Kirk-Othmer Encyclopedia of Chemical Technology.

FUELS, SYNTHETIC, LIQUID FUELS

The creation of liquids to be used as fuels from sources other than natural crude petroleum (qv) broadly defines synthetic liquid fuels. Hence, fuel liquids prepared from naturally occurring bitumen deposits qualify as synthetics, even though these sources are natural liquids. *Synthetic liquid fuels* have characteristics approaching those of the liquid fuels in commerce, specifically gasoline, kerosene, jet fuel, and fuel oil (see Aviation and other gas turbine fuels; Gasoline and other motor fuels). For much of the twentieth century, the synthetic fuels emphasis was on liquid products derived from coal (qv) upgrading or by extraction or hydrogenation of organic matter in coke liquids, coal tars, tar sands (qv), or bitumen deposits. More recently, however, much of the direction involving synthetic fuels technology has changed. There are two reasons.

The potential of natural gas, which typically has 85–95% methane, has been recognized as a plentiful and clean alternative feedstock to crude oil (see Gas, natural). Estimates (1–3) place worldwide natural gas reserves at ca 1×10^{14} m^3 (3.5×10^{15} ft^3) corresponding to the energy equivalent of ca 1×10^{11} m^3 (637×10^9 bbl) of oil. As of this writing, the rate of discovery of proven natural gas reserves is increasing faster than the rate of natural gas production. Many of the large natural gas deposits are located in areas where abundant crude oil resources lie such as in the Middle East and Russia. However, huge reserves of natural gas are also found in many other regions of the world, providing oil-deficient countries access to a plentiful energy source. The gas is frequently located in remote areas far from centers of consumption, and pipeline costs can account for as much as one-third of the total natural gas cost (1) (see Pipelines). Thus tremendous strategic and economic incentives exist for on-site gas conversion to liquids.

In general, the proven technology to upgrade methane is via steam reforming to produce synthesis gas, $CO + H_2$. Such a gas mixture is clean and when converted to liquids produces fuels substantially free of heteroatoms such as sulfur and nitrogen. Two commercial units utilizing the synthesis gas from natural gas technology in combination with novel downstream conversion processes have been commercialized.

The direct methane conversion technology, which has received the most research attention, involves the oxidative coupling of methane to produce higher hydrocarbons (qv) such as ethylene (qv). These olefinic products may be upgraded to liquid fuels via catalytic oligomerization processes.

A second trend in synthetic fuels is increased attention to oxygenates as alternative fuels (4) as a result of the growing environmental concern about burning fossil-based fuels. The environmental impact of the oxygenates, such as methanol (qv), ethanol (qv), and methyl *tert*-butyl ether (MTBE) (see Octane improvers) is still under debate, but these alternative liquid fuels are gaining new prominence. The U.S. Alternative Fuels Act of 1988, and the endorsement of oxygenate fuels that act contains, clearly underscore the idea that economics is no longer the sole consideration with regard to alternative fuels production (5).

Despite reduced prominence, coal technology is well positioned to provide synthetic fuels for the future. World petroleum and natural gas production are expected ultimately to level off and then decline. Coal gasification to synthesis gas is utilized to synthesize liquid fuels in much the same manner as natural gas steam reforming technology (see Coal conversion processes). Although as of this writing world activity in coal liquefaction technology is minimal, the extensive development and detailed demonstration of processes for converting coal to liquid fuels should serve as solid foundation for the synthetic fuel needs of the future.

Coal, tar, and heavy oil fuel reserves are widely distributed throughout the world. In the Western hemisphere, Canada has large tar sand, bitumen (very heavy crude oil), and coal deposits. The United States has very large reserves of coal and shale. Coal comprises ca 85% of the U.S. recoverable fossil energy reserves (6). Venezuela has an enormous bitumen deposit and Brazil has significant oil shale (qv) reserves. Coal is also found in Brazil, Colombia, Mexico, and Peru. Worldwide, the total resource base of these reserves is immense and may constitute $>90\%$ of the hydrocarbon resources in place (see Fuel resources).

The driving force behind the production of combustible liquids before 1900 was the search for low cost lighting. Gas produced during coal distillation was used to light homes at the end of the eighteenth century (7). Large-scale use of coal, which began in England in the nineteenth century, led to significant reductions in the costs of hydrocarbon liquids. The production of coal tar, and the separation therefrom of various coal liquids concomitant to the production of illuminating gas, probably predates production from the coking operations associated with iron (qv) production. The coal tars produced in gas works may have been the first synthetic liquids turned to fuel use in quantity.

Proof of the existence of benzene in the light oil derived from coal tar (8) first established coal tar and coal as chemical raw materials (see Feedstocks, coal chemicals). Soon thereafter the separation of coal-tar light oil into substantially pure fractions produced a number of the aromatic components now known to be present in significant quantities in petroleum-derived liquid fuels. Indeed, these separation procedures were for the recovery of benzene–toluene–xylene (BTX) and related substances, ie, benzol or motor benzol, from coke-oven operations (8) (see BTX processing).

By the middle of the nineteenth century it was realized, both in England and in the United States, that kerosene, or coal oil, distilled from coal, could produce a luminous combustion flame. Commercialization was rapid. By the time of the U.S. Civil War, $\sim$87 m^3/yr (23,000 gal/yr) of lamp oil was produced in the United States from the distillation not only of coal, but also of oil shale and natural bitumen. In 1859, high gravity, low sulfur crude oil was discovered in the United States. This produced high quality kerosene with minimal processing, and the world's first oil boom erupted. Until the end of the nineteenth century, kerosene was the only substance of value extracted from natural crude oil. It cost too much for heating purposes, but was used widely for lighting until replaced by electricity. Refiners slowly learned to use the residues from kerosene production, and as the market for lamp oil collapsed, gasoline increased in value. The widespread use of liquids as fuels dates from that time.

Liquid fuels possess inherent advantageous characteristics in terms of being more readily stored, transported, and metered than gases, solids, or tars. Liquid fuels also are generally easy to process or clean by chemical and catalytic means. The energy densities of clean hydrocarbon liquids may be very high relative to gas, solid, or semisolid fuel substances. Moreover, liquid fuels are the most compatible with the twentieth century world fuel infrastructure because most fuel-powered conveyances are designed to function only with relatively clean, low viscosity liquids. In general, liquid hydrocarbon fuels possess an intermediate hydrogen-to-carbon content. Production of synthetic fuels from alternative feedstocks to natural petroleum crude oil is based on adjusting the hydrogen-to-carbon ratio to the desired intermediate level.

There is an inherent economic penalty associated with producing liquids from either natural gas or solid coal feedstock. Synthetic liquid fuels technologies are generally not economically competitive with crude oil processing in the absence of extraneous influences such as price supports or regulations.

1. Indirect Liquefaction/Conversion to Liquid Fuels

Indirect liquefaction of coal and conversion of natural gas to synthetic liquid fuels is defined by technology that involves an intermediate step to generate synthesis gas, $CO + H^2$. The main reactions involved in the generation of synthesis gas are the coal gasification reactions:*Combustion*

$$C + O_2 \rightleftharpoons CO_2 \qquad \Delta H_{298\ K} = -394\ kJ/mol\ (-94.2\ kcal/mol) \qquad (1)$$

Gasification

$$C + 1/2\ O_2 \rightleftharpoons CO \qquad \Delta H_{298\ K} = -111\ kJ/mol\ (-26.5\ kcal/mol) \qquad (2)$$

$$C + H_2O\ (g) \rightleftharpoons CO + H_2 \qquad \Delta H_{298\ K} = +131\ kJ/mol\ (31.3\ kcal/mol) \qquad (3)$$

$$C + CO_2 \rightleftharpoons 2\ CO \qquad \Delta H_{298\ K} = +172\ kJ/mol\ (41.1\ kcal/mol) \qquad (4)$$

Water gas shift

$$CO + H_2O\ (g) \rightleftharpoons CO_2 + H_2 \qquad \Delta H_{298\ K} = -41\ kJ/mol\ (-9.8\ kcal/mol) \qquad (5)$$

the methane steam reforming reactions:*Partial oxidation*

$$CH_4 + 1/2\ O_2 \rightleftharpoons CO + 2\ H_2 \qquad \Delta H_{298\ K} = -36\ kJ/mol\ (-8.6\ kcal/mol) \qquad (6)$$

Reforming

$$CH_4 + H_2O\ (g) \rightleftharpoons CO + 3\ H_2 \qquad \Delta H_{298\ K} = 206\ kJ/mol\ (49.2\ kcal/mol) \qquad (7)$$

and the water gas shift reaction (eq. 5), used to increase the H_2/CO ratio of the product synthesis gas.

Coal gasification technology dates to the early nineteenth century but has been largely replaced by natural gas and oil. A more hydrogen-rich synthesis gas is produced at a lower capital investment. Steam reforming of natural gas is applied widely on an industrial scale (9, 10) and in particular for the production of hydrogen (qv).

The conversion of coal and natural gas to liquid fuels via indirect technology can be achieved by the routes shown in Figure 1. Two pathways from synthesis gas can be taken. Both have been commercialized. One pathway involves coupling with Fischer-Tropsch technology to produce fuel range hydrocarbons directly or upon further processing. Using coal feedstock, this route has been commercialized in South Africa since the 1950s and a process using natural gas was commercialized in Malaysia by Shell Oil Co. in 1993. An alternative route relies on the production of methanol from synthesis gas and subsequent transformation of the methanol to fuels using zeolite catalyst technology introduced by Mobil Oil Corp. (see Molecular sieves). This route was commercialized using indigenous natural gas in New Zealand in 1985.

1.1. Coal Upgrading via Fischer-Tropsch

The synthesis of methane by the catalytic reduction of carbon monoxide and hydrogen over nickel and cobalt catalysts at atmospheric pressure was reported in 1902 (11).

$$CO + 3\ H_2 \longrightarrow CH_4 + H_2O\,(l) \qquad \Delta H_{298\ K} = -250\ kJ/mol\ (-59.8\ kcal/mol) \qquad (8)$$

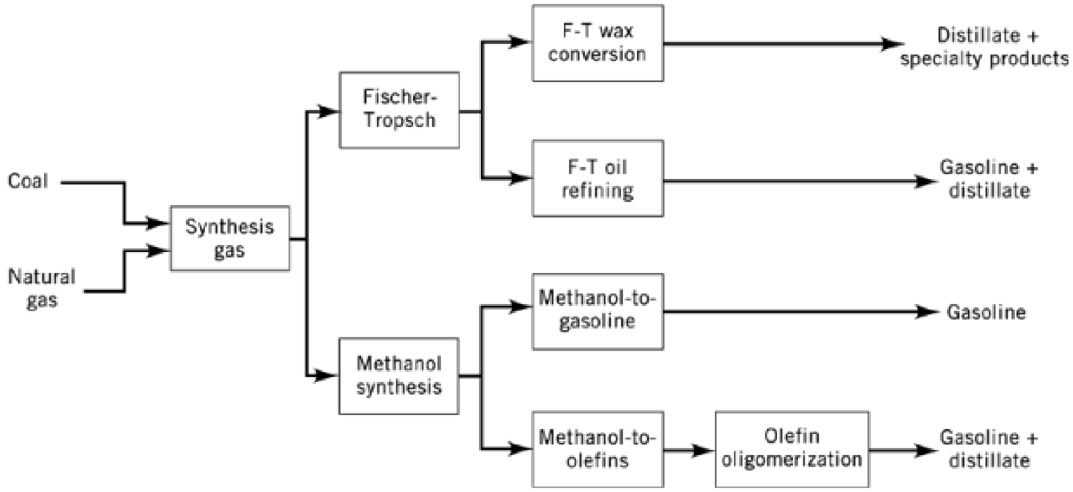

Fig. 1. Routes to liquid fuels from natural gas and coal via synthesis gas. F-T is the Fischer-Tropsch process.

$$2\,\mathrm{CO} + 2\,\mathrm{H_2} \longrightarrow \mathrm{CH_4} + \mathrm{CO_2} \qquad \Delta H_{298\ \mathrm{K}} = -247\ \mathrm{kJ/mol}\ (59.0\ \mathrm{kcal/mol}) \qquad (9)$$

In the early 1920s Badische Anilin- und Soda-Fabrik announced the specific catalytic conversion of carbon monoxide and hydrogen at 20–30 MPa (200–300 atm) and 300–400°C to methanol (12, 13), a process subsequently widely industrialized. At the same time Fischer and Tropsch announced the Synthine process (14, 15), in which an iron catalyst effects the reaction of carbon monoxide and hydrogen to produce a mixture of alcohols, aldehydes (qv), ketones (qv), and fatty acids at atmospheric pressure.

In the classical normal pressure synthesis (16), higher hydrocarbons are produced by net reactions similar to those observed in the early 1900s, but at temperatures below the level at which methane is formed:

$$n\,\mathrm{CO} + 2n\,\mathrm{H_2} \longrightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\,\mathrm{H_2O} + \text{heat} \qquad (10)$$

$$2n\,\mathrm{CO} + n\,\mathrm{H_2} \longrightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\,\mathrm{CO_2} + \text{heat} \qquad (11)$$

In the mid-1930s improvements in catalysts and techniques (17–19) culminated in the licensing of the process to Ruhrchemie to produce liquid hydrocarbons and paraffin waxes using precipitated cobalt-on-kieselguhr catalysts. Subsequently, a medium pressure synthesis was developed (20) at 0.5–2 MPa (5–20 atm) using dispersed cobalt catalysts which improved hydrocarbon yields by 10–15%. The yields of paraffin wax, in particular, could be increased to 45% of the total liquid product. Hydrotreating of catalyst (required in the normal pressure process) was avoided, and catalyst life was extended (21–23). There is a marked influence of pressure on product yields. Beyond the optimum pressure of about 2 MPa (20 atm), paraffin yield decreases. Little change is found in the gasoline and gas oil yields, however.

Furthermore it was discovered that reasonable yields could be obtained using precipitated iron catalysts at 1–3 MPa (10–30 atm), and that very high melting waxes could be synthesized at 10–100 MPa (100–1000 atm) over ruthenium catalysts. At the same time a related process, the oxo synthesis, was announced (24) (see Oxo process). Early in World War II, the iso-synthesis process was developed for the production of low molecular weight isoparaffins at high temperatures and pressures over thoria and mixtures of alumina and zinc oxide (25–28). In the early 1960s polymethylenes were synthesized using activated ruthenium catalysts at high pressures.

Industrial operation of the Fischer-Tropsch synthesis involved five steps: (*1*) synthesis gas manufacture; (*2*) gas purification by removal of water and dust, and hydrogen sulfide and organic sulfur compounds; (*3*) synthesis of hydrocarbons; (*4*) condensation of liquid products and recovery of gasoline from product gas; and (*5*) fractionation of synthetic products. Only the synthesis reactor and its method of operation were unique to the process. For low pressure synthesis the reactor incorporated elaborate bundles of cooling tubes immersed in the catalyst, whereby circulating water removed the heat of reaction, limiting the conversion to methane which produced high temperatures. In the pressure process, bundles of concentric tubes, with catalyst arranged in the annuli, through and around which cooling water flowed, served as conversion units. In both systems, the conversion units each contained about 10 m^3 (ca 350 ft^3) of catalyst, and were rated at a capacity of ca 4.8 m^3 (30 bbl) of liquid product per day.

During World War II, nine commercial plants were operated in Germany, five using the normal pressure synthesis, two the medium pressure process, and two having converters of both types. The largest plants had capacities of ca 400 m^3/d (2500 bbl/d) of liquid products. Cobalt catalysts were used exclusively.

1.1.1. Developments Outside Germany

In the late 1930s experimental work in England (29–31) led to the erection of large pilot facilities for Fischer-Tropsch studies (32). In France, a commercial facility near Calais produced ca 150 m^3 (940 bbl) of liquid hydrocarbons per day. In Japan, two full-scale plants were also operated under Ruhrchemie license. Combined capacity was ca 400 m^3 (2500 bbl) of liquids per day.

In the mid-1930s Universal Oil Products reported (33, 34) that gasoline of improved quality could be produced by cracking the high boiling fractions of Fischer liquids, and a consortium, the Hydrocarbon Synthesis, Inc., entered into an agreement with Ruhrchemie to license the Fischer synthesis outside Germany.

