

IV

TECHNOLOGY AND PROCESSES

A. BACKGROUND

The production of liquids from coal is one option for supplying the liquid hydrocarbons estimated to be needed within this century.² Coal liquefaction via hydrogenation at high temperatures and pressures was developed by Bergius between 1910 and 1927. This effort culminated in the construction of 12 plants that produced a total of about 100,000 barrels of oil per day from coal. The process was directed largely to the production of gasoline with a high octane rating for aviation use before and during World War II. Operating conditions were severe (i.e., pressures were greater than 200 atmospheres and temperatures were in excess of 400 °C), expensive high-pressure vessels that were limited in diameter were required, and operating costs, particularly for hydrogen compression, were high. Current coal liquefaction research within the United States is directed toward developing liquefaction processes that require less severe operating conditions and are less expensive.

As noted in Chapter III, the chemical objectives of coal liquefaction are: (1) to break up weak van der Waals-type and hydrogen bonds, freeing fairly large units of coal structure, (2) to break up the interconnected aromatic-aliphatic linkages in the coal structure to form smaller organic fragments, and (3) to increase the hydrogen-to-carbon (H/C) atomic ratio from about 0.8 (equivalent to about 6 percent hydrogen) to a value greater than 1.0 to chemically stabilize the fragments formed. As the H/C atomic ratio is increased, the resulting liquid products range from a low-sulfur content, ash-free material with a melting point of between 150 and 200 °C to a liquid stock comparable to crude oil or petroleum distillates. Typical H/C atomic ratios for crude oil, gasoline, and methane are 1.5, 1.8, and 4.0, respectively.

The H/C atomic ratio in the volatile fraction can be increased by rearranging the hydrogen in the coal itself and forming residual char; by adding hydrogen from external sources, such as molecular hydrogen (H_2) or hydroaromatics; or by gasifying the coal with steam to form synthesis gas ($H_2 + CO$) and reacting this to form hydrocarbons. At least 1 to 2 percent hydrogen must be added to stabilize the organic fragments resulting from the initial break-up of the coal structure.

Considerably more hydrogen must be added (4 to 8 weight percent) to produce a liquefied product similar to crude oil or typical petroleum products. Hydrogen consumption represents a major process cost item, and several process variations are designed to limit or control hydrogen consumption or increase the H/C atomic ratio of the liquefied product without the need for gas-phase hydrogen. Coal-derived liquids typically contain higher concentrations of oxygen, sulfur, and nitrogen heteroatoms than typical crude oils, and removal of these heteroatoms results in additional hydrogen consumption. The high nitrogen concentration in coal-derived liquids is a particular problem because removal is difficult and involves large amounts of hydrogenation and very high hydrogen consumption.

The separation of solids from the liquefied product is another major consideration in liquefaction processes and may represent a major processing cost. While process variations have evolved that reduce solids separation problems and costs and the effect of coal solids on catalysts used to upgrade the liquids formed, separation remains a major problem in many hydrogenation processes.

Several reactor types are used in coal liquefaction processes because each type can have a significant effect on the results. The simplest type is the idealized plug-flow noncatalytic reactor (Figure 3a) that consists of an open tube through which the reacting fluid flows. The fluid may be a gas and/or a liquid, and the liquid phase may contain solids, as is the case for a coal slurry being pumped through an open tube. This reactor type usually is used for coal liquefaction by solvent extraction, and frequently no added catalyst is involved. The essential feature is that fluid elements pass through the reactor without mixing with elements in front or in back.

The second noncatalytic flow reactor is the continuous-flow stirred-tank reactor (Figure 3c). Its essential feature is complete mixing of all fluid and solid elements in the reactor. Generally no catalyst is added, but if this is not the case, the added particulate catalyst is suspended in the fluid phase, and the reactor is referred to as a slurry reactor (Figure 3d).

A fixed-bed catalytic reactor contains a bed of catalyst particles through which the reacting fluid flows (Figure 3b). Catalysis of desired reactions takes place as the fluid flows through the reactor. The fluid-flow scheme is similar to that in the plug-flow noncatalytic reactor, with no mixing of fluid elements. Very frequently when a gas and a liquid are passing through the reactor the liquid flows downward, essentially trickling over the particles of catalyst, and the gas also flows downward through the catalyst bed. This is the main reactor type used in the hydroprocessing of heavy liquids such as coal-derived liquids, and it is referred to as a trickle-bed reactor.

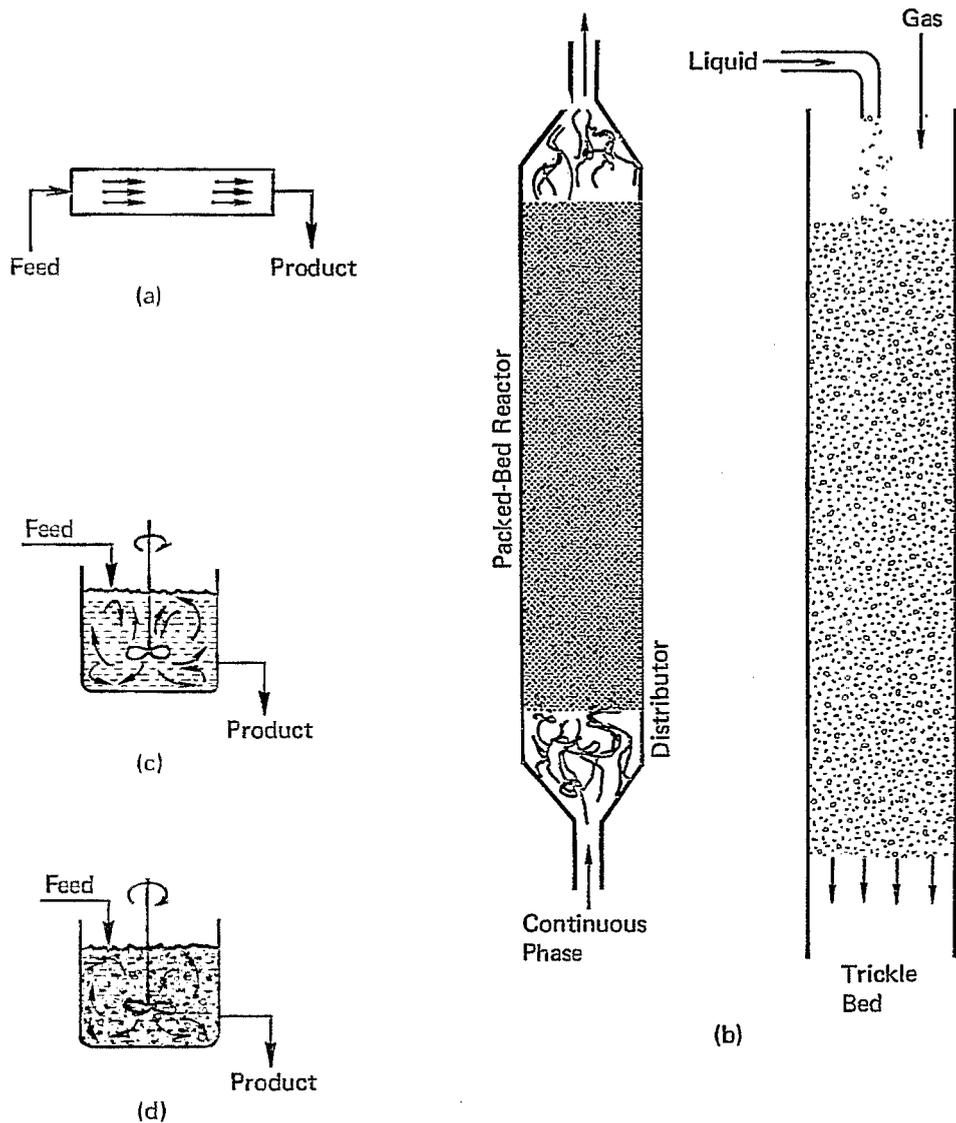


Figure 3 Plug-flow and well-mixed reactor types: (a) plug flow noncatalytic reactor, (b) plug-flow packed-bed reactors, (c) continuous-flow stirred-tank reactor, (d) slurry reactor.

In the fluidized-bed reactor, fine solid particles are suspended in a stream of upward-flowing fluid, which may be gas or liquid (Figure 4a). The particles may be reacting as is the case for coal being liquefied in a fluidized bed or the particles may be a catalyst that promotes reaction between species in the fluid phase. When the particles are suspended in a liquid and a gas is bubbling up through the liquid phase, the reactor is often referred to as an ebullating-bed reactor (Figure 4b), an important type used in catalytic coal liquefaction. The essential flow features of a fluidized-bed reactor are uniform mixing of the solid particles throughout the reactor and essentially plug-flow operation of the fluid phase through the reactor.

When the solid particles are suspended in the fluid phase and are traveling with it through the reactor, the reactor is referred to as an entrained-flow reactor or as a dilute- or lean-phase fluidized bed with pneumatic transport of solids (Figure 4c). Both the fluid phase and the solids exhibit plug-flow behavior. This type of reactor is important in coal pyrolysis and in indirect liquefaction.

