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THE SHELL MIDDLE DISTILLATE SYNTHESIS PROCESS (SMDS) *

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Since the early 1970s Shell's research has been involved in syngas chemistry with special focus on routes to convert (remote) natural gas into easily transportable liquid hydrocarbons. This has resulted in the development of the SMDS process. The world's first commercial SMDS plant is being constructed on a site adjoining the Bintulu LNG plant in Sarawak, Malaysia, and will come on stream in the last quarter of 1992.

The heart of SMDS is an enhanced Fischer-Tropsch process. However, direct FT synthesis does not allow the selective production of materials of narrow carbon number range. To overcome this limitation the flexible two-stage concept of SMDS has been developed, which combines the chain-length-independent FT chain-growth reaction with a chain-length-dependent cracking process. Naphtha, kerosene and gas oil yield ratios can be varied from 15 : 25 : 60 to 25 : 50 : 25. Both the kerosene and gas oil show excellent combustion properties: the smoke point of the kerosene can be over 45 mm and the gas oil has a cetane number in excess of 70.

Further attention is paid to the production of the synthesis gas because of its impact on overall process efficiency, to the selection of multitubular FT reactors, and to the environmental merits of the SMDS process and its clean, aromatics-free products.

1. Introduction

Today, the energy requirements of the transport sectors are dominated by liquid fuels derived from crude oil and this dominance is expected to continue. Gaseous fuels such as liquified petroleum gas (LPG) and compressed natural gas (CNG) have had only limited success, even where considerable fiscal incentives have been given. Forecasts indicate, however, a further growth of the consumption of transportation fuel till the year 2000 and thereafter, while the oil reserves

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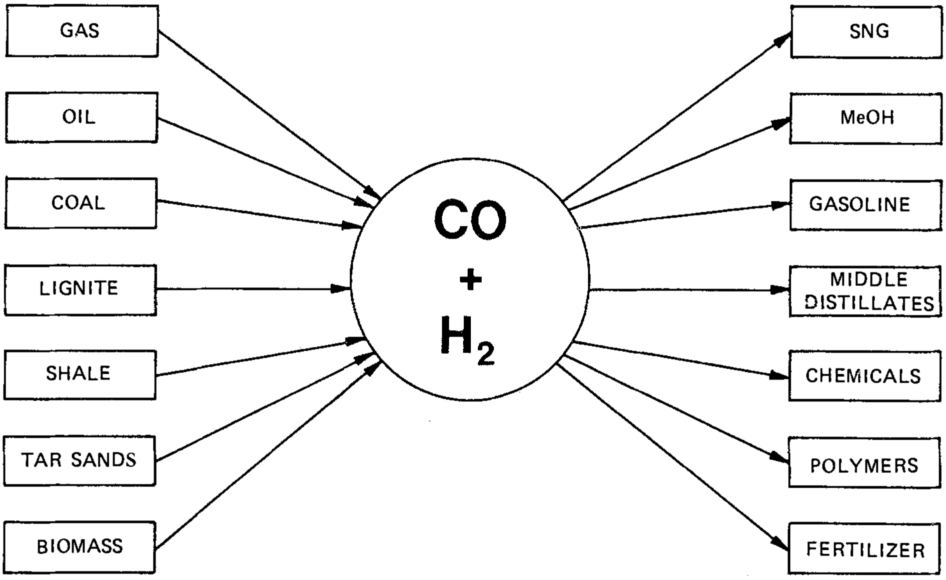


Fig. 1. CO/H_2 technology.

are limited and in fact decreasing in many parts of the world. Interest has therefore grown in creating liquid fuels, suitable for use in existing engines, from alternative resources, particularly from the world's abundant gas and coal resources.

Different conversion processes have been proposed. Generally they are classified into two groups: *direct* and *indirect* processes. The indirect processes all consist of a high-temperature stage to break up the raw materials in synthesis gas, a mixture of carbon monoxide and hydrogen, followed by a synthesis stage to selectively yield the desired products (fig. 1). The first synthesis catalyst was developed by Fischer and Tropsch in 1925. These catalysts were used in Germany during the second world war and are still in use on a large scale in South Africa (Sasol 4000 kt/a). After the oil crisis in 1973 and 1979 interest in synthetic fuels increased substantially. Two examples are ethanol from sugar waste in Brazil and gasoline via methanol: a Mobil process, commercialized in 1985 in New Zealand.

The direct processes have no common denominator other than the avoidance of an intermediate product and they may differ widely as to the chemical principles and technology involved. Examples here are the high-pressure hydrogenation of coal [1] and the oxidative coupling of methane, as in the ARCO process [2]. The term "direct" may suggest simplicity: generally speaking, though, the direct processes are far from simple and, like the indirect processes, usually consist of a high-temperature endothermic process and a low-temperature exothermic stage. Further, direct processes tend to be less selective towards the desired products, so that complex product work-up sections are required and product quality is more difficult to control. In both coal and gas upgrading, therefore, Shell has primarily focused its efforts on the indirect routes.

Shell researchers have been working on non-crude-oil-based liquid transport fuels since the late 1940s. The intensified research activity since the early 1970s has resulted in the development of the Shell Middle Distillate Synthesis (SMDS) process, and in August 1989 came the official announcement that the world's first commercial SMDS plant was going to be built in Bintulu in Sarawak, Malaysia, and would come on stream in the last quarter of 1992.

