2. LIQUEFACTION

This is the process of converting coal from a solid material to a hydrocarbon liquid. In the process the ash (mineral matter) in the coal is removed and there is also a reduction in the sulfur, nitrogen and other undesirable elements in the final products when compared to the original coal. The spectrum of products that is produced depends on the process used. In all cases the ratio of hydrogen to carbon is higher in the coal-derived liquid fuels ready for market than it is in the starting coal.

Indirect liquefaction starts with breaking down of the coal, using steam and oxygen in a gasifier, to produce a synthesis gas that is a mixture of hydrogen and carbon monoxide. The synthesis gas can then be converted to methanol or hydrocarbon liquids over a suitable catalyst. In the case of methanol a further reaction step can be added to process it into hydrocarbons—mainly gasoline.

By contrast, direct liquefaction breaks down the coal structure only as far as is necessary to produce the desired liquid hydrocarbon products. Hydrogen, generated in a gasifier, is added to the coal and recycled liquid slurry at elevated temperatures and pressures. Product recovery yields gaseous, liquid and solid products which are further refined. Some of these materials are recycled.

The technologies of both indirect and direct liquefaction have, with a few exceptions, been known since the early part of this century. While the manufacture or gasoline and diesel fuels from coal did not come to a high degree of fruition in Germany until the war years, the inventions on which this technology is based go back to 1913.[R] By 1927, three methods of coal liquefaction had been developed in Germany:

- The Bergius and Pier process (coal hydrogenation),
- The Pott-Broche process (hydrogen donor), and
- The Fischer-Tropsch process (hydrocarbon synthesis).

Aside from low-temperature carbonization and hydrolysis processes, these three basic processes comprise virtually all the technical possibilities of coal liquefaction. All other processes developed in recent times are based on one of these three fundamental techniques.

The basic aim of the process developed by Bergius and Pier was the production of motor fuels. Essentially, the process is carried out in two stages: the liquid phase hydrogenation of coal and the vapor phase hydrogenation of coal liquids. In the initial hydrogenation stage, coal is finely crushed, dried and mixed to form a paste with a medium-heavy oil mixture (recycled oil) which is generated in the process itself. In addition, certain catalysts are added to assist the hydrogenation process. Hydrogenation is brought about by adding hydrogen gas at high pressure and at a temperature of about 480°C (900°F). This produces gases (chiefly hydrocarbon gases), straight-run gasoline and medium and heavy oils. The straight-run gasoline and the medium oils are further processed in a vapor hydrogenation stage in a pressurized hydrogen atmosphere, again in the presence of catalysts. The main product is gasoline, but the process can also be operated in such a way that larger proportions of the end product consist of heavy or light fuel oils.

As in the Bergius-Pier process, the process of coal extraction developed by Pott and Broche is also based on the principle of hydrogenation, although it makes use not of hydrogen under pressure but of a solvent which contains disposable hydrogen which can be transferred to the coal. This produces a pitch or tar-like extract which becomes liquid at about 180°C (360°F). When the mineral components of the coal have been separated by filtration, a product is obtained which is low in sulphur and can be burned in power stations as heavy fuel oil.

The Fischer-Tropsch process of hydrocarbon synthesis works on a completely different principle. In the extraction and hydrogenation processes, coal is broken down slowly; by the splitting of the large coal molecules and the simultaneous addition of hydrogen, smaller and smaller hydrocarbon molecules containing more and more hydrogen are gradually formed. In the Fischer-Tropsch process, the coal is first of all completely broken down and converted into very small molecules.

Technically, this is achieved by gasification of the coal with oxygen and steam at temperatures in excess of 1000°C (1830°F). The "synthesis gas" thus produced contains chiefly carbon monoxide (CO) and hydrogen (H_2), the basic elements of hydrocarbon synthesis. It is again possible, by the use of certain catalysts, under pressure and at relatively low temperatures, to bring about the selective combination of these basic elements to form light or even heavy hydrocarbons, fuels and raw materials for the chemical industry.

By far the most widely used technique employed in the German hydrogenation plants was the Bergius-Pier process. Germany had a total of 12 plants with an output capacity of 4 million tonnes (4.4 million tons = 30 million barrels) of liquid fuel (1943/44). As early as 1927, the first plant in Leuna was producing an annual quantity of 100,000 tonnes (110,000 tons) and was later extended to produce a total of 650,000 tonnes/yr (715,000 tons/yr). The territory of the present Federal Republic of Germany contained the Scholven and Gelsenberg plants with capacities of 200,000 tonnes (220,000 tons) based on lignite and Welheim near Bottrop producing 180,000 tonnes (200,000 tons) from coal tar. In addition, one plant each was built in the United Kingdom, Japan and France. The nine German Fischer-Tropsch plants had a combined annual output capacity of only 600,000 tonnes (660,000 tons = 4.4 million barrels).

Interest in these technologies revived strongly after the 1973 oil crisis and there are now many projects being pursued in the United States and abroad. This chapter examines some of the foreign technologies (or U.S. technologies being used in other countries) that are moving towards commercialization and for which information is available.

The first section covers the synthesis part of indirect liquefaction. The gasification, gas purification and shift reactions were not specified as part of this study. The second section deals with direct liquefaction processes while the third section focuses on gasifiers that have been suggested as hydrogen producers for various direct liquefaction flow schemes. These same gasifiers could be used to generate synthesis gas for indirect liquefaction.

2.1 Indirect Liquefaction

The best known indirect liquefaction process is that of gasification followed by Fischer-Tropsch synthesis. This is used by Sasol Ltd. at Sasolburg (Sasol One) and Secunda (Sasols Two and Three) in South Africa. Because of the amount of material that is available on Sasol's experience it was covered in a separate report to Oak Ridge National Laboratory by T. David Pay of Gilbert/Commonwealth, *Foreign Coal Liquefaction Technology Survey and Assessment. Sasol - The Commercial Experience,* ORNL/Sub-79/13837/4, November 1980.

The conversion of coal into hydrogen and carbon monoxide using gasification is a technology that has been known for a long time. So has the technology for producing methanol from synthesis gas. However, the emphasis in this section is on the newer, lower-pressure processes that have been in commercial use for only ten years or so. Interest in methanol synthesis has increased because methanol is now being given serious consideration as a fuel in its own right, as an extender of gasoline and as a raw material that can be converted into gasoline. This last option was made possible by the discovery by Mobil Corporation of a class of shape-selective, zeolite catalysts that allow conversion of methanol directly into high grade gasoline.