As shown in Figure 5, coal liquefaction processes can be divided into four categories: pyrolysis, solvent extraction, catalytic liquefaction, and indirect liquefaction. In this section each coal liquefaction process for which an adequate amount of information is available in the literature is described and its current status is summarized; the Panel's evaluation of these processes is presented in Chapter V. Process yields and thermal efficiencies are frequently not defined on the same basis; in this report they are based on moisture and ash-free coal and are expressed per ton of coal fed to the reaction zone. Yields based on coal fed to a self-sufficient integrated plant would be significantly lower, but such data are only infrequently available. In general, the order of discussion will proceed from the most completely demonstrated processes to those in early stages of development.

B. PYROLYSIS AND HYDROCARBONIZATION

Pyrolysis, or carbonization, is perhaps the oldest technique for obtaining liquids directly from coal. This process involves heating coal in the absence of air or oxygen to obtain heavy oil, light liquids, gases, and char. When pyrolysis is carried out in the presence of a circulating stream of hydrogen, it is referred to as hydrocarbonization. Other gases such as inert gases or the vapors driven from the coal also may be used. The composition and relative amounts of the products formed are influenced by heat-up rate of the coal, pressure, maximum temperature reached, coal and product residence time, atmosphere in which the pyrolysis is carried out, coal particle size, coal type, and reactor configuration. Pyrolysis processes typically convert 50 percent or more of the coal to char, which does not now have a ready market. For this and other reasons, the pyrolysis processes appear best suited to multiproduct plants that involve char gasification to produce needed hydrogen, fuel gas, or synthesis gas ($\text{CO} + \text{H}_2$) for methanation, Fischer-Tropsch, methanol, or other synthesis.

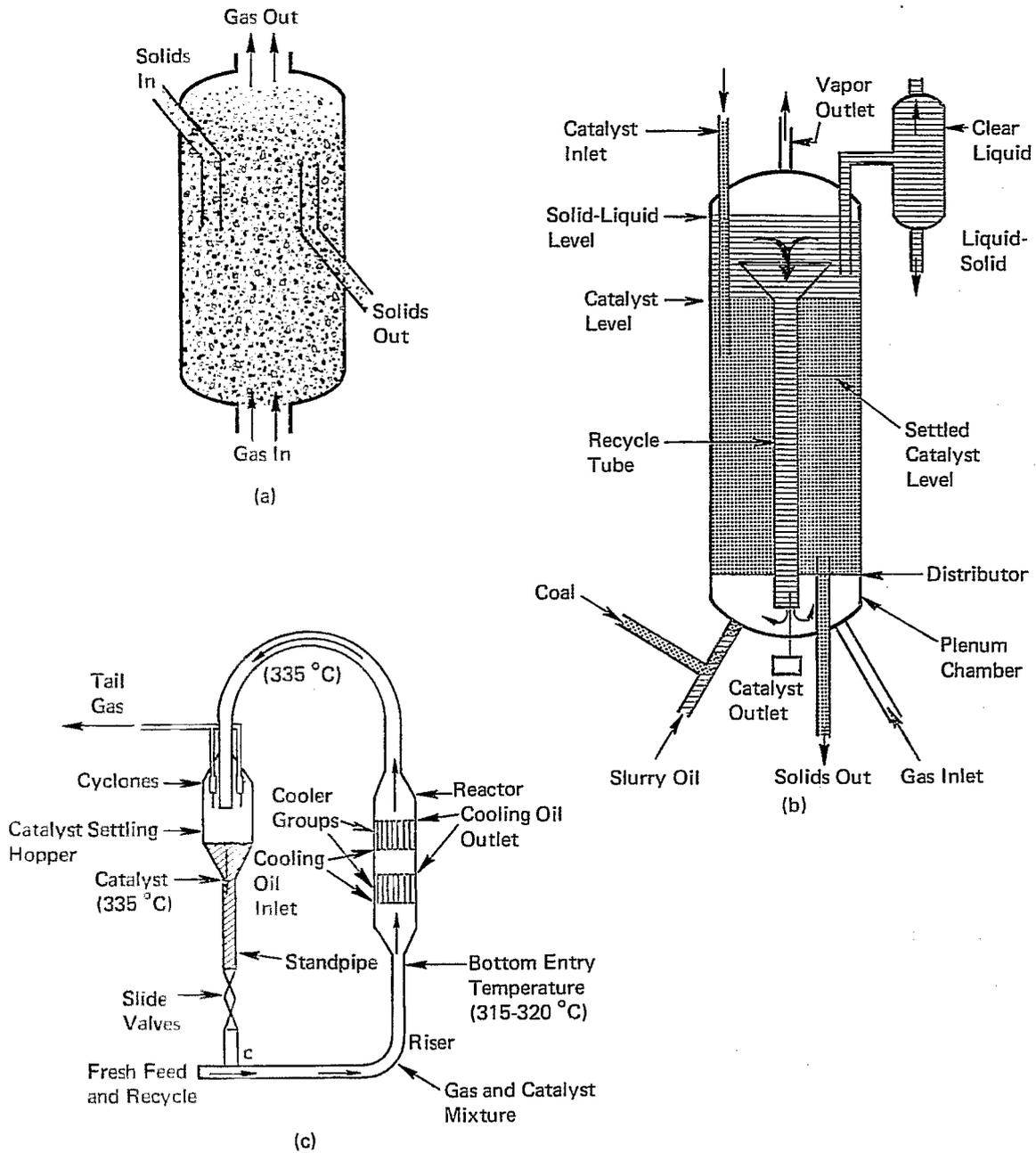


Figure 4 Fluidized-bed reactor types: (a) typical fluidized-bed reactor, (b) ebullating-bed reactor, (c) entrained-flow or dilute-phase transport reactor for Fischer-Tropsch synthesis.

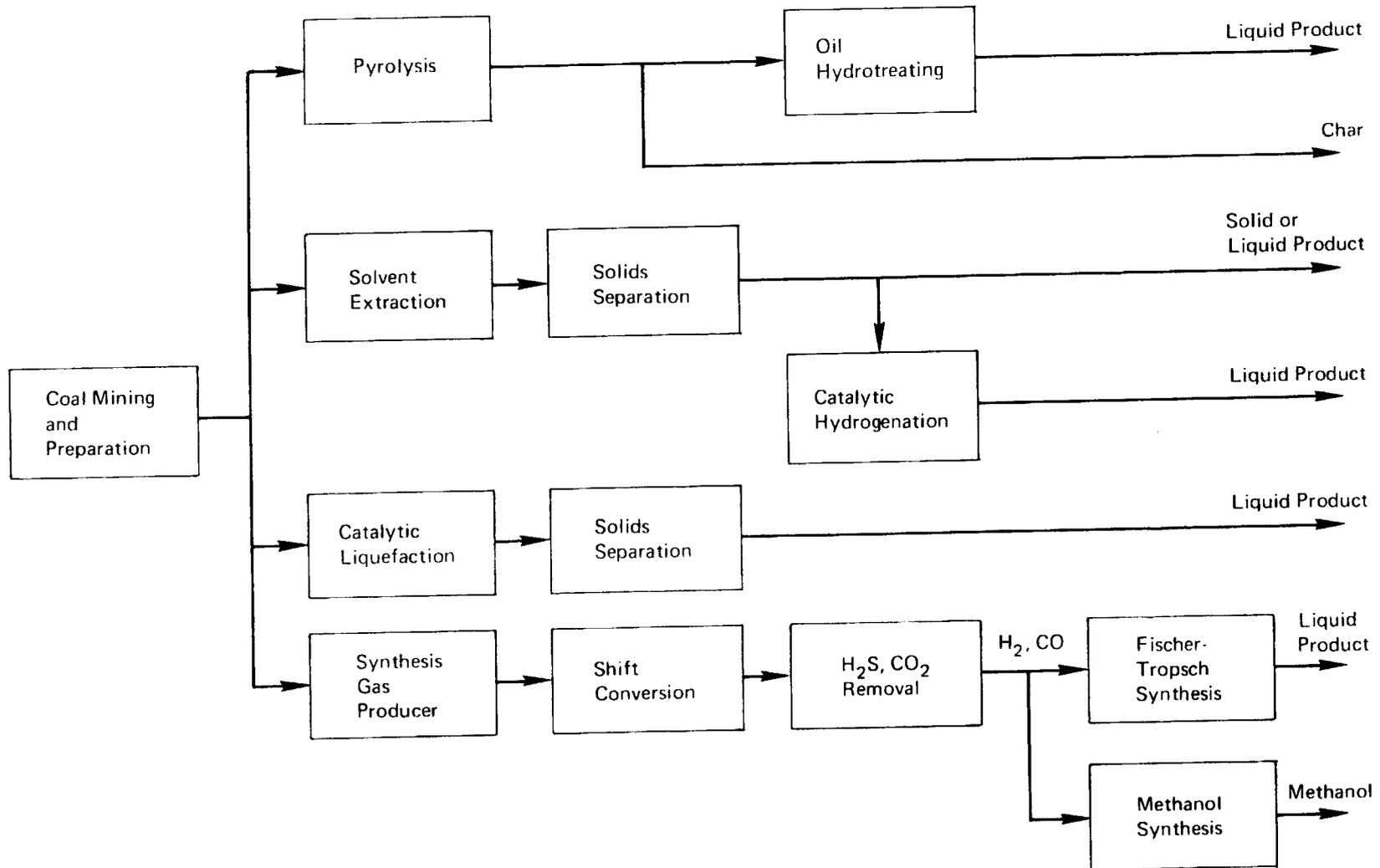


Figure 5 Coal liquefaction routes (only major products are shown). The bottom line represents the indirect liquefaction processes.