2. Natural gas as feedstock for middle distillate synthesis

The composition of the hydrocarbon feedstock indicates preferred conversion routes for the production of liquid transportation fuels, such as gasoline or middle distillate fuels (kerosene and gas oil). When feedstock and product carbon/hydrogen ratios are well matched, as when aromatic gasoline is produced from coal or paraffinic middle distillates from natural gas, a relatively high theoretical conversion efficiency is possible. If the carbon/hydrogen ratios of the feedstock and product differ substantially, rejection of carbon or hydrogen, as the case may be, is inevitable, and lower conversion efficiencies result. Fig. 2 shows, schematically, a resource selection route for conversion processes.

Because of the vast amounts of coal reserves, much attention was initially paid to developing the indirect liquefaction of coal (coal gasification followed by synthesis). The high level of investment, however, remains a major constraint on commercial application. The conversion of natural gas into liquid hydrocarbons, on the other hand, is seen as an attractive alternative, since the specific capital expenditure is significantly lower. To illustrate this, table 1 shows the chemical reactions in the conversion of coal and natural gas, the efficiency of conversion and the relative capital expenditure needed.

Other factors that favour the use of natural gas for synthesis of liquid transportation fuels are [3,4]:

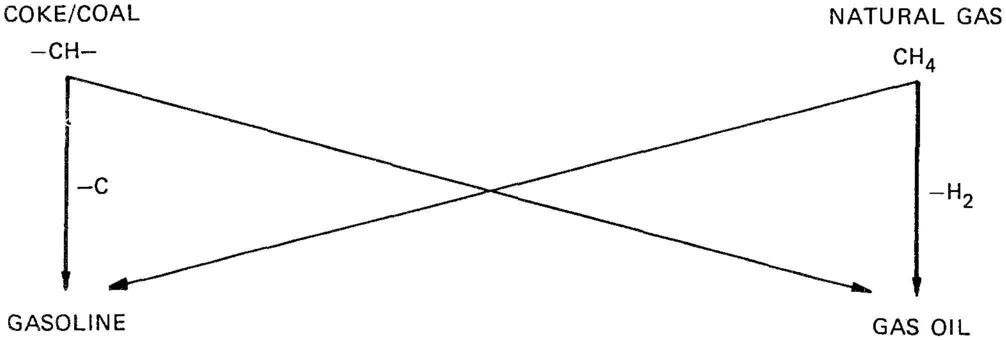


Fig. 2. Transport fuels from coal and natural gas.

Table 1
Chemistry of Middle Distillate Synthesis

Syngas manufacture	Fischer-Tropsch	Thermal * efficiency	Reactive capital expenditure
Coal:			
$2(\text{-CH-}) + O_2 \rightarrow 2CO + H_2 \rightarrow$	$(\text{-CH}_2\text{-}) + CO_2$	60%	200
Natural gas:			
$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \rightarrow$	$(\text{-CH}_2\text{-}) + H_2O$	80%	100

* Theoretical maximum.

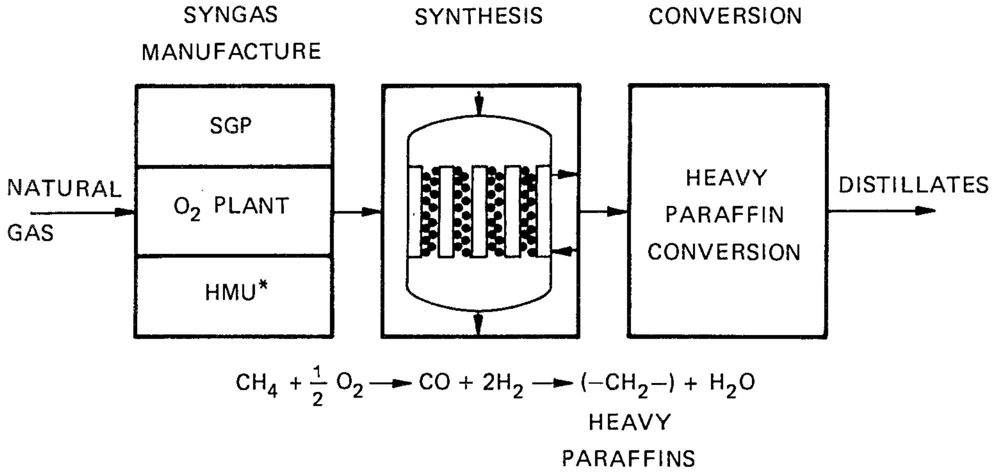
- the continuously growing proven natural gas reserves, which are now at about the same level as the crude oil reserves
- the remote and/or small gas fields which cannot support the high costs of a gas pipeline system or a liquified natural gas (LNG) production plant and may well otherwise remain unused
- associated gas, which is often flared off as waste
- the fact that synthetic fuels made from indigenous natural resources may be cheaper than imported transportation fuels
- the growing demand for middle distillates
- the high quality of synthetic middle distillates, which can be used to improve conventional products.

3. The SMDS concept

The SMDS process consists of three stages (fig. 3):
(1) Syngas manufacturing
(2) Heavy Paraffin Synthesis (HPS)
(3) Heavy Paraffin Conversion (HPC).

