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OVERVIEW OF INDIRECT LIQUEFACTION PROCESSES AND PROSPECTS

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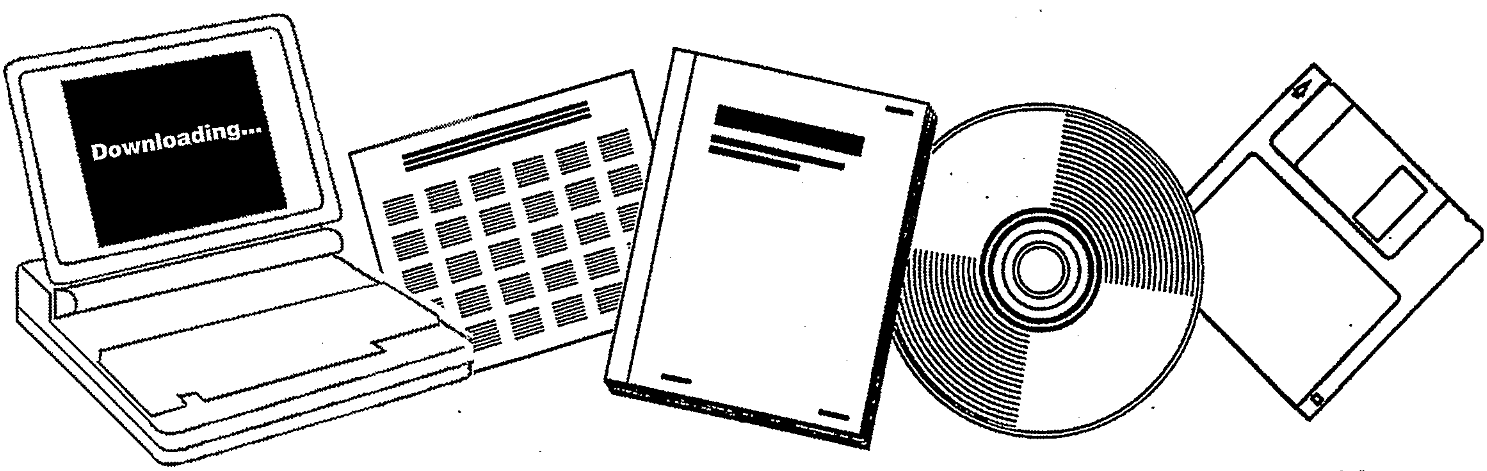

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OVERVIEW OF INDIRECT LIQUEFACTION PROCESSES AND PROSPECTS

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rrocesses for the hydrogenation of carbon monoxide have had commercial importance since about 1920, when the commercial production of methanol and higher alcohols on oxide catalysts began. Soon thereafter, Fischer and Tropsch discovered that liquid hydrocarbons could be synthesized from carbon monoxide and hydrogen over Group VIII metal catalysts. Following extensive development efforts, this technology provided Germany with a source of liquid fuels during World War II. The period following the War saw an acceleration in research and development on the Fischer-Tropsch process, but the only commerical application that was to emerge was the SASOL process in the Union of South Africa.

The oil crisis of the 1970's has rekindled worldwide interest in indirect liquefaction technologies for the production of clean, high-quality motor fuels from coal. The development of more efficient coal gasification processes and the advent of molecular sieve catalysts that allow tailoring of product distribution have set the stage for revolutionary improvements in process designs.

A brief discussion of the historical development of this 60-year-old technology is followed by more detailed descriptions of (a) the process used in South Africa; (b) the Mobil processes, based on their novel zeolite catalyst; and (c) the promising new applications that are in the R&D pipeline.