In 1955 the South African Coal, Oil, and Gas Corp. (Sasol) commercialized the production of liquid fuels utilizing Fischer-Tropsch technology (35). This Sasol One complex has evolved into the streaming of second-generation plants, known as Sasol Two and Three. The Sasol One process, shown in Figure 2**a** (36), combines fixed-bed Ruhrchemie-Lurgi Arge reactor units with fluidized-bed Synthol process technology (37). For Sasol One, 16,000 t/d of coal is crushed and gasified with steam and oxygen. After a number of gas purification steps in which by-products and gas impurities are removed, the pure gas is processed in both fixed- and fluidized-bed units simultaneously. Table 1 gives product selectivity comparisons of fixed-bed and Synthol operations. Conversion to hydrocarbons is higher in the Synthol unit and the H_2/CO ratio is also higher. Because the fixed-bed Arge reactor favors the formation of straight-chain paraffins, there is greater production of diesel and wax fractions than the Synthol unit. The Arge reactor products have lower gasoline octane number but higher diesel cetane number relative to Synthol. The high wax production using the Arge reactor was disadvantageous at the time owing to market limitations of wax fuels. Sasol One produced a vast array of chemical and fuel products, including gasoline at 1.5×10^6 t/yr.

The 1973 oil crisis resulted in the Sasol Two unit which started up in early 1980 followed by the nearly identical Sasol Three unit two years later. Figure 2**b** gives the schematic flow diagrams for the Sasol Two and Three processes. Sasol Two uses 36 Lurgi gasifiers in parallel to process ca 31,000 t/d of sized coal. By-product effluents and gas impurities are removed in Rectisol (sulfur compounds and CO_2 removal), Phenosolvan (oxygen compounds and ammonia removal), and tar separation units. Synthol fluid-bed units were employed because of the product distribution and ease of design scale-up. Approximately 80,000 t/d of coal are needed for the two plants. Composition and manufacturing information for Sasol Fischer-Tropsch catalysts are trade secrets, but the catalyst is widely accepted as being an alkali-metal promoted iron-based material.

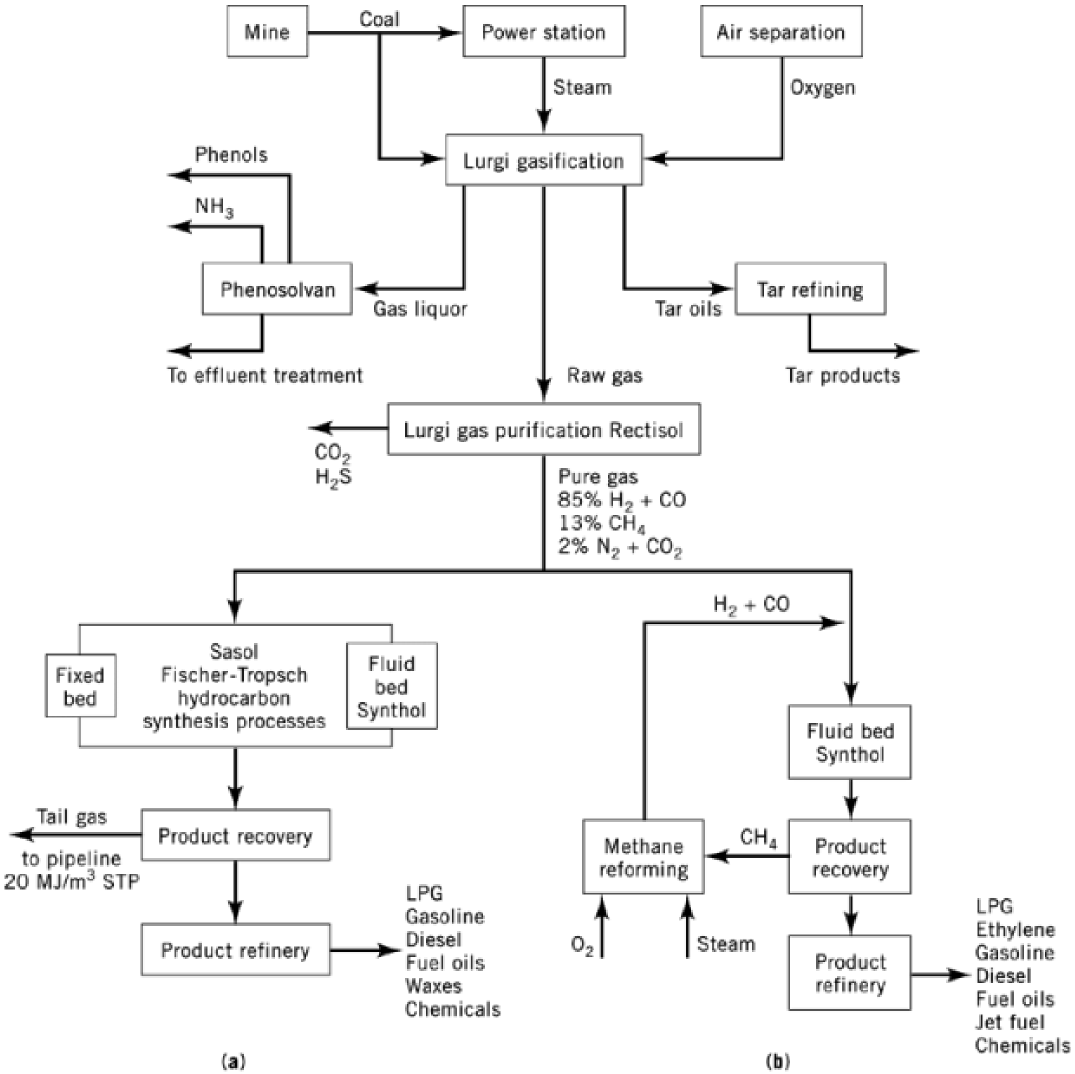

Fig. 2. Process flow sheet of (**a**) Sasol One and (**b**) the Sasol synfuel process for Sasol Two and Three (36). LPG is liquefied petroleum gas; other terms are defined in the text. To convert J to cal, divide by 4.184.

More recently, Sasol commercialized a new type of fluidized-bed reactor and was also operating a higher pressure commercial fixed-bed reactor (38). In 1989, a commercial scale fixed fluid-bed reactor was commissioned having a capacity similar to existing commercial reactors at Sasol One (39). This effort is aimed at expanded production of higher value chemicals, in particular waxes (qv) and linear olefins.

1.1.2. Properties

Fischer-Tropsch liquid obtained using cobalt catalysts is roughly equivalent to a very paraffinic natural petroleum oil but is not so complex a mixture. Straight-chain, saturated aliphatic molecules predominate but monoolefins may be present in an appreciable concentration. Alcohols, fatty acids, and other oxygenated compounds may represent less than 1% of the total liquid product. The normal pressure synthesis yields ca 60%

Table 1. Product Selectivities for Commercial Fixed-Bed and Synthol Units[a]

Product	Fixed-bed	Synthol
methane	2.0	10
ethylene	0.1	4
ethane	1.8	4
propylene	2.7	12
propane	1.7	2
butenes	3.1	9
butanes	1.9	2
C_5 and higher	83.5	51
soluble chemicals	3.0	5
water-soluble acids	0.2	1

[a] Ref. 36.

gasoline, 30% gas oil, and 10% paraffin (mp 20–100°C). The medium pressure synthesis yields 35% gasoline, 35% gas oil, and 30% paraffin. The octane rating of the gasoline is too low for direct use as motor fuel (40).

Most of the German gasoline production was blended into motor fuels using benzene derived from coking. The gas oil could be used directly as a superior diesel fuel; some was also used in soap (qv) manufacture. The paraffin (referred to as gatsch) was used primarily for the synthesis of fatty acids and hard soaps. The propane and butane gases were also used as motor fuels. Some propylene and butylenes were polymerized over phosphoric acid to high octane gasoline, and some olefins to lubricating oils. Typical values for the composition of the technical-scale reaction products of the normal and medium pressure synthesis are available (41).

1.2. Natural Gas Upgrading via Fischer-Tropsch

In the United States, as in other countries, scarcities from World War II revived interest in the synthesis of fuel substances. A study of the economics of Fischer synthesis led to the conclusion that the large-scale production of gasoline from natural gas offered hope for commercial utility. In the Hydrocol process (Hydrocarbon Research, Inc.) natural gas was treated with high purity oxygen to produce the synthesis gas which was converted in fluidized beds of iron catalysts (42).

1.2.1. Shell Middle Distillate Synthesis

The *Shell middle distillate synthesis (SMDS)* process developed by Shell Oil Co., uses remote natural gas as the feedstock (43–45). A simplified flow scheme is given in Figure 3. This two-step process involves Fischer-Tropsch synthesis of paraffinic wax called the heavy paraffin synthesis (HPS). The wax is subsequently hydrocracked and hydroisomerized to yield a middle distillate boiling range product in the heavy paraffin conversion (HPC). In the HPS stage, wax is maximized by using a proprietary catalyst having high selectivity toward heavier products and by the use of a tubular, fixed-bed Arge-type reactor. The HPC stage employs a commercial hydrocracking catalyst in a trickle flow reactor. The effect of hydrocracking light paraffins is shown in Figure 4. The HPC step allows for production of narrow range hydrocarbons not possible with conventional Fischer-Tropsch technology.

After years of bench-scale and pilot-plant studies, construction was begun on a gca 1600 m^3/d (10,000 bbl/d) unit in Sarawak, Malaysia, by Shell in a joint venture with Mitsubishi and the Malaysian government. Plant commissioning was in early 1993 at a capital investment of ca $\$600 - 700 \times 10^6$. The plant uses natural gas from offshore fields and is located adjacent to the existing Malaysian liquefied natural gas (LNG) plant. The production of liquid transportation fuels via SMDS cannot compete economically with fuels derived from crude oil. However, economics vary greatly with site location, and subsidies from the Malaysian government,

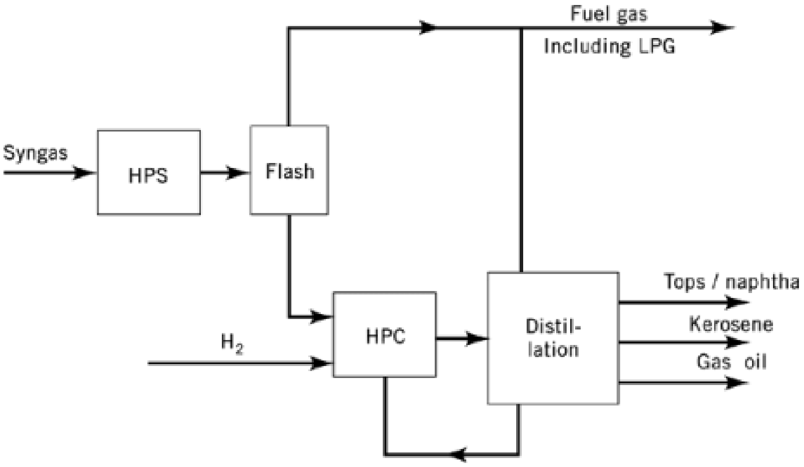

Fig. 3. The Shell middle distillate synthesis (SMDS) process. HPS=heavy paraffin synthesis. HPC=heavy paraffin conversion.

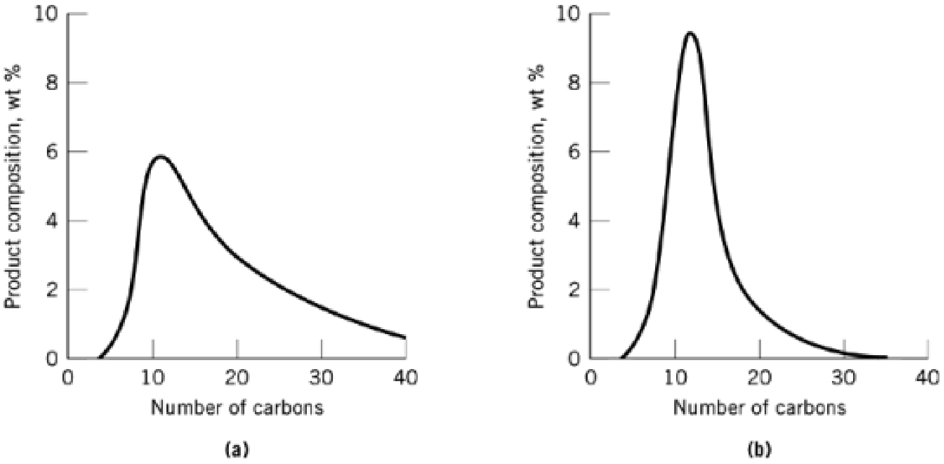

Fig. 4. Product compositions as a function of carbon number for the Shell middle distillate synthesis process: (**a**) the Fischer-Tropsch product following HPS, and (**b**) the final hydrocracking product following HPC. See text (45).

eg, reduced natural gas cost, brought this plant to commercialization. In addition, premium selling prices for the high quality products made from SMDS are a primary influence on commercialization potential (44).

A similar process to SMDS using an improved catalyst is under development by Norway's state oil company, den norske state olijeselskap AS (Statoil) (46). High synthesis gas conversion per pass and high selectivity to wax are claimed. The process has been studied in bubble columns and a demonstration plant is planned.

1.2.1.1. Properties. Shell's two-step SMDS technology allows for process flexibility and varied product slates. The liquid product obtained consists of naphtha, kerosene, and gas oil in ratios from 15:25:60 to 25:50:25, depending on process conditions. Of particular note are the high quality gas oil and kerosene. Table 2 gives SMDS product qualities for these fractions.

The products manufactured are predominantly paraffinic, free from sulfur, nitrogen, and other impurities, and have excellent combustion properties. The very high cetane number and smoke point indicate clean-burning

Table 2. SMDS Product Quality[a, b]

Parameter	SMDS	Specification
	Gas oil	
cetane number	70	40 to 50
cloud point, °C	−10	−10 to +20
	Kerosene	
smoke point, mm	45	19
freezing point, °C	−47	−47

[a] Ref. 44.

[b] The tops/naphtha fraction is similar to straight-run material.

hydrocarbon liquids having reduced harmful exhaust emissions. SMDS has also been proposed to produce chemical intermediates, paraffinic solvents, and extra high viscosity index (XHVI) lubeoils (see Lubrication and lubricants) (44).

1.3. Liquid Fuels via Methanol Synthesis and Conversion

Methanol is produced catalytically from synthesis gas. By-products such as ethers, formates, and higher hydrocarbons are formed in side reactions and are found in the crude methanol product. Whereas for many years methanol was produced from coal, after World War II low cost natural gas and light petroleum fractions replaced coal as the feedstock.

1.3.1. Methanol-to-Gasoline

The most significant development in synthetic fuels technology since the discovery of the Fischer-Tropsch process is the Mobil *methanol-to-gasoline (MTG) process* (47–49). Methanol is efficiently transformed into C_2–C_{10} hydrocarbons in a reaction catalyzed by the synthetic zeolite ZSM-5 (50–52). The MTG reaction path is presented in Figure 5 (47). The reaction sequence can be summarized as

$$n/2\ \left[2\,CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O\right] \longrightarrow C_nH_{2n} \longrightarrow n\left[CH_2\right] \qquad (12)$$

where $[CH_2]$ represents an average paraffin–aromatic mixture.

How the initial $C—C$ bond is formed from the C_1 progenitor is unknown and much debated (48, 53–55). Light olefins are key intermediates in the reaction sequence. These undergo further transformation, ultimately forming aromatics and light paraffins. Table 3 lists a typical MTG product distribution. A unique characteristic of these products is an abrupt termination in carbon number at around C_{10}. This is a consequence of molecular shape–selectivity (56–58), a property of ZSM-5. The composition and properties of the C_5 + fraction are those of a typical premium aromatic gasoline. Interestingly, C_{10} also is the end point of conventional gasoline.

The MTG process was developed for synfuel production in response to the 1973 oil crisis and the steep rise in crude prices that followed. Because methanol can be made from any gasifiable carbonaceous source, including coal, natural gas, and biomass, the MTG process provided a new alternative to petroleum for liquid fuels production. New Zealand, heavily dependent on foreign oil imports, utilizes the MTG process to convert vast offshore reserves of natural gas to gasoline (59).

