-hexadecane shows that very little methane and ethane, if any at all, is formed. In addition, process conditions can be chosen such as to allow partial evaporation of the lighter hydrocarbons so that they escape easily from the reactor. Since the heavier paraffins may then preferentially condense or absorb on the catalyst surface, they will remain longer in the reactor and thus have a better chance to react. Initially, one might expect the curve to follow an approximately exponential increase with an increase in carbon number as the absorption coefficient is an exponential function of the heat of absorption, while this heat of absorption for normal paraffins is known to increase about linearly with increasing carbon number. The increment per carbon number amounts to some 10-15 kJ/mol. Above a certain chain length, however, one may expect the effect to level out as the degree of absorption approaches 100%. The result would be a chain-length-dependent reactivity, which shows a very steep increase in the lower carbon number range and an about linear increase in for the higher carbon numbers.

Taking this into account and assuming an equimolar production ratio for all cracked components except for those resulting from breakage of the first three bonds, one can calculate that a C-20 paraffin can be converted into some 80% wt of C-10 - C-20 material, while only some 20% wt ends up in the lighter fraction.

The principle of combining the length-independent chain growth process with a selective, chain-length dependent conversion process has been applied to selectively produce middle distillate paraffins from synthesis gas. To take full advantage of this concept, the Fischer-Tropsch catalyst and the operating conditions were chosen as to produce a heavy product with a high alpha-value, minimizing the formation of undesired light hydrocarbons. The

effectiveness of the two stage approach also creates flexibility creating selective distributions of Fischer-Tropsch liquid products after heavy paraffin conversion at different cracking severities.

The HPC product is subsequently fractionated in a conventional distillation section. The product fraction which is still boiling above the gas oil range is recycled to the HPC section. By varying the process severity or the conversion per pass one can influence the selectivity towards a preferred product. Hence one may opt for a kerosene mode of operation yielding some 50% kerosene on total liquid product or for a gas oil mode of operation producing some 60% gas oil. In practice the following variability has been proven:

<u>% wt</u>	<u>Gas Oil mode</u>	<u>Kerosene mode</u>
Tops/naphtha	15	25
Kerosene	25	50
Gas Oil	60	25

Compared to syngas requirements of the total complex, the hydrogen demand for the HPC step is very modest. This hydrogen can be recovered from a slipstream of the syngas by any of several methods; one modern method makes use of membranes. Steam reforming of the synthesis purge gas and/or natural gas is also a possibility.

THE PLANT

Shell, together with its partners Petronas, Sarawak State Government and Mitsubishi Corporation, are the shareholders in the first commercial SMDS plant in Bintulu, Malaysia, adjacent to the Malaysia LNG plant. The plant will convert 100 million cubic ft/day of natural gas from offshore fields into approximately 500,000 metric tons/year of hydrocarbons. The Malaysian SMDS project, based on the conversion of natural gas to transportation fuels, like kerosene and gas oil, has through its development and in particularly the efforts spent at Shell's Research Laboratories, gained new grounds. For petrochemicals, the ability to produce naphtha as chemical feedstock is a further advantage. The tops/naphtha fraction is completely paraffinic and therefore makes an ideal cracker feedstock for ethylene manufacture. Obviously, taking into account the paraffinic nature of the hydrocarbons specific solvents provide another market opportunity for the SMDS products.

Further more the SMDS Bintulu project has taken advantage of producing high quality waxes by diverting part of the HPS product stream to the Wax Production Unit. After a hydrogenation step the C17 minus fraction is distilled off in various distillation columns. Subsequently, the various wax qualities are produced by further distillation. The wax grades are either produced and transported as bulk liquids or as solids, in which case transportation will take place in containers, in the form of slabs or granulates.

Since November 1989 when the ground breaking ceremony took place, there has been a flurry of activities: detailed engineering, ordering of critical equipment, recruitment and training, formation of the start-up and operating crew, construction, commissioning and start-up. Construction was completed by end 1992. Commissioning of a complex plant, introducing new technology, is a time-consuming exercise. Starting with the pre-commissioning in December 1992, it has been progressing in the first quarter of 1993. As a result, in the second quarter of 1993 the first middle distillates were produced.