In the second stage, the heart of SMDS, carbon monoxide and hydrogen are converted into paraffins via the Fischer-Tropsch (FT) reaction. The synthesis catalyst and the associated reactor design represent the essential technology of the SMDS process. Another feature which, however, is equally important in view of the selective production of middle distillate fuels is the two-stage, HPS-HPC concept, shown in fig. 4.

The paraffinic hydrocarbons produced via the FT reaction are highly linear. From this it can be derived that the synthesis reaction can be considered as a stepwise addition of a C_1 segment at the end of an existing chain. Since atoms of the alkyl chain remote from the end will hardly be capable of influencing the reactions at this terminal growth centre, it is plausible that the relative probabili-



$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \rightarrow (-CH_2-) + H_2O$$

Fig. 3. Shell Middle Distillate Synthesis (SMDS): basic concept. * HMU = Hydrogen Manufacturing Unit.

ties of chain growth and chain termination (α and $1-\alpha$, respectively) will be independent of the length of the alkyl chain (fig. 5). The carbon number distributions of FT product can therefore be described fairly accurately by a simple statistical model with α as a single parameter (the Anderson-Flory-Schulz (AFS) distribution [5]), the value of α being dependent upon the catalyst and reaction conditions. In a few hundred independent FT synthesis experiments with

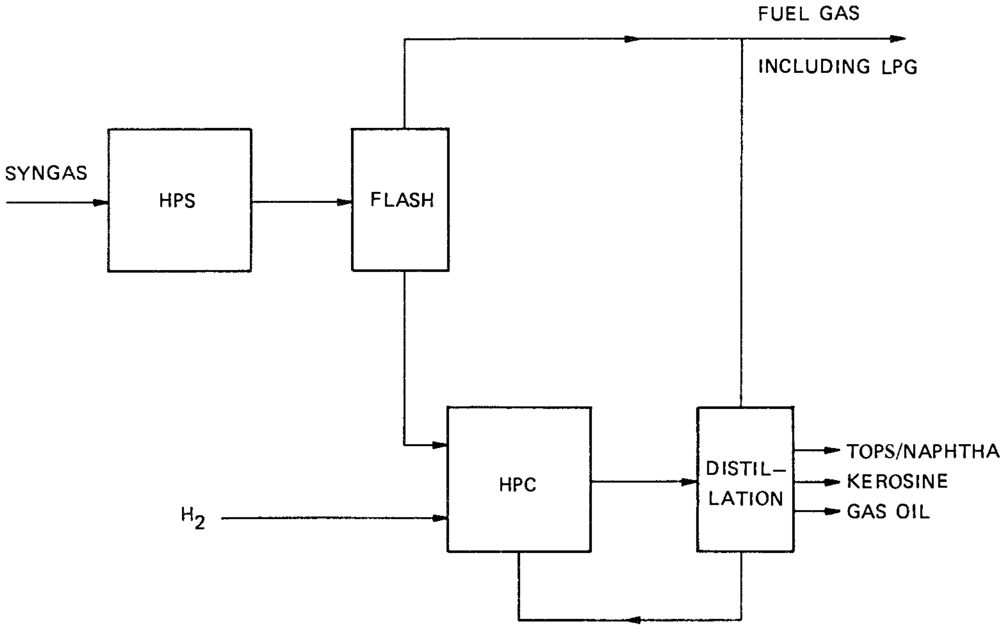


Fig. 4. Shell Middle Distillate Synthesis (SMDS) simplified flow scheme.

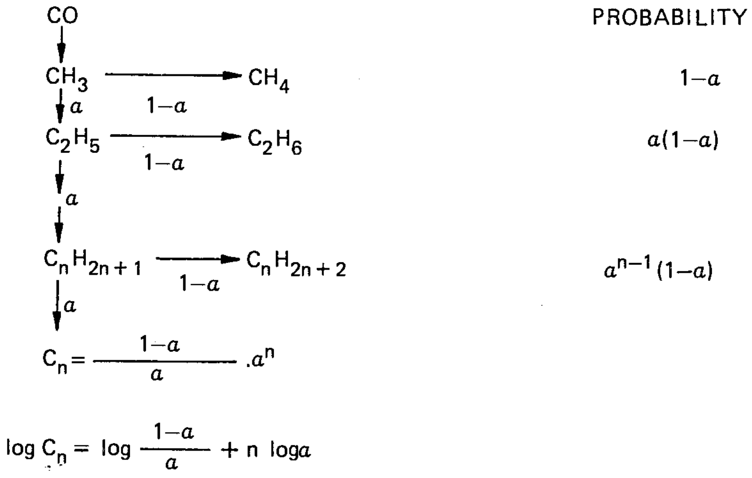


Fig. 5. Schulz-Flory kinetics.