Other indirect liquefaction routes have been technically feasible since the early part of this century when the catalytic synthesis stage of the process was discovered. Work by Sabatier and Senderens in 1902 led to the synthesis of methane with reduced nickel catalyst, and similar work by Badische Anilin and Soda-Fabrik, A.G. (BASF) synthesized a liquid containing alcohols, ketones, aldehydes, fatty acids and aliphatic hydrocarbons using high-pressure catalysis. When Franz Fischer and Hans Tropsch published their work on the synthesis of oxygenated hydrocarbons, attention quickly focused on the ability of the Fischer-Tropsch (F-T) reaction to selectively produce hydrocarbons in the gasoline-boiling range. By using lower pressures and temperatures than in the BASF process, Fisher and Tropsch were able to shift production away from oxygenates towards hydrocarbons. Work on F-T catalysts continues in many parts of the world as does work on other hydrocarbon synthesis routes that may provide more selectivity for desired products.

2.1.1 Methanol synthesis

2.1.1.1 Process Licensers

1) Lurgi Kohle and Mineraloeltechnik GmbH (Low pressure system) (Germany)
2) ICI (Low-pressure system) (United Kingdom)
3) Mitsubishi Gas Chemicals Corporation (Low-pressure system) (Japan)
4) Chem Systems (Liquid-phase methanol synthesis) (U.S.)

2.1.1.2 Status/History

In the original high-pressure methanol synthesis process, pressures of 30 MPa (4350 psi) at 200°C (390°F) were used in the presence of a zinc-chromium oxide catalyst, and yields of over 60 percent were obtained. In 1968 Imperial Chemical Industries (ICI) of the United Kingdom developed a low-pressure process using 5 MPa (725 psi) at 250°C (480°F) and a highly selective, copper-based catalyst.[1] Methanol processes are offered by several companies: Vulcan-Cincinnati (U.S.), ICI (U.K.), Lurgi (Germany), Mitsubishi (Japan), Nissui-Topsoe (Japan and Denmark), and Selas-Polimex (Poland). In recent years, contract awards have been dominated by ICI and Lurgi. The ICI process is used in about 26 plants and the Lurgi process is used in 15 in operation or under construction. A recent development in this field is the Chem Systems' liquid-phase methanol synthesis. However, this process is commercially unproven.

?.1.1.3 Reactants and Operating Conditions

Synthesis gas which has a ratio of H_2/CO of slightly greater than two can be obtained by natural gas reforming or coal gasification. The operating conditions for high and low pressure processes are shown in Table 2.1.

Table 2.1 Operating conditions for methanol synthesis

	High-pressure process	Low-pressure process
Temperature, °C	350	300
°F	660	570
Pressure, KPa	5,300 - 10,000	450 - 5,300
psi	2,900 - 4,350	725 - 1,450

2.1.1.4 Catalyst

High-pressure process: catalyst containing zinc oxide and chromic oxide in various proportions with or without other metal oxides as promoters. Low-pressure process: copper-based catalyst.

2.1.1.5 Products

The outlet gas from the methanol synthesis reactor contains about 5.5 mole % methanol together with large amounts of unreacted CO, CO_2, and H_2; inerts such as N_2, argon, and CH_4; and some quantities of byproducts such as water, dimethyl ether and higher alcohols.[2]

2.1.1.6 Description[2]

Figure 2.1 shows a two-step process flow diagram for producing methanol from either coal or natural gas. For both routes, the two steps are commercially proven.

Synthesis gas from the first step (coal gasification or steam reforming, shift conversion, and acid gas removal) is passed through desulfurizer drums containing activated carbon, which act as a sulfur guard for the methanol synthesis catalyst. The ICI process uses zinc oxide for this function.

From the desulfurizer drums, the gas enters the synthesis makeup compressor, and is compressed to high pressure. The discharge gas from the compressor is combined with recycle synthesis gas and cooled in an air cooler to 55°C (130°F). The feed gas then enters the synthesis loop which consists of a synthesis converter, heat exchange train, and recycle compressor. In the ICI process loop, the gas is divided with a portion of the gas being sent as quench for the converter and the remainder being sent as feed to the converter. In order to achieve the temperature necessary for reaction to methanol, the feed gas is first passed through the converter feed preheater, where the gas is heated by hot reactor effluent.

The preheated feed gas enters the top of the converter vessel and flows downward through several catalyst beds to the converter outlet. At the exit of each catalyst bed, cold quench is injected to control the temperature of the material entering the next catalyst bed.