R.R. Schehl, Overview of Indirect Liquefaction Processes and Prospects, Proceedings of the Eleventh Energy [illegible] Conference, March 19-21, 1984, Washington

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INTRODUCTION

Indirect coal liquefaction refers generically to the production of liquid fuels from synthesis gas derived from the gasification of coal. Research efforts directed at the production of hydrocarbon fuels from synthesis gas date back to the turn of the century (1), but it was not until 1923, when Franz Fischer and Hans Tropsch reported that passing synthesis gas over alkalized iron catalyst produced mixtures of hydrocarbons and oxygenated compounds, that the potential of this method for producing transportation fuels from coal was fully recognized. Interest spread very rapidly, and soon catalyst development studies were conducted in the U.S., Great Britain, and Japan. With encouragement from the German government, Fischer and Tropsch actively pursued their research throughout the 1920's and were eventually led to the choice of $Co-ThO_2-MgO$-kieselguhr as the best catalyst for commercial operation. Nine Fischer-Tropsch installations were erected and put into operation in Germany during the period from 1935 to 1945. At the height of production in 1943-44, the annual output from these plants reached nearly 570,000 metric tons of primary product, or 15% of the total German synthetic fuels production. During this time the bulk of the coal-derived liquids was obtained from high-pressure direct hydrogenation. In addition to the German plants, Ruhrchemie AG licensed Fischer-Tropsch plants abroad. Before 1945, plants based on the Ruhrchemie process were operated in France, Japan, and Manchuria.

Following the Second World War, research and development activities intensified in the United States. The U.S. Bureau of Mines at Bruceton, Pa., now the Pittsburgh Energy Technology Center concentrated its efforts on the development of the [illegible] and oil-slurry Fischer-Tropsch systems, and in 1949, [illegible] based on the oil circulation process was built in Louisiana, Mo. (2). The pilot plant had a capacity of 50 to 80 barrels per day and was supplied by coal gasification. New discoveries of petroleum shortly thereafter, however, caused decreased government interest in synthetic fuels from coal, and consequently operation of the plant ceased in 1953.

Hydrocarbon Research, Inc., also made an important contribution to Fischer-Tropsch technology at about this same time with the development of a fluidized-bed process known as the "Hydrocol" process. A synthetic gasoline and by-product chemicals plant based on this process was brought into operation in 1951 in Brownsville, Tex. The plant was designed to produce about 7000 bbl/day of products from reformed natural gas. Operation of the plant was suspended in 1957 because of economics.

The German work and the early developments at the U.S. Bureau of Mines were described in great detail by Storch, Golumbic, and Anderson (3), and a more recent summary of the Bureau of Mines work has been presented by Baird et al. (4)

SASOL TECHNOLOGY

The only large-scale Fischer-Tropsch plants in operation in the world today are found in South Africa. The South African Coal, Oil, and Gas Corporation (SASOL) brought the first plant into operation in 1955. This plant, SASOL I, is located at Sasolburg, 50 miles south of Johannesburg, and, after a quarter century of operation, is still in production today.

The SASOL I technology consists of coal gasification via Lurgi dry-ash gasifiers, gas purification using Rectisol scrubbing, and hydrocarbon synthesis using two types of Fischer-Tropsch reactor systems, namely, the Synthol and Arge reactors (5). Schematics of these two types of reactors are shown in Figure 1. The Arge is a fixed-bed tubular reactor based on German technology and uses a precipitated iron-based catalyst operated at relatively low temperatures (ca. 230°C). It produces primarily higher-boiling hydrocarbons, including a range of solid waxes. The Synthol reactor is an entrained fluidized-bed unit that produces lighter hydrocarbons concentrated in the gasoline and diesel fuel range. The Synthol reactor employs a fused-iron catalyst and operates at a temperature nearly 100°C higher than the Arge. Table 1 shows a comparison of the product distributions from the two processes (6).

When the international price of petroleum was raised in October 1973, South Africa intensified efforts to cut its dependence on foreign oil imports. The decision was made shortly thereafter to build a much larger synthetic fuels plant, SASOL II. Later, when the Shah of Iran was deposed, oil imports from that country were no longer directly available, and South Africa quickly decided to build a third plant, SASOL III virtually identical to SASOL II. Since the current emphasis is on transportation fuels, only the Synthol [illegible] reactors are used in SASOL II and III. SASOL II went on [illegible] the end of 1980, and SASOL III was commissioned in 1982.