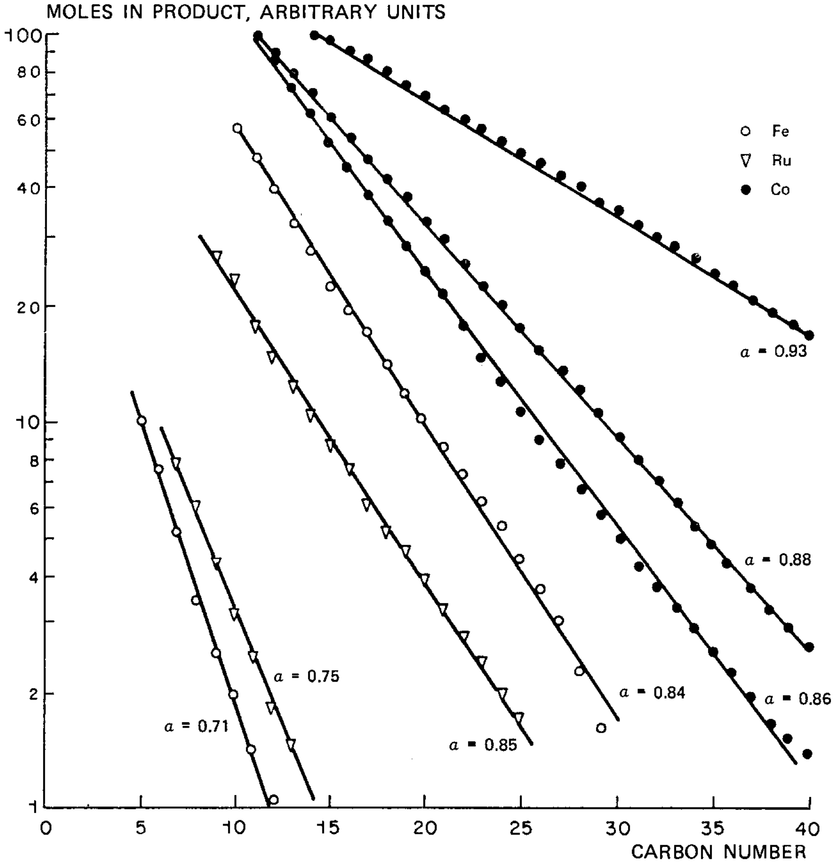


Fig. 6. Typical carbon number distributions.

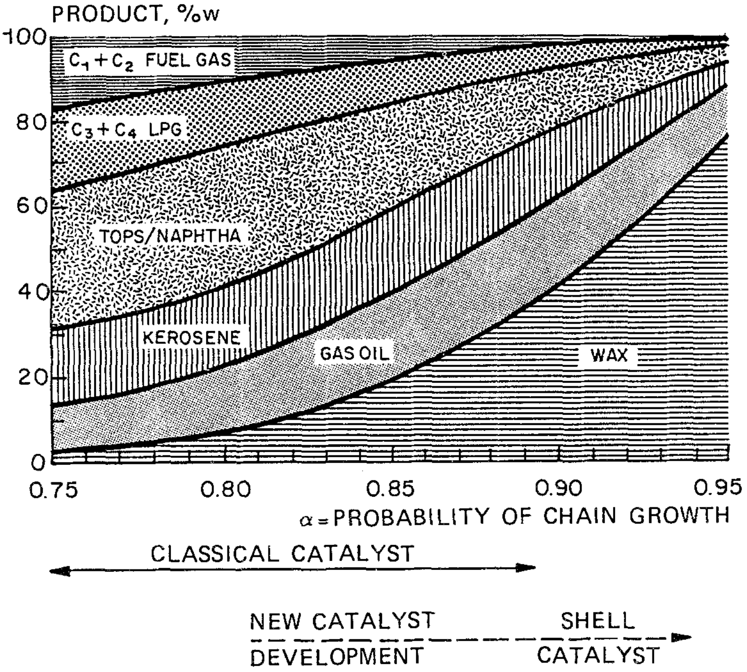


Fig. 7. Product distribution in Fischer-Tropsch synthesis.

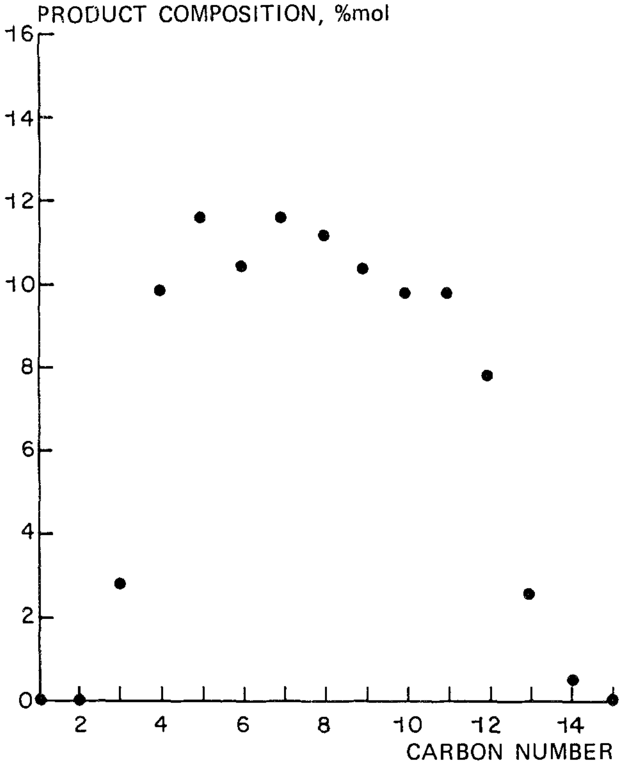


Fig. 8. Molar product distribution after hydrocracking a mixture consisting of 88% w C_{16} and 12% w C_{17} over a dual-functional catalyst.

various catalyst formulations under different operating conditions it was confirmed that the carbon number distribution were in close agreement with the AFS chain growth kinetics discussed above, with α values varying between 0.70 and 0.95 (fig. 6).