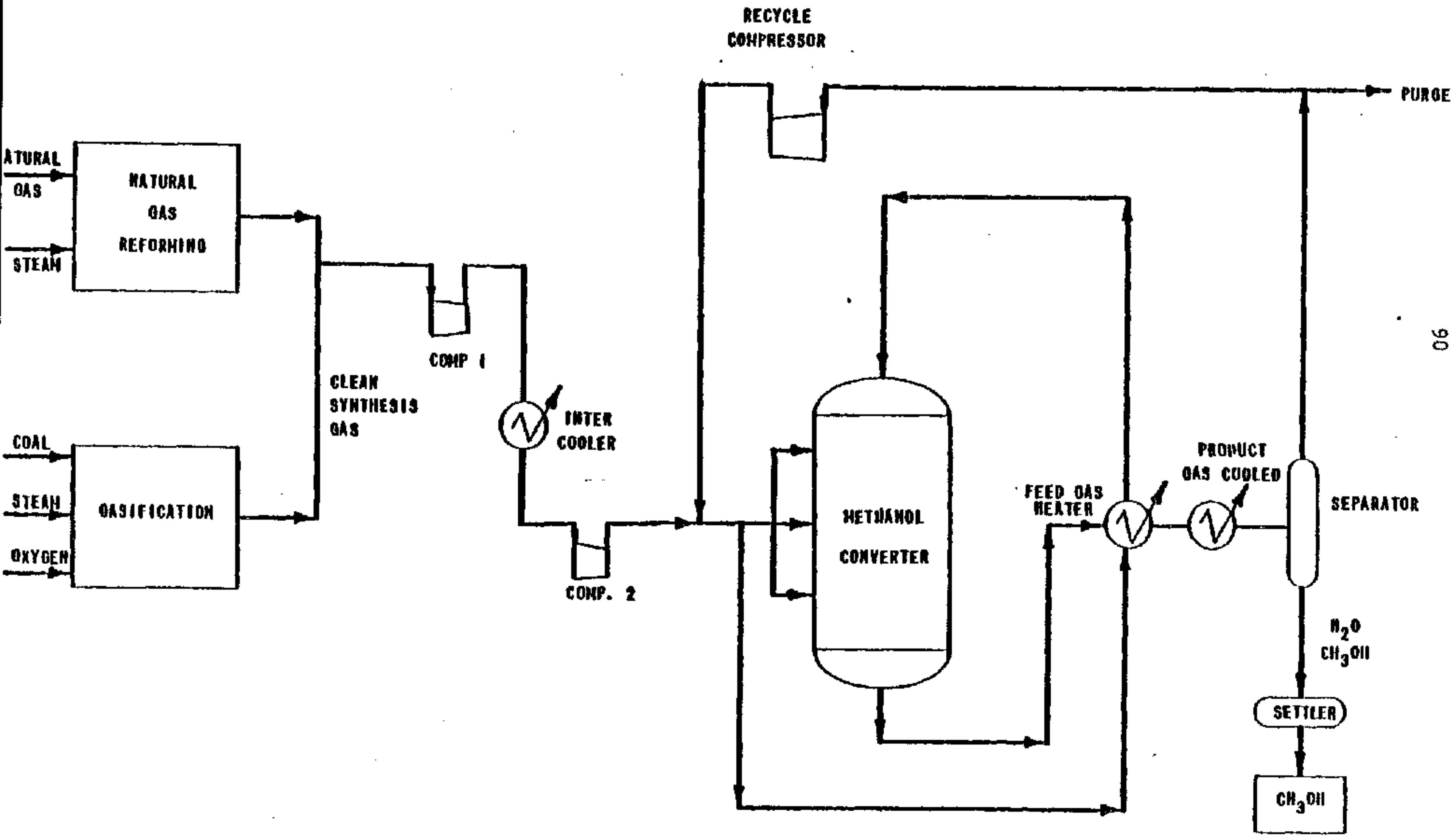

FIGURE [illegible].1
METHANOL FROM COAL OR NATURAL GAS

The outlet gas is cooled in a heat exchanger train. The two-phase mixture is separated and the unreacted gases are sent to the recycle compressor. The condensed liquid contains methanol and water.

In the Lurgi process which utilizes a tubular type converter, the conditions are isothermal in the reactor. Boiler feed water flows around the catalyst tubes and vaporizes to form medium pressure steam. The reactor temperature is controlled by adjusting the steam pressure.[3]

2.1.1.7 Process Features

Advantages:

1. The coal-to-methanol step, precursor to Mobil's methanol-to-gasoline scheme, is considered proven technology.

2. Thermal efficiency is higher than Fischer-Tropsch synthesis even if the methanol is processed into gasoline.[3]

2.1.1.8 Disadvantages:

1. Possibly lower overall thermal efficiency than direct hydroliquefaction processes, but product quality is high.
2. Problems with consumption in motor cars such as corrosion, starting difficulties and possible absorption of water.

Foreign Interest

Automotive use of methanol is getting strong attention abroad. Volkswagen of Germany has sponsored automotive fleet tests on methanol use and the results have been encouraging. This work has primarily been involved with blending up to 15 percent methanol into gasoline.[4] Many other countries are considering using methanol as an automotive fuel either by itself or as a gasoline extender.

2.1.2 Methanol-to-gasoline

2.1.2.1 Process name - Mobil MTG (methanol-to-gasoline)

2.1.2.2 Developer - Mobil Research and Development Corporation, Paulsboro, New Jersey

2.1.2.3 Status/History

Bench scale process research was initiated in 1975 and 1976 with 1.3 inch internal diameter fixed bed and 1.6 inch internal diameter fluidized bed units. From 1976 to 1978 process demonstration unit studies were performed with 1 BPD fixed bed and 4 BPD fluid bed process demonstration units.[5] Mobil is also developing a heat-exchanger-type tubular reactor[7,8] as a means of controlling the temperature rise during this exothermic reaction. A four-year plan to construct and operate a 100 BPD (barrel per day) of gasoline fluidized bed unit has been proposed to demonstrate scale-up. The U.S. Department of Energy and the West German government have completed an agreement in which a catalyst plant will be in the U.S. and the 100 bbl/Mgasoline/day pilot plant in Wesseling, West Germany.[6] Also, the government of New Zealand has decided to pursue the Mobil MTG Process. On April 1, 1980, Mobil Corporation and New Zealand's Petrocorp entered into an agreement whereby Mobil will build a 530,000 tonne/year (583,000 ton/yr = 5×10^6 barrel/hr) (gasoline) synthetic fuel facility costing about $500 million. The methanol would be manufactured from offshore natural gas.

Reactants and Operating Conditions

Crude methanol with up to 17% H_2O can be utilized.[8] Synthesis gas required to produce methanol can be obtained by hydrocarbon gas reforming and oil or coal gasification. Operating conditions for the MTG fixed-bed and fluidized-bed reactors are given in Table 2.2.

Catalyst[6]

Mobil's patented ZSM-5 class of zeolite catalysts (family of crystalline aluminosilicates) are used in a fixed-bed or fluidized-bed. The channel structure in the zeolite catalyst is important in limiting the size of the product to hydrocarbons in the gasoline range.[4] The catalyst used in the first stage of the process (conversion of part of the methanol to dimethyl ether) differs from the zeolite used in the gasoline production stage.

Table 2.2 Operating conditions for the methanol-to-gasoline process

	Fixed-bed	Fluid-bed
Inlet temperature, °C	360	
°F	680	
Outlet temperature, °C	415	
°F	780	
Average bed temperature, °C		410
°F		770
Pressure, MPa	2.0-2.1	
psi	290-305	
Recycle ratio (mole)	7.0-9.0	<<7.0
Space velocity, WHSV*	2.0	1.0

*WHSV - weight hourly space velocity (hr^{-1})

2.1.2.6 Products

Table 2.3 and Table 2.4 give product distribution and quality for the fixed bed and fluidized bed processes.

2.1.2.7 Description[6,7]

Figure 2.2 shows a process flow diagram for producing gasoline commercially from crude methanol.

Equipment used in the methanol-to-gasoline step is similar to that used in petroleum hydrotreating. Crude methanol isfirst passed through the dehydration reactor to form the mixture of methanol, dimethyl ether, and water. Effluent is diluted with recycle gas and passed through a conversion reactor.

Recycle gas provides a heat sink to pick up heat of reactor, 80% of which is liberated in the conversion reactors, and limit temperature rise. Reactor inlet temperature is typically 360°C (680°F) and with a 9:1 recycle ratio, adiabatic temperature rise is about 55°C (100°F).