Two versions of the MTG process, one using a fixed bed, the other a fluid bed, have been developed. The fixed-bed process was selected for installation in the New Zealand *gas-to-gasoline (GTG)* complex, situated on the North Island between the villages of Waitara and Motonui on the Tasman seacoast (60). A simplified block flow diagram of the complex is shown in Figure 6 (61). The plant processes over $3.7 \times 10^6\ m^3/d$ (130×10^6 SCF/d) of gas from the offshore Maui field supplemented by gas from the Kapuni

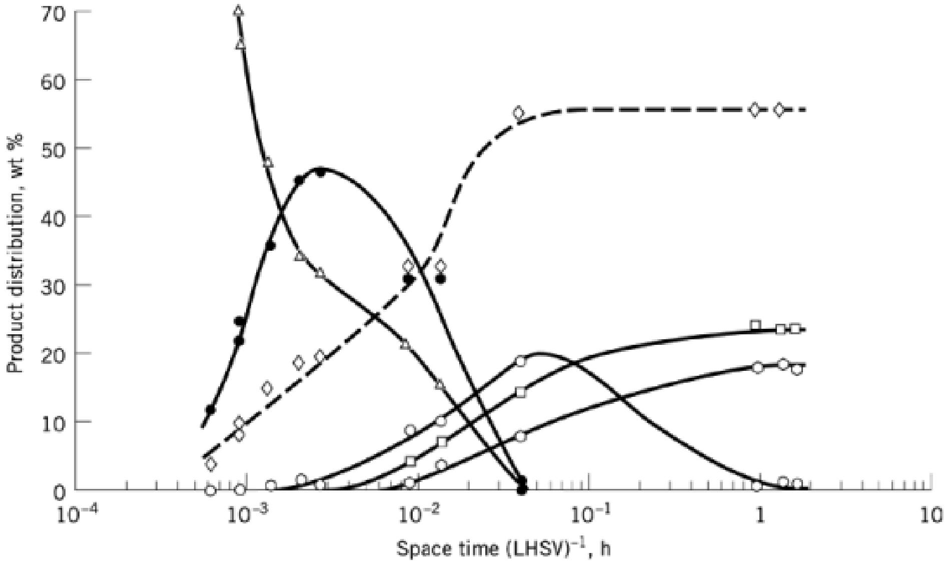

Fig. 5. Methanol-to-hydrocarbons reaction path at 371°C, where (△) is methanol; (●), dimethyl ether; (◇), water; (□), paraffins (and C_6+olefins); (), aromatics; and (○), C_2–C_5 olefins. LHSV=Liquid hourly space velocity.

field, first to methanol, and thence to 2.3×10^3 m^3/d (14,500 bbl/d) of gasoline. Methanol feed to the MTG section is synthesized using the ICI low pressure process (62) in two trains, each with a capacity of 2200 t/d.

A flow diagram of the MTG section is shown in Figure 7. Methanol feed, vaporized by heat exchange with reactor effluent gases, is converted in a first-stage reactor containing an alumina catalyst to an equilibrium mixture of methanol, dimethyl ether (DME), and water. This is combined with recycle light gas, which serves to remove reaction heat from the highly exothermic MTG reaction, and enters the reactors containing ZSM-5 catalyst. As indicated in Figure 7, five parallel swing reactors are used. Four reactors are on feed while the fifth is under regeneration. The multiple-bed configuration is used to minimize pressure drop as well as to control product selectivity. Reaction conditions are 360–415°C, 2.17×10^3 kPa (315 psia), and 9/1 recycle/fresh feed ratio. The overall thermal efficiency of the plant is ca 53%.

A fluid-bed version of the MTG process has been developed (60, 63–65) and demonstrated in semiworks scale of 15.9 m^3/d (100 bbl/d), but has not been commercialized to date (ca 1993). Heat management of the exothermic MTG reaction is greatly facilitated by use of fluid-bed reactors. The turbulent bed, with its excellent heat-transfer characteristics, ensures isothermality through the reaction zone and permits steam generation by direct exchange with steam coils in the bed. A schematic diagram appears in Figure 8. The reactor system consists of three principal parts: the reactor, the catalyst regenerator, and an external catalyst cooler. The reactor is also equipped with internal heat-exchanger tubes. Methanol is converted in a single pass at 380–430°C, 276–414 kPa (40–60 psia). The methanol feed rate is 500–1050 kg/h. The fluid-bed demonstration was carried out in 1982–1983 (66).

1.3.1.1. Properties. Table 4 contains typical gasoline quality data from the New Zealand plant (67). MTG gasoline typically contains 60 vol % saturates, ie, paraffins and naphthenes; 10 vol % olefins; and 30 vol % aromatics. Sulfur and nitrogen levels in the gasoline are virtually nil. The MTG process produces ca 3–7 wt % durene [95-93-2] (1,2,4,5-tetra-methylbenzene) but the level is reduced to ca 2 wt % in the finished gasoline product by hydrodealkylation of the durene in a separate catalytic reactor.

Table 3. MTG Product Distribution[a, b]

Hydrocarbon	Distribution, wt %
methane	1.0
ethane	0.6
ethylene	0.5
propane	16.2
propylene	1.0
i-butane	18.7
n-butane	5.6
butenes	1.3
i-pentane	7.8
n-pentane	1.3
pentenes	0.5
C_6 + aliphatics	4.3
benzene	1.7
toluene	10.5
ethylbenzene	0.8
xylenes	17.2
C_9 aromatics	7.5
C_{10} aromatics	3.3
C_{11}+ aromatics	0.2

[a] Reaction conditions of 371°C and LHSV of $1.0\ h^{-1}$.
[b] 100% conversion.

Table 4. MTG Gasoline Quality[a]

Parameter	Average	Range
density at 15°C, kg/m^3	730	728–733
Reid vapor pressure, kPa[b]	86.2	83.4–91.0
octane number		
research	92.2	92.0–92.5
motor	82.6	82.2–83.0
durene content, wt %	2.0	1.74–2.29
induction period, min	325	260–370
distillation, % evaporation		
at 70°C	31.5	29.5–34.5
at 100°C	53.2	51.5–55.5
at 180°C	94.9	94.0–96.5
distillation end point, °C	204.5	196–209

[a] Ref. 67.
[b] To convert kPa to psia, multiply by 0.145.

1.3.2. Methanol-to-Olefins and Olefins-to-Gasoline-and-Distillate

Because the MTG process produces primarily gasoline, a variation of that process has been developed which allows for production of gasoline and distillate fuel (68). This process integrates two known technologies, *methanol-to-olefins (MTO)* and *Mobil olefins-to-gasoline-and-distillate (MOGD)*. The MTO/MOGD process schematic is shown in Figure 9. The combined process produces gasoline and distillate in various proportions and, if needed, olefinic by-products.

In the MTO process, methanol is converted over ZSM-5 giving high (up to ca 80 wt % hydrocarbons) olefin yields and low ethylene and light saturate yields. The low ethylene yields are desirable in achieving high distillate yields using MOGD. Figure 5 shows that the production of olefins rather than gasoline from methanol

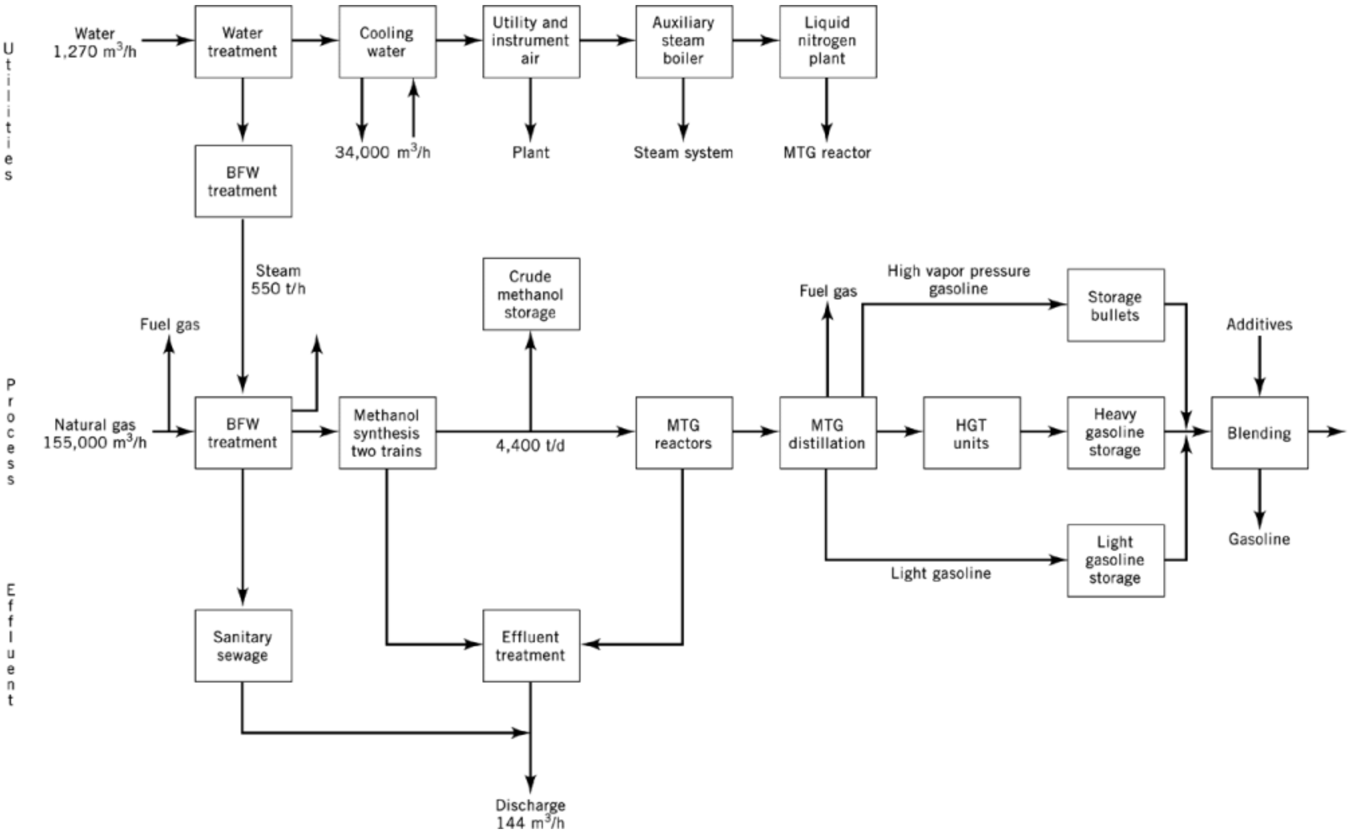

Fig. 6. Simplified block flow diagram for the New Zealand gas-to-gasoline (GTG) plant (61). To convert m^3/h to gal/min, multiply by 4.40. HGT=heavy gasoline treatment facility; MTG=methanol−to−gasoline ; BFW=boiler feed water.

is governed by the kinetics of methanol conversion over ZSM-5 catalyst (69). Generally, catalyst and process variables which increase methanol conversion decrease olefins yield.

The MTO process employs a turbulent fluid-bed reactor system and typical conversions exceed 99.9%. The coked catalyst is continuously withdrawn from the reactor and burned in a regenerator. Coke yield and catalyst circulation are an order of magnitude lower than in fluid catalytic cracking (FCC). The MTO process was first scaled up in a 0.64 m^3/d (4 bbl/d) pilot plant and a successful 15.9 m^3/d (100 bbl/d) demonstration plant was operated in Germany with U.S. and German government support.

The MOGD process oligomerizes light olefins to gasoline and distillate products over ZSM-5 zeolite catalyst. Gasoline and distillate selectivity is $>95\%$ of the feed olefins and gasoline/distillate product ratios can vary, depending on process conditions, from 0.2 to >100. High octane MTO gasoline is separated before the MOGD section and blended with MOGD gasoline. Some MOGD gasoline may be recycled. The distillate product requires hydrofinishing. Generally, the process scheme uses four fixed-bed reactors, three on-line and one in regeneration. A large-scale MOGD refinery test run was conducted by Mobil in 1981.

1.3.2.1. Properties. The gasoline product from the integrated MTO/MOGD process is predominately olefinic and aromatic. The gasoline quality (ca 89 octane) is comparable to FCC gasoline. Typical distillate product properties are given in Table 5. After hydrofinishing, the distillate product is mostly isoparaffinic and has high cetane index, low pour point, and negligible sulfur content. MOGD diesel fuel has somewhat lower

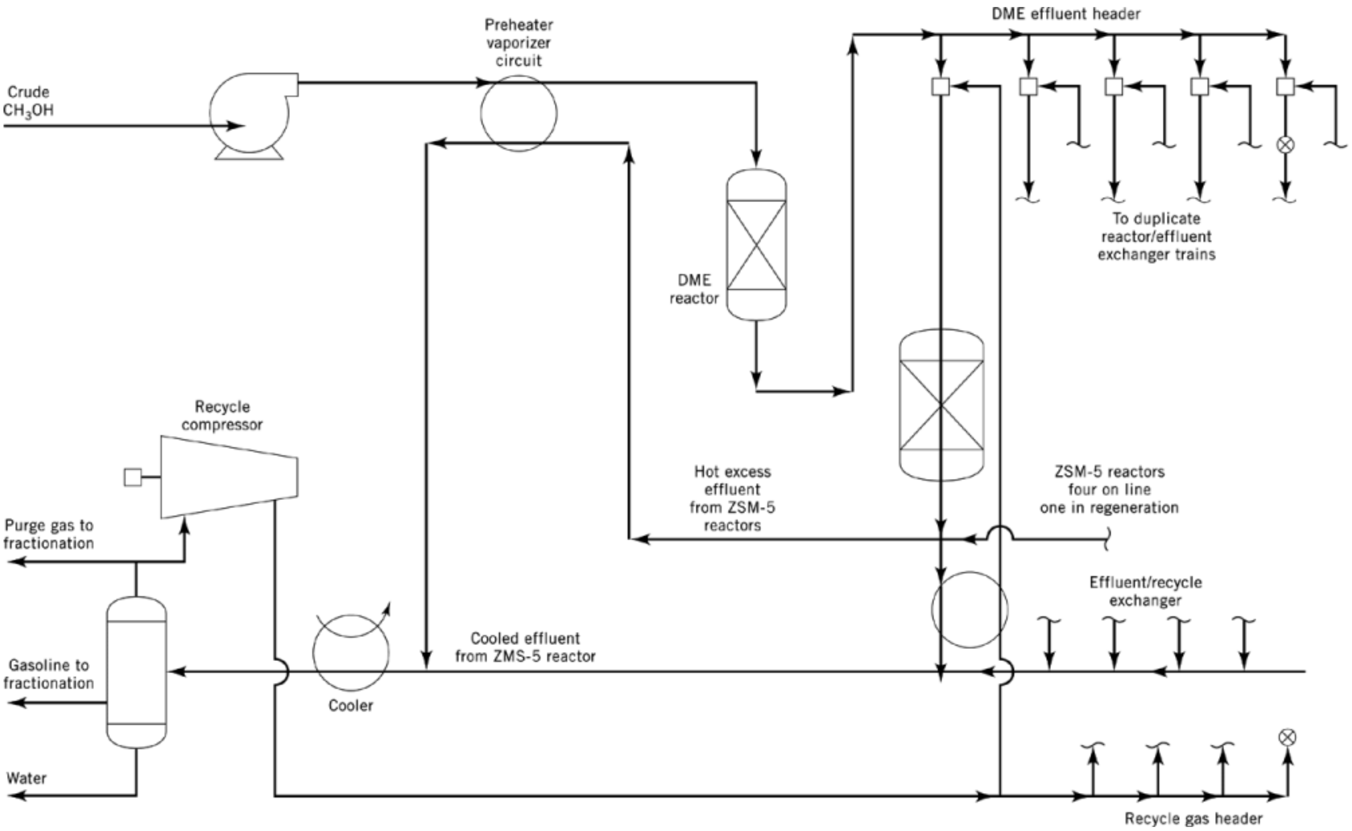

Fig. 7. A methanol-to-gasoline (MTG) fixed-bed process flow diagram. DME = dimethyl ether.

Table 5. MTO/MOGD Distillate Properties

Parameter	Total distillate	Jet fuel	Diesel fuel
quantity, vol %	100	30	70
density, g/mL	0.792	0.774	0.800
pour point, °C	−50		−30
freeze point, °C	−60	−60	
flash point, °C	60	50	100
cetane number	50		52
smoke point, mm	25	25	
aromatics, vol %	4	5	
sulfur, ppm	50		

density than typical conventional fuels (0.8 vs 0.86). Low aromatics levels contribute to a stable jet fuel with very little smoke emission during combustion. MOGD diesel and jet fuels meet or exceed all conventional specifications.