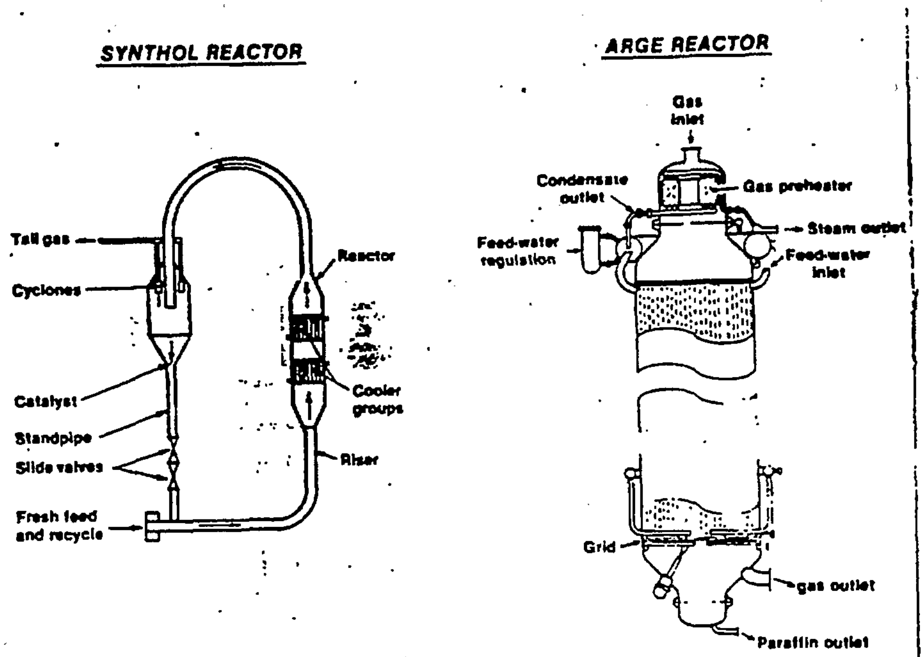

Figure 1. SYNTHOL and ARGE Reactors used for Fischer-Tropsch Synthesis

TABLE 1. Comparison of Fischer-Tropsch Product Distributions From the Synthol and Arge Processes

roduct, wt%	SYNTHOL	ARGE
CH_4	11.0	3.5
C_2H_4	4.0	0.0
C_2H_6	3.4	1.9
C_3H_6	11.4	2.6
C_3H_8	1.4	1.9
C_4H_8	9.3	2.1
C_4H_{10}	2.0	2.4
C_5-160°C	32.6	15.0
160°C-350°C	13.0	19.5
+ 350°C	5.4	48.1
Water-Soluble Oxygenates	6.5	3.0

Reference: Dry, M. E., paper presented at the International Conference on Coal Utilization, Pretoria, South Africa, August 1982.

A simplified schematic of SASOL II is shown in Figure 2. After the coal is crushed and screened, the coal fines are sent to utility boilers to produce steam and electricity for the process, and the coarse material (12-50 mm) is transferred to the gasifiers. The gasification section consists of 36 Mark IV Lurgi high-pressure gasifiers with 30 units on line and 6 on standby.