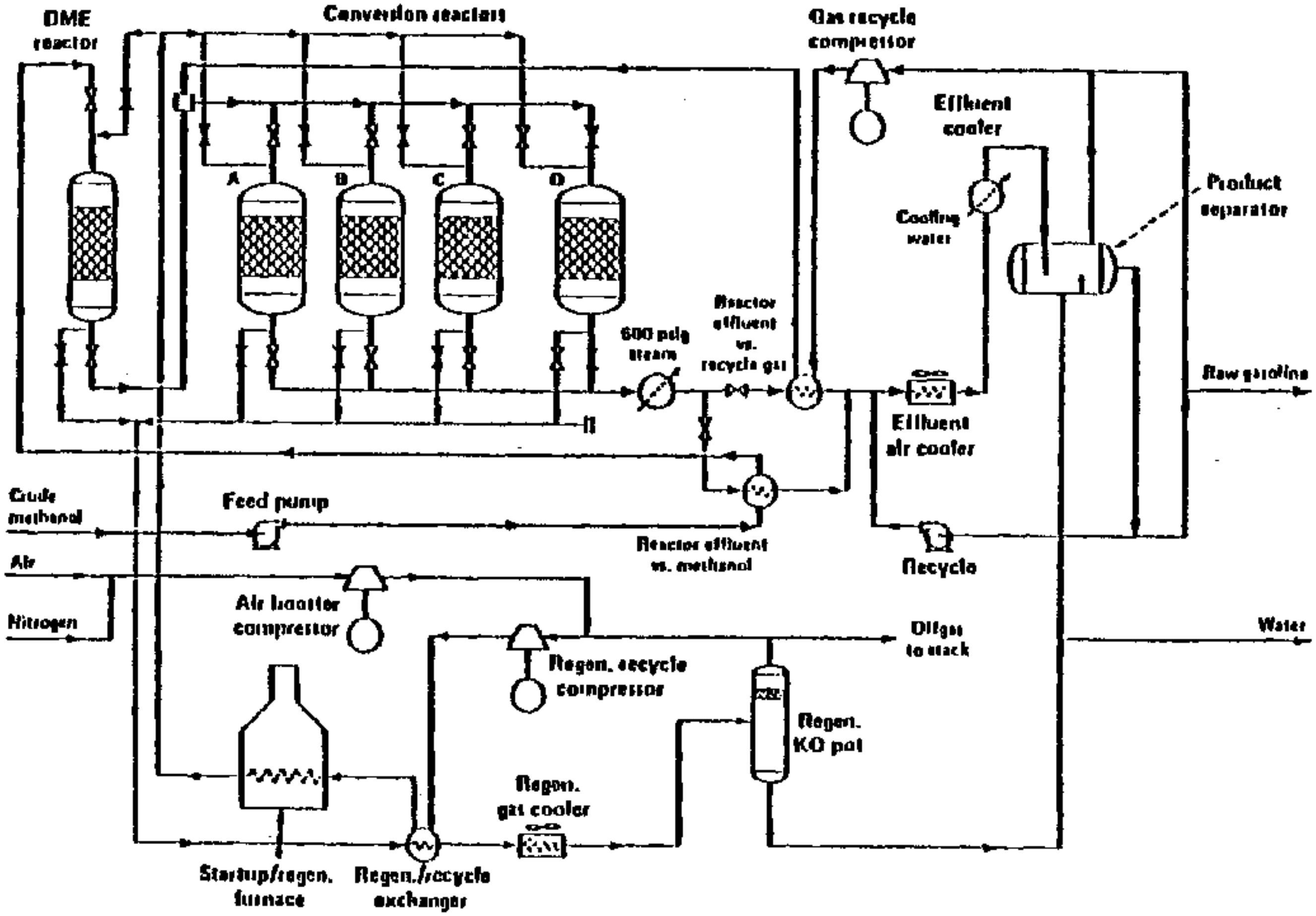

FIGURE 2.2
COMMERCIAL MOBIL METHANOL TO
GASOLINE FLOW SHEET (4)

Table 2.3 Methanol-to-gasoline process product distribution[6]

	Fixed-bed	Fluidized-bed
Yield, wt % of methanol charge		
Methanol + ether	0.0	0.2
Hydrocarbons	43.4	43.5
Water	56.0	56.0
$CO + CO_2$	0.4	0.1
Coke & Other	0.2	0.2
Total	100.0	100.0
Hydrocarbon distribution, wt %		
Light gas	1.4	5.6
Propane	5.5	5.9
Propylene	0.2	5.0
i-Butane	8.6	14.5
n-Butane	3.3	1.7
Butenes	1.1	7.3
C_5+ gasoline	79.9	60.0
Total	100.0	100.0
Product distribution, wt %		
Gasoline including alkylate	85.0	88.0
LPG	13.6	6.4
Fuel gas	1.4	5.6
Total	100.0	100.0

Table 2.4 Methanol-to-gasoline product quality[6]

	Fixed bed	Fluidized bed
Components, wt %		
Butanes	2.7	3.2
Alkylate	3.2	28.6
C_5 + synthesized gasoline	94.1	68.2
Total	100.0	100.0
Components, wt %		
Paraffins	51.0	56.0
Olefins	13.0	7.0
Naphthenes	8.0	4.0
Aromatics	28.0	33.0
Total	100.0	100.0
Research octane rating		
Clear	93.0	96.8
Leaded, 0.8 cm^3 TEL/liter	100.0	102.6
Reid vapor pressure, kPa (psi)	62 (9)	62 (9)
Specific gravity	0.730	0.730
Durene, wt %	3.8	3.8

Reactor effluent is condensed, water and liquid hydrocarbon phases are separated, and the gas is recycled. Liquid and gaseous hydrocarbons are processed through a conventional gas plant. To make additional gasoline, the propylene, butenes, and isobutane are separated and alkylated using conventional petroleum technology. Small amounts of CO, CO_2 and coke are formed as by-products.

Only a small band of catalyst in the conversion reactor is active at any time. The reaction zone moves through the reactor slowly as coke accumulates. The catalyst is ready for regeneration when there is a break through of uncoverted methanol. The time between regenerations is approximately 20 days. By contrast the DME reactor requires regeneration only about once a year. Activity is restored by burning off the coke with air.[8]

2.1.2.8 Process Features[6,7]

Advantages:

1. Liquid-product yield is significantly higher than from Fischer-Tropsch options if only liquid products are desired.
2. Raw product quality is better than that from F-T options (higher RON - 93 vs. 91-and lower olefin content - 11% vs. 75%).
3. Overall thermal efficiency is higher than a single-liquid product F-T synthesis route.
4. More simplified process flow scheme than F-T process.