This 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 percent selectivity. All other products, including fractions boiling in specific ranges, for example gasoline, kerosene or gas oil, can be produced only with relatively low selectivities (fig. 7). The only product fraction, besides 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 is designed to produce a long-chain hydrocarbon wax.

The Heavy Paraffin Conversion process has now been developed to selectively convert the heavy paraffins into the desired middle distillates, kerosene and gas oil. It is a mild hydrocracking process using a dual-functional (Shell proprietary) catalyst. To achieve the high selectivity the catalyst and conditions have to be selected so that:

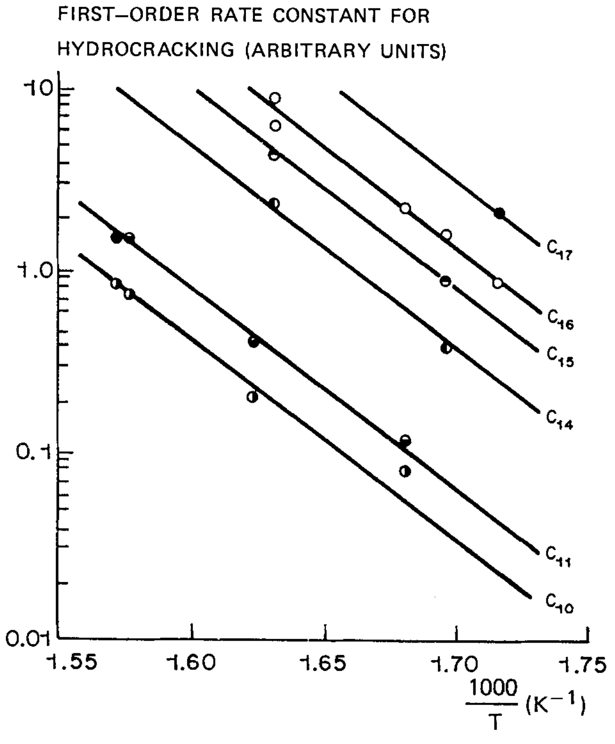


Fig. 9. Hydrocracking reactivity of n-paraffins of different chain length using a dual-functional catalyst.

- heavier molecules display much higher reactivity than lighter components, in order to prevent overcracking of materials in the desired boiling range into light gaseous products, and that
- the heavier molecules are cracked selectively into the desired boiling range.

The experimental data from hydrocracking experiments with three narrow-carbon-number-range fractions (C_{10-11}, C_{14-16}, C_{16-17}) obtained from a total FT product clearly proved the above features.

Fig. 8 shows that the hydrocracking reaction produces lighter (iso-)paraffins on an equimolar basis, except for methane, ethane, which are hardly formed, and propane, which is also underproduced. Such a product distribution has also been reported by others [6,7] and may be explained from the reaction mechanism, sometimes referred to as the "ideal-cracking mechanism", which may be represented by isomerization followed by β scission [6]. The result is that, on a weight basis, the production of light molecular components is low relative to that of higher-molecular-weight products.

Fig. 9 illustrates the reactivity distribution: a C_{17} displays a reactivity that is about 90 times that of a C_{10}. Here again, it is not only the reaction mechanism but also the process conditions that are responsible for this remarkable difference. Process conditions are so chosen as to allow lighter hydrocarbons to be partially evaporated; they then have only limited contact with the catalyst and hence display a low reactivity.

To take full advantage of the above concept of combining the length-independent chain growth process with a selective, chain-length-dependent conversion process, the FT process should be tuned so as to yield the heaviest possible product mixture, hence to operate a high α value, thereby minimizing the formation of undesired light products. To illustrate this, some calculated product distributions have been included in table 2 as a function of α. The effectiveness of the two-stage approach is further illustrated in fig. 10, which shows experimen-

Table 2
Product distribution in direct FT synthesis and in the two-stage process as a function of the chain growth chance α

AFS distribution of Fischer-Tropsch products				Calculated distributions in the two-stage process	
Growth chance α	Product %w			Product %w	
	$< C_{10}$	$C_{10}-C_{20}$	$> C_{20}$	$< C_{10}$	$C_{10}-C_{20}$
0.80	62.4	31.8	5.8	63.6	36.4
0.85	45.6	38.9	15.5	48.7	51.3
0.90	26.4	37.1	36.5	33.7	66.3
0.95	8.6	19.8	71.7	22.9	77.1
0.98	1.6	4.9	93.5	20.3	79.1
0.99	0.4	1.4	98.2	20.0	80.0