Processes currently under investigation are Lurgi-Ruhrgas, COED (FMC), Occidental, Toscoal (Tosco Corp.), U.S. Steel Clean Coke, Coalcon (Union Carbide hydrocarbonization), and others. Table 3 summarizes certain details of these processes.

1. Lurgi-Ruhrgas Process

This low-pressure pyrolysis process^{4,5} was developed for the liquefaction of European brown coals and is the only pyrolysis process presently in commercial use. The process flow diagram is shown in Figure 6. Crushed coal is fed into a mechanical mixer where it is rapidly heated to between 450 and 600 °C by direct contact with hot, recirculated char particles previously heated by partial oxidation with air in an entrained-flow reactor. A portion of the carbonized char is withdrawn as product; that required to provide process heat to the incoming coal is routed to the entrained-flow reactor. The pyrolysis gases from the mixer are passed through a cyclone for particulate removal and then through condensers to collect the liquid that is further hydro-treated to form a range of products. The heating value of the product gases is from 700 to 850 Btu per standard cubic foot (scf).

Products of the process are 50 weight percent devolatilized char, about 18 weight percent liquids (about 1 barrel per ton of coal fed to the reactor), and about 32 weight percent gases. The high gas yield occurs because of the fairly long residence time at high temperature in the reactor resulting in cracking of the liquids. Product gases may be used for hydrogen generation for hydrotreating or methanation.

A 1,600-ton-per-day Lurgi-Ruhrgas plant was built in 1963 in Yugoslavia to process lignite and is still operating. Additional commercial installations have been made since then using both caking and noncaking coals without difficulty in the mixer-carbonizer operation. Sulfur in the coal largely ends up in the char. Fine grinding of the coal by the flash pyrolysis step results in a product char of very small particle size, which requires special handling, particularly if it must be transported long distances to power plants.

2. COED (FMC) Process

The COED (Char-Oil-Energy-Development) process^{5,6,7} produces synthetic crude oil by pyrolysis of crushed coal at 1.4 to 1.7 atmospheres in a series of fluidized beds in which agglomeration is prevented by operating at successively higher temperatures (Figure 7). In the first bed, the wet coal is heated to about 315 °C by hot flue gases that dry and devolatilize the coal. Each subsequent bed, operating at higher temperature, removes an increasing fraction of the volatile matter. The temperature in each bed is just below the temperature at which agglomeration takes place. The stages typically operate at 315, 455, 540, and 870 °C, respectively, but both the temperatures and the number of stages depend on the agglomerating properties of the coal. Highly

Table 3 Summary of Pyrolysis and Hydrocarbonization Processes

Process	Developer	Coal	Reactor type	Reaction temp. ^a °C	Reaction Pressure ^a atm abs	Coal hold-up time ^a	Yield, ^b weight percent				Status of Process Development
							Char	Oil	Water	Gases	
Lurgi-Ruhrgas	Lurgi-Ruhrgas	European Brown Coal	Mechanical mixer	450-600	1	<20 sec	55-45 ^c	15-25	-	30	1,600 ton/day plant 1963; several other plants built since
COED	FMC Corp.	Illinois No. 6	Multiple fluidized beds	288-816	1.4-1.7	1-4 hr	60.7	20.1	5.7	15.1	36 ton/day pilot plant has operated
Occidental Coal Pyrolysis	Occidental	Western Kentucky	Entrained flow	579	1	.2 sec	56.7	35.0	1.7	6.6	Results based upon 1 in. diameter reactor. Process to be tested in an available 3.6 ton/day pilot plant
Toscoal	Tosco	Subbituminous bituminous	Kiln-type retort vessel	425-540	1	.5 min ^c	80-90 ^c	5-10	-	5-10	25 ton/day coal test. 1,000 ton/day plant for oil shale has been operated
Clean Coke	U.S. Steel Corp.	Illinois No. 6	Fluidized bed	650-750	6.5-11	.50 min	66.4	13.9	5.1	14.6	A 0.25 to 0.5 ton/day PDU under development; 100 ton/day pilot plant under design
Union Carbide Corp.	Union Carbide Corp.	Lake de Smet	Fluidized bed	566	69	5-11 min	38.4	29.0	19.2	16.2	18 ton/day pilot plant has been operated successfully on noncaking coals
CSIRO	CSIRO	Wallarrah, Australia	Fluidized bed	460	20-50	37 min	83.0	9.5	5.5	3.0	0.5 ton/day pilot plant has been operated

Note: It is difficult to compare results of the various processes because of the wide variation in conditions and differences in coals used.

^a Exact operating conditions will depend on the coal being processed and the products desired.

^b Yields are presumably based on moisture- and ash-free (MAF) coal fed to the reaction zone; for several cases the exact basis could not be verified, and yields are reproduced as published. Yields based on coal fed to a self-sufficient integrated plant would be significantly lower.

^c Not available, estimated as best possible. Amount in excess of 100 percent represents hydrogen added.

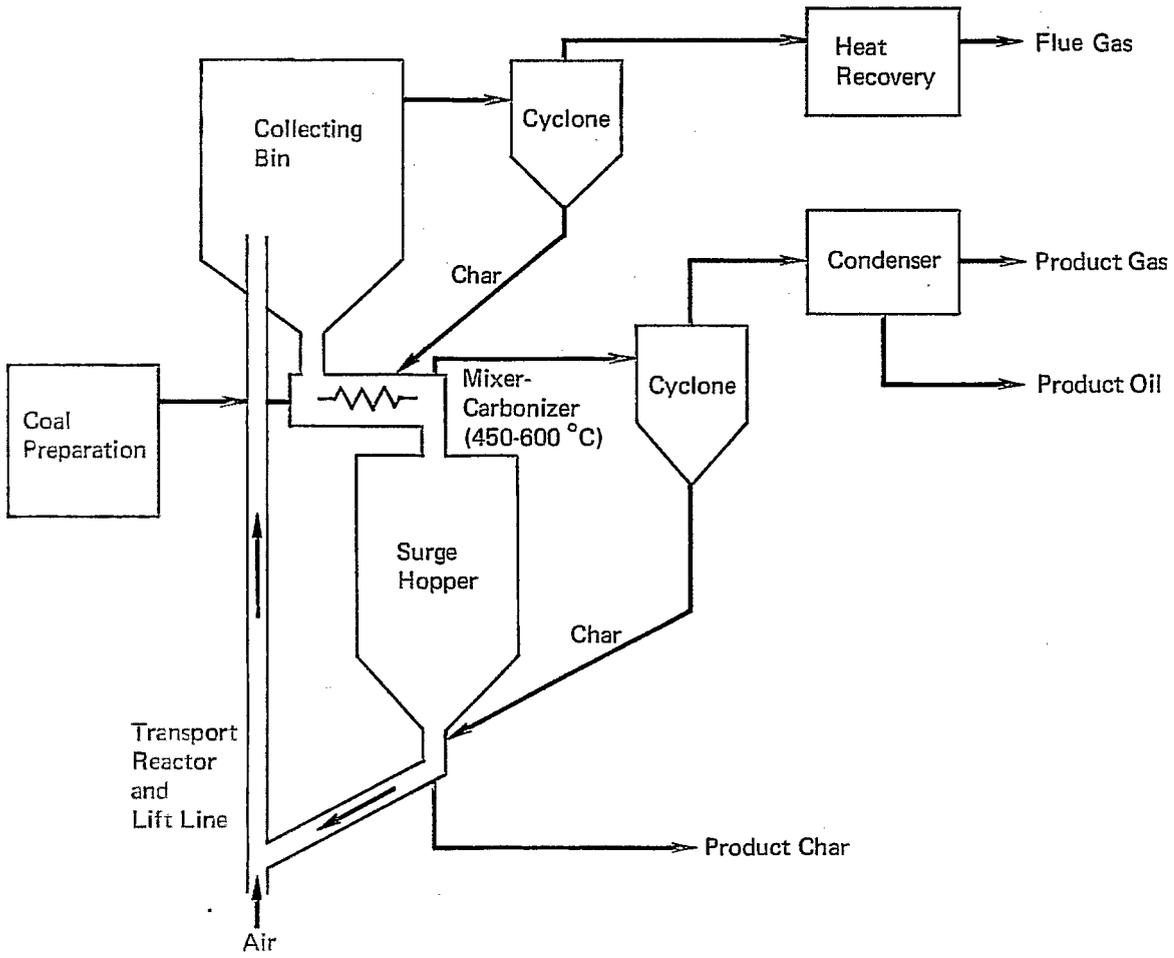


Figure 6 Schematic of Lurgi-Ruhr gas process.