Disadvantages:

1. Inability to directly produce diesel, jet fuel, or distillate fuel oil.
2. F-T technology offers all the required range of transportation fuels and some chemicals.
3. Lower overall thermal efficiency than direct hydroliquefaction processes.
4. The F-T process is commercial. The MTG process is being developed and first commercial applications may have some risk.

2.1.2.9 Foreign country interests[6,7]

1. 100 BPD (barrel per day) fluidized-bed demonstration plant costing under $35 million for construction in Wessling, West Germany. Besides US and FRG government participation, Mobil will be joined by the German firms of Union Rheinische Braunkohlen Kraftstoff AG and Freidrich Uhde GmbH.[8]

2. 13,000 BPD fixed-bed commercial plant planned for construction in New Zealand. The proposed plant will use natural gas as a raw material.

2.1.3 Direct syngas-to-gasoline

2.1.3.1 Name

Syngas to gasoline

2.1.3.2 Developers

Mobil Research and Development, Corporation, Paulsboro, New Jersey

Shell Internationale Petroleum Maatschappij B.V., The Hague, The Netherlands

2.1.3.3 Status/History[5]

Bench-scale process development was initiated by Mobil in 1976. In 1977, a 1 bbl/day process demonstration unit was set up and is presently operating. Sufficient data are expected to be obtained for the design of a 100 bbl/day pilot plant from this ongoing research. Results obtained so far have proved that direct catalytic conversion of syngas is technically feasible on the bench-scale. Present efforts include establishing catalyst life and activity of regenerated catalysts, determining scale-up factors, effect of changes in feed composition, and product acceptability.

In conjunction with the Shell-Koppers gasifier program, Shell has developed two new indirect liquefaction processes. In one of these processes shifted syngas is reacted over a synthetic zeolite/promoted iron catalyst to form gasoline, LPG and diesel fuels. In the other, the syngas is converted directly over a proprietary catalyst (suspected to be a synthetic zeolite containing promoted iron) without prior water gas shift, and the conversion of the syngas is sufficient to make recycle unnecessary. Shell is planning scaleup of the process to demonstration scale by 1990.[9]

Shell has also developed a simpler syngas conversion system which exhibits a high conversion per pass and doesn't require recycling of syngas.[F] In addition, it converts syngas with a high CO/H_2 ratio such that water gas shift of the syngas is not required. This process is called the "KSLA" (Royal Dutch Shell Laboratories Amsterdam) process.

A comparison of the yields for these two system is as follows:

Product	Shell direct gasoline system (%)	Shell KSLA system (%)
Gasoline	66	45-63
LPG	26	15-23
Kerosene and diesel	8	40-14

Economic data for these two processes were compared with methanol production costs based on mid-1979 costs:

Process	Shell direct gasoline process	Shell KSLA process	Methanol[a] production process
Thermal efficiency	50	52.4	53.3
Tons coal/ton liquid products	3.76	3.57	
Conversion of syngas, %	89	95	97
Selectivity			
C_3 + % wt	92.7	90	
C_5 + % wt	68	75	
Liquid composition, wt %			
LPG	26	15-23	
Gasoline	67	45-63	
Kerosene + diesel	8	40-14	
Capital cost, $/daily ton	274,000	241,000	255,000
Capital cost, $/daily bbl[b]	39,000	34,500	36,500
Product price, $/bbl (coal at $22/ton)	43	39	40

[a] Converted to gasoline equivalent.

[b] 1 ton = 7 bbl.

A projection by Shell for the commercialization of these two indirect processes indicated that a process-development scale unit is planned upon completion of the scouting program currently in progress. They hope to have a demonstration plant ready by 1990 and a commercial plant by 1992. Data comparing production costs for Exxon Donor Solvent raw and upgraded products with the results for the Shell indirect processes indicate that upgrading the EDS products to fuels comparable to those made by the indirect liquefaction processes would be more costly even though the overall process efficiencies are lower for the indirect processes.

2.1.3.5 Mobil Syngas-to-Gasoline Process Description[5]

The syngas-to-gasoline process is not yet well defined, but its central element will be a reactor containing the Mobil catalyst either in a fixed or fluidized-bed. The product from the reactor will be a mixture of hydrocarbons in the gasoline range, LPG materials, C_2 hydrocarbons, methane, water vapor, carbon dioxide, and unreacted components of the syngas fed to the reactor. Minor amounts of oxygenated organics and hydrocarbons above the gasoline range may also be produced. The gasoline and LPG hydrocarbons and some of the C_2 hydrocarbons and methane will be separated from the mixture. Part or all of the remainder, possibly after removal of the carbon dioxide and water vapor, will be recycled to the reactor along with fresh syngas.

Unlike the Fischer-Tropsch catalysts, the Mobil catalysts produce high yields of high-octane gasoline and only trace amounts of oxygenated organics or hydrocarbons having molecular weights higher than those in gasoline. Some of the Mobil catalysts produce olefinic gasolines and others produce aromatic gasolines. Some reject oxygen in the form of water and others do so in the form of carbon dioxide. The other byproducts of the Mobil catalysts are LPG materials, C_2 hydrocarbons, and methane.

Preliminary aging tests suggest that some of the catalysts can be regenerated and some also exhibit relatively long service lives.

2.1.3.6 Process Features[5]

Advantages:

1. Requires less capital starting from raw coal and going to unleaded 92-94 research octane gasoline than the coal-to-methanol-to-gasoline process.
2. Has a higher thermal efficiency than Fischer-Tropsch, although the overall efficiency is still in the 50-60% range even with second-generation gasifier technology and, more likely, near the lower end of the range.
3. Produces no by-products other than a small amount of readily marketable and ethane readily usable in the natural gas pipeline system.

Disadvantages:

1. The capital cost of syngas production is expected to be the controlling factor in economics. The bulk of the plant investment and operating cost is tied up in the conversion of coal into purified synthesis gas at operating temperature and pressure.
2. This technology is still at an early stage of development.