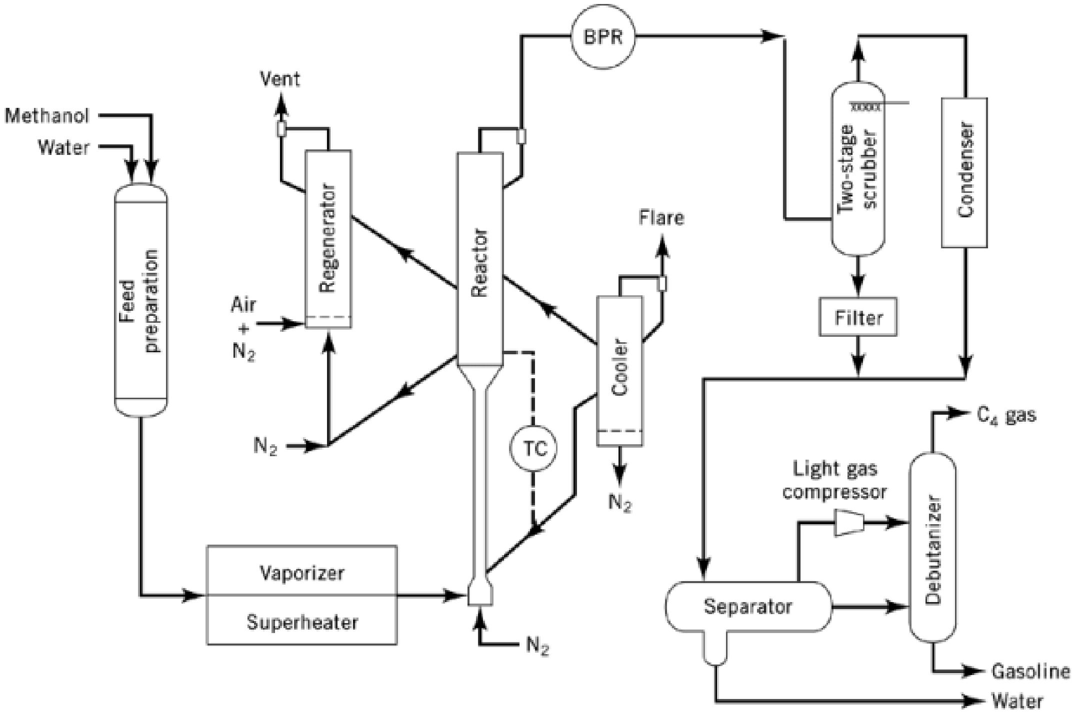

Fig. 8. Fluid-bed MTG demonstration plant schematic diagram. BPR=Back pressure regulator; TC=temperature controller.

2. Direct Conversion of Natural Gas to Liquid Fuels

The capital costs associated with indirect natural gas upgrading technology are high, thus research and development has focused on direct conversion of natural gas to liquid fuels. Direct conversion is defined as upgrading methane to the desired liquid fuels products while bypassing the synthesis gas step, ie, direct transformation to oxygenates or higher hydrocarbons. Direct upgrading routes which have been extensively studied include direct partial oxidation to oxygenates, oxidative coupling to higher hydrocarbons, and pyrolysis to higher hydrocarbons. Owing to the inert nature of methane, the technology is limited by the yields of desired products which in turn affects the process economics. Only one direct oxidative methane conversion process has been commercialized. A plant at Copsa Mica (Romania) in the 1940s (70) produced formaldehyde directly from methane and air by partial oxidation. This plant is no longer in operation. Plants to produce acetylene from methane by high temperature pyrolysis routes have been commercialized (see Hydrocarbons, acetylene).

Generally, the most developed processes involve oxidative coupling of methane to higher hydrocarbons. Oxidative coupling converts methane to ethane and ethylene by

$$2\ CH_4 + 1/2\ O_2 \longrightarrow H_3CCH_3 + H_2O \qquad (13)$$

$$H_3CCH_3 + 1/2\ O_2 \longrightarrow H_2C{=}CH_2 + H_2O \qquad (14)$$

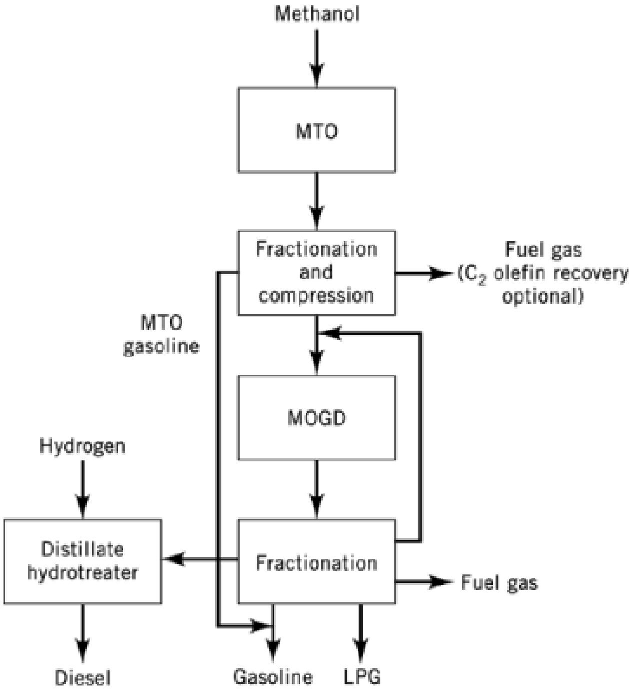

Fig. 9. Methanol-to-olefins (MTO) and Mobil olefins-to-gasoline (MOGD) and distillate process schematic.

The process can be operated in two modes: co-fed and redox. The co-fed mode employs addition of O_2 to the methane/natural gas feed and subsequent conversion over a metal oxide catalyst. The redox mode requires the oxidant to be from the lattice oxygen of a reducible metal oxide in the reactor bed. After methane oxidation has consumed nearly all the lattice oxygen, the reduced metal oxide is reoxidized using an air stream. Both methods have processing advantages and disadvantages. In all cases, however, the process is run to maximize production of the more desired ethylene product.

Direct conversion of natural gas to liquids has been actively researched. Process economics are highly variable and it is unclear whether direct natural gas conversion technologies are competitive with the established indirect processes. Some emerging technologies in this area are presented herein.

2.1. ARCO Gas-to-Gasoline Process

A two-step process using oxidative coupling to upgrade natural gas to liquid fuels has been proposed by ARCO (Atlantic Richfield Co.) (71, 72). A simplified process scheme is given in Figure 10. Methane is passed through a redox-mode oxidative coupling reactor which generates C_2+ hydrocarbons such as ethylene. The olefinic products are then oligomerized over a zeolite catalyst in a second reactor to produce gasoline and distillate. Unreacted methane is recycled. ARCO claims 25% conversion of methane with 75% C_2+ selectivity (ethylene to ethane ratio up to 10) in the oxidative coupling first stage and 95% ethylene conversion with 70% selectivity to gasoline and distillate in the olefin oligomerization second stage. This technology has been developed through bench-scale and pilot-plant stages.

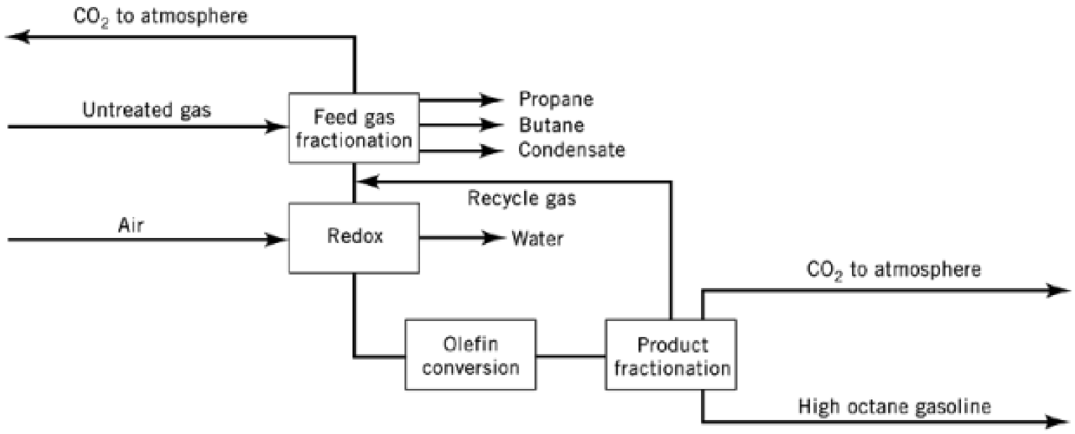

Fig. 10. Simplified flow diagram depicting the ARCO gas-to-gasoline process for a conceptual gasoline production plant (72).

2.2. OXCO Process

The OXCO process for upgrading natural gas has been proposed by the Commonwealth for Scientific and Industrial Research Organization (CSIRO) in Australia (73, 74). This process involves C_2+ pyrolysis and oxidative coupling of natural gas in a two-stage reactor; the entire concept is shown schematically in Figure 11. The methane in natural gas is separated and oxidatively coupled in a fluidized-bed reactor operating in co-fed mode to produce ethylene and ethane. The higher alkanes from the natural gas as well as the product ethane from the first stage are injected into an oxygen-free pyrolysis stage to make additional ethylene. The heat from the coupling reactor is used in the pyrolysis reaction. The overall carbon conversion to unsaturates plus CO_2 per pass is 30% with an overall carbon selectivity to unsaturates of 86%. The ethylene may be subsequently upgraded by oligomerization to liquid fuels. This process, which produces higher yields of ethylene and has a more favorable heat balance than conventional oxidative coupling technology, has been demonstrated in 30- and 60-mm fluidized-bed reactors.

2.2.1. Properties

Liquid fuels derived from oxidative coupling/olefin oligomerization processes would be expected to have properties similar to those derived from olefin oligomerization pathways such as MTO/MOGD.

3. Oxygenate Fuels

Alcohols and ethers, especially methanol, ethanol, and methyl *tert*-butyl ether [1634-04-4] (MTBE), have been widely used separately or in blends with gasolines (reformulated gasoline) and other hydrocarbons to fuel internal combustion engines. Fuel properties of key oxygenates are presented in Table 6 (5). These compounds, as a class, may be considered to be partially oxidized, ie, each has a mole of oxidized hydrogen. They differ from the hydrocarbons that make up gasoline principally in lower heating values and in higher vaporization heat requirements. This constitutes a serious disadvantage to the substitution of oxygenates, especially lower alcohols, for motor gasoline. For example, the heating value of methanol is about half that of gasoline on an equivalent volume basis. Other properties which greatly influence the potential of oxygenates as fuels include octane performance, solubility in gasoline, effect on gasoline vapor pressure, sensitivity to water,

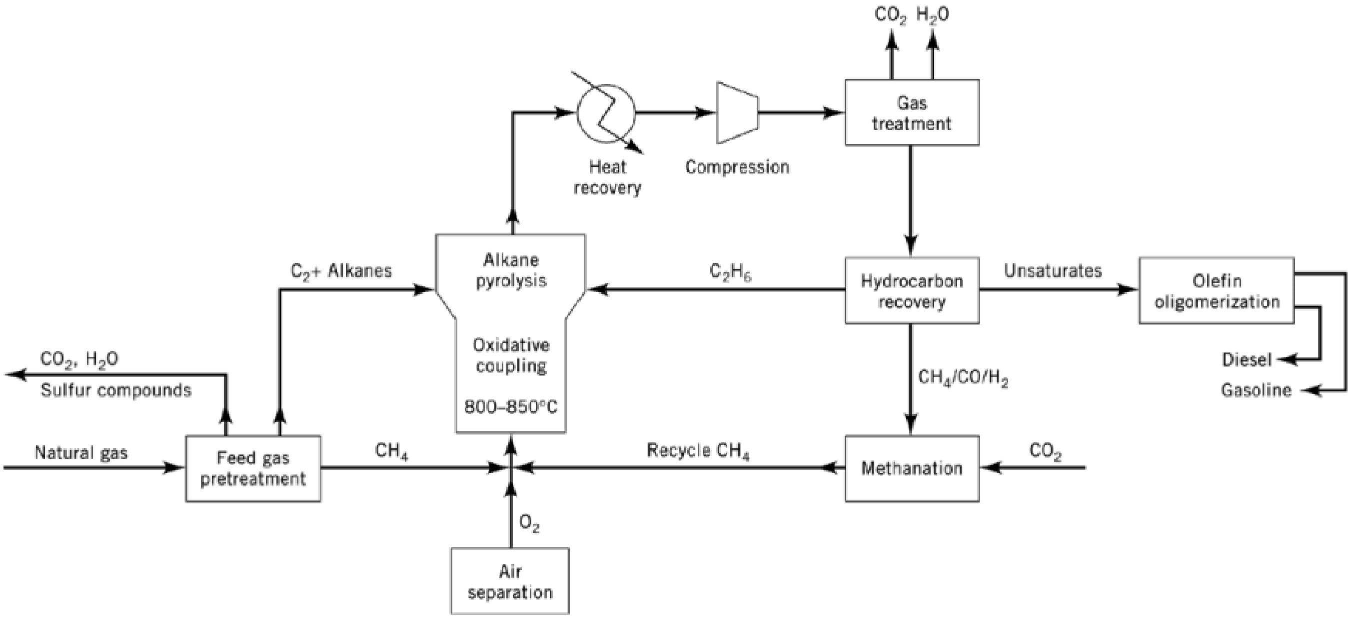

Fig. 11. The OXCO process for natural gas conversion (74).

Table 6. Fuel Oxygenates Properties[a]

Oxygenate	Blending octane, 1/2(RON + MON)[b]	Heat of combustion, MJ/L[c]	Specific gravity	Boiling point, °C
methanol	101	18.0	0.79	64.6
ethanol	101	21.3	0.79	78.5
2-propanol	106	26.4	0.79	82.4
2-butanol	99	28.3	0.80	99.5
tert-butyl alcohol	100	28.1	0.80	82.6
MTBE[d]	108	30.2	0.75	55.4
ETBE[e]	111	32.5	0.74	72.8
TAME[f]	102	31.2	0.77	86.3
gasoline	87	34.8	0.74	

[a] Ref. 5.

[b] RON = research octane number; MON = motor octane number.

[c] To convert MJ/L to Btu/gal, multiply by 3589.

[d] MTBE = methyl *tert*−butyl ether.

[e] ETBE = ethyl *tert*−butyl ether.

[f] TAME = *tert*−amyl methyl ether.

and evaporative/exhaust emissions. Oxygenate fuels tests are often debated because the tests employed were developed for conventional gasolines.

The addition of small percentages of oxygenates to gasoline can produce large gains in octane. Thus, as blending components in gasoline, oxygenates improve octane quality. As neat fuels for spark-ignition engines, octane values for oxygenates are not useful in determining knock-limited compression ratios for vehicles because of the lean carburetor settings relative to gasoline. Neither do these values represent the octane performance of oxygenates when blended with gasoline.

In part because neat alcohols are insufficiently volatile to enable a cold engine to start, even at moderate temperatures, the use of neat alcohols for automotive motor fuel is problematic (see Alcohol fuels). Manufacturers have, however, reported that alcohol-powered cars, after being started and warmed up, can have the same or better driveability as gasoline cars (75–77). As for gasoline vehicles, port fuel injector fouling has occurred in some methanol vehicles and has affected driveability and emissions. Other problems related to high alcohol content gasoline in conventional engines include vapor lock and corrosion. Flexible-fuel vehicles (FFV), which can operate on either neat methanol or gasoline, or mixtures thereof, are being evaluated.

Gasoline blends containing oxygenates change the emissions characteristics of a motor vehicle designed for gasoline. Oxygenates and oxygenate-blends approved for use by the U.S. government are expected to have desirable emissions features as automotive fuels, and governmental environmental mandates and regulations have necessitated increased examination and implementation of oxygenates as fuels. As of this writing, however, no process can produce alcohols or ethers at equivalent or lower cost per volume than gasolines derived from natural petroleum.

3.1. Methanol

Methanol (qv) production in the 1990s is dominated by reaction of synthesis gas produced from natural gas. The economics of producing methanol as fuel are highly variable and site-specific. The natural gas feedstock has a broad range of values depending on location. Delivered costs for methanol are probably double that for gasoline from petroleum. Impurities, including water, vary according to the synthesis process employed. The term *methyl fuel* describes certain methanol products that may also contain significant quantities of water and higher alcohols as well as other oxygenated compounds. Water removal from such mixtures by distillative processes is generally complicated because of the formation of azeotropes. Methanol is used to produce MTBE, another oxygenate fuel.

Methanol as a fuel has been proposed in various ratios with gasoline. In gasoline formulations having relatively low methanol content, eg, M3 (3% methanol) and M15 (15% methanol), solubilizers are used and stringently dry conditions must be maintained. High methanol content fuels, M85 (85% methanol) and M100 (neat methanol), have special engine requirements. The use of high methanol content fuels is limited by methanol cost plus poor compatibility with the existing gasoline infrastructure.