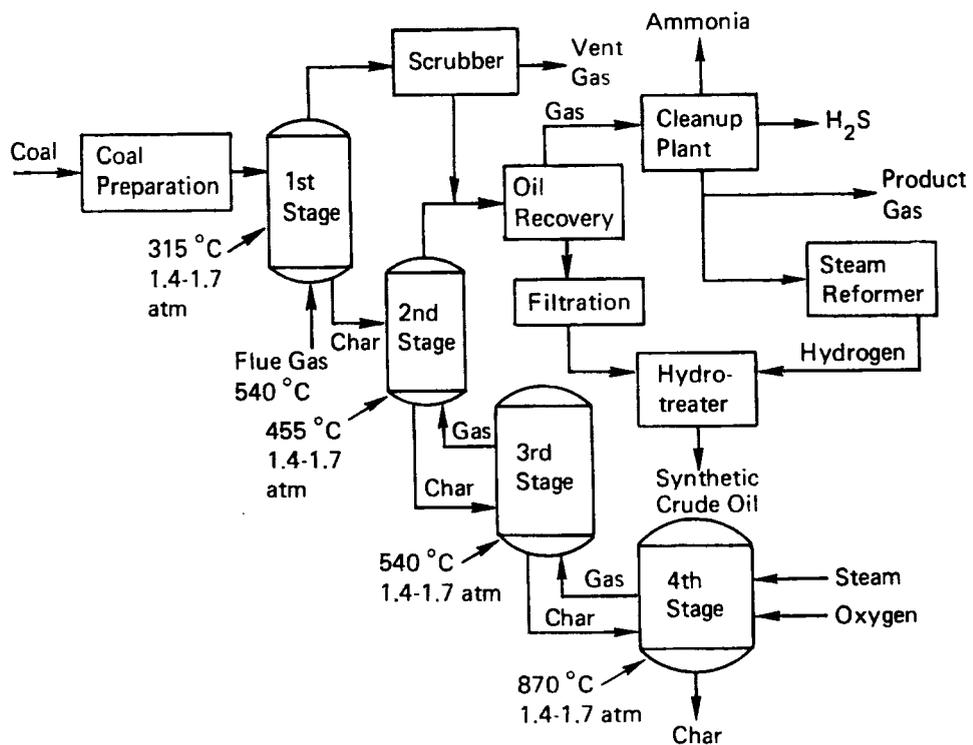


Figure 7 Schematic of COED (FMC) process.

caking coals require an oxidative pretreatment by addition of excess air in the first stage via the fluidizing gas originating from the preheating furnace to avoid agglomeration problems in the second and third stages.

Some of the char is fluidized by steam and burned with oxygen in the fourth stage to maintain the bed temperature and to provide hot gases for heating the second and third stages. Gases from the fourth stage flow countercurrent to the solids through the third to the second stage and produce the fluidization in these stages. Most of the volatile products are produced in these stages.

The volatile matter released from the coal is condensed in a product recovery system. Condensation of the coal pyrolysis vapors is accomplished by direct contact with a water-rich stream in Venturi scrubbers, and the resulting oil-water mixture is separated by gravity in a decanter vessel. Further water is removed by steam-heated dehydrators. The pyrolysis oil product is filtered by a pressurized, rotary-drum, precoal filter to remove solids (char fines) that are carried through the cyclones of the fluidized-bed reactors. Gas separated in the oil recovery section is scrubbed to remove NH_3 , CO_2 and H_2S and then is steam-reformed to produce hydrogen. A typical process yield is given in Table 3. The yields of gas (about 8,000 scf per ton) are low, apparently because of the slower stagewise rate of heating.

The filtered oil is further stabilized in a fixed-bed catalytic reactor by hydrogenation, which also reduces sulfur, nitrogen, and oxygen. The catalyst used is commercial nickel-molybdenum operating at 375 to 425 °C and 100 to 200 atmospheres.

The COED process has been under development by FMC Corporation since May 1962 under the sponsorship of the Office of Coal Research. Successful operation of a 100-pound-per-hour process development unit led to the design, construction, and operation of a pilot plant at Princeton, New Jersey, which processed 36 tons of coal per day and produced about 6 tons of oil, 18 tons of char, and 4 tons of gas. Pilot-plant operation began in 1970 and runs in excess of 30 days were completed. Design capacities were demonstrated in all parts of the pilot plant except the oil absorber tower section. Some of the most significant accomplishments were the demonstration of solids circulation between multiple fluidized-bed reactors, the filtration of the product oil, and the upgrading of the coal oil to synthetic crude oil through fixed-bed hydrotreating.

The oil absorber tower section, which was concurrently to separate the entrained solids and condense the vapors from the second-stage pyrolysis reactor, experienced plugging problems due to the high load of fines in the feed stream. Design changes involving low-temperature (180 °C) drying of the coal have been proposed to reduce fines.

Pilot-plant studies are considered completed, and the plant is being dismantled. Two process flow schemes have been designed for a commercial-

scale plant to process 25,000 tons of Illinois No. 6 seam coal per day. The project is now going forward under sponsorship by ERDA and Northern Illinois Gas Company, Peoples Gas Light and Coke Company, Central Illinois Light, North Shore Gas Company, and Central Illinois Public Service Company. A demonstration plant is to be built and operated using 2,200 tons of Illinois coal a day to produce 18×10^6 scf of high-Btu gas and 2,400 barrels of crude oil per day.

Construction of another pilot plant to evaluate the gasification of the char from the COED plant was initiated in 1974 for a process referred to as the COGAS process. Upon successful completion of the char gasification program, the COED process could move into the commercial stage since it is based on reasonably well established technology.

3. Occidental Pyrolysis Process

The Occidental pyrolysis process^{4,5,10-13} for converting volatile bituminous coal into synthetic crude oil is an entrained-flow low-pressure pyrolysis scheme with very short coal residence time and rapid heating rates (Figure 8). The process produces a high yield of liquid product. When small coal particles are heated very rapidly to high temperature, substantial quantities of liquid products are formed because of the rapid break-up of the coal structure into fragments and their vaporization, followed by rapid removal, which retards cracking, repolymerization, and coke formation. The stream leaves the reactor and passes through a cyclone for gas-solids separation and then to a gas-liquids collection-separation train. The product char is cooled; the quantity required for process heat requirements is sent to the char heater to elevate the temperature to about 760 °C by partial combustion with a controlled amount of air in a short residence time.

The hot vapors leaving the cyclone are cooled and scrubbed. The non-condensable gases are split to provide one stream for fuel requirements in the plant and another to be processed to form hydrogen for use in the liquids hydroprocessing system or to be upgraded to substitute natural gas.

The product yield is about 57 weight percent char (12,000 Btu/lb), 35 weight percent liquids (about 2 barrels of oil per ton of coal fed to the reactor), and 6.6 weight percent gas with a heating value of 700 Btu/scf. These high yields are without high-pressure operation or hydrogen, and the short contact times reduce the reactor volumes. The condensed liquids are hydrotreated under pressure to produce either a synthetic crude or a low-sulfur fuel oil.

Occidental Research Corporation (formerly Garrett R&D) has been developing this pyrolysis process since 1969 entirely with its own funds. A 3.6-ton-per-day pilot plant in La Verne, California, has been operated extensively over a wide range of conditions since 1972. Design of a 250-ton-per-day pilot plant is under way. Operation with noncaking coals has been well characterized; caking coals produced agglomeration problems in