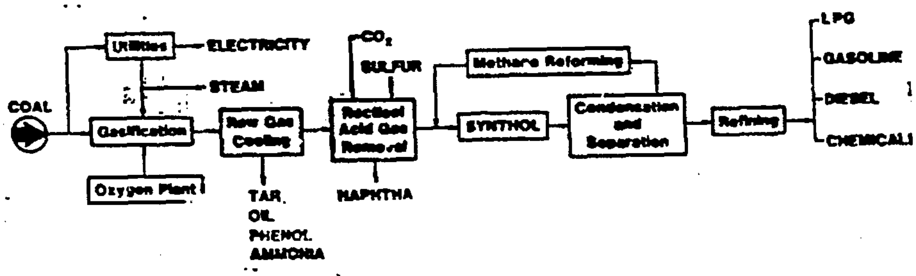

Figure 2. SASOL Fischer-Tropsch Synthesis Process

The raw gas leaving the Lurgi gasifiers is cooled; and tar, dust, oil, phenols, and ammonia present in the effluent are removed. The CO_2 and H_2S are then removed by Rectisol acid gas scrubbers; at this point, the process gas stream consists primarily of CO, H_2, and CH_4. The naphtha fractions from the gasification area and from the acid gas removal section are hydrotreated and become part of the gasoline pool. Synthol reactors are used in SASOL II to convert CO and H_2 to hydrocarbons. The choice of the Synthol over the Arge reactor was dictated by the spectrum of products desired and the ease of scale-up of the design. There are eight Synthol reactors in SASOL II. Each reactor is about 75-m high and consists of a reaction chamber containing two banks of cooling coils to remove the reaction heat, and a catalyst settling chamber. Promoted iron catalyst in powder form is made from mill scale. The catalyst is metered through special slide valves in the standpipe into the preheated feed and recycle gas stream, and is carried by entrainment to the reaction zone. The synthesis reaction takes place at a temperature of 310°C to 340°C and a pressure of 2300 kPa. Catalyst and product vapor are separated in the settling chamber, with the vapor leaving the system and the catalyst being recycled back to the standpipe. The synthesis product is then fractionated and the methane that is produced in the gasifier as well as that produced during synthesis is routed to partial oxidation reformers to provide further synthesis gas feed for the Synthol reactors. The remaining product streams go to the refinery area, where liquid petroleum gas (LPG), transportation fuels, and a variety of chemicals are made ready for distribution.

METHANOL TO GASOLINE

One shortcoming of classical Fischer-Tropsch catalysts (Fe, Co, Ru, etc.) is the lack of product selectivity. It has become recognized generally that Fischer-Tropsch reactions are governed by what is known as "Anderson-Schulz-Flory" polymerization kinetics (3, 7). Simply stated, this mechanism assumes that each hydrocarbon chain developing on the surface of a catalyst has the same probability, α, of continuing to grow by adding one more carbon. This polymerization probability is given by the following:

$$\alpha = \frac{r_p}{r_p + r_d}$$

where r_p is the rate of chain propagation by carbon addition, and r_d is the rate of desorption of the chain from the catalyst surface. Although α can be controlled, to some extent, by catalyst composition and reaction conditions, an upper limit is placed on the amount of product that can be formed within a given desired carbon number range. This is clearly illustrated in Figure 3. For a value of α in the range where gasoline or diesel selectivity is high, significant quantities of fuel gas (C_1 and C_2) and wax (C_{21}+) are also produced.

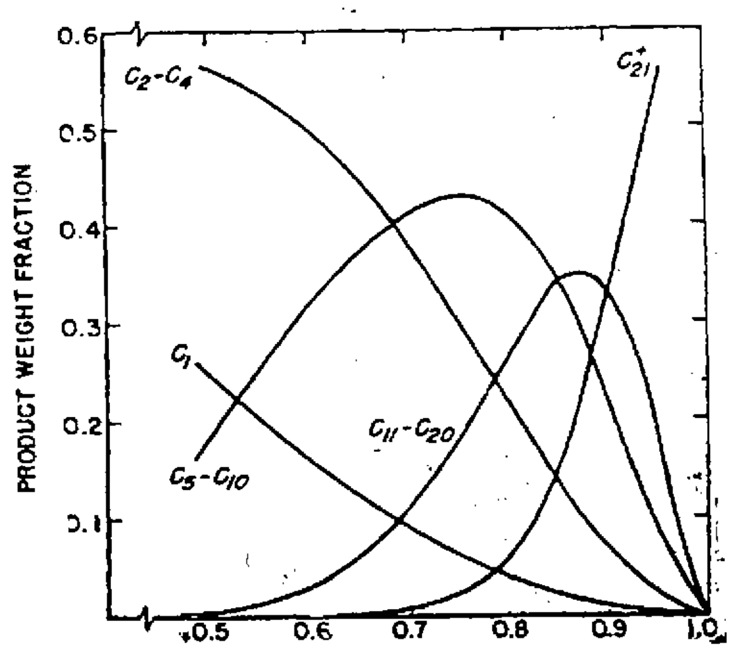

Figure 3. Effect of Polymerization Probability, α, on Fischer-Tropsch Product Distribution