Methanol is more soluble in aromatic than paraffinic hydrocarbons. Thus varying gasoline compositions can affect fuel blends. At room temperature, the solubility of methanol in gasoline is very limited in the presence of water. Generally, cosolvents are added to methanol–gasoline blends to enhance water tolerance. Methanol is practically insoluble in diesel fuel.

Concerns about using methanol–gasoline blend fuels include problems with vapor lock, cold start, and warmup. Oxygenate–gasoline blends, and in particular those containing methanol, have unusual volatility characteristics and cannot be accurately characterized using test methods developed for gasoline. Vapor pressure is an important volatility parameter that is adversely affected by the addition of methanol. Gasoline blends containing oxygenates form nonideal solutions with varying characteristics. In general, methanol–gasoline blend fuels exhibit increases in Reid vapor pressure (RVP) over that of gasoline itself. This effect contributes to vapor lock and evaporative emissions. The data available for assessing methanol's impact on exhaust emissions, and consequently on air quality, are limited. Formaldehyde (qv) has been reported in the exhausts of cars fueled with straight methanol or methanol–gasoline blends (see also Exhaust control, automotive).

The use of methanol as a motor fuel has been discussed since the 1920s. Straight methanol has long been a preferred fuel for racing engines because of the much higher compression ratios at which methanol may be combusted relative to gasolines. This is translatable for racing purposes at equivalent power outputs to engines of considerably reduced weight. However, fuel consumptions are roughly three times that of gasoline on a km/L (mi/gal) basis, and extremely high emissions of unburned fuel and carbon monoxide can result (78).

In Germany in the early 1950s, a 50:50 mixture of methanol and 2-propanol was blended with gasoline, first at a level of 7.5% and later at 1.5% (79). Complaints about stalling, power loss, and phase separation caused the ratio to be changed to 60:40::methanol:2-propanol but this apparently aggravated the problems. The practice was discontinued in 1970 when a tax was placed on alcohol.

In the United States, the Clean Air Act of 1970 imposed limitations on composition of new fuels, and as such methanol-containing fuels were required to obtain Environmental Protection Agency (EPA) waivers. Upon enactment of the Clean Air Act Amendments of 1977, EPA set for waiver unleaded fuels containing 2 wt % maximum oxygenates excluding methanol (0.3 vol % maximum). Questions regarding methanol's influence on emissions, water separation, and fuel system components were raised (80).

In 1979 Sun Oil Co. was granted a waiver for a gasoline blend containing 2.75 vol % methanol and an equal volume of *tert*-butyl alcohol (TBA) (2 wt % total oxygen). Cosolvents such as TBA were shown to reduce adverse effects of methanol on volatility and water tolerance. ARCO obtained EPA waiver in 1981 for a 3.5 wt % oxygen fuel blending containing Oxinol, also comprising equal parts of methanol and TBA. In 1985 a waiver was granted to Du Pont, Inc. for a gasoline blend containing 5 vol % maximum methanol with at least 2.5 vol % higher alcohol cosolvents. The waiver incorporated a water tolerance or phase separation requirement (81).

The most extensive worldwide program on methanol blend gasoline was in Italy where from 1982 to 1987 a 1.9×10^4 m^3/yr (5×10^6 gal/yr) plant produced a mixture containing 69% methanol. The balance contained higher alcohols. This mixture was blended into gasoline at the 4.3% level and marketed successfully as a premium gasoline known as Super E (82).

Methanol, a clean burning fuel relative to conventional industrial fuels other than natural gas, can be used advantageously in stationary turbines and boilers because of its low flame luminosity and combustion temperature. Low NO_x emissions and virtually no sulfur or particulate emissions have been observed (83). Methanol is also considered for dual fuel (methanol plus oil or natural gas) combustion power boilers (84) as well as to fuel gas turbines in combined methanol/electric power production plants using coal gasification (85) (see Power generation).

Owing to its properties, methanol is not recommended for aircraft or marine fuel uses. Methanol cannot be used in conventional diesel-powered vehicles without modifications to the fuel system and engine. Simple methanol–diesel blends are not possible because of insolubility. Heavy-duty diesel engines have been adapted to use neat methanol by many U.S. manufacturers, and several are being used in field demonstrations (82) (see Alcohol fuels).

3.2. Ethanol

Ethanol (qv) is produced both from ethylene (qv) derived from the cracking of petroleum fractions and by the fermentation of sugars derived from grains or other biomass (see Sugar). Many of its relevant properties are similar to those of methanol. Although ethanol may be a more desirable fuel or fuel component than methanol, its significantly higher cost (volume basis) may outweigh these advantages. Broad implementation of ethanol-containing fuels would require government action, eg, in the form of subsidies to farmers and fuel waivers.

The term *gasohol* has come into wide usage to identify, generally, a blend of gasoline and ethanol, with the latter derived from grain. The term may also be applied to blends of methanol or other alcohols in gasolines or other hydrocarbons, without regard to sources of components.

3.2.1. Brazil's Alcohol Program

In Brazil, the enactment of legislation in 1931 made ethanol addition to gasoline compulsory at a level of 5% (86). Excess molasses and sugar were converted to alcohol in distilleries attached to sugar mills as a means to stabilize sugar prices. Production of fuel ethanol in the 1990s is mostly from biomass.

Starting in the city of Sao Paulo in 1977, and extending to the entire state of Sao Paulo in 1978, a gasohol incorporating 20% ethanol was mandated. Brazil's National Alcohol Program (Proalcool) set an initial goal of providing the 20% fuel mixture nationwide by 1980–1981 and a system of special tax, warranty, and price considerations were enacted to advance the aims of Proalcool.

For a considerable period, $>90\%$ of the new cars in Brazil operated on E96 fuel, or a mixture of 96% ethanol and 4% water (82). The engines have high compression ratios (ca 12:1) to utilize the high knock resistance of ethanol and deliver optimum fuel economy. In 1989 more than one-third of Brazil's 10 million automobiles operated on 96% ethanol/4% water fuel. The remainder ran on gasoline blends containing up to 20% ethanol (5).

3.2.2. Gasohol in the United States

Over 90% of the fuel ethanol in the United States is produced from corn. Typically, 0.035 m^3 (1 bushel) of corn yields 9.5 L (2.5 gal) of ethanol. Ethanol is produced by either dry or wet milling (87). Selection of the process depends on market demand for the by-products of the two processes. More than two-thirds of the ethanol in the United States is produced by wet milling. Depending on the process used, the full cost of ethanol after by-product credits has been estimated to be between \$0.25–0.53/L (\$1–2/gal) for new plants (88). Feedstock costs are a significant factor in the production of fuel ethanol. A change in corn price of \$0.29/m^3 (\$1.00/bushel) affects the costs of ethanol by \$0.08/L (\$0.30/gal).

Ethanol can also be produced from cellulose (qv) or biomass such as wood (qv), corn stover, and municipal solid wastes (see Fuels from biomass; Fuels from waste). Each of these resources has inherent technical or economic problems. The Tennessee Valley Authority (TVA) is operating a 2 t/d pilot plant on converting cellulose to ethanol.

After the oil embargo in 1973, gasohol use was stimulated by tax incentives. An application for EPA waiver of gasohol fuels (up to 10 vol % ethanol) was granted in 1979. From 1981 to 1983 the California Energy Commission field tested alcohol-powered cars equipped with a gasoline-assist starting system, ie, having an onboard auxiliary supply of volatile fuel for cold start tests. In 1989 about 8% of U.S. gasoline contained 10% ethanol plus a corrosion inhibitor (82). As of this writing, government waivers of RVP standards for gasohol fuels are being considered (89).

3.3. Methyl *t*-Butyl Ether

MTBE is produced by reaction of isobutene and methanol on acid ion-exchange resins. The supply of isobutene, obtained from hydrocarbon cracking units or by dehydration of *tert*-butyl alcohol, is limited relative to that of methanol. The cost to produce MTBE from by-product isobutene has been estimated to be between \$0.13 to \$0.16/L (\$0.50–0.60/gal) (90). Direct production of isobutene by dehydrogenation of isobutane or isomerization of mixed butenes are expensive processes that have seen less commercial use in the United States.

More than 95% of MTBE produced worldwide is used to blend with gasoline. In 1987 U.S. production of MTBE exceeded 3.8×10^6 m^3/yr $(1 \times 10^9$ gal/yr) (82). The worldwide capacity for MTBE is increasing, especially in the United States and Europe, and has been projected to exceed production for years to come.

MTBE's gain in prominence as a fuel-blend component is a result of inherent technical advantages over other oxygenates, especially the lower alcohols. MTBE has a high blending octane number (Table 6) although this number varies somewhat with gasoline composition. The low vapor pressure relative to the lower alcohols results in no increase in RVP for MTBE-gasoline blends and consequently better evaporative emission and vapor lock characteristics. No phase separation occurs in blends with other fuels. MTBE, in blends of <20 vol % with gasoline, does not deleteriously affect other fuel or driving characteristics such as cold start, fuel consumption, and engine materials compatibility.

MTBE has been used in motor fuels in Europe since the early 1970s and is undergoing rapid growth, particularly in the United States. MTBE-blended gasoline containing up to 11 vol % MTBE received EPA waiver in 1981. Later legislation increased the MTBE waiver up to 15 vol %. In 1987–1988 Colorado began mandating use of winter oxygenate-based fuels in the Denver region. About 90% of the fuel in this period used a gasoline blend containing 8 vol % MTBE and in 1988–1989 the fuel was required to contain at least 2% oxygen (11 vol % MTBE). Based on the success of this program and EPA assessments that CO reductions of 10–20% over the next decade were possible with oxygenate-blend fuels, numerous state governments enacted legislation requiring the use of these fuels in winter and in cities having high ozone (smog) concentrations. The Clean Air Act Amendments of 1990 have mandated the use of reformulated gasolines, especially in serious ozone problem areas, by 1995.

The effectiveness of MTBE, however, is under discussion (91). Based on Denver, Colorado vehicle emissions data from 1981 to 1991 and theoretical models, Colorado scientists have claimed that the use of MTBE-blended fuels had no statistically significant effect on atmospheric CO levels, but increased pollutants such as formaldehyde. A drop in CO levels in Denver during this time period was attributed to fleet turnover of older, more polluting cars being replaced by newer cars having cleaner burning engines. In addition, health problems associated with direct exposure to MTBE in Fairbanks, Alaska has resulted in EPA exemption of the oxygenated fuel requirement in that area (91).

4. Direct Liquefaction of Coal

Direct liquefaction, the production of liquids from feed coal in a single processing scheme without a synthesis gas intermediate step, includes two routes for the upgrading of coal: hydrogenation and pyrolysis. In hydrogenation, the conversion of coal to liquids having higher hydrogen-to-carbon ratio involves the addition of hydrogen. Generally, the additional hydrogen required is added either from molecular hydrogen or from a hydrogen-donor solvent such as tetralin. Processes classified under pyrolysis are those which produce liquids by removal of carbon. This occurs when coal is thermally processed under inert or reducing atmospheric conditions. The use of hydrogen in a pyrolytic process to increase yields of distillate products is known as hydropyrolysis. Coal carbonization to produce metallurgical coke involves much the same chemistry as pyrolysis.

4.1. Coal and Coal-Tar Hydrogenation

If paraffinic and olefinic liquids are extracted from solid fuel substances, the hydrogen content of the residual material is reduced even further, and the residues become more refractory. The yields of liquids so derivable are generally low, even when a significant fraction of the hydrogen is extractable. Thus production of fuel liquids from nonliquid fuel substances such as coal and coal tars may be enhanced only by the introduction of additional hydrogen in a synthesis process. The principal differences in the processes are from the modes in which hydrogen is introduced and the catalysts used.

Hydrogenation of coal and other carbonaceous matter using high pressure hydrogen has been patented (92), and subsequently the Nobel Prize in chemistry was won for this accomplishment. By 1922, a 1 t/d plant was operating and using hydrogen at 10 MPa (100 atm) and 400°C to treat brown coal tar to give a liquid that comprised 25 wt % gasoline boiling at 75–210°C and 40 wt % middle oil, 210–300°C (see Lignite and brown coal). The pitch residue had a specific gravity of 1.04, and a solidification point of 15°C. The degree of liquefaction was shown to increase with decrease in oil rank (93). Liquid products were of low quality, being high in oxygen, nitrogen, and sulfur content, owing to low hydrogenation rates and polymerization of primary products (94).

In 1935 an ICI coal hydrogenation plant at Billingham, U.K., produced ca 136,000 t/yr motor fuel from bituminous coal and coal tar. By 1936, 272,000 t/yr of motor fuel were produced by improved hydrogenation of brown coal and coal tar at a facility constructed at Leuna and some 363,000 t/yr was being produced in three other German plants (95). Two years later the total German output from these facilities was ca 1.4×10^6 t/yr

(96). The number of coal hydrogenation plants in Germany increased during World War II to 12, with total capacity of about 4×10^6 t/yr (100,000 bbl/d) of aviation and motor gasolines.

Experimental plants for hydrogenating coal or coal tar were operated in Japan, France, Canada, and in the United States before or during World War II. Much of that technology has remained proprietary. In general, coal-in-oil slurries containing iodine or stannous oxalate catalyst were subjected to liquid-phase hydrogenation at pressures of 25–70 MPa (250–700 atm). Liquids produced were fractionated, and the middle oils were then subjected to vapor-phase hydrogenation over molybdenum-, cobalt-, or tungsten sulfide-on-alumina catalysts (97). About 1 t of crude motor fuel was recovered from 4.5 t of coal, from which all necessary hydrogen and power requirements for the production were also obtained.

4.1.1. Developments in the United States

A large number of proprietary coal hydrogenation process variants have been proposed. Much of the technology originally directed to the catalytic hydrogenation of coals and coal tars in Germany has been applied to the hydrorefining of petroleum fractions, but U.S. commercial interest in coal hydrogenation was offset by the relative abundance of domestic petroleum up to World War II.

The huge demand for liquid fuels during World War II prompted the passage of the Synthetic Liquid Fuels Act of 1944. There were various programs relating to demonstration plants to produce liquid fuels from coal, oil shale, and other substances, including agricultural and forestry products. The Bureau of Mines had begun work on coal liquefaction in 1936, at which time a 45 kg/d experimental coal hydrogenation unit was constructed (98). The expanded program, after 1944, culminated in the construction and operation of a 45 t/d coal hydrogenation demonstration plant at Louisiana, Missouri, in 1949 (99), where a variety of problems and processing variations were investigated (100, 101). Cost studies (102) showed that production of gasoline from coal hydrogenation could not compete with using natural petroleum as a gasoline source. The demonstration plant operations were terminated in 1953.

Work on coal hydrogenation continued by the Bureau of Mines on a laboratory scale (103–105). In one of these variants (106) coal-oil pastes admixed with catalyst in tubular reactors were hydrogenated at high pressure and low residence times to give improved yields of liquid products. The original thrust of the work was to hydrodesulfurize coal economically to produce environmentally acceptable boiler fuel (107). In the mid-1970s, a process sponsored by the Bureau of Mines named Synthoil (108) was developed, but the efforts were terminated by 1978 owing to limited catalyst lifetimes.

4.1.2. H-Coal Process

The *H-coal process* (Hydrocarbon Research, Inc., HRI, subsidiary of Dynalectron Corp.), for the conversion of coal to liquid products (109), is an application of HRI's ebullated-bed technology for the conversion of heavy oil residues into lighter fractions. Coal is dried, pulverized, and slurried with coal-derived oil (110). The coal-oil slurry is charged continuously with hydrogen to a reactor of unique design (111) containing a bed of ebullated catalyst, where the coal is hydrogenated and converted to liquid and gaseous products. The liquid product is a synthetic crude oil that can be converted to gasoline or heating oil by conventional refining processes. Alternatively, under milder operating conditions, a clean fuel gas and low sulfur fuel oils may be produced. The relative yields of these products depend on the desired sulfur level in the heavy fuel oil. In general, reaction products are separated by fractionation and absorption (qv). Unreacted coal may be fed into a fluid coker that produces gas, gas oil, and dry char. The coker gas oil, along with gas oils separated from the main reactor effluent, may be subjected to hydrocracking for conversion to lighter products.