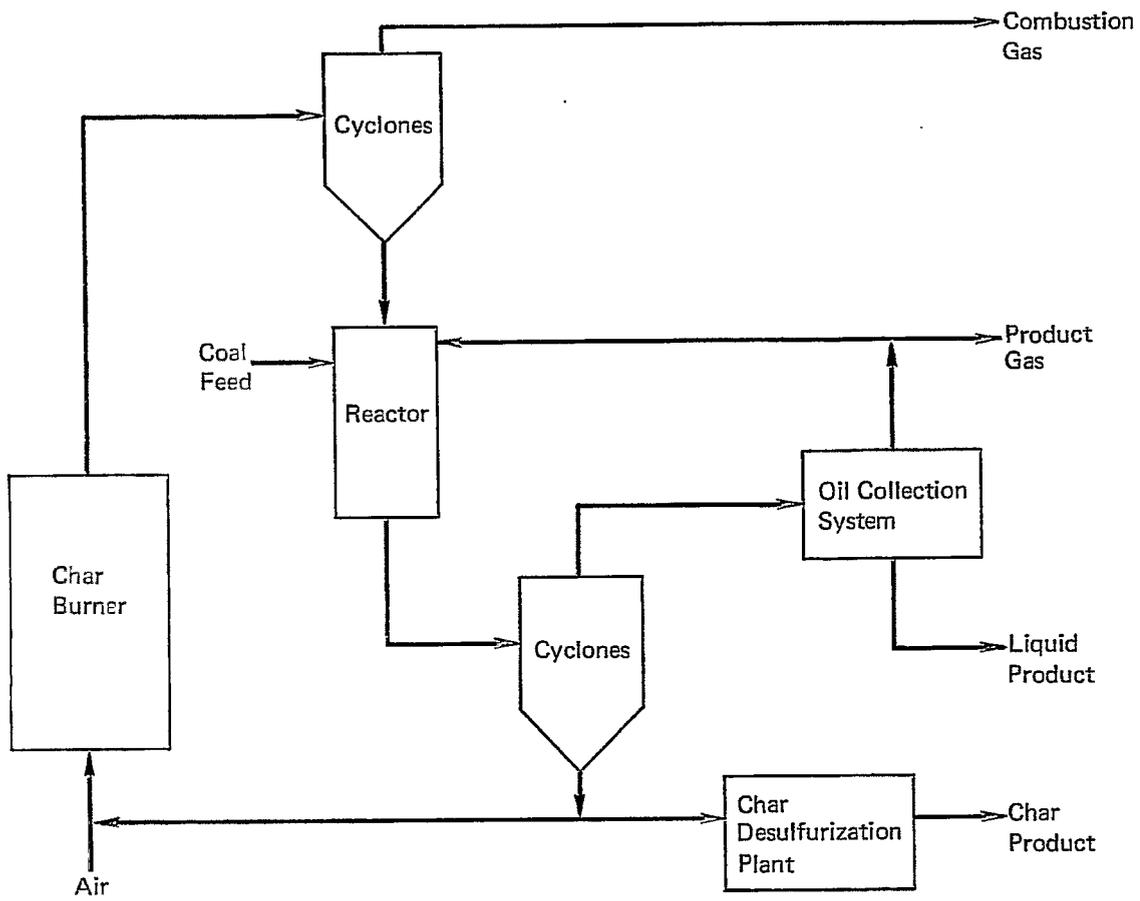


Figure 8 Schematic of Occidental coal pyrolysis process.

the original reactor design, but modification has resulted in a reportedly operational system for caking coals.

A large fraction of the sulfur remains in the char and investigations of its removal are under way. ERDA support (\$3.7 million) for producing development-unit-scale studies of reactor design and operating parameters for handling caking coals began in 1976. A conceptual design for a pilot plant will be initiated in 1977.

4. Toscoal Process

The Toscoal process (Figure 9) is an adaptation of oil-shale retorting technology to the production of oil and gas from coal.^{5,14,15} The process was developed by Tosco (formerly the Oil Shale Corporation). Coal is crushed, dried, and heated to a low temperature level with hot flue gas and then is transferred to a rotating drum where it is heated to pyrolysis temperature (425 to 540 °C) by contact with hot ceramic balls. The balls then are separated from the coal, reheated, and recycled to the rotating drum. The product mix is 5 to 10 weight percent liquids (about 0.3 to 0.5 barrel per ton of coal fed to the retort), 5 to 10 weight percent gas (500 to 650 Btu/scf) and 80 to 90 weight percent char based on the coal processed.⁵ The liquid products are condensed, hydrotreated, and fractionated.

Tosco has investigated this process for coal pyrolysis since 1970, and it has proved operable on a 25-ton-per-day pilot-plant scale. Since it is similar to the Tosco oil-shale pyrolysis process, which has been demonstrated on the 1,000-ton-per-day scale, it is not believed necessary to carry out testing on a larger scale.

5. U.S. Steel Clean-Coke Process

U.S. Steel's Clean-Coke Process (Figure 10) is a combination of low-temperature pyrolysis and solvent extraction integrated to produce metallurgical grade coke and some gases and liquids.^{4,5,16,17} Half of the feed coal is fluidized by a hydrogen-rich stream of recycle gas and pyrolyzed in a fluidized-bed reactor at 650 to 750 °C and 6.5 to 11 atmospheres. This treatment devolatilizes and partially desulfurizes the coal to produce gas, oil, and char, which serves as the base material for production of metallurgical coke. The second portion of the feed coal is slurried with the process-derived oil and subjected to solvent extraction at about 470 °C and 205 to 275 atmospheres hydrogen pressure. Solids separation involves flash vaporization of volatile material, after which the residual solids are quenched and removed from the system.

Liquid products from the pyrolysis and solvent extraction steps are combined and upgraded by hydrotreating to low-sulfur liquid fuels, chemical feedstocks, and oil fractions that are recycled to the slurry preparation unit and used in compounding the char to make coke pellets. The very heavy oils are recycled to the pyrolysis unit for further cracking. Yields are given in Table 3.

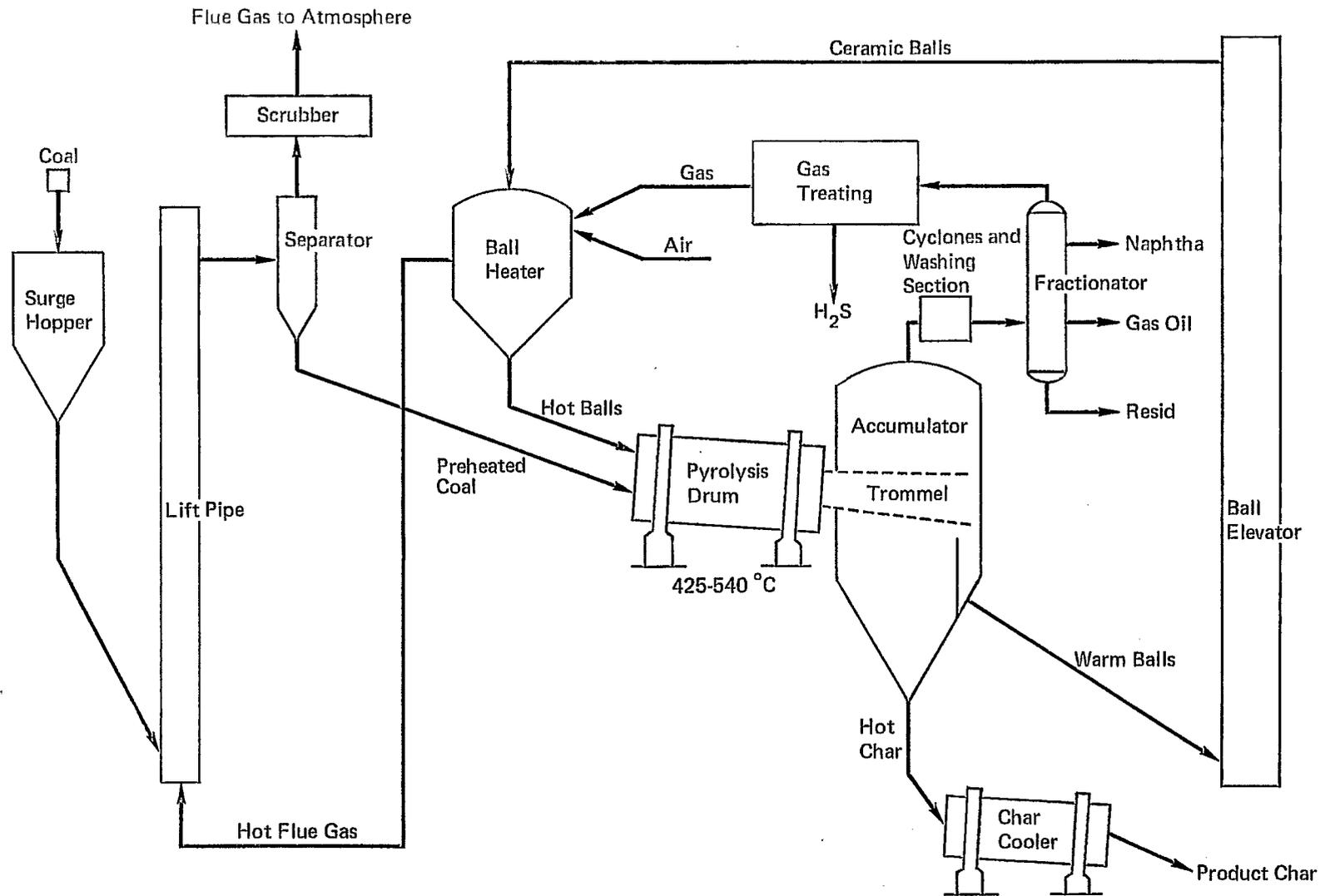


Figure 9 Schematic of the Toscoal process.