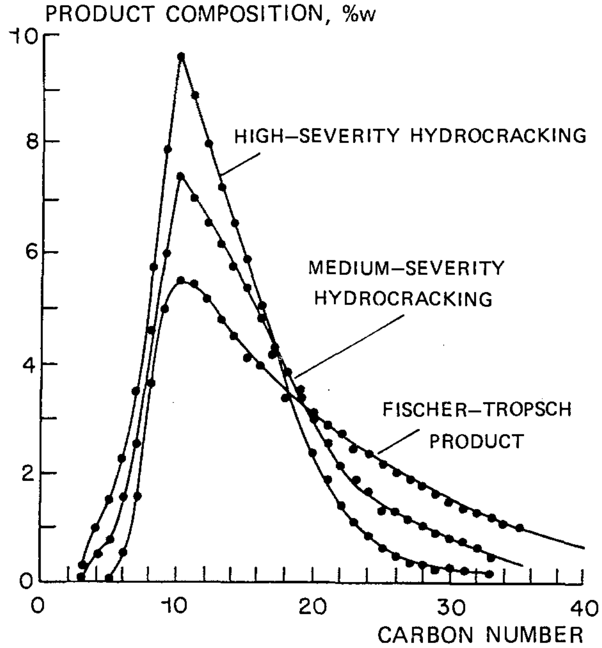


Fig. 10. Distribution of a Fischer-Tropsch product before and after selective hydrocracking.

tally determined distributions of a FT liquid product before and after hydroconversion at two different severities. Under the conditions applied, too heavy paraffins were preferentially cracked, so that the ultimate product distribution shows a peak in the desired middle distillate fuel range while the amount of additionally formed light products was minimal.

4. Process description

As mentioned before the SMDS process consists of three stages (see fig. 4): conversion of natural gas (methane) to synthesis gas (H_2/CO), followed by a Fischer-Tropsch process referred to as Heavy Paraffin Synthesis (HPS) and by a selective hydrocracking process referred to as Heavy Paraffin Conversion (HPC). All three will be discussed briefly below.

SYNGAS MANUFACTURING

This first stage is very important for the total process, not only from a technical point of view but also economically, since some 50–60% of the process capital cost relates to the syngas manufacturing units.

Steam reforming of methane (SMR) is a well-known option. SMR makes use of a nickel catalyst and operates at about 850°C. It produces, however, a

Table 3
Synthesis gas production from natural gas

Chemical reaction	H_2/CO ratio in practice
A. Partial oxidation (Shell Gasification Process or catalytic partial oxidation $2CH_4 + O_2 = 2CO + 4H_2$	2
B. Steam reforming $CH_4 + H_2O = CO + 3H_2$ Water gas shift reaction $CO + H_2O = CO_2 + H_2$	>3

synthesis gas with an H_2/CO ratio of at least 3, unless an expensive CO_2 recycle is incorporated or the natural gas used as a feed already contains carbon dioxide. As the H_2/CO usage ratio of the FT reaction amounts to about 2.1 mol/mol, it is clear that the combination will always result in surplus hydrogen production, to be burned in the SMR furnace. Theoretically, such a system is still water-balanced; in practice, schemes based solely on SMR as a syngas manufacturing process will require substantial amounts of make-up water. Another disadvantage is the maximum SMR pressure of about 30 bar, while the FT reaction is preferably carried out at somewhat higher pressures.

A gas with an H_2/CO ratio of about two can be produced by noncatalytic autothermal partial oxidation using, for example, the Shell Gasification Process (SGP) (see table 3). SGP was developed in the 1950s, primarily with the objective

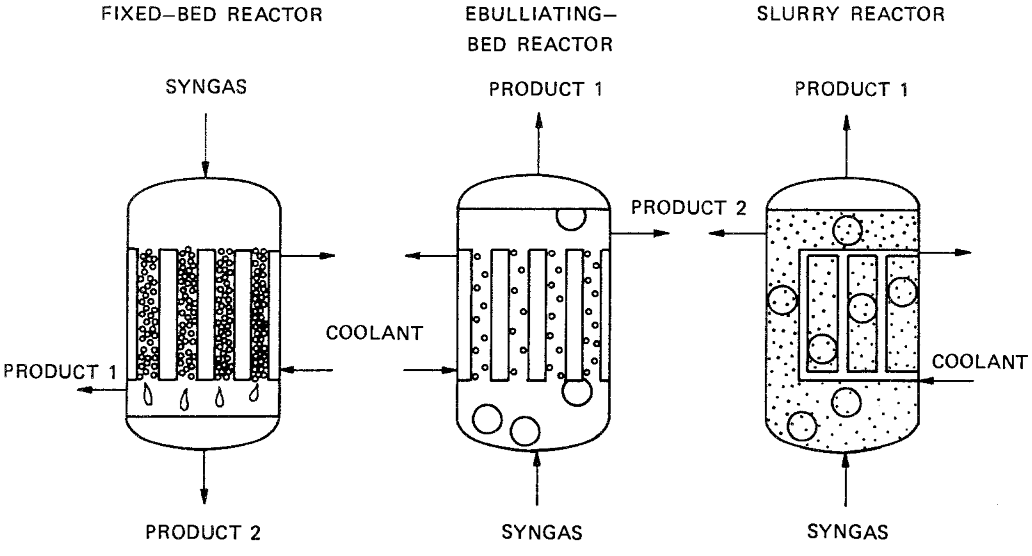


Fig. 11. Reactors considered for HPS.

of converting heavy residues, and plants have been in operation since 1956. The process operates at 1300 to 1500°C and pressures up to 70 bar and the carbon efficiency is in excess of 95% with a methane slip about 1%. For the natural gas to middle distillate route the SGP gas requires little adjustment of the H_2/CO ratio, giving a high overall process efficiency, and produces only water as a by-product.