In 1976, Ashland Oil (Ashland Synthetic Fuels, Inc.) was awarded the prime contract to construct a 540 t/d H-coal pilot plant adjacent to its refinery at Catlettsburg, Kentucky, by an industry–government underwriting consortium. Construction was completed in 1980 (112). The pilot-plant operation ended in early 1983.

Table 7. Properties of Syncrude from H-Coal Process[a]

Property	Boiling range			Total
	Initial to 190°C	190–343°C	343–524°C	
specific gravity, (°API)[b]	0.767 (53.0)	0.915 (23.2)	1.05 (3.5)	0.863 (32.4)
vol % of total	40.0	54.2	5.8	100.0
analysis, wt %				
carbon	84.5	88.8	89.4	87.3
hydrogen	13.6	11.0	10.2	11.9
oxygen	1.7			0.6
nitrogen	0.1	0.1	0.1	0.1
sulfur	0.1	0.1	0.3	0.1
Total	*100*	*100*	*100*	*100*

[a] Ref. 111.

[b] $°\text{API} = \frac{141.5}{\rho} - 131.5$ where ρ is specific gravity.

4.1.2.1. Properties. The properties of naphtha, gas oil, and H-oil products from an H-coal operation are given in Table 7. These analyses are for liquids produced from the syncrude operating mode. Whereas these liquids are very low in sulfur compared with typical petroleum fractions, they are high in oxygen and nitrogen levels. No residual oil products (bp $> 540°C$) are formed.

4.1.3. Solvent-Refined Coal Process

In the 1920s the anthracene oil fraction recovered from pyrolysis, or coking, of coal was utilized to extract 35–40% of bituminous coals at low pressures for the purpose of manufacturing low cost newspaper inks (113). Tetralin was found to have higher solvent power for coals, and the I. G. Farben Pott-Broche process (114) was developed, wherein a mixture of cresol and tetralin was used to dissolve ca 75% of brown coals at 13.8 MPa (2000 psi) and 427°C. The extract was filtered, and the filtrate vacuum distilled. The overhead was distilled a second time at atmospheric pressure to separate solvent, which was recycled to extraction, and a heavier liquid, which was sent to hydrogenation. The bottoms product from vacuum distillation, or solvent-extracted coal, was carbonized to produce electrode carbon. Filter cake from the filters was coked in rotary kilns for tar and oil recovery. A variety of liquid products were obtained from the solvent extraction-hydrogenation system (113). A similar process was employed in Japan during World War II to produce electrode coke, asphalt (qv), and carbonized fuel briquettes (115).

In the United States there was little interest in solvent processing of coals. A method to reduce the sulfur content of coal extracts by heating with sodium hydroxide and zinc oxide was, however, patented in 1940 (116). In the 1960s the technical feasibility of a coal deashing process was studied (117), and a pilot plant able to process ca 45 t/d was completed in late 1974 (118).

A flow diagram of the solvent-refined coal or *SRC* process is shown in Figure 12. Coal is pulverized and mixed with a solvent to form a slurry containing 25–35 wt % coal. The slurry is pressurized to ca 7 MPa (1000 psig), mixed with hydrogen, and heated to ca 425°C. The solution reactions are completed in ca 20 min and the reaction product flashed to separate gases. The liquid is filtered to remove the mineral residue (ash and undissolved coal) and fractionated to recover the solvent, which is recycled.

The liquid remaining after the solvent has been recovered is a heavy residual fuel called solvent-refined coal, containing less than 0.8 wt % sulfur and 0.1 wt % ash. It melts at ca 177°C and has a heating value of ca 37 MJ/kg (16,000 Btu/lb), regardless of the quality of the coal feedstock. The activity of the solvent is apparently more important than the action of gaseous hydrogen in this type of uncatalyzed hydrogenation. Research has been directed to the use of petroleum-derived aromatic oils as start-up solvents (118).

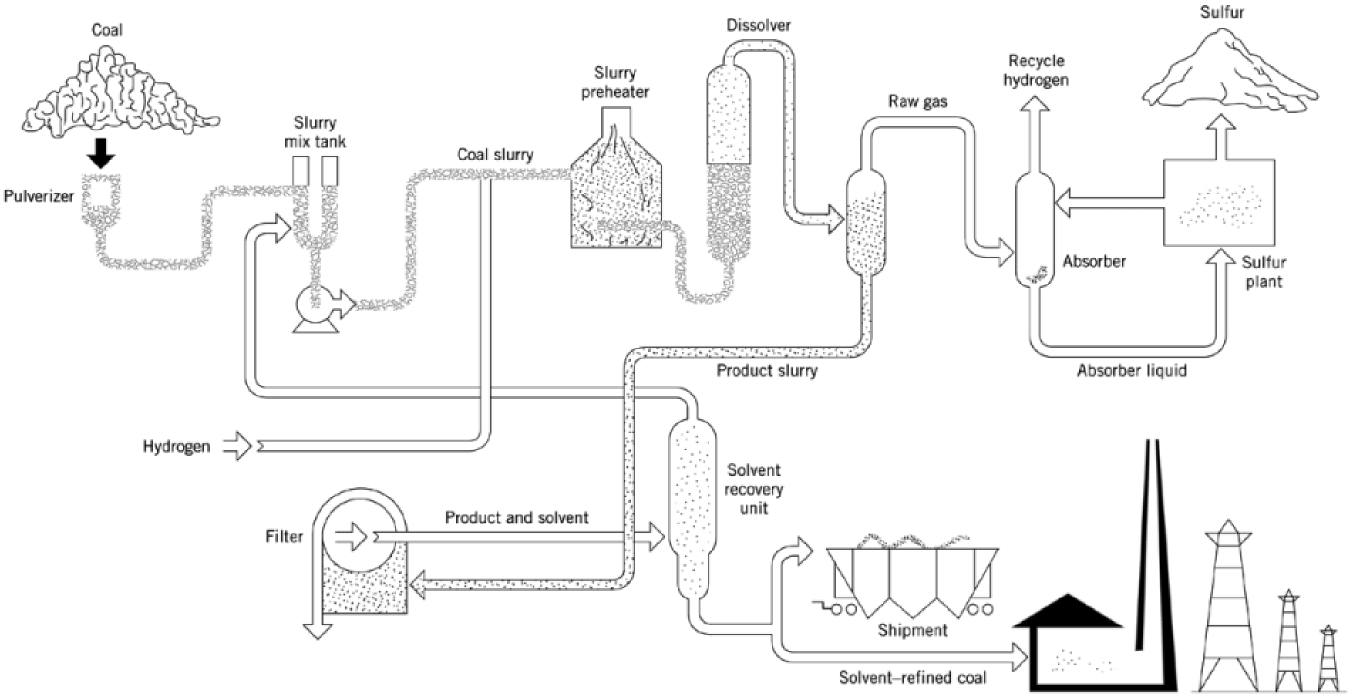

Fig. 12. Solvent-refined coal process (119).

In the early 1970s production of low sulfur, ashless (solid) boiler fuel was the preferred commercial application (119). This basic process (SRC-I) yielded small amounts of liquid oil products with additional processing. Liquid output was significantly increased by the coal-oil-gas (COG) refinery concept (120–122) which incorporated high degrees of hydroconversion and hydrotreating. A SCR-II process has been developed, in which hydrocracking occurs in the solution (hydrogenation) vessels (123). A low viscosity fuel oil is the primary distillate product in this case, although naphtha and LPG are also recovered.

Two pilot plants have been built and operated to demonstrate the feasibility of the SRC process. These included a 6 t/d plant at Wilsonville, Alabama (*vide infra*) and a 50 t/d plant at Ft. Lewis, Washington which was operated from 1974 to 1981.

In an effort to obtain higher value products from SRC processes, a hydrocracking step was added to convert resid to distillate liquids. The addition of a hydrocracker to the SRC-I process was called *nonintegrated two-stage liquefaction (NTSL)*. The NTSL process was essentially two separate processes in series: coal liquefaction and resid upgrading. NTSL processes were inefficient owing to the inherent limitations of the SRC-I process and the high hydrocracker severities required.

4.1.3.1. Properties. The properties of the liquid fuel oil produced by the SRC-II process are influenced by the particular processing configuration. However, in general, it is an oil boiling between 177 and 487°C, having a specific gravity of 0.99–1.00, and a viscosity at 38°C of 40 SUs (123). Pipeline gas, propane and butane (LPG), and naphtha are also recovered from an SRC-II complex.

4.1.4. Exxon Donor Solvent-Coal Liquefaction Process

The *EDS process* from Exxon is a hydrogenation process using a donor solvent for the direct conversion of a broad range of coals to liquid hydrocarbons (124). In the process sequence, shown in Figure 13, the feed coal is

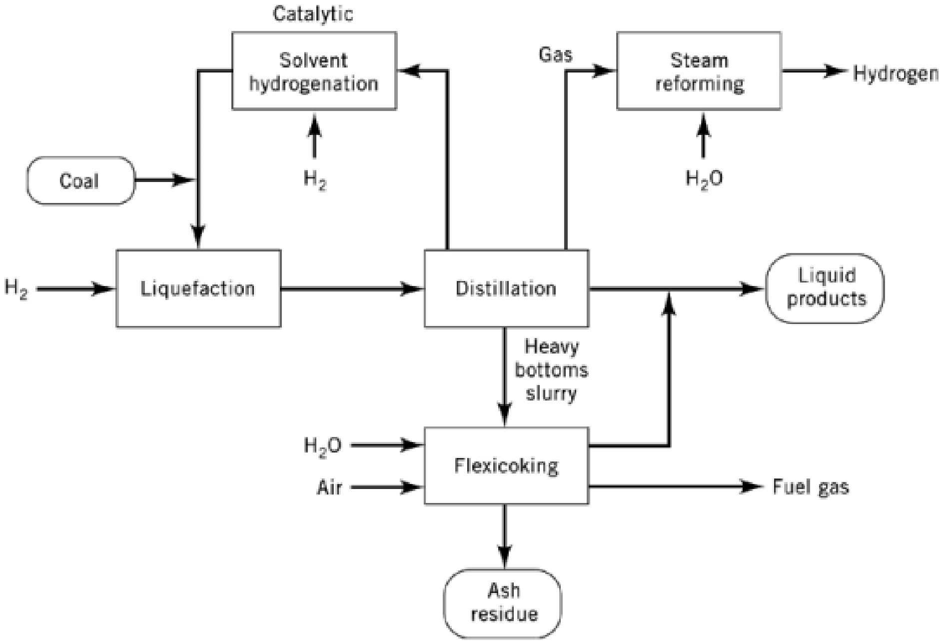

Fig. 13. Exxon donor solvent process (124).

crushed, dried, and slurried with hydrogenated recycle solvent (the donor solvent) and fed to the reactor with hydrogen. The reactor is an upward plug-flow design operating at 430–480°C and at ca 14 MPa (2000 psi) total pressure.

The reactor effluent is separated by conventional distillation into recycle solvent, light gases, C_4 to 537°C bp distillate, and a heavy vacuum bottoms stream containing unconverted coal and ash. The recycle solvent is hydrogenated in a separate reactor and sent back to the liquefaction reactor.

The heavy vacuum bottoms stream is fed to a Flexicoking unit. This is a commercial (125, 126) petroleum process that employs circulating fluidized beds at low (0.3 MPa (50 psi)) pressures and intermediate temperatures, ie, 480–650°C in the coker and 815–980°C in the gasifier, to produce high yields of liquids or gases from organic material present in the feed. Residual carbon is rejected with the ash from the gasifier fluidized bed. The total liquid product is a blend of streams from liquefaction and the Flexicoker.

The EDS process was developed starting from 1976 in a 10-year joint undertaking between DOE and private industry (127). Under the direction of Exxon Co. USA, a 250 t/d pilot plant was operated at Baytown, Texas. Operation of this unit began in 1980 and was completed by late 1982.

4.1.4.1. Properties. Pilot-unit data indicate the EDS process may accommodate a wide variety of coal types. Overall process yields from bituminous, subbituminous, and lignite coals, which include liquids from both liquefaction and *Flexicoking*, are shown in Figure 14. The liquids produced have higher nitrogen contents than are found in similar petroleum fractions. Sulfur contents reflect the sulfur levels of the starting coals: ca 4.0 wt % sulfur in the dry bituminous coal; 0.5 wt % in the subbituminous; and 1.2 wt % sulfur in the dry lignite.

Table 8 shows that the naphthas produced by the EDS process have higher concentrations of cycloparaffins and phenols than do petroleum-derived naphthas, whereas the normal paraffins are present in much lower concentrations. The sulfur and nitrogen concentrations in coal naphthas are high compared to those in petroleum naphthas.

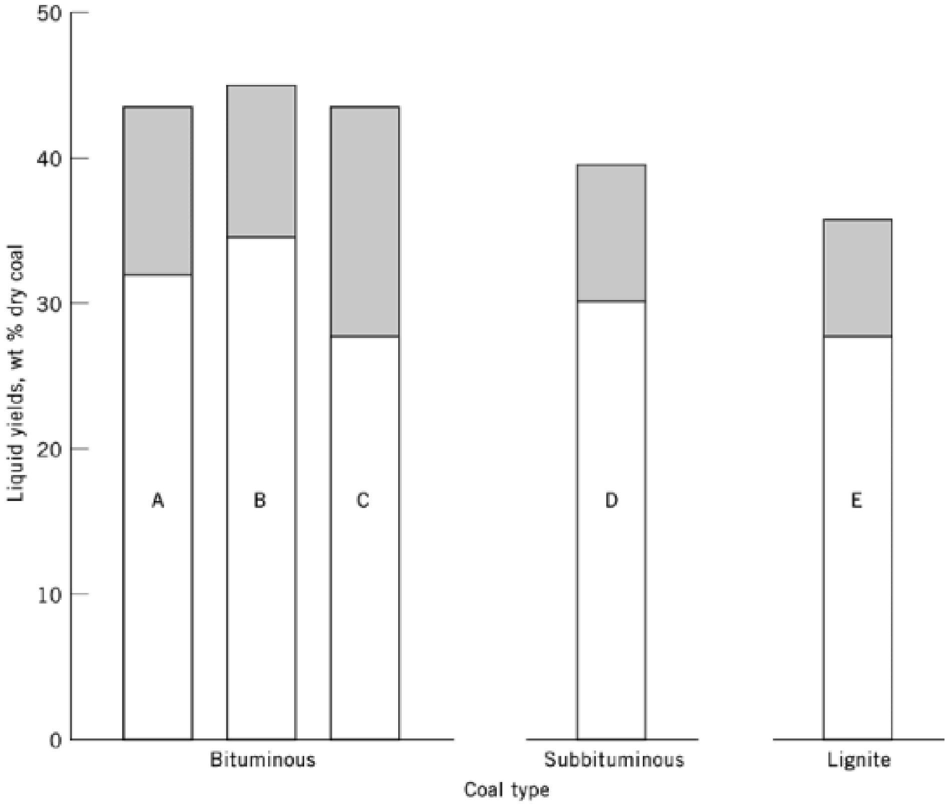

Fig. 14. Preferred liquefaction-coking liquid yields in the EDS process for various coals where ■ represents Flexicoking liquids and □, liquefaction liquids (124). A, Ireland (West Virginia); B, Monterey (Illinois); C, Burning Star (Illinois); D, Wyodak (Wyoming); and E, Big Brown (Texas).

Gas oil fractions (204–565°C) from coal liquefaction show even greater differences in composition compared to petroleum-derived counterparts than do the naphtha fractions (128). The coal-gas oils consist mostly of aromatics (60%), polar heteroaromatics (25%), asphaltenes (8–15%), and saturated compounds ($<10\%$). Petroleum-gas oils, on the other hand, contain more than 50% saturated compounds, less than 5% polar heteroaromatics, and no asphaltenes. Furthermore, the aromatics of petroleum-gas oils have longer side chains.

4.1.5. Coal Liquefaction at Wilsonville

Starting in 1974 the Advanced Coal Liquefaction R&D Facility at Wilsonville, Alabama operated a 6 t/d pilot plant and studied various coal liquefaction processing schemes. The facility, cosponsored by the DOE, the Electric Power Research Institute (EPRI) and Amoco Oil Co, was shut down in early 1992.

Initial operation at the Wilsonville pilot plant was in SRC-I mode and later evolved into a two-stage process (129) by operation in NTSL mode. NTSL limitations described previously combined with high hydrogen consumptions resulted in subsequent focus on a staged integrated approach, which was to be the basis for all further studies at Wilsonville.

