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TRANSPORTATION FUELS FROM INDIRECT COAL LIQUEFACTION

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ABSTRACT

Coal can be converted to liquid fuels via three generically defined technologies: pyrolysis, direct hydroliquefaction, and indirect liquefaction. This paper presents a general overview of the indirect liquefaction technology and a discussion of processes that are commercially available as well as those in the development stage. Finally, the objective of the DOE research and development program in conversion of synthesis gas derived from coal to transportation fuels is summarized.

TECHNOLOGY BACKGROUND

Indirect coal liquefaction is distinguished from other methods of producing coal-derived liquids in that the coal structure is first essentially destroyed through steam-oxygen gasification to produce synthesis gas (hydrogen plus carbon monoxide). The synthesis gas thus produced can then be converted to chemicals, gaseous fuels, or clean liquid transportation fuels by a variety of catalytic processes. A generalized block diagram of various indirect liquefaction routes is shown in Figure 1.

The genesis of indirect liquefaction is considered to be the work of Sabatier and Senderens in 1902.[1] They reported the synthesis of methane from hydrogen-carbon monoxide and hydrogen-carbon dioxide mixtures over reduced nickel catalyst at temperatures between 473° and 573°K. More than a decade later, Badische Anilin and Soda Fabrik (BASF) observed that alkalized cobalt and osmium oxides catalyzed the reaction of carbon monoxide and hydrogen to produce mixtures of aliphatic hydrocarbon and oxygenated products.[2] After an interruption caused by the 1914-1918 European conflict, BASF continued their research efforts and in 1923 disclosed a process for synthesizing methanol from synthesis gas to the exclusion of other products. This high pressure process (20,000-35,000 kPa) was first put to commercial use at Leuna, Germany, and until 1966, was the basis for all commercial methanol plants. Imperial Chemical Industries, Ltd., (ICI) introduced their low pressure (5,000-10,000 kPa) methanol synthesis process in 1966.[3] The more active ICI copper-zinc-chromium catalyst resulted in lower capital and operating costs than did the BASF zinc-chromium based catalyst.

Research directed at the synthesis of higher molecular weight hydrocarbons was first reported by Franz Fischer and Hans Tropsch in 1923 as a result of several years work at the Kaiser Wilhelm Institut für Kohlenforschung.[4] The product they obtained at 10,000-15,000 kPa and 673°-723°K using an alkalized iron catalyst consisted primarily of oxygenated compounds with a very small quantity of hydrocarbons. It was subsequently found that operation at lower pressures (700 kPa) shifted the product distribution to chiefly aliphatic hydrocarbons. At that time, the German government was highly interested in the production of synthetic motor fuel, and Fischer and Tropsch actively pursued their research throughout the 1920's and reported their findings on a number of catalyst systems. During this time, interest in the possibility of synthesizing motor fuels spread, and Smith and coworkers at the U.S. Bureau of Mines performed tests a using synthetic-ammonia catalyst (fused iron oxide promoted with potassium and aluminum oxides).[5] By the late 1920's, catalyst development studies were also being conducted by the British and Japanese.

Significant advances were made in the development of Fischer-Tropsch catalysts a few years later with the preparation of the nickel-thoria-kieselguhr and the cobalt-thoria-

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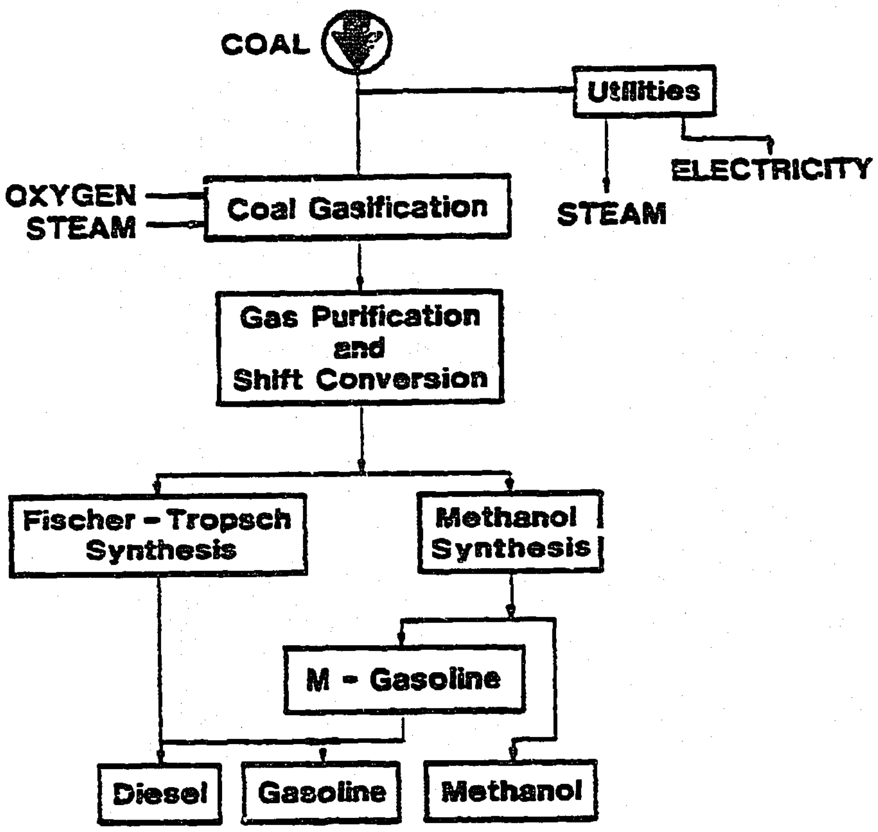