THE PRODUCT

As can be expected from a Fischer-Tropsch process of this type, products manufactured by the SMDS process are completely paraffinic and free from nitrogen and sulphur. Both the kerosene and gas oil have excellent combustion properties, as the typical product data, given below, show. In this paper particular focus will be given to the excellent properties of the SMDS gas oil and its potential in the market.

	<u>SMDS Gas Oil</u>	<u>CARB Specs.</u>	<u>CEN Specs.</u>
Cetane number	76	40 min	49 min
Density (kg/cu.m)	780	N/S	820-860
Sulphur (ppm)	zero	500	500 (1996)
Aromatics (% m/m)	zero	10 max	N/S
Cloud point (deg. C)	1	-5	N/S
CFPP (deg. C)	-2	N/S	+5 to -20*
Distillation:			
90% recovery (deg. C)	340	288-338	
95% recovery (deg. C)	350		370 max

* depending on climatic band chosen

Because of these excellent properties, which are far in excess of the minimum specifications in terms of smoke point and cetane number, these products make excellent blending components for upgrading of lower-quality stock derived from catalytic and thermal cracking operations; for example cycle oils. Alternatively the products could enter in a market where premium specifications are valued to meet local requirements. Examples include the California diesel market, where the California Air Resources Board (CARB) has imposed a fuel specification with low sulphur and aromatics and the Committee for European Norms (CEN) which has established a fairly high cetane number requirement.

OUTLOOK

As is well known, capital and operating costs for synfuel complexes are highly dependent on location and product slate produced. It has been found that the specific capital cost of a 10,000 bbl/d plant built on a developed site in an industrialized country would be around US\$ 30,000 per daily barrel, whereas for a similar plant in a remote and undeveloped location the cost could be up to double that amount. The uniqueness of the SMDS products, though, including their added value, gives the SMDS process excellent opportunities to provide return on investment.

If feedstock is natural gas priced at US\$ 0.5/MMBtu, the feedstock cost element in the product is about US\$ 5/bbl. The total fixed and other variable operating costs are estimated at a further US\$ 5/bbl. The total required selling price for the product will depend on numerous factors, including fiscal regimes, local incentives, debt/equity ratio, type of loans and corporate return requirements. The premium that may be realized for the high quality products is also a locally influenced and important aspect; it may be as high as 6-8 US\$/bbl over and above the normal straight run middle distillate value.

Another important factor is whether the products are for inland use or for export. For countries with sufficient gas, but that need to import oil or oil products to meet their local demand, SMDS products manufactured in that country should realize at least, import parity values. In some cases these may be far above the normal world spot market values. For such countries therefore, the national benefit of the SMDS process may 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 25,000 to 50,000 bbl/d range, have a much better economy of scale. Moreover, whilst the process is ready for commercialization, further developments are underway, directed at increasing the efficiency of the process even further and reducing the capital cost. An important area for these efforts is the synthesis gas manufacturing plant, which constitutes more than 50% of the total process capital cost. Other fields of interest include further catalyst improvement, the design of the synthesis reactors and general process integration within the project. It is expected that work in this area combined with further improvements for larger size plants, will bring the specific capital costs for remote areas to the range of US\$25,000 to 30,000/daily barrel.

SMDS technology has been developed to a stage where it can be considered as technically proven and, subject to local circumstances, commercially viable. Installation of SMDS plants can bring significant national benefits to countries with uncommitted gas reserves, either through export from the plant or inland use of the products, thereby reducing the need to import oil and oil products and saving on foreign exchange.

REFERENCES

Eilers, J., Posthuma, S.A., and Sie, S.T., (1990), 'The Shell Middle Distillate Process (SMDS)', paper presented at the AIChE Spring National Meeting, Orlando, Florida, USA, March 18-20.

Oerlemans, T.W., Van Wechem, H.M.H., and Zuideveld, P.L., (1991), 'Conversion of Natural Gas to Middle Distillates via the SMDS Process', paper presented at the 18th World Gas Conference, Berlin, FRG, July 8-11.

Tijm, P.J.A., Van Wechem, H.M.H., and Senden, M.M.G., (1993), 'New Opportunities for Marketing Natural Gas: The Shell Middle Distillate Synthesis Process', paper presented at the GASTECH 93, 15th International LNG/LPG Conference & Exhibition, Paris, February 16-19.