The integrated two-stage process (ITSL) combined short contact time liquefaction in one reactor with ebullated-bed hydrocracking in a second stage (130). The short contact time conditions permitted better hydrogen transfer from the solvent rather than from the gas phase. The hydrocracking step operated at lower

Table 8. Composition of Naphthas[a] from Various Sources[b]

	EDS coal liquefaction		Petroleum naphthas	
Component, wt %	Illinois coal	Wyodak coal	Cycloparaffinic[c]	Paraffinic[d]
saturated compounds	69.9	60.8	77.9	81.3
paraffins	13.4	19.4	36.0	58.2
cycloparaffins	56.5	41.4	41.9	23.1
olefins[e]	0.5	3.7		
aromatics	17.0	28.6	22.1	18.7
benzenes	11.7	25.1	20.8	17.2
indans, tetralins	5.1	3.5	1.0	1.2
indenes	0.2	0.0		
naphthalenes	0.01	0.0	0.3	0.3
phenols	12.6	6.9	traces	traces
Total	*100.0*	*100.0*	*100.0*	*100.0*
sulfur	0.57	0.10	0.035	0.049
nitrogen	0.15	0.18	0.0001	0.0001
oxygen	1.60	2.49		

[a] C_5 to 204°C bp.
[b] Ref. 128.
[c] Prudhoe Bay.
[d] Arab Light.
[e] Values are approximate.

severity resulting in lowered gas make and improved hydrogen efficiency. Recycle solvent was generated from the hydrocracked distillates and coupled the two reaction stages. Results of ITSL processing of Illinois No. 6 coal at Wilsonville are given in Table 9. Distillate yields and coal throughput for ITSL were higher than those obtained by NTSL.

Further developments of the ITSL process resulted in incremental gains in distillate yields (131). Reconfigured integrated two-stage liquefaction (RITSL) involved placing the solvent deasher after the hydrocracker thus producing a recycle solvent consisting of deashed resid and distillate. This resulted in reduction of feed to the deasher and reduced organic rejection. Close coupled integrated two-stage liquefaction (CC-ITSL) linked the two reactors and removed several operations between the two stages. A deleterious effect of these two processing modes was increased hydrogen consumption over ITSL.

From 1985 to 1992, development activity at Wilsonville was on catalytic two-stage liquefaction (CTSL). CTSL, initiated by HRI (132), consists of catalytic processing in two ebullated-bed reactors which lower reaction temperatures and increase distillate yields, up to 78% yield. CTSL results from Wilsonville for Illinois No. 6 coal are also given in Table 9. Distillate yields were shown to be significantly higher for CTSL over ITSL; however, hydrogen consumption was somewhat increased.

4.1.5.1. Properties. CTSL distillates have qualities comparable to or better than No. 2 fuel oil and have good hydrogen content and low heteroatom contents. Distillates having a higher boiling point distribution from Wilsonville CTSL operation (131) showed 26.8° API gravity with heteroatom levels of 0.11 wt % sulfur, <1 wt % oxygen, and 0.16 wt % nitrogen.

4.2. Coal Pyrolysis

Pyrolysis is the destructive distillation of coal in the absence of oxygen typically at temperatures between 400 and 500°C (133). As the temperature of carbonaceous matter is increased, decomposition ultimately occurs. Melting and dehydration may also occur. Coals exhibit more or less definite decomposition temperatures, as indicated by melting and rapid evolution of volatile components, including potential fuel liquids, during

Table 9. Wilsonville Plant Operating Conditions and Yields for ITSL and CTSL Modes[a]

	Mode of operation[b]	
Parameter	ITSL	CTSL
Operating conditions		
run number	7242BC; 243JK/244B	253A
catalyst	Shell 32M	Shell 317
First stage[c]		
average reactor temperature, °C	460; 432	432
space velocity	690; 450[d]	4.8[e]
pressure, MPa[f]	17; 10–17	17.9
Second stage		
average reactor temperature, °C	382	404
space velocity, feed/catalyst[e]	1.0	4.3
catalyst age, resid/catalyst	278–441; 380–850	100–250
Yields[g]		
C_1–C_3 gas	4; 6	6
C_4 + distillate	54; 59	70
resid	8; 6	−1
hydrogen consumption	4.9; 5.1	6.8
Other		
hydrogen efficiency, C_4 + distillate/H_2 consumed	11; 11.5	10.3
distillate selectivity, C_1–C_3/C_4+ distillate	0.07; 0.10	0.08
energy content of feed coal reject to ash concentrate, %	24; 20–23	20

[a] Feed is Illinois No. 6 coal.

[b] CTSL = catalytic two-stage liquefaction; ITSL = integrated two-stage liquefaction.

[c] First stage is thermal for ITSL.

[d] Value given is coal space velocity at temp $>371°C$ in kg/m^3.

[e] Value given is in h^{-1}.

[f] To convert MPa to psia, multiply by 145.

[g] Wt % on a moisture- and ash-free (MAF) coal basis.

destructive distillation (134). Table 10 summarizes an extensive survey of North American coals subjected to laboratory pyrolysis. The yields of light oils so derived average no more than ca 8.3 L/t (2 gal/short ton), and tar yields of ca 125 L/t (30 gal/short ton) are optimum for high volatile bituminous coals (135).

Coal pyrolysis has been studied at both reduced and elevated pressures (136), and in the presence of a variety of agents and atmospheres (137). Although important to the study of coal structure and reactions, coal pyrolysis, as a means to generate liquids, has proved to have limited commercial value.

4.2.1. COED Process

Sponsored by the Office of Coal Research of the U.S. Department of the Interior, the COED process was developed by FMC Corp. as Project Char-Oil-Energy Development (COED) through 1975 (138–140). Bench-scale experiments led the way to construction in 1965 of a process development unit employing multistage, fluidized-bed pyrolysis to process 45 kg/h (141). Correlated studies included hydrotreating of COED oil (142), high temperature hydrodesulfurization of COED char, and investigations of char-oil and char-water slurry pipelining economics (143). A pilot plant capable of processing up to 33 t/d and hydrotreating 4.7 m^3/d (30 bbl/d) was started up in 1970 (144), and was operated successfully for a number of years (145).

The COED concept (139), designed to recover liquid, gaseous, and solid fuel components, consists of four stages. Heat is generated by the reaction of oxygen with a portion of the char in the last pyrolysis stage and is also introduced by the air combustion of gas to dry feed coal. The number of stages in the pyrolysis, and the

Table 10. Average Yields and Range of Yields of Fischer Assay of Various Coals[a, a]

	Coke, %		Tar, L/t[c]		Light oil, L/t[c]		Gas, m^3/t[d]		Water, %	
Rank of coal	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range
semianthracite			3.2		0.14					
low volatile bituminous	89.7	85.8–93.3	39.6	29.0–58.4	4.69	3.36–7.41	59.8	54.4–66.6	3.2	1.1–6.6
medium volatile bituminous	83.3	77.4–90.4	86.9	44.6–117.8	7.68	4.92–10.58	66.0	47.3–76.2	4.1	2.8–7.0
high volatile A bituminous	75.5	68.8–81.4	142.1	105.3–187.2	10.53	6.81–15.09	67.0	57.5–80.2	6.0	3.0–9.2
high volatile B bituminous	70.4	66.0–73.2	139.4	111.8–198.3	10.03	7.13–15.82	68.3	56.4–82.3	11.1	10.2–13.1
high volatile C bituminous	67.1	65.4–68.6	124.2	85.1–178.5	8.65	5.93–12.47	61.2	53.0–70.4	15.9	12.0–19.1
high volatile C bituminous or subbituminous A	59.1		94.3	84.6–112.2	7.59	6.26–8.88	90.4		23.4	
subbituminous A			81.9	81.0–82.8	6.21	6.12–6.26				
subbituminous B	57.6	54.8–59.9	70.8	60.7–76.8	6.12	5.24–7.13	90.4	62.2–93.8	27.8	23.3–30.4
lignite	36.5		69.9	30.8–124.2	5.47	2.90–8.69	71.4		44.0	
cannel	58.8	44.1–69.0	338.1	247.0–498.2	23.28	16.84–34.13	61.5	51.0–72.1	3.7	2.0–4.8

[a] Ref. 135.

[b] As-received basis; maximum temperature, 500°C.

[c] To convert L/t to gal/short ton, divide by 4.6.

[d] To convert m^3/t to ft^3/short ton, multiply by 29.4.

Table 11. Properties of COED Char Product[a]

Property	Utah coal	Illinois No. 6
volatile matter, wt %	6.1	2.7
fixed carbon, wt %	80.2	77.0
ash, wt %	13.7	20.3
higher heating value, MJ/kg,[b] dry	28.6	25.6
elemental analysis, wt %, dry		
carbon	81.5	73.4
hydrogen	1.3	0.8
nitrogen	1.5	1.0
sulfur	0.5	3.4
oxygen	1.5	1.0
chlorine	0.006	0.1
iron[c]	0.28	

[a] Ref. 139.
[b] To convert MJ/kg to Btu/lb, multiply by 430.
[c] Included in ash above.

operating temperatures in each, may be varied to accommodate high volatile bituminous and subbituminous feed coals with widely ranging caking or agglomerating properties.

Oil condensed from the released volatiles from the second stage is filtered and catalytically hydrotreated at high pressure to produce a synthetic crude oil. Medium heat-content gas produced after the removal of H_2S and CO_2 is suitable as clean fuel. The pyrolysis gas produced, however, is insufficient to provide the fuel requirement for the total plant. Residual char, 50–60% of the feed coal, has a heating value and sulfur content about the same as feed coal, and its utilization may thus largely dictate process utility.

4.2.1.1. Properties. The properties of char products from two possible coal feeds, a low sulfur Western coal, and a high sulfur Midwestern coal, are shown in Table 11. The char derived from the low sulfur Western coal may be directly suitable as plant fuel, with only minor addition of clean process gas to stabilize its combustion. Flue gas desulfurization may not be required. Flue gas from the combustion of the char derived from the high sulfur Illinois coal, however, requires desulfurization before it may be discharged into the atmosphere.

Typical COED syncrude properties are shown in Table 12. The properties of the oil products depend heavily on the severity of hydroprocessing. The degree of severity also markedly affects costs associated with hydrogen production and compression. Syncrudes derived from Western coals have much higher paraffin and lower aromatic content than those produced from Illinois coal. In general, properties of COED products have been found compatible with expected industrial requirements.

4.2.2. Occidental Petroleum Coal Conversion Process

Garrett R&D Co. (now the Occidental Research Co.) developed the Oxy Coal Conversion process based on mathematical simulation for heating coal particles in the pyrolysis unit. It was estimated that coal particles of 100-mm diameter could be heated throughout their volumes to decomposition temperature (450–540°C) within 0.1 s. A large pilot facility was constructed at LaVerne, California, in 1971. This unit was reported to operate successfully at feed rates up to 136 kg/h (3.2 t/d).

Hot product char carries heat into the entrained bed to obtain the high heat-transfer rates required. Feed coal must be dried and pulverized. A portion of the char recovered from the reactor product stream is cooled and discharged as product. The remainder is reheated to 650–870°C in a char heater blown with air. Gases from the reactor are cooled and scrubbed free of product tar. Hydrogen sulfide is removed from the gas, and a portion is recycled to serve as the entrainment medium.

Table 12. Typical COED Syncrude Properties[a]

Property	Utah A-seam	Illinois No. 6 seam
specific gravity, (° API)[b]	0.934 (20)	0.929 (22)
pour point, °C	16	−18
flash point, closed cup, °C	24	16
viscosity, at 38°C, mm^2/s (=cSt)	8	5
ash, wt %	0.01	0.01
moisture, wt %	0.1	0.1
metals, ppm	10	10
elemental analysis, wt %		
C	87.2	87.1
H	11.0	10.9
N	0.2	0.3
O	1.4	1.6
S	0.1	0.1
ASTM distillation initial bp, °C	138	88
10%	221	134
30%	277	199
50%	349	270
70%	416	316
90%	493	362
end point (95%)	510	397
hydrocarbon type analysis, liquid vol %		
paraffins	23.7	10.4
olefins	0	0
naphthenes	42.2	41.4
aromatics	34.1	48.2

[a] Ref. 139.

[b] $°\text{API} = \frac{141.5}{\rho} - 131.5$ where ρ is specific gravity.

4.2.2.1. Properties. A high volatile western Kentucky bituminous coal, the tar yield of which by Fischer assay was ca 16%, gave a tar yield of ca 26% at a pyrolysis temperature of 537°C (146–148). Tar yield peaked at ca 35% at 577°C and dropped off to 22% at 617°C. The char heating value is essentially equal to that of the starting coal, and the tar has a lower hydrogen content than other pyrolysis tars. The product char is not suitable for direct combustion because of its 2.6% sulfur content.

4.2.3. The TOSCOAL Process

The Oil Shale Corp. (TOSCO) piloted the low temperature carbonization of Wyoming subbituminous coals over a two-year period in its 23 t/d pilot plant at Rocky Falls, Colorado (149). The principal objective was the upgrading of the heating value in order to reduce transportation costs on a heating value basis. Hence, the solid char product from the process represented 50 wt % of the starting coal but had 80% of its heating value.

Furthermore, 60–100 L (14–24 gal) oil, having sulfur content below 0.4 wt %, could be recovered per metric ton coal from pyrolysis at 427–517°C. The recovered oil was suitable as low sulfur fuel. Figure 15 is a flow sheet of the Rocky Flats pilot plant. Coal is fed from hoppers to a dilute-phase, fluid-bed preheater and transported to a pyrolysis drum, where it is contacted by hot ceramic balls. Pyrolysis drum effluent is passed over a trommel screen that permits char product to fall through. Product char is thereafter cooled and sent to storage. The ceramic balls are recycled and pyrolysis vapors are condensed and fractionated.

4.2.3.1. Properties. Results for the operation using subbituminous coal from the Wyodad mine near Gillette, Wyoming, are shown in Table 13. Char yields decreased with increasing temperature, and oil yields

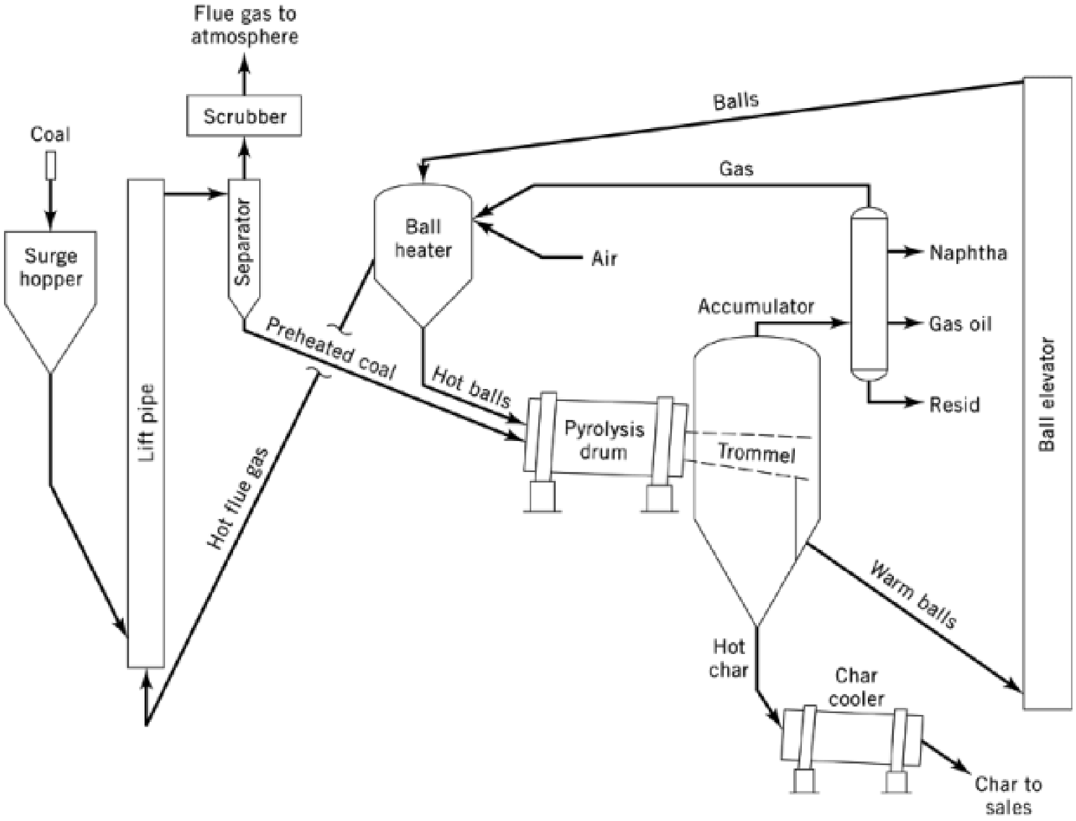

Fig. 15. TOSCOAL process (149).