Figure 1- Generalized indirect coal liquefaction process.

kieselguhr catalysts. An intensive catalyst development program in Germany in the period 1933-1939 resulted in the choice of Co-ThO_2-MgO-kieselguhr (100:5:8:200 parts by weight) as the best catalyst for commercial operation. The first large-scale Fischer-Tropsch plant was brought into operation by Ruhrchemie at Sterkrade-Holten about 1935. Nine Fischer-Tropsch installations were erected and put into operation in Germany in the period from 1935 to 1945. All of these plants were of the Ruhrchemie type operating at either normal pressure or medium pressure (100 kPa) and temperatures of 453°-473°K. 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. The product slate was reported to consist of approximately 46% gasoline, 23% diesel oil, 3% lubricating oil, and 28% waxes, detergents, and synthetic fat and oil.[6] The bulk of the coal-derived liquids at this time were obtained from high-pressure direct hydrogenation. Intensive Allied bombing raids between May and October of 1944 resulted in almost complete destruction of the nine Fischer-Tropsch plants (only three of the plants could be put back into operation). A plant in Bergkamen continued operation after the war under Schering AG until it was shut down in March 1962 due to economic considerations.

In addition to the German plants, Ruhrchemie AG also licensed Fischer-Tropsch plants abroad. Before 1945, plants based on the Ruhrchemie process were operated in France (one plant), Japan (four plants), and Manchuria (one plant) and had a total production capacity of 340,000 metric tons of primary products per annum.

In April 1944, the U.S. Congress enacted the Synthetic Liquid Fuels Act, which commissioned the Department of the Interior, more specifically, the U.S. Bureau of Mines, to conduct laboratory and pilot plant studies that would hopefully lead to the construction of demonstration plants and the subsequent development of a synthetic liquid fuels industry in the United States. Extensive research was carried out at Bruceton, PA, now the Pittsburgh Energy Technology Center of the U.S. Department of Energy, during the period of 1944 to 1949. Studies were concentrated on the oil-circulation and oil-slurry Fischer-Tropsch systems, and in 1949 a pilot plant based on the oil-circulation process was built in Louisiana, MO.[7] This plant had a capacity of 50 to 80 barrels per day and was supplied by synthesis gas produced by the gasification of coal. New discoveries of petroleum in the United States, Canada, and Middle East, however, caused decreased government interest in synthetic fuels from coal, and consequently operation of the plant ceased in 1953. Research on Fischer-Tropsch synthesis continued at the Bureau of Mines' Bruceton station until about 1960. This work has recently been summarized by Baird et al.[8]

With financing from several petroleum companies, a synthetic gasoline and by-product chemicals plant using a fluidized-bed Fischer-Tropsch converter was brought into operation in 1951 in Brownsville, Texas. The plant, known as the Carthage Hydrocol, was designed by Hydrocarbon Research, Inc., to produce about 7,000 bbl/day of products from reformed natural gas. Scale-up problems plagued the plant from the beginning, and the modification required to reach design conditions was considered too costly in view of the availability of cheap petroleum at that time. The complex finally suspended operations in 1957.

SOUTH AFRICAN TECHNOLOGY

The only commercial operation that produces hydrocarbons from synthesis gas today is found in South Africa. The South African Coal, Oil, and Gas Corporation (SASOL) brought the plant into operation in 1955. This plant, SASOL I, is located at Sasolburg, 50 miles south of Johannesburg.

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.[9] The Arge reactor is a fixed-bed system developed by Lurgi in West Germany. It produces primarily higher-boiling hydrocarbons, including a range of solid waxes. The Synthol reactor is an entrained fluid-bed unit that produces lighter hydrocarbons concentrated in the gasoline and diesel fuel range. The Synthol reactor was designed by M.W. Kellogg in cooperation with Uhde of West Germany and built by Kellogg.