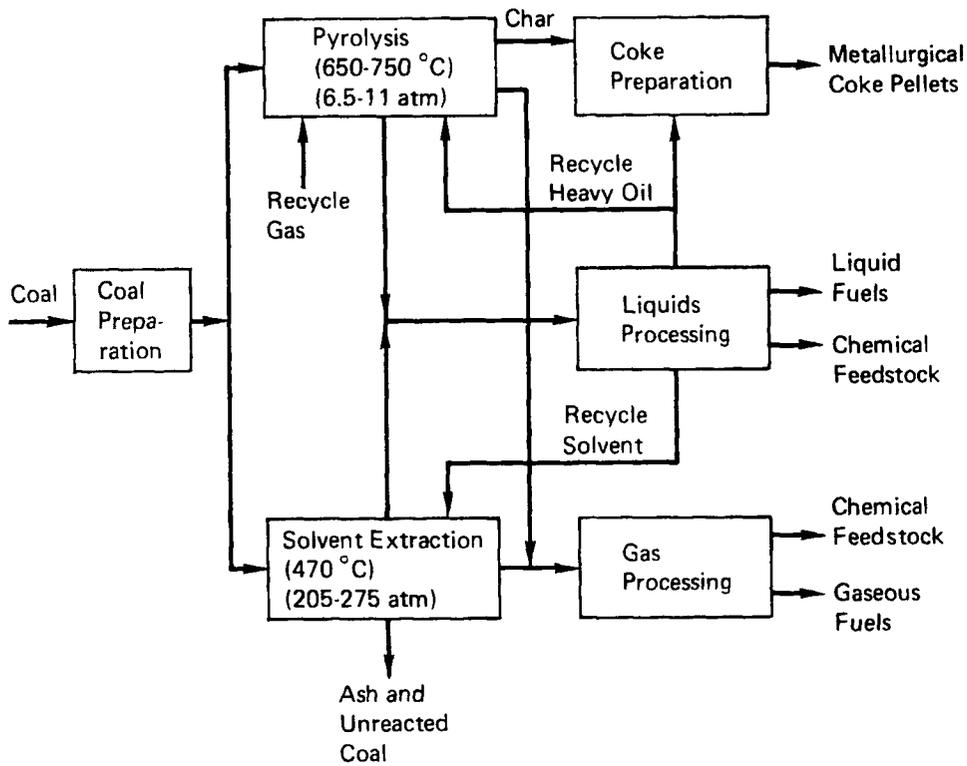


Figure 10 Block diagram of the U. S. Steel clean-coke process.

Studies of pyrolysis and solvent extraction have been completed in a 3-inch-diameter fluidized-bed reactor and a batch autoclave, respectively. Process development studies began in 1975 in an integrated unit incorporating a 10-inch fluidized-bed pyrolysis reactor, a fluidized-bed oxidation unit for preoxidation of the coal feedstock to the pyrolysis unit, and a 10-inch solvent extraction process development reactor. Initial design studies for a 240-ton-per-day pilot plant are under way.

6. Coalcon Process

The Coalcon process (Figure 11) is an outgrowth of Union Carbide's hydrocarbonization studies¹⁹ and is an intermediate hydrogen pressure process for the hydrocarbonization of finely divided, low-rank coal or high-boiling-point oils in a fluidized-bed reactor to produce char, heavy oil, intermediate and low-boiling-point liquids, and gases. It offers potentially high phenolic yields, which are of interest as a chemical feedstock.

Dried and heated 60 to 325 mesh coal, suspended in a preheated H₂ stream, is introduced into the base of a fluidized-bed reactor with an expanded upper section that permits good gas-solids separation. The coal is heated rapidly by the H₂ stream, and pyrolysis reactions occur simultaneously with hydrogenation. Increasing hydrogen pressure increases the oil yield and shifts the gas composition to higher concentrations of methane and water. The unreacted char is discharged through an overflow pipe in the expanded section of the fluidized-bed reactor. Condensers operating at different temperatures are used to remove liquids from the vapors leaving the top of the reactor, and the remaining gases are converted to hydrogen, burned as fuel, or returned to the process upgraded. In commercial-scale operations, the char formed would be gasified to provide part of the hydrogen required for the process or used for combustion purposes.

Process development studies were made at temperatures from 480 to 570 °C, hydrogen partial pressure from 0 to 1,000 psig, and solids residence time from 5 to 11 minutes. Under favorable operating conditions with a subbituminous coal, about 40 percent of the coal is converted to char, slightly less than 30 percent to liquids (about 1.8 barrels of oil per ton of coal fed to the reactor), and about 20 percent to gases (remainder ash) (Table 3). Projected demonstration-scale plant operating conditions include 560 °C, 39 atmospheres, 25 minutes solids residence, and 25 seconds gas residence time.¹⁹

Developmental work on this process ceased in the early 1960s. At that time studies of the hydrocarbonization process had been conducted at a bench scale of 1 pound of coal per hour and at two scale-ups of about 0.15 and 20 tons per day with a subbituminous coal from Lake de Smet, Wyoming. The process has been operated only with noncaking coal to date, and the ability to use caking coal in the fluidized bed without loss of fluidization is yet to be established.

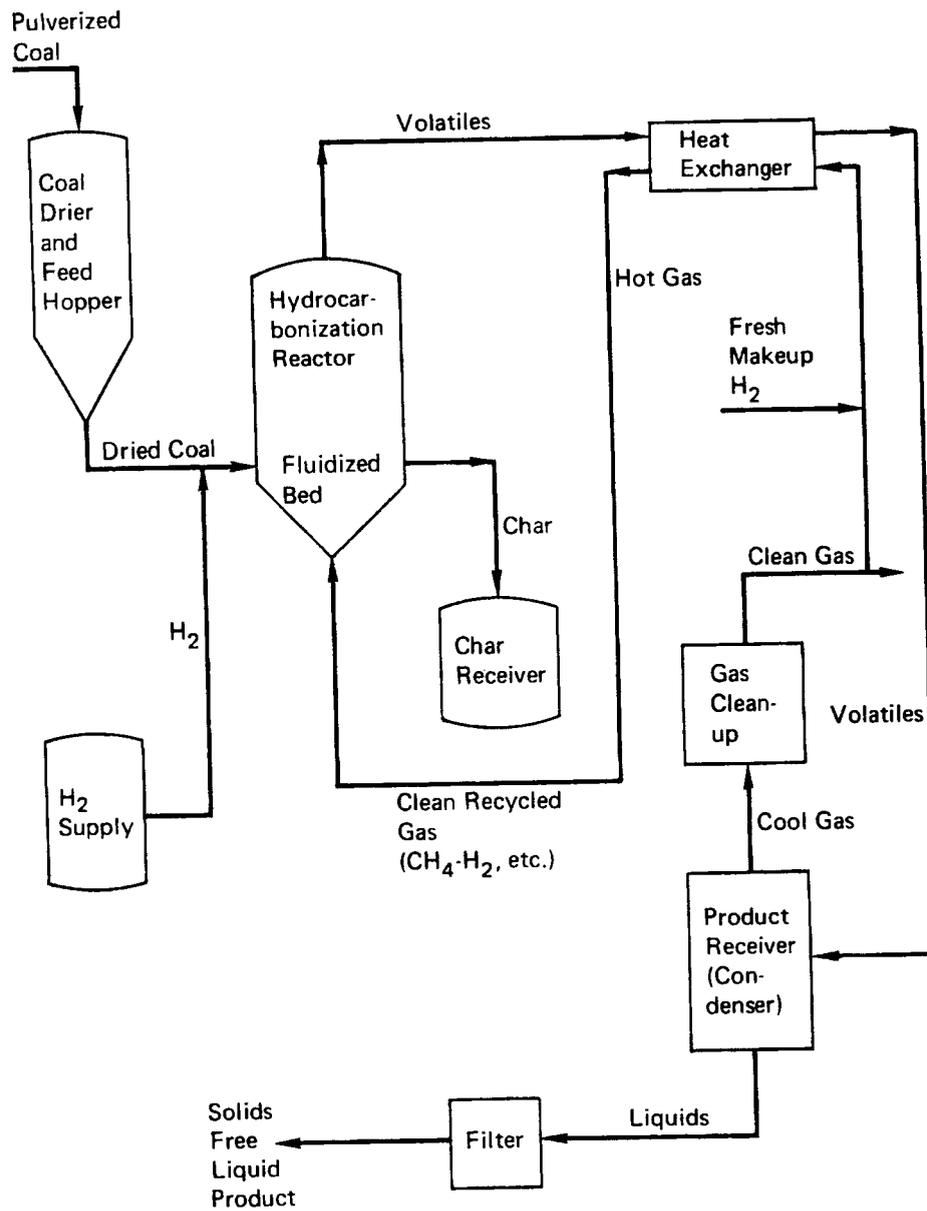


Figure 11 Flow diagram of Coalcon hydrocarbonization process.

In mid-1974 the Chemical Construction Corporation and the Union Carbide Corporation formed Coalcon, and in January 1975 Coalcon contracted with ERDA to develop a process and, if feasible, to design, construct, and operate a Clean Boiler Fuel Demonstration Plant to convert 2,600 tons per day of high-sulfur coal to 3,900 barrels of clean liquid fuel and 22 million cubic feet of high-Btu synthetic pipeline gas without any char by-products. The project is being conducted in four phases: (a) preliminary conceptual commercial process designs and engineering and site selection; (b) detailed final demonstration plant design, plant engineering and planning activities, and preparation of detailed specifications, drawings, and a construction bid; (c) plant site preparation, construction, equipment purchase, field erection, and plant acceptance and checkout; and (d) plant operation to produce synthetic products to obtain data for evaluating the potential of this process for commercial development. The first and second phases are proceeding, and two alternate designs--a high-pressure and a low-pressure reactor system--are being considered. The process design for the high-pressure system was proposed in a response to the request for proposal. Efforts are concentrated on developing a preliminary design for the low-pressure system, which is more attractive from an operation and economic standpoint. Selection and approval of a plant site at New Athens, Illinois, were completed at the end of 1975. Procurement of equipment requiring long lead times was initiated at the start of the fourth quarter of 1975.