With the recent discovery of a novel family of medium pore (5-6 Å), shape-selective zeolites by Mobil, an entirely new avenue was opened for the production of fuels and chemicals from synthesis gas. The most publicized member of this family, ZSM-5, converts alcohols and olefins to gasoline in high yield without rapid coking (8). The unique structural characteristics of this zeolite not only inhibit the formation of carbonaceous deposits within the catalyst pores but also restrict the formation of hydrocarbons greater than about C_{11}. Fortuitously, this corresponds very closely to the end point of the gasoline boiling range.

After having discovered the properties of ZSM-5, Mobil began work to optimize the catalyst and to develop a process to convert methanol to gasoline. These studies were continued in 1975-1976 under a DOE (formerly ERDA) contract. This work was jointly funded by DOE and Mobil. The results of this project provided data for the fixed-bed Mobil MTG process (9).

Commercialization of the MTG process is in progress. The New Zealand government has decided to build a 14,000 bbl/day liquefaction plant based on the MTG fixed-bed process (10). Natural gas from the offshore Maui Field will be steam-reformed to synthesis gas, which will then be converted into methanol and finally to high octane gasoline via the MTG process (11). About 85% of the total hydrocarbons formed from methanol fall in the gasoline range. This includes the alkylate that can be formed from the light olefins produced. The remaining product consists of LPG and fuel gas (C_1-C_2).

Mobil is also conducting process development studies on a fluidized-bed MTG process. Again, under a cost-shared contract with ERDA that began in 1976, the Mobil Research and Development Corporation designed, built, and successfully operated a 4 bbl/day fluidized-bed unit (12). Operation of the unit was so promising that soon thereafter the foundation was laid for a cooperative effort to demonstrate the process in a semiworks unit in the Federal Republic of Germany (FRG).

The fluidized-bed version of the MTG process offers several potentially significant advantages over the fixed bed. The fluidized bed allows low pressure operation (270 kPa) and, as a result of good fluidized-bed heat transfer characteristics, may be operated nearly isothermally, with no gas recycle requirements. Another important feature of the fluidized-bed catalytic reactor is that it provides for the continuous withdrawal and regeneration of catalyst so that optimal catalytic activity can be maintained. The fixed-bed MTG reactors must be taken off-stream periodically to regenerate the catalyst beds by coke burn-off. Operating conditions and product yields for the fixed-bed and fluidized-bed processes are compared in Table 2 (13).

The semiworks unit in Germany is designed to be [redacted] converting 100 to 200 bbl/day of methanol into gasoline, [redacted] began in early 1980 as a cooperative agreement between [redacted]

TABLE 2. Comparison of Operating Conditions and Product Yields For Fixed-Bed and Fluidized-Bed MTG Process

OPERATING CONDITIONS	FLUIDIZED-BED	FIXED-BED
Temperature, Avg. Bed, °C	410	-
Inlet, °C	-	360
Outlet, °C	-	415
Pressure, kPa	270	2170
Recycle Ratio, Mole	0.0	9.0
Methanol Space Velocity, WHSV	1.0	1.6
YIELDS, WT% OF METHANOL CHARGE		
Methanol + Ether	0.2	0.0
Hydrocarbons	43.5	43.6
Water	56.0	56.0
CO, CO_2, Coke, Other	0.3	0.4
HYDROCARBON PRODUCT, WT%		
Light Gas	5.6	1.4
Propane	5.9	5.5
Propylene	5.0	0.2
i-Butane	14.5	8.6
n-Butane	1.7	3.3
Butenes	7.3	1.1
C_5 + Gasoline	60.0	79.9
Gasoline (including alkylate)	88.0	85.0
LPG	6.4	13.6
Light Gas	5.6	1.4

Reference: Fitch, F. B., and Lee, W., paper presented at International Pacific Conference on Automotive Engineering, Honolulu, Hawaii, November 16-19, 1981.