Although SASOL I has been in production for 25 years, operation of the plant has not always been without difficulties. When first started up, the Synthol reactors did not function as designed. It required five years for SASOL to develop better catalysts and modify the reactors before they could be brought into reliable commercial production. A third Synthol unit was later added. SASOL has also significantly refined the Lurgi gasifiers.

When the international price of oil 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. SASOL II and III, which are based on SASOL I technology, are located in Secunda, about 90 miles east of Johannesburg. The Fluor Corporation of California is managing the construction of these plants, which are reported to cost a total of $ 7 billion.[10] Since the current emphasis is on the production of transportation fuels, only the Synthol-type reactors are used in SASOL II and III. SASOL II went on stream at the end of 1980, and SASOL III is scheduled to be commissioned in late 1982.

A simplified schematic of SASOL II is shown in Figure 2. After coal crushing and screening, the coal fines are sent to the utility boilers to produce steam and electricity for the process while 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. Oxygen is supplied to the gasifiers by six air separators designed by L'Air Liquide. With the capability of delivering more than 12,000 tonne/day, this is the largest oxygen facility in the world.

The raw gas leaving the Lurgi gasifiers is cooled, and the 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 fraction from the gasification area and from the acid gas removal section is hydrotreated and becomes 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 8 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 a 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° 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

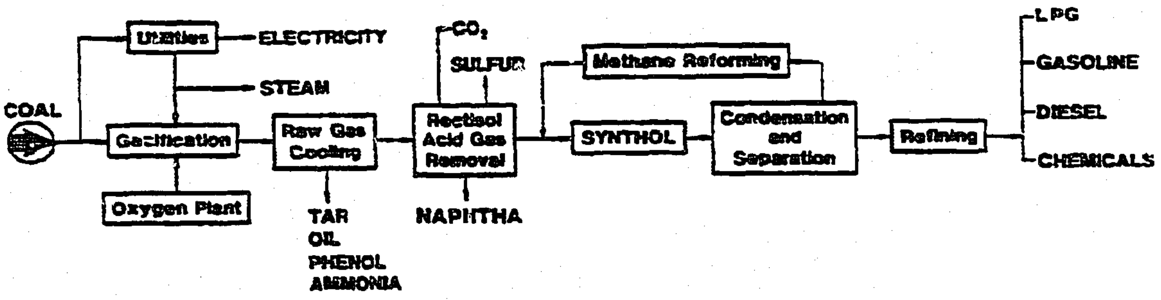

Figure 2- SASOL Fischer-Tropsch synthesis

fractionated and the methane that is produced in the gasifiers 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 LPG, transportation fuels, and a variety of chemicals are made ready for distribution.

MOBIL TECHNOLOGY

With the recent discovery of a novel family of medium-pore (5-6Å), shape-selective zeolites by Mobil, an entirely new approach to the production of fuels and chemicals from synthesis gas was made available. The most publicized member of this family, ZSM-5, was found to convert alcohols and olefins to gasoline in high yield without rapid coking.[11] 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 the process to convert methanol to gasoline. These studies were continued in 1975-1976 under 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 M-Gasoline process. The methanol-to-gasoline reaction is highly exothermic (approximately 1700 kJ/kg of methanol converted), and in order to control catalyst temperature, special precautions must be taken. The crude methanol is first partially dehydrated to an equilibrium mixture of methanol, water, and dimethylether in a first stage reactor, liberating a portion of the total heat of reaction (Figure 3). The