2.1.4 Liquid-Phase Fischer-Tropsch Process[X]

Liquid-phase Fischer-Tropsch process development was started in 1938 by Kölbel and Ackermann in Germany. The process utilizes a reactor filled with a high-boiling hydrocarbon liquid with finely powdered catalyst dispersed in the liquid. Pressurized synthesis gas feed is bubbled upward through the catalyst slurry at a velocity sufficient to maintain good catalyst dispersion and mixing in the three-phase system. Reaction heat from the Fischer-Tropsch reaction occurring in the reactor is removed by internal cooling coils which produce medium-pressure steam. Products are removed overhead in the vapor phase and condensed downstream. The liquid-phase Fischer-Tropsch system can accept synthesis gas having much lower H_2/CO molar ratios than the Synthol entrained bed reactors (as low as 0.67 compared to 2.0-2.5 required for the Synthol reactor). Also, a product selectivity exhibiting a lower methane content and higher motor fuel fractions is claimed.

2.1.4.1 History and Status. - Development of the liquid-phase process began in 1938 by Kölbel and Ackermann.[R1-R4] It was interrupted in 1944 by the events of World War II, but was resumed in 1951. In 1953 it led to the startup of a pilot plant (Rheinpreussen-Koppers) with a production rate of 11.5 tons of hydrocarbons per day operated under a cooperative agreement among Kölbel at the Technische Universitat, Berlin-Charlottenburg, Rheinpreussen A. G. fur Bergbau und Chemie, Hamburg, and Heinrich Koppers G.m.b.H., Essen. The pilot plant represented a successful scale-up from the laboratory reactor by a factor of 1667-fold in volume. The primary goal was the production of fuels as well as products for further chemical processing.

Further investigations with the same objectives were conducted during the war by BASF, and after the war by the U.S. Bureau of Mines, the Fuel Research Station (London), the Indian Institute of Technology, and the University of Tokyo. Variants of the liquid-phase process were developed. With the exception of the BASF process modified by the Bureau of Mines, development work did not exceed pilot-plant scale.

Since 1974, new activities in the use of the liquid-phase process for the production of primary chemical products have become apparent. Interest is being shown mainly in short-chain C_2 to C_4 olefins,[R5] the medium-chain C_5 to C_{14} olefin fraction, and in oxygen-containing products (aldehydes).

2.1.4.2 Liquid-Phase Fischer-Tropsch Process Flow Diagram. - The process used in the Rheinpreussen-Koppers Demonstration Plant is briefly described by the flow chart of Fig. 2.3.[R1] Synthesis gas was produced in a Koppers water gas generator and CO_2 from the synthesis tail gas was added to the steam during the gas production period. The synthesis gas contained an average of 54 to 56% CO, 36 to 38% H_2, 3 to 5% CO_2, and 2.6 to 4% N_2. The gas was subjected in the usual manner to a rough purification over iron oxide to remove H_2S, and over a hot purifying mass (Lauta mass and soda) to remove organic sulfur compounds to a residual sulfur content of 1 to 2 mg of S/m^3 (0.0004 to 0.0008 grains/ft^3). The gas flowed through two compressors a, the gas meter b, the measuring orifice plate c, through the heat exchanger g, where it was preheated by the tail gas stream coming from the reactor e, and entered at the bottom of the reactor e through a gas distributor with jets about 2 to 3 mm (0.08 to 0.12 in.) in diameter. The reactor consisted of a pressure-resistant steel cylinder with a diameter of 1.55 m (5.1 ft) and a height of 8.6 m (28.2 ft). At the top of the reactor was a steam collector f. From the latter, the feedwater supply went to the inner down pipes of the cooling tube exchanger located in the reactor, and steam was removed through the annular space in the cooling pipes. The internal heat exchanger ended about 1.3 m (4.3 ft) above the gas distributor. The reaction temperature was kept constant by controlling the saturated steam pressure in the steam collector.

The tube exchanger in the reactor was used during the activation of the catalyst to heat the suspension by the addition of steam, which is compressed by the compressor to a pressure corresponding to the catalyst activation temperature. The catalyst suspension was introduced or withdrawn by means of pumps k through nozzles at the bottom of the reactor from or to the stirred tank o. The height of the suspension [~8 m (26 ft)] was kept constant by a regulator either by filtering off the high-boiling fractions in the pressure filter n or by adding higher-boiling synthesis products from containers i. The reactor temperature was measured by 12 resistance thermometers attached at different heights, and recorded. Nine smaller nozzles mounted at different levels permit the removal of suspension samples from the reactor.

The tail gas exited the reactor through a swan-neck and was precooled with fresh gas in heat exchanger g. Higher-boiling products partially condensed by