A small SMR is installed to provide the hydrogen to compensate for the slight shortage in the hydrogen balance in the HPS stage and to be used as the feed gas for the HPC stage.

HEAVY PARAFFIN SYNTHESIS

In the HPS stage, the heart of SMDS, the syngas is converted into paraffins via the highly exothermic FT reaction. The synthesis catalyst and the associated reactor design (together with the HPC) represent the essential technology of the SMDS process.

HPS REACTORS

The selection of a reactor for the highly exothermic process needed careful attention. In principle, three different types of reactors might be used for the synthesis (see fig. 11):

- a fixed-bed reactor;
- an ebulliating (three-phase fluidized-) bed reactor; or
- a slurry reactor.

A fluidized-bed reactor can only be used when the reactants are essentially in the gaseous phase. It has been derived theoretically that, for this reason, stable fluid-bed operation is only possible when the chain growth chance α is less than 0.71 [8]. Analysis of data from commercial FT processes which operate in a fluidized regime, viz. Hydrocol [9] and Synthol [10], confirmed the above statement by showing α values of 0.68 and 0.67, respectively. In middle distillate synthesis, where a heavy wax is formed, this type of reactor is unsuitable.

Slurry and ebulliating-bed reactors, with a three-phase system having excellent heat transfer characteristics, could be used for middle distillate and wax synthesis. In fact, the first studies go back to the 1930s. As yet slurry processes have not been employed on a commercial scale, though Statoil recently reported on the development of a slurry-bed-based FT process [11]. The continuous separation and regeneration of the catalyst may be difficult, and erosion of both catalyst and plant may cause problems. Other drawbacks of slurry-bed reactors are the need to overcome gas-liquid mass transfer and back-mixing, as well as the long lead time and costs associated with the scaling-up of reactors of this type.

A tubular fixed-bed reactor has been chosen for the FT reaction in the SMDS HPS stage. It is inherently simple in design and operation and is proven technology in, for example, methanol synthesis. The catalyst is packed in tubes which are cooled by boiling water which surrounds them. Considerable heat can thus be removed by boiling heat transfer. The tube dimensions have to be designed in accordance with the heat that is released and the thermal stability criteria that have been defined.

HPS CATALYST

A Shell proprietary catalyst has been developed which gives a high selectivity towards heavy products, as the result of a probability of chain growth of well over 0.90 (fig. 7). Life tests in a single-tube pilot plant showed the commercial HPS catalyst to possess very good stability, with respect to both activity and selectivity. Moreover, an in-situ regeneration procedure has been developed which gives full recovery of the original performance. A useful catalyst lifetime of at least 5 years is therefore expected.

HEAVY PARAFFIN CONVERSION

The HPC is a mild trickle-flow hydrocracking process employing a Shell proprietary catalyst and operating typically at 30–50 bar total pressure and a temperature of about 300–350°C. The plant lay-out is very similar to that of a conventional gas oil hydrotreater. The HPC stage actually performs four functions:

- hydrogenation of the olefins present in the FT product
- removal of the small amount of oxygen-containing compounds, mainly primary alcohols
- hydroisomerization and
- hydrocracking of the n-paraffins to isoparaffins of the desired chain length and/or boiling range.

The HPC product is subsequently fractionated in a conventional distillation section. The product fraction boiling above the gas oil range is recycled to the HPC. By varying the process severity and/or the conversion per pass one can influence the selectivity towards a preferred product. Hence one may opt for a kerosene mode of operation, which will yield some 50% kerosene on total liquid product, or for a maximum gas oil mode, in which some 60% gas oil will be produced (see fig. 12).

5. Product quality

The products of the SMDS process are pure paraffins, free from impurities such as nitrogen and sulphur and from aromatic species. Consequently, both the kerosene and the gas oil have excellent combustion properties–smoke point and cetane number–and show very low particle emissions. Their cold-flow character-

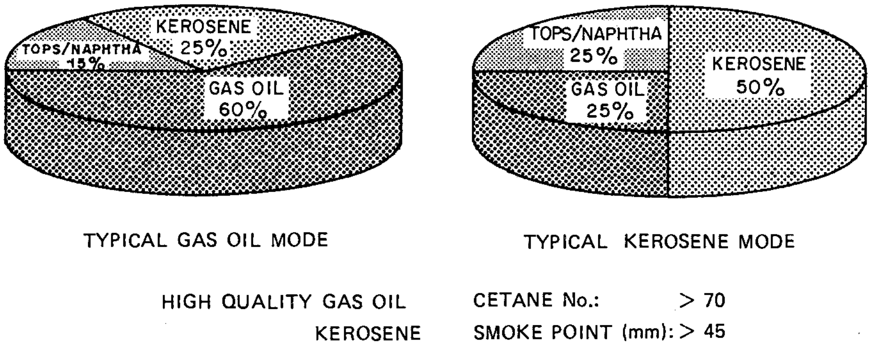


Fig. 12. Product breakdown.

istics meet all relevant specifications–even the stringent freezing-point requirements of aviation turbine fuel. The SMDS products therefore make excellent blending components for upgrading refinery fractions that would otherwise only be used in fuel oil.