Development studies are being conducted at Tonawanda, New York, and in South Charleston, West Virginia. In Tonawanda, a 2-ton-per-day pilot plant is being used to develop kinetics and yield data for agglomerating high-sulfur bituminous coals (Pittsburgh Seam No. 8, Illinois Seam No. 6, and Kentucky Seam No. 11). In South Charleston tests are being conducted to evaluate alternative methods for deagglomerating high-sulfur bituminous coals for use in the hydrocarbonization process.

7. Other Processes

a. CSIRO

CSIRO (The Commonwealth Scientific and Industrial Research Organization) of Australia has developed a process using a fluidized-bed reactor and recirculating a gas of high hydrogen content at pressures up to 52 atmospheres absolute. Noncaking brown coal has been successfully carbonized in a 0.5-ton-per-day process development unit.

The process^{20,21} considered a two principal systems: a hydrogenation unit for the production of predominantly methane from Yallourn brown coal, and a low-temperature pyrolysis unit designed to maximize yields of char and/or liquids from Wallarah Seam, New South Wales coal. The crushed coal in suspension in the fluidizing gas was introduced continuously at the base of the fluidized bed, where rapid heat-up and pyrolysis occurred; for weakly caking coals the feed coal was blended with char to prevent defluidization. Char was removed from the top of the bed, and pyrolysis gases were passed through cyclone dust collectors, condensers, and scrubbers for product recovery.

When the reactor was operated in the pyrolysis mode alone, atmospheric pressure air was used as the fluidizing medium and as a source of heat through combustion. The product mix was then about 8 percent liquids; the remainder was char. The gases were largely oxidized. During hydrocarbonization operation, which was at 20 to 52 atmospheres H_2 pressure and 450 to 750 °C, the optimum product yield was about 10 percent liquids, 3 percent gases, and 83 percent char; the gas was mainly methane and light hydrocarbons.

The process has been tested in a 0.5-ton-per-day unit and larger scale tests were conducted with a 20-foot-deep fluidized-bed reactor. All reported work was completed by 1960.

b. Rapid Hydrocarbonization

The Rocketdyne Division of Rockwell International is working (with ERDA support) on a hydrocarbonization process based on the same concepts used in Occidental's processes (i.e., rapid heating to high temperature with short residence times) except that pyrolysis is carried out in the presence of hydrogen. Injection and mixing techniques originally developed for liquid propellant rocket engines will be used. The reactor rapidly mixes pulverized coal with a minimum amount of hydrogen heated to about 815 °C. The reaction period is expected to be in the 10 to 1,000 milliseconds range at 1,000 °C and 69 atmospheres; the products are quenched immediately thereafter by a water spray. The program is in a very early developmental stage and no results are available.

c. Miscellaneous

A number of other pyrolysis processes have been developed but are not being worked on at present for various reasons. One example was a fluidized-bed process for coal carbonization developed by the U.S. Bureau of Mines in the 1950s.²² It was concerned with the production of industrial carbons for thermal power and for blending material for metallurgical-coke manufacture from Wyoming noncaking or slightly caking coals. Emphasis was centered on the processing of fine and lump coal in externally heated fluidized-bed reactors at atmospheric pressure and temperatures up to 750 °C. Average residence time of the coal was about 12 minutes; gas residence time was on the order of 1 second. The char, liquids, and gases were separated and cleaned by a series of cyclone separators, precipitators, condensers, and scrubbers. The yield of liquid oils varied from 11 percent for Lake de Smet to 22 percent for Hanna area coal and with the rate of heating but not with temperatures above 500 °C. No further work has been done on this process. A second example was the Consolidation Coal Company development of a low-temperature coal carbonization process²³ in the late 1950s. The results indicated that the yields were too low to make the process economic.

A number of other pyrolysis processes are under study that have not been reported in any detail or are in very early stages of development.

Among these are the CECO process developed by Atlantic Richfield, high-hydrogen-pressure hydrocarbonization studies carried out by Arthur Squires at New York University, and rapid heating hydrocarbonization studies under way at the Institute of Gas Technology.

C. SOLVENT EXTRACTION

Solvent extraction designates a liquefaction process in which coal is mixed with a solvent capable of transferring relatively loosely bound hydrogen atoms to the coal at temperatures up to 500 °C and pressures to 275 atmospheres absolute. Heating first breaks many of the physical interactions in the coal such as van der Waals forces and hydrogen bonding and promotes swelling and solvation. Heat also breaks weak chemical bonds in the coal structure, and the donor solvent transfers hydrogen atoms to the broken bonds, thereby helping to terminate the combination of free radicals and to prevent repolymerization. If molecular hydrogen is present, it may attached directly to the free radicals, but the rate is thought to be low. Molecular hydrogen may also hydrogenate donor solvent molecules that then can transfer hydrogen atoms to the coal. These processes involving molecular hydrogen are probably affected significantly by the mineral matter in the coal, but the mechanisms generally are not well understood.

Extraction of coal in the presence of a recycle solvent has been developed in three different configurations: (1) extraction in the absence of hydrogen using a recycle solvent that has been hydrogenated in a separate step, (2) extraction in the presence of hydrogen with a recycle solvent that has not been hydrogenated, and (3) extraction in the presence of hydrogen with a hydrogenated recycle solvent. In all three cases, middle oil distillates of process-derived liquids have been successfully used as the recycle solvent. The recycle solvent is recovered continuously and recycled to the extraction step; rehydrogenation takes place in a separate step over a metal sulfide hydroprocessing catalyst in two of the process configurations but also may occur in the extraction step.

Solvent extraction can be operated under "milder" conditions to result in a product containing about 1 percent sulfur from a coal containing about 3 percent sulfur; however, the nitrogen content of the product is not significantly reduced, and the product is a solid below 100 °C or a very heavy oil along with some lighter oils and gases. More severe conditions result in more effective sulfur removal and produce a lighter liquid product that is more amenable to handling like crude oils and heavy fuel oils. The liquids may be further hydrogenated to produce lighter oils and to remove sulfur and nitrogen.

The processes, identified in terms of the above configurations, currently under active development are the Consol synthetic fuel (CSF) process (Configuration 1), solvent-refined coal (SRC) process (Configuration 2), solvent-refined lignite (SRL) process (Configuration 2), Costeam process (Configuration 2), and Exxon donor solvent (EDS) process (Configuration 3). The important elements of these processes are summarized in Table 4.

Table 4. Summary of Solvent Extraction Processes

Process	Consol Synthetic Fuel (CSF)	Solvent Refined Coal (SRC)	Solvent Refined Lignite (SRL)	Costeam	Exxon Donor Solvent (EDS)
Developer	Conoco Coal Development Co.	Pittsburgh & Midway Coal Mining Co.	Univ. of North Dakota	U.S. Bureau of Mines (ERDA)	Exxon Research & Engineering Co.
Coal	Lignite Subbituminous	Subbituminous Bituminous	Lignite	Lignite Subbitumi- nous	Subbituminous Bituminous
Reactor Type	Stirred-tank (CFSTR) extractor; ebullated-bed catalytic hydrotreater	Vertical tubular plug flow	Tubular plug flow	Stirred tank (CFSTR)	Tubular plug flow
Reaction Temp., °C	400	~450	370-480	375-450	425-480
Reaction Pressure ^a , atm abs	10-30 extractor; 205 hydrotreater	69-103	69-205	137-275	100-140
Residence Time, ^a hr	<1	<1	~1.4	1-2	0.25-2.0
<u>Product Yield, per ton^{a, b}</u>					
Char or Product	492 lb char	1,400 lb product	1,100-1,400 lb SRL product	550 lb char	~400 lb char
Oil	3.5 bbl	~0.75 bbl (~270 lb)	No net production	1,200 lb	3.0 bbl
Gas	4,600 scf (933 Btu [scf])	80 lb	200-500 lb	250 lb	600 lb
Recycle	Heavy middle cut fraction of hydrogenated product	Fraction distilled from SRC product not hydrogenated	Fraction distilled from SRL product not hydrogenated solvent balance not closed yet	Anthracene oil	Middle cut process derived oil, hydrogenated before return
Hydrogen Consumption per ton of Coal Reacted & Source	7,300 scf in extractor 15,000 scf in hydrotreater, Lurgi gasification	3,000-7,000 scf Bi-gas gasifier	H ₂ equivalent contained 1.5 to 2.5 wt % added to coal MAF	---	About 15,000 scf H ₂ from Flexi- coking process but mainly re- forming of product gases
Current Status	20-ton-per-day plant operated at Cresap, W. Va. until 1970. Revamped plant to restart in 1977	6-ton-per-day plant operating at Wilsonville, Ala. 50 ton per day plant at Ft. Lewis, Washington	0.5-ton-per-day pilot plant in start-up stage	Bench scale continuous flow unit	1-ton per-day automated pilot plant operated; 250-ton-per-day plant designed

^a Exact operating conditions and yield will depend on coal being processed and on products desired.

^b Yields are typical values observed or ranges reported; yields are based on moisture- and ash-free (MAF) coal fed to the reaction zone. Yields based on coal fed to a self-sufficient integrated plant would be significantly lower and yields will vary with the coal fed.