Table 13. TOSCOAL Retorting of Wyodak Coal[a, b]

	Retort temperature		
Component	427°C	482°C	521°C
char	524.5	505.8	484.4
gas, C_3 and lighter	59.5	78.4	63.0
oil, C_4 and heavier	57.0	71.5	93.1
water[c]	351.0	351.0	351.0
Total	*992.0*	*1006.7*	*991.5*
Recovery, %	*99.2*	*100.7*	*99.1*

[a] Ref. 150.

[b] Product yields, kg/t, of as-mined coal.

[c] Value assumed from Fischer assay and moisture content. The addition of steam to the process prevented accurate measurement of water produced in retorting.

increased. The Fischer assay laboratory method closely approximated the yields and product assays that were obtained with the TOSCOAL process.

The volatiles contents of product chars decreased from ca 25–16% with temperature. Char (lower) heating values, on the other hand, increased from ca 26.75 MJ/kg (11,500 Btu/lb) to 29.5 MJ/kg (12,700 Btu/lb) with temperature. Chars in this range of heating values are suitable for boiler fuel application and the low sulfur

Table 14. TOSCOAL Oil Properties[a]

Properties	Retort temperature		
	427°C[b]	482°C	521°C
analysis, wt %			
carbon	81.4	80.7	80.9
hydrogen	9.3	9.1	8.7
oxygen	8.3	9.4	9.3
nitrogen	0.48	0.7	0.7
sulfur	0.43	0.2	0.2
chlorine	0.0	0.0	0.0
ash	0.0	0.2	0.1
Total	*99.91*	*100.3*	*99.9*
heating values			
gross, MJ/kg[c]	38.59	37.72	37.13
net, MJ/kg[c]	36.61	35.75	35.26
specific gravity, (°API)[d]			
primary oil	1.015 (7.9)	1.040 (4.5)	1.061 (1.9)
calculated, with C_4 and heavier components of gas added	0.978 (13.2)	0.985 (12.1)	1.027 (6.2)
pour point, °C	32	38	35
Conradson carbon, wt %	7.6	9.9	11.4
distillation,[e] °C			
2.5 vol %	212	216	199
20 vol %	302	288	235
50 vol %	407	413	385
viscosity, SUs			
at 82°C	122	123	128
at 90°C	63	66	69

[a] Ref. 150.

[b] Feed coal was different from that used for 482 and 521°C.

[c] To convert MJ/kg to Btu/lb, multiply by 430.

[d] $°\mathrm{API} = \frac{141.5}{\rho} - 131.5$ where ρ is specific gravity.

[e] Combination of true boiling point and D1160 distillations.

content (about equal to that of the starting coal) permits direct combustion. These char products, however, are pyrophoric and require special handling in storage and transportation systems.

Properties of the tar oil products are given in Table 14. The oils change only slightly with change in the retorting temperature; sulfur levels are low. The fraction boiling up to 230°C contains 65 wt % of phenols, cresols, and cresylic acids.

TOSCO tar oils have high viscosity and may not be transported by conventional pipelines. Heating values of product gas on a dry, acid gas-free basis are in the natural gas range if butanes and heavier components are included.

4.2.4. Coal Carbonization

In the by-product recovery of a modern coke oven, coal tar is removed first by cooling the gases emanating, and light oil is removed last by scrubbing the gas with solvents. Other products, including ammonia, phenols, pyridine, or naphthalene, may be recovered between these operations. The constituents of coal tar, light oil, and gas usually overlap considerably, ie, the fractional condensation does not effectively separate individual components. Assuming the lowest boiling coal tar constituent to be benzene (bp 80.09°C), and the highest boiling to be naphthalene, the overlapping compositions of gas, light oil, and tar may be as shown graphically in Figure 16. Many chemical compounds have been identified (8) in these substances. Included are most of

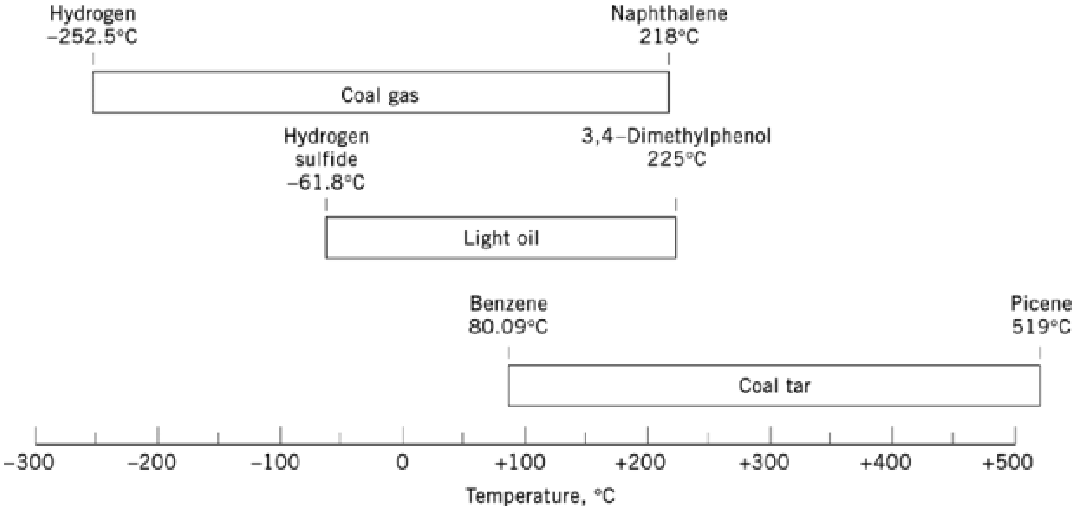

Fig. 16. Boiling ranges of carbonization products (8).

the significant constituents of petroleum-derived fuel liquids, although only a few components are present in sufficient quantity to make commercial recovery feasible.

The precise compositions of the light oil and coal tar recovered from coke-oven gas is a distinct function of the design of the recovery system, as well as of the properties of the starting coal. In general, 12.5–16.7 L/t (3–4 gal/m light oil per short ton) of coal carbonized is recovered from high temperature coke-oven operations. Light oil may contain 55–70% benzene, 12–20% toluene, and 4–7% xylene. Unrecovered light oil appearing in the effluent coal gas may comprise ca 1 vol % and contribute ca 5% of the gas's heating value. Refining of light oil consists mainly of sulfuric acid washing, followed by fractional distillation.

Large-scale recovery of light oil was commercialized in England, Germany, and the United States toward the end of the nineteenth century (151). Industrial coal-tar production dates from the earliest operation of coal-gas facilities. The principal bulk commodities derived from coal tar are wood-preserving oils, road tars, industrial pitches, and coke. Naphthalene is obtained from tar oils by crystallization, tar acids are derived by extraction of tar oils with caustic, and tar bases by extraction with sulfuric acid. Coal tars generally contain less than 1% benzene and toluene, and may contain up to 1% xylene. The total U.S. production of BTX from coke-oven operations is insignificant compared to petroleum product consumptions.

5. Other Processes

5.1. Shale Oil

In the United States, shale oil, or oil derivable from oil shale, represents the largest potential source of liquid hydrocarbons that can be readily processed to fuel liquids similar to those derived from natural petroleum. Some countries produce liquid fuels from oil shale. There is no such industry in the United States although more than 50 companies were producing oil from coal and shale in the United States in 1860 (152, 153), and after the oil embargo of 1973 several companies reactivated shale-oil process development programs (154, 155). Petroleum supply and price stability has since severely curtailed shale oil development. In addition, complex environmental issues (156) further prohibit demonstration of commercial designs.

5.2. Heavy Oil

The definitions used to distinguish among naturally occurring heavy petroleum oils, bitumens, asphalts, and tars, are subject to broad variations. More than 10% of the world's current crude oil production has an API gravity below 20°, or a specific gravity greater than $0.934^{15}{}_{15}$. Oils having sp $\mathrm{gr}^{15}_{15} > 0.904 - 0.934$ (20–25°API) are considered heavy oils in most classifications. However, Safaniyah crude oil produced in Saudi Arabia having sp $\mathrm{gr}^{15}{}_{15}$ of 0.893 (27°API) carries the designation Arabian heavy, and in petroleum parlance is generally referred to as heavy crude oil. Yet its production method does not differ from that of Arabian medium or Arabian light crude oils.

Energy in the form of injected water or CO_2 may be supplied to increase the rate of production of light crude oils. Application of heat to the reservoirs, eg, using hot water, steam, heated CO_2, fireflood, or *in situ* combustion, however, is generally associated with the production of heavier, viscid crudes.

Heavy crude oil is widely distributed, and it is difficult to estimate reserves separate from normal crude oil reserves or from tar sands deposits. Estimates of petroleum reserves frequently include a large heavy oil component, which can only be produced at significantly higher cost than light oil.

Most heavy oil production is concentrated in California, Canada, and Venezuela. There is significant production of heavy oil in California from the Kern River field near Bakersfield and in Canada from the Cold Lake deposit in Alberta. Production generally involves steam drives, or the injection of steam into reservoirs through special wells in prescribed sequences. Oil–water mixtures are recovered, and often separated water is treated and reinjected.

Heavy oil may be upgraded through two main routes: coking and hydroprocessing. Virtually all established upgrading schemes involve some variant of those two routes. The challenges in upgrading and refining are from the low hydrogen content and specific gravity and high sulfur, nitrogen, and metals content of the heavy oil.

5.3. Tar Sands

Tar sands (qv) are considered to be sedimentary rocks having natural porosity where the pore volume is occupied by viscous, petroleum-like hydrocarbons. The terms oil sands, rock asphalts, asphaltic sandstones, and malthas or malthites have all been applied to the same resource. The hydrocarbon component of tar sands is properly termed bitumen.

Distinctions between tar sands' bitumens and heavy oils are based largely on differences in viscosities. The bitumen in oil sand has a specific gravity of less than 0.986 g/mL (12°API), and thus oil sands may be regarded as a source of extremely heavy crude oil. Whereas heavy oils might be produced by the same techniques used for the lighter crude oils, the bitumens in tar sands are too viscous for these techniques. Consequently these oil-bearing stones have to be mined and specially processed to recover contained hydrocarbon.

Tar sands have been reported on every continent except Australia and Antarctica. The best known deposits are the Athabasca of Canada, where almost 60,000 km^2 in northeastern Alberta is underlain with an estimated $138 \times 10^9\ \mathrm{m}^3$ $(870 \times 10^9\ \mathrm{bbl})$ of recoverable bitumen (157). The Alberta deposits may contain up to $215 \times 10^9\ \mathrm{m}^3$ $(1350 \times 10^9\ \mathrm{bbl})$ of bitumen reserves. Venezuela may have the largest accumulations in the world; the Orinoco heavy-oil belt has been estimated by some (157) to contain as high as $636 \times 10^9\ \mathrm{m}^3$ $(4000 \times 10^9\ \mathrm{bbl})$. The Olenek reserves in the former USSR may contain ca $95 \times 10^9\ \mathrm{m}^3$ $(600 \times 10^9\ \mathrm{bbl})$. The United States is estimated to have deposits of about $4.5 \times 10^9\ \mathrm{m}^3$ $(28 \times 10^9\ \mathrm{bbl})$.

The Great Canadian Oil Sands, Ltd. (GCO) (Sun Oil Co.) has been operating a plant at Fort McMurray, Alberta, Canada, since 1967. Initially, some 8050 t/d (55,000 bbl/d) of synthetic crude oil was produced from coking (158) with the project expanding to 9220 t/d (63,000 bbl/d). Since 1978, Syncrude Canada has been producing ca 22,000 m^3/d (140,000 bbl) synthetic crude oil by fluid coking from their plant at Cold Lake, Alberta, Canada (159) with expansion planned for ca 35,000 m^3/d (225,000 bbl/d).

6. Economic Aspects of Synthetic Fuels

As of this writing, processes for production of synthetic liquid fuels by upgrading natural gas, coal, or heavy oil are generally not directly competitive with crude oil upgrading (160). The key controlling factors in the economics are crude oil price and availability. Many economic analyses for synthetic liquid fuels give a crude oil price target whereupon the alternative technology becomes attractive, but these studies sometimes neglect the fact that the natural gas, coal, and heavy oil prices often track those of crude oil. In addition, conversion of a refractory gas (methane) or solid (coal) to liquids is a greater technical challenge than that of processing crude oil. Thus there are processing cost penalties which inevitably exist even after considerable technological development. Nevertheless, synthetic fuels technology is projected to play a primary role in providing liquid fuels once crude oil depletion is of concern. Economic competitiveness plays a reduced role in commercialization only when environmental legislation mandates the use of certain fuels such as oxygenates.

The commercialization potential of synthetic fuels technology relies on site-specific economic and political factors. This complex network of factors may include capital costs, crude oil price, product yields and value, government subsidies, strategic impact, alternative uses for the feed, and environmental and geographical constraints. Whereas no direct coal liquefaction process has gone to commercial stage, technologies involving indirect conversion of natural gas or coal have been commercialized. In all cases, special conditions allowed the technology to progress. In the Sasol project at South Africa, coal upgrading was possible due to factors such as no indigenous petroleum, minimal environmental standards, and cheap labor (160). The New Zealand GTG process became economically feasible owing to high oil prices, abundance of indigenous natural gas, and government commitment to energy self-sufficiency (59). Government support and long-term strategic benefits were also keys to Shell's SMDS project in Malaysia.

At 1994 crude oil prices of ca \$94–125/m^3 (ca \$15–20/bbl), conversion of natural gas to liquid fuels exists only in unique situations. For natural gas upgrading via New Zealand-type technology, economics by Mobil for a 1987 plant start-up on the U.S. Gulf Coast (161) indicated an investment of $\$895 \times 10^6$ was required for a 2.3×10^3 m^3/d (14,600 bbl/d) gasoline production unit. Thus this and other natural gas-to-fuels processes are highly capital-intensive and capital recovery remains the dominant factor even with incremental advances in conventional technology. This is especially the case using indirect upgrading of natural gas because the cost of synthesis gas manufacture may account for more than 50% of the total process capital cost (44). An analysis by Shell of the SMDS process published in 1988 showed capital expense for a 1600 m^3/d (10,000 bbl/d) plant to be $\$300 \times 10^6$ for a developed site in an industrialized country and $\$600 \times 10^6$ for a developing site in a developing country (44). Direct upgrading of natural gas to gasoline and distillate by oxidative coupling plus olefin oligomerization has been evaluated to be ca 10% costlier in capital than upgrading via indirect technologies (162).

Natural gas upgrading economics may be affected by additional factors. The increasing use of compressed natural gas (CNG) directly as fuel in vehicles provides an alternative market which affects both gas price and value (see Gasoline and other motor fuels; Gas, natural). The hostility of the remote site environment where the natural gas is located may contribute to additional costs, eg, offshore sites require platforms and submarine pipelines.

The economic feasibility of coal upgrading, and in particular direct coal liquefaction, are closely tied to crude oil price and capital expense. H-coal technology was evaluated as a base case in 1981 and the results showed economic feasibility was possible only at crude oil price of \$630/m^3 (\$100/bbl) or greater (160). A more recent analysis by HRI on coal/oil coprocessing technology indicated the required light crude price was \$138–182/m^3 (\$22–29/bbl) for economic feasibility (163). The cost of capital could add over \$60/m^3 (\$10/bbl) to the cost of products. A study of EDS, H-coal, ITSL, and two-stage Wilsonville systems showed capital costs for a 30,000 t/d plant processing Illinois No. 6 coal to run between $\$4100-\$4700 \times 10^6$ (131). Required break-even selling prices for products from these technologies ranged from \$226–314/m^3 (\$36–50/bbl). The two-stage system was the most economical at \$229.94/m^3 (\$36.56/bbl). An evaluation of coprocessing Cold Lake vacuum bottoms using Alberta subbituminous coal in a 3200 m^3/d (20,000 bbl/d) synthetic crude oil production unit indicated a selling price of \$189–220/m^3 (\$30–35/bbl) was necessary for the process to be competitive (164). In general, the economics of direct coal liquefaction depend more on the high cost of liquefaction rather than the cost for upgrading product coal liquids (165).

Factors which may affect the cost of coal upgrading are environmental considerations such as toxicity, hazardous waste disposal, and carcinogenic properties (131). These and other environmental problems from process streams, untreated wastewaters, and raw products would figure significantly into the cost of commercialization.

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