Federal Ministry for Research and Technology, the U. S. Department of Energy, and three industrial partners: Mobil, Uhde, and Union Rheinische Braunkohlen Kraftstoff (URBK). The development program, scheduled to be completed in 1986, will examine two methods for removing the exothermic heat of reaction from the fluidized-bed (14). In one mode of operation, the catalyst is continuously circulated to an external heat exchanger where it is fluidized with inert gas. The catalyst, at a lower temperature, is then returned to the reactor The second mode of operation involves the direct removal of reaction heat by heat exchanger tubes submerged in the reactor fluidized-bed.

DIRECT SYNGAS - GASOLINE CONVERSION

The emergence of the methanol-to-gasoline technology [illegible] spawned the idea of combining a Fischer-Tropsch type catalyst [illegible] shape-selective catalysts, such as ZSM-5, to produce high [illegible] gasoline directly from synthesis gas. Chang et al. (15) [illegible] et al. (16) demonstrated that intimate mixture [illegible] methanol or Fischer-Tropsch synthesis catalysts are capable of producing gasoline-range hydrocarbons, high in aromatic content, in yields greater than those predicted by Anderson-Schulz-Flory polymerization kinetics. In one example, a 25% fused-iron ammonia synthesis catalyst mixed with 75% ZSM-5 increased the gasoline-range product by as much as 50% over that produced when fused-iron catalyst was tested under identical conditions but without ZSM-5 present. Furthermore, the composite catalyst produced only trace amounts of hydrocarbons greater than C_{11}. Since other experiments, conducted in such a way that the iron and zeolite were arranged sequentially, did not result in the same synergism, Caesar and coworkers (16) were led to propose that at higher temperatures, α-olefins are free intermediates in the Fischer-Tropsch reaction and are capable of readsorption on catalytic sites and of initiating new growing chains. In the presence of ZSM-5, however, these α-olefins may be intercepted by the zeolite and converted to internal olefins, aromatics, or branched aliphatics that do not readily complex with the iron sites to undergo further reaction.

Research groups have continued studies of the metal-zeolite catalyst system that are directed toward developing a better understanding of such things as the effect of method of metal incorporation with the zeolite on metal-zeolite interactions (17). The Union Carbide Corporation is also working under a cost-shared research contract with the U. S. Department of Energy to investigate the direct conversion of synthesis gas to gasoline- and diesel-range hydrocarbons using Carbide molecular sieve catalysts in conjunction with Fischer-Tropsch components (18). Two major problems remain a challenge to researchers: (a) The one-step approach necessitates that both catalyst components function at the same reaction temperature. Reported data for the MTG process would indicate that the optimum operating temperature for ZSM-5 may be 100°C to 150°C higher than temperatures used for typical Fischer-Tropsch catalysts. Thus, one is forced to compromise and operate at some intermediate temperature, which sometimes leads to excessive yields of methane and ethane and/or inefficient conversion of the reaction intermediates to high octane components by the ZSM-5. (b) Dual-functional, direct-synthesis gas conversion catalysts deactivate with use and require periodic regeneration in order to maintain useful activity. Brennan (19) demonstrated that multiple oxidative or hydrogenative reactivation was possible in a fluidized-bed system, although frequently activity and selectivity deterioriate with increasing number of regenerations. Once again, conditions required to regenerate one component of the catalyst may have adverse effects on the other component. For example, repeated high temperature coke burn-off of the zeolite component may cause irreversible deactivation of the transition metal component through sintering of metal crystallites and loss of active metal surface area.