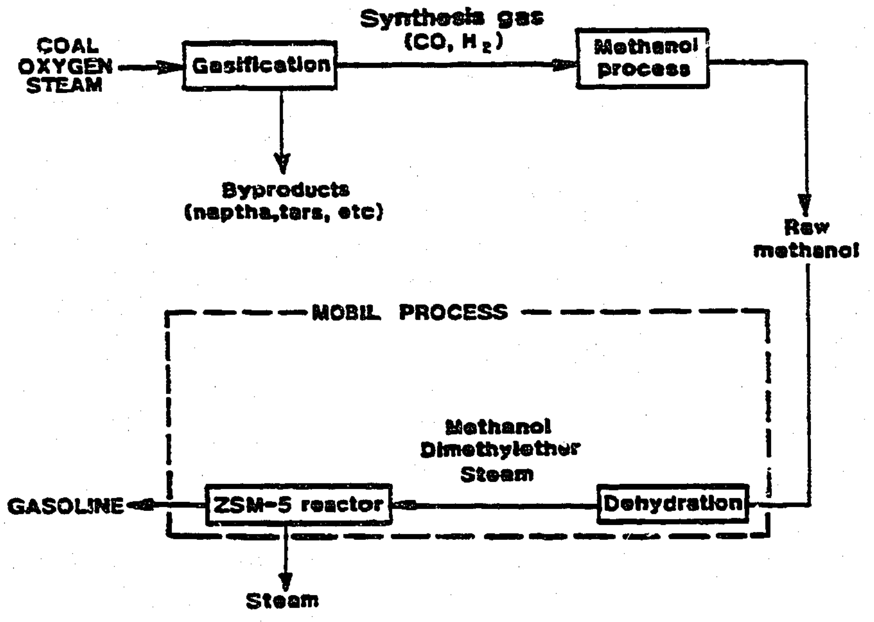

Figure 3- Mobil m-gasoline process .

second stage reactor, containing ZSM-5 catalyst, then converts the methanol and dimethylether to hydrocarbons and water. The temperature rise in the second reactor is controlled by recycling light product gases back to the reactor inlet. About 85% of the total hydrocarbons formed fall in the gasoline range. This includes the alkylate formed from the light olefins that are produced.

The remaining hydrocarbon product consists of liquid petroleum gas (LPG) and fuel gas (C_1-C_2).

The New Zealand government has decided to build a 13,000 bbl/day plant based upon the M-Gasoline fixed bed process.[12] New Zealand plans to utilize its abundant supply of natural gas as feedstock to the plant. The natural gas will be steam reformed to synthesis gas, which will then be converted to methanol and finally to high octane gasoline.

U.S. DEPARTMENT OF ENERGY RESEARCH AND DEVELOPMENT PROGRAM

The production of liquids from coal <u>via</u> indirect liquefaction has gained new interest in this country as a result of recent technical discoveries and improvements in gasification technology and in low pressure methanol synthesis catalysts, and of Mobil's discovery of a process for converting methanol to high octane gasoline.

Reflecting this renewed interest in indirect liquefaction, the Department of Energy has formulated a research program directed at developing improved processes to convert synthesis gas from coal to high quality transportation fuels.[13] The program activities fall within three general areas:

1. Improved integration of the gasification step with the liquefaction step. Recent studies have indicated that second generation gasifiers, such as the Slagging Lurgi or Shell-Koppers, with reduced steam requirements, have the potential of producing a synthesis gas at higher thermal efficiency and at a lower syngas cost.[14,15] This synthesis gas, however, has a H_2 to CO ratio in the range of 0.6 to 0.7. Methanol synthesis as well as 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 strong incentive for developing catalysts and reactor systems capable of directly converting low ratio synthesis gas to liquid hydrocarbons.

2. Increased yield of premium transportation fuels through use of shape-selective catalysts. "Classical" Fischer-Tropsch catalysts yield a broad spectrum of products ranging from methane to solid waxes. For the U.S. market, extensive product upgrading would be required in order to improve the quality and/or yield of transportation fuels. Mobil's Methanol-to-Gasoline process is one route to the production of high quality liquids in high yield. Studies have also shown that shape-selective catalysts may be used to convert synthesis gas directly to gasoline.[16] Catalysts of this type possess both a CO reduction function and a zeolite to restrict the product molecular size. Another alternative for increasing gasoline yields is to use shape-selective catalysts in a second stage "refining" step that is coupled to a "standard" Fischer-Tropsch synthesis unit.

3. Development of improved thermally efficient synthesis reactors. The conversion of synthesis gas to hydrocarbons and oxygenates is a highly exothermic reaction, and careful control of reaction temperature is necessary to prevent excessive formation of light gas (C_1 and C_2) and to avoid rapid deactivation of the catalyst. The three-phase slurry reactor,[17] first investigated by the Germans during the 1930's, offers attractive alternatives to the gas-phase

reactors now employed for methanol synthesis and at SASOL. The excellent temperature control provided by the slurry reactor enables high single-pass conversions, thus reducing recycle requirements; results in reduced yield of methane and ethane; and inhibits deactivation of the catalyst by coke formation. Coupled with the appropriate catalyst, the slurry reactor is expected to be capable of processing low H_2/CO ratio synthesis gas without the rapid catalyst deactivation that is observed in vapor phase systems.

CONCLUSION

The current outlook for indirect liquefaction is encouraging. New facilities are being built in South Africa and New Zealand, and commercial plants could be designed and built for operation in the United States using proven technology. At the same time, developments in gasification as well as liquefaction catalyst and reactor technology promise significant improvements in indirect liquefaction processes in the years to come.

DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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