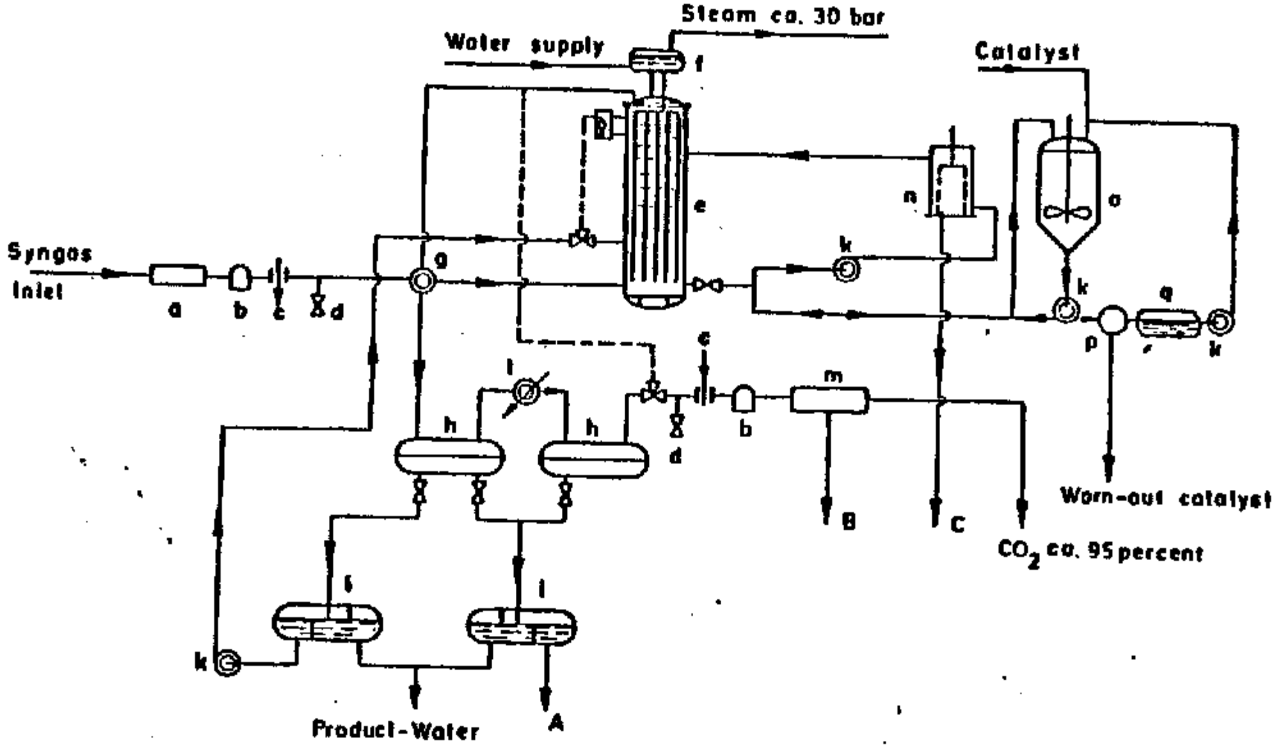

Fig. 2.3. Flow diagram of the large-scale demonstration plant (Rheinpreussen Process). A: Freely separated primary products. B: Final gas for recovery of low-boiling hydrocarbons. C: High-boiling primary products. a: Compressor. b: Gas meter. c: Orifice plate. d: Sampling intake. e: Bubble volume reactor. f: Steam collector. g: Heat exchanger. h: Separator. i: Container for separated substances. k: Pump. l: Condenser. m: CO_2 expulsion unit. n: Pressure filter. o: Contact stirring container and container for suspension removed from reactor. p: Centrifuge. q: Wash oil.

the boiling range of the liquid medium were stored in containers h or i. Indirect cooling with water in l at about 30°C (86°F) condensed products of the medium boiling range, and, out of the residual gas, the major portion of the water formed by the synthesis. After the carbon dioxide was washed out in m, the residual gas was conveyed into the recovery plant for light-boiling and gaseous products (oil pressure washing and activated charcoal plant). The carbon dioxide was cycled to the generator for the production of CO-enriched synthesis gases. In the case of a multistage process, most of the CO_2 and H_2O is removed from the outlet gas which is then recycled in the process.

The pump filled the reactor with fresh catalyst from agitator tank o where the ground catalyst was mixed with the high-boiling synthesis products. When the reactor was emptied, pump k conveyed the suspension into centrifuge p which separated the catalyst from the liquid medium, which could then be used again. Deactivated catalyst can be regenerated.

If the synthesis is adjusted for the production of low-molecular weight compounds, the removal of the liquid medium is often greater than the addition because of synthesis. In this case the higher molecular weight product collecting in heat exchanger g is fed into the reactor by pump k, its flow regulated by a liquid level regulator. If the process is geared toward products of higher molecular weights these products must be separated from the catalyst by continuous separation in filter n and removed. The catalyst flows back into the reactor. After being removed under pressure in liquid form, the primary products are separated in separators i from the water of reaction. The separator yields oxygen-containing products, especially alcohols. The hydrocarbons from the containers are separated into fractions by distillation in the usual manner, depending on their intended use.

The pilot plant useful reactor volume was 10 m^3 (353 ft^3), the overall dimensions being 155 cm (5.1 ft) ID x 8.6 m (28.2 ft) high. At the feed throughputs employed, the total internal cooling surface required to maintain nearly isothermal operation [+1°C (1.8°F) gradient] was <115 m^2 (1237 ft^2).

2.1.4.3 Catalysts. - Development of catalysts for the liquid-phase synthesis was based on extensive work done with iron catalysts that were intended for use in the fixed-bed process. Compared to other types of processes, work in the liquid phase offers greater possibilities for the flexible use of catalysts because it is not necessary to maintain certain temperature ranges and high gas velocities, or a high hydrogen content of the synthesis gases. Basically, all the catalysts which are suitable for Fischer-Tropsch synthesis can also be used in the liquid phase. In contrast to other types of processes, mechanical strength of the catalyst is not required. On the contrary, it is advantageous to have the catalyst particles break up during the synthesis as a result of carbide formation, because this leads to a good dispersion in the liquid. Catalysts with a high content of supports are less suitable since they lead to unusually high viscosities as compared to support-free catalysts, hindering the gas distribution and reducing the boundary area between gas and liquid, which area in turn determines the mass transfer.

It is for this reason that primarily support-free iron precipitation catalysts were considered during the developmental stage. They made it possible to use the highest concentration of iron in suspension, they can be formed easily in a liquid medium, they possess high activity, and they produce stable suspensions. The optimum concentration of catalyst in suspension proved to be about 10 wt % in terms of the iron present in the catalyst. Lower concentrations reduced the reactor efficiency, and higher concentrations up to 20% can be used, but they increase the viscosity of the suspension and thus decrease the interfacial area, which affects the mass transfer and hence may cause a decrease in conversion. An optimum equilibrium is required between catalyst concentration, gas throughput, and operating temperature.[R3]

The iron-based catalyst was of the unsupported precipitation type which is relatively inexpensive and could be easily prepared at the plant site. It was prepared by rapid precipitation from nitrate solutions by ammonium hydroxide. Copper promoter (as nitrate) was added before precipitation and potassium promoter (as carbonate) was added to the filter cake. The final precipitate was dried, ground, charged to the reactor in the oxide form, and then activated in situ by reduction at 15-30°C (27-54°F) above reaction temperature. The catalyst concentration in the slurry was 88 g/ℓ (5.50 lb/ft^3). A typical composition was Fe : Cu : K_2O = 100 : 0.1 : 0.05-0.5, this being an unusually low alkali level. Catalysts for slurry operation were claimed not to have stringent requirements for mechanical attrition resistance. However, data on long-term catalyst particle size diminution are not available. The key physical property was stated to be good dispersability. The final particle size [a few µm (0.04 in.)] resulted from internal carbon deposition during activation and reaction.

The superficial upward gas velocity was ~10 cm/sec (0.3 ft/sec). At this velocity, a bubble size of a few mm (0.1 in.) was achieved without elaborate gas dispersion devices. The key item in successful scale-up from the laboratory [6 ℓ (1.5 gal or 0.2 ft^3) reactor] to pilot plant-scale [10,000 ℓ (350 ft^3) reactor] was said to be maintenance of constant gas bubble residence time. Kolbel stressed that the low viscosity and surface tension of the paraffinic dispersing liquid used were crucial for maintaining small bubble size and hence good gas-liquid mass transfer characteristics. Under this set of flow conditions, the reactor was claimed to be reaction rate-limited with no mass transport limitations.