FISCHER-TROPSCH SYNTHESIS IN SLURRY PHASE

Recent studies have indicated that second generation gasifiers [illegible] such as the slagging Lurgi or Shell-Koppers, with reduced [illegible] requirements, have the potential of producing synthesis gas [illegible] thermal efficiency and at lower syngas cost (20). This [illegible] gas, however, may have a H_2 to CO ratio of 0.5 to [illegible] synthesis, as well as the SASOL-type Fischer-Tropsch synthesis, requires a syngas ratio of about 2.0 or greater. If this syngas must be shifted to a 2.0 ratio for synthesis conversion, then much of the advantage gained in the gasification step is lost. Consequently, there is a strong incentive for developing catalysts and reactor systems capable of directly converting low ratio synthesis gas to liquid hydrocarbons. The three-phase slurry reactor (21, 22), first investigated by the Germans during the 1930's, appears to satisfy this requirement. The three-phase reactor is essentially a bubble column in which the Fischer-Tropsch catalyst particles are suspended in a molton wax and the synthesis gas is bubbled through the suspension. Excellent temperature control is provided by the high heat capacity and thorough mixing of the slurry. Coupled with appropriate catalysts having both Fischer-Tropsch synthesis and water-gas shift activity, the slurry reactor is capable of processing low H_2/CO ratio syngas without the rapid catalyst deactivation that is observed in vapor phase systems.

Air Products and Chemicals, Inc., is exploring the application of three-phase reactors to the synthesis of both hydrocarbons and methanol. In one project (23), jointly funded with the U. S. Department of Energy, a 35 bbl/day unit located in La Porte, Tex. will soon go into operation to provide engineering scale-up data for a liquid phase process developed by Chem Systems, Inc., to convert synthesis gas to methanol. A second project (24), also jointly funded with the U. S. Department of Energy, involves the application of new catalytic materials to three-phase Fischer-Tropsch synthesis with the objective of improving the yield of gasoline- and diesel-range hydrocarbons.

The advantages of the three-phase reactor led the Mobil Research and Development Corporation to investigate the feasibility of converting low H_2/CO ratio synthesis gas to high octane gasoline in a two-stage process, using a slurry phase Fischer-Tropsch reactor in the first stage, followed by an upgrading reactor containing a ZSM-5 class catalyst (25). Mobil is currently conducting this study, under a jointly funded contract with the U. S. Department of Energy, with a slurry bubble-column reactor (5.2-cm-diameter x 7.6-m-tall), followed by a fixed-bed reactor containing the zeolite upgrading catalyst (26). Heavy hydrocarbons (C_{12}^+ liquid) produced in the slurry reactor are effectively converted to lower boiling range material, and significant amounts of aromatics are formed in the second-stage reactor. This approach offers the advantage of allowing the Fischer-Tropsch catalyst and the zeolite catalyst to be operated at their preferred process conditions. An additional advantage is that each catalyst could be regenerated, as required, under its own optimum conditions.

The slurry-phase reactor also appears capable of high diesel oil yields if operated under conditions such that a large fraction of the product boils above 350°C. Recent studies at SASOL indicate that as much as 87% of the total upgraded C_5+ product can be diesel oil with a cetane number of 67 (6). The diesel fraction consists of straight run diesel, oligomerized C_3 to C_6 olefins, and hydrocracked wax. Thus, by varying the upgrading process configuration and/or processing conditions, high degree of product flexibility [illegible] octane gasoline vs. high cetane diesel oil) is seen to be possible with the two-stage concept.

SUMMARY

It has been 60 years since Fischer and Tropsch found that H_2 and CO could be reacted catalytically to form liquid hydrocarbons. The technology has advanced over the years, usually in surges brought about because of strategic or emergency circumstances. Motivated by Middle East crises and escalating costs for crude petroleum, great strides have been made in the last decade toward improving process thermal efficiency and selectivity to high-quality transportation fuels. New indirect liquefaction technology based on shape-selective zeolites is ready for commercialization, given the proper economic climate, and R&D programs now underway promise even more attractive routes from coal to motor fuels.

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