The tops/naphtha fraction is equivalent in quality to "straight-run" naphtha obtained via crude-oil distillation and is suitable for blending into gasoline after its octane number has been increased by catalytic reforming. In view of its paraffinic nature it is also an ideal chemical feedstock.

The strategic decision to develop the SMDS route was based on medium-and longer-term expectations that the demand for middle distillate fuels would continue to grow while the factor "quality" could eventually place limits on the production of these transportation fuels from crude oil.

6. Environment

The production of middle distillates from natural gas has a low environmental impact (fig. 13). Off-gases from the different process units are used inside the plant for utility generation: for instance, to fire the SMR. Flue gases leaving the plant are free of SO_x and low in NO_x and fulfil the stringent European specifications.

As a general principle, process water and condensate should be re-used to minimize the discharge of waste water. The process based on partial oxidation of natural gas is, however, a net producer of water. Waste water leaving the plant would first be treated to an extent such that discharge would be permitted. In areas of water scarcity, though, this water may even be turned to advantage: for example, for irrigation purposes.

The spent catalyst will be recycled for recovery of the metallic components.

Finally, the exceptional quality of both the kerosene and gas oil manufactured via SMDS means that, if used as transportation fuels, their emission of harmful exhaust products would be very low.

7. Overall energy efficiency

The theoretical maximum thermal efficiency for the conversion of methane into paraffins is 78% (based on lower heating values). The efficiency attainable in practice is, of course, lower.

Proper heat integration means that the SMDS plant is heat-balanced: that is to say, no extra natural gas has to be burned for utility purposes. For example, the steam produced in both the SGP and the HPS processes is used in the turbines of the oxygen manufacturing plant and the different process off-gases are used to fire the SMR. As a result, the Bintulu SMDS plant will operate at an overall thermal efficiency of 63% or, in other words, 80% of the theoretical maximum.

8. Economics and outlook

Capital and operating costs of synfuel complexes are considerable and depend to a great extent on the location. The total investment for the first commercial project (12000 bbl/d Bintulu project) is about $660 million. Future plants are expected to be up to 50000 bbl/d and significant economies of scale apply in this capacity range.

For gas at US $0.5 per million BTU, the feedstock cost element in the product is about US $5/bbl. The total fixed and variable operating costs are estimated at a further US $4/bbl. The total required selling price for the product will depend on fiscal regimes, debt/equity ratio, type of loans, and corporate return requirements.

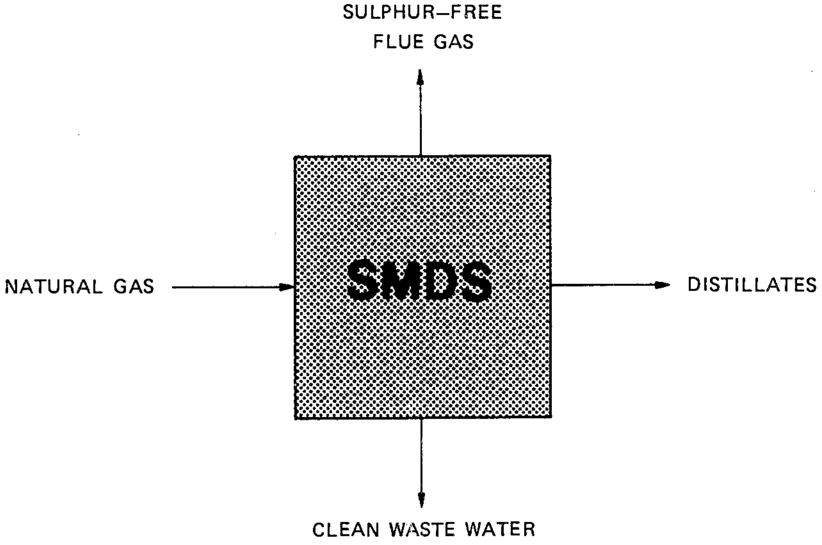


Fig. 13. Environmental aspects.

Table 4
Characteristics of SMDS process

- High overall thermal efficiency above 60%
- Flexibility kerosene/gas oil ratio 1:2 to 2:1
  kerosene + gas oil 75–85% product
- Simple process line-up, only one intermediate product
- Environmentally benign
- Self-sufficient in heat and power
- Product quality very favourable
- Synthesis catalyst selective, active and stable, allowing simple, reliable fixed-bed operation

The premium to be realized for the high-quality products is also an aspect influenced locally, which might become increasingly important as environmental pressure increases.

New process developments are very much focussed on the reduction of the costs per unit of product. For this reason, though the unit as designed for Bintulu is a full-scale commercial plant, scaling-up to still larger units is a possibility still being actively pursued.

9. Conclusions

- Natural gas feedstock and middle distillate products are well matched in terms of hydrogen and carbon content.
- The conversion package, which consists of both the syngas manufacturing technology and SMDS synthesis, is well balanced.
- At its heart is a flexible, two-stage concept to overcome the selectivity constraints of a direct Fischer-Tropsch process.
- The process is environmentally benign.
- The products are of exceptional quality and have significant environmental merits.
- The first commercial plant is under construction in Bintulu, Malaysia.
- On the basis of a number of favourable characteristics (shown in table 4) further commercial projects are to be expected.

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