2.1.4.4 Rheinpreussen-Koppers Pilot Plant Results. - The production goal for the plant was to make gasoline. An analysis of such a synthetic "gasoline" product according to boiling range and properties is shown in Table 2.5. The product analyzed was a sample from large storage tanks which contained the products from one of the longer operating periods. The operating conditions under which this product was made are listed in Table 2.6. The olefin content, which is of importance for petrochemical processing, is given as 70-85% for the C_3-C_4 fraction. It is fluctuated between these limits because of a change in operating conditions over the long period of operation to which the analyses are referred. Note the high olefin content (70%) of the 40-180°C (104-356°F) fraction, which is of interest as raw material for the oxo process. Almost one-half of the 180-220°C (356-428°F) fraction (important for the production of surface-active agents) consists of olefins.

Gasoline was obtained in the proportion of 85% in the C_3-synthesis products. The raw primary gasoline [25-190°C (77-374°F)], with a Reid vapor pressure of 0.55 atm (8.1 psi), had an intermediate octane rating of 73 which, after thermal treatment with Al_2O_3, rose to 83. Mixing with polymer gasoline without adding lead gave an octane rating of 93. About 12% of the liquid products were diesel fuels [190-310°C (374-590°F)] with a solidification point of -13°C (9°F) and an ignition value of over 70 (cetane number). As products of the Fischer-Tropsch synthesis, the materials were free of sulfur and thus meet present requirements for environmentally safe automotive fuels.

Table 2.5. Composition and properties of a product from the Rheinpreussen pilot plant

	g/Nm^3 of CO + H_2	lb/ft^3 of CO + H_2	Wt % of total product C_1^+	% olefin	Avg. molecular weight	Density, 20°C (68°F)
Methane + ethane	5.7	0.0004	3.2	0		
Ethylene	613.0	0.0382	3.6	100		
C_3	40.3	0.0025	22.6	75–85		
C_4	9.1	0.0006	5.1	70–80		
40–180°C (104–356°F)	95.5	0.0059	53.6	70	93.9	0.683
180–220°C (356–428°F)	7.1	0.0004	4.0	48	139.4	0.760
220–320°C (428–608°F)	10.7	0.0007	6.0	37	218.0	0.781
>320°C (>608°F)	3.3	0.0002	1.9	7	300.5	0.811
Total	178.0	0.0111	100.0			

Table 2.6. Operating data and results of liquid-phase synthesis for one-step operation with a single passage of the gas over iron catalysts[R10]

	Laboratory plant	Pilot plant
Effective reaction space (volume of suspension, including dispersed gas), λ	6	10,000
Catalyst, kg Fe (lb Fe)	0.4 (0.9)	800 (1760)
Synthesis gas pressure, bars (psi)	11 (165)	12 (180)
Synthesis gas volume ratio of $CO:H_2$	1.5	1.5
Synthesis gas flowrate, Nm^3/hr (ft^3/hr)	1.3 (46)	2,700 (95,350)
Linear velocity of synthesis gas at operating temperature referred to free reactor cross-section, cm/s (ft/s)	3.5 (0.1)	9.5 (0.3)
$CO + H_2$ flowrate, Nm^3/hr (ft^3/hr)	1.1 (39)	2,300 (81,200)
$CO + H_2$ flowrate, Nm^3/hr per m^3 of reaction chamber volume (ft^3/hr per ft^3 of reaction chamber volume)	183 (183)	230 (230)
$CO + H_2$ flowrate, Nm^3/hr per kg of Fe (ft^3/hr per lb of Fe)	2.45 (39.3)	2.6 (41.7)
Average synthesis temperature, °C (°F)	266 (510)	268 (514)
CO conversion, %	88	89
Synthesis products per amount of $CO + H_2$ consumed, g/Nm^3 (lb/ft^3)		
Hydrocarbons		
C_1^+	178 (0.011)	176 (0.011)
$C_1 + C_3$	11 (0.001)	12 (0.001)
C_3^+	165 (0.010)	166 (0.010)
Oxygen-containing products in synthesis water, g/Nm^3 (ppm)	2 (2)	3 (3)
Space-time yield of C_3^+ products including oxygen-containing products in 24 hr, kg/m^3 of reaction chamber volume (lb/ft^3)	740 (46)	930 (58)

A recent study performed by Gray[R6] in the U.S. compared the Kölbel synthesis reactor with an entrained-bed Sasol system designed for a site in the U.S. Results showed higher gasoline yields, higher overall plant thermal efficiencies and lower capital costs for the Kölbel case. This represented a savings in plant production costs of about 40% for the Kölbel process over the Sasol-type system.

Schering AG in Bergkamen, West Germany has been investigating liquid-phase Fischer-Tropsch reactors in bench-scale reactors. Although their objective is to optimize the C_2/C_4 olefin yields for chemical feed stock production, they have published information on a number of different type catalysts including one prepared in a manner similar to that used by Rheinpreussen-Koppers. Other small pilot plant experiments using Kölbel slurry reactors at the United States Bureau of Mines (1951)[R7] and at the Department of Scientific and Industrial Research in the United Kingdom (1953-61)[R8] and in Japan[R9] failed to replicate the success of the Rheinpreussen plant.

Table 2.7 shows a comparison of product selectivities for the Kölbel and Sasol reactors. The liquid-phase results are shown which include the Rheinpreussen pilot plant data,[R1] data developed by Schering[R10] using catalysts similar to Kölbel's and Schering's results using a catalyst manufactured by Ruhrchemie. The C_5^+ selectivities observed by Schering using "Kölbel-type" catalysts are below those claimed for the pilot plant, but reasonable C_5^+ selectivity agreement was observed using a Ruhrchemie proprietary catalyst.

Table 2.7. Product selectivity for Synthol and liquid-phase Fischer-Tropsch synthesis reactors

	Product wt % of total hydrocarbons			
		Liquid-phase Fischer-Tropsch		
Product fraction	Synthol	Kölbel[a]	Kölbel[b]	Ruhrchemie catalyst[c]
$C_1 + C_2$	22.8	6.8	25.8	15.0
C_3	15.3	22.6	14.5	11.2
C_4	10.6	5.1	10.6	9.0
C_5-320°C (608°F)	46.6	63.6	49.1	64.8
>320°C (608°F)	4.6	1.9		

[a] Rheinpreussen pilot plant average results.

[b] Schering data — Kölbel-type catalyst.

[c] Schering data — catalyst supplied by Ruhrchemie.