1. Consol Synthetic Fuel (CSF) Process

The CSF process, under development by the Conoco Coal Development Company (formerly the Consolidation Coal Company), produces either a low-sulfur boiler fuel of less than 0.9 percent sulfur or a distillate fuel of less than 0.3 percent sulfur, depending on the extent of treatment. It is based on technology developed as part of Project Gasoline, which was supported by the Office of Coal Research in a 20-ton-per-day pilot plant from 1967 to 1970 at Cresap, West Virginia. Numerous technical and operational problems caused shutdown of the plant.

The CSF or hydrogen-donor solvent process^{4,5,9,24} is represented schematically in Figure 12. The coal feed is crushed, dried, and preheated to about 250 °C in a fluidized-bed reactor and then slurried with a process-derived recycle oil in a stirred extraction vessel (CFSTR) operated at about 400 °C and 11 to 30 atmospheres with an average residence time of less than 1 hour. Hydrogen transfer from solvent to coal is between 1.0 and 2.5 percent to liquefy about 75 percent of the coal. The slurry then passes to a separation step (typically hydroclones) where unreacted coal and ash are removed at temperatures above 200 °C. Filtering, centrifuging, hydrocloning, and solvent precipitation have been tried for this separation step.

Mixed solid liquid residue from the separation is conveyed to a low-pressure pyrolyzer (450 to 500 °C) for solvent recovery and char oil separation. The heavy liquids are further treated to produce residuum, distillate, and fuel gas. The liquid is fractionated to recover recycle solvent, synthetic crude, and extract.

The extract from the separation step, still containing about 25 percent of the solvent, flows to a catalytic hydrotreater consisting of an ebullating-bed reactor operating at 205 atmospheres and 425 to 450 °C, where the distillate product and recycle solvent are produced. These materials then may be separated and further refined from a possible product mix from a Pittsburgh Seam coal (Table 5).

Table 5 Typical Products from CSF Process Using Pittsburgh Seam Coal (Ireland Mine)

Product	Product/Ton of Raw Coal Processed ^a	Characteristics of Products		
		API Gravity	Btu	% of Total Product
Gas	3.424 mscf		933/scf	
Naphtha	0.52 lb	58°	5.22x10 ⁶ /bbl	5.6
Fuel Oil	1.52 lb	10.3°	6.4x10 ⁶ /bbl	12.8
Ammonia	11.00 lb			
Sulfur	71.00 lb			
Ash	213.60 lb			

^aCoal contained 14.4 weight percent moisture and 10.8 weight percent ash.

The process has been developed from bench-scale studies started in 1963 under a contract between Consolidation Coal Company and the Office of Coal Research through construction of the 20-ton-per-day pilot plant at Cresap, West Virginia. The plant currently (mid-1976) is being re-ramped by the Fluor Corporation for operation to produce clean boiler fuel and distillate rather than gasoline and to evaluate several coal liquefaction processes including components that are critical to a number of the processes.

2. Solvent Refined Coal (SRC) Process

The solvent refined coal (SRC) process^{9,25} (or PAMCO process) is a noncatalytic hydrogenation developed by the Pittsburgh and Midway Coal Mining Company, a subsidiary of Gulf Oil Corporation. Coal is first crushed, dried, and slurried with an unhydrogenated process-derived solvent (Figure 13). Gaseous hydrogen is added to the slurry, and the mixture is preheated to 450 °C and pumped into a tubular plug-flow extractor-dissolver at 69 to 137 atmospheres, where extraction-hydrogenation takes place at about 450 °C. The pressure in the extracted solution then is reduced in a flash separator, which also separates gases from liquids. Hydrogen is recovered from the gas stream. Make-up hydrogen (about 1.5 to 3.0 percent is added to the coal during dissolution) is added to the recycle gas stream and the stream is returned to the pre-heater. Bottoms from the gas-liquid separator are filtered to separate solids from liquid. The liquid is sent to a vacuum flash evaporator to remove solvent for recycle to slurry preparation. The SRC product (16,000 Btu/lb), which melts at 150 to 200 °C, is allowed to solidify and may then be transported. Approximately 65 percent of the original coal is converted to SRC product, about 15 percent to distillable liquids, and the remainder to ash and gases.

Table 6 gives a typical composition for the SRC product as compared with the coal from which it originated. The process removes almost all of the inorganic material, including the pyritic sulfur. A small amount of organically bound sulfur is removed, giving a total removal of about 65 to 75 percent. None of the nitrogen is removed.

The process has been developed from the bench scale through a 0.6-ton-per-day pilot plant under a research and development program beginning in 1966 under the Office of Coal Research. This program culminated in the design, construction, and successful operation of a 50-ton-per-day plant at Fort Lewis, Washington. It currently is being operated to make 3,000 to 4,000 tons of SRC product for commercial-scale boiler tests on a 22.5-MW boiler of the Georgia Power Company in the summer of 1977. The Fort Lewis plant also is being used to evaluate the effects of process variables on operation and product quality and to assess solids separation problems.

Modifications that will permit recycle of unconverted coal and ash will be completed on the Fort Lewis plant in 1977. It is hoped this may

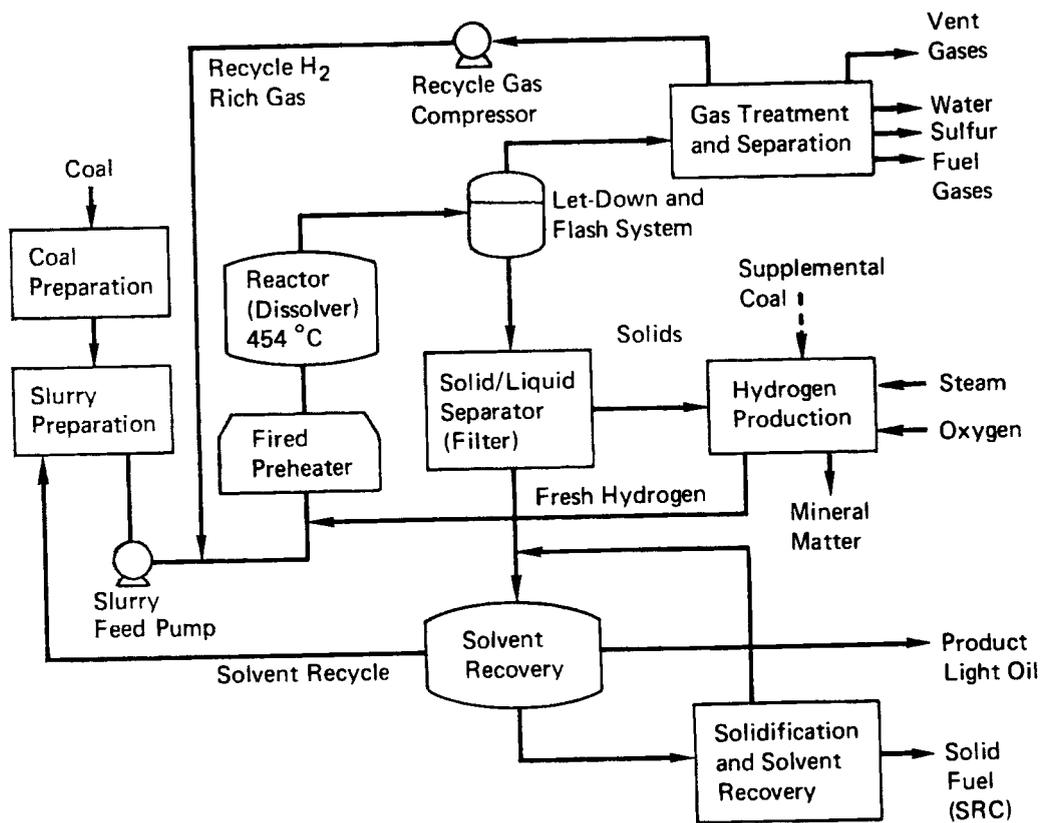


Figure 13 Block flow diagram for the solvent refined coal (SRC) process.

TABLE 6 Typical Product Composition from the Solvent Refined Coal Process

Component	Typical Analysis, weight percent	
	Raw Coal	SRC Product
Carbon	70.7	88.2
Hydrogen	4.7	5.2
Nitrogen	1.1	1.5
Sulfur	3.4	1.2
Oxygen	10.3	3.4
Ash	7.1	0.5
Moisture	<u>2.7</u>	<u>0.0</u>
	100.0	100.0
Volatile matter	38.7	36.5
Fixed Carbon	51.5	63.0
Ash	7.1	0.5
Moisture	<u>2.7</u>	<u>0.0</u>
	100.0	100.0
	12,821 Btu/lb	15,768 Btu/lb

increase the hydrogen addition from 3.0 to 3.5 weight percent to yield an oil of higher fluidity (essentially a No. 6 furnace oil) that can be further hydrotreated to reduce the sulfur concentration.

A 6-ton-per-day SRC pilot plant under the joint sponsorship of the Electric Power Research Institute and Southern Services, Inc., was constructed at Wilsonville, Alabama, and started up in January 1974. The plant has operated successfully and is being used as a pilot plant to test equipment operation, particularly in the filtration step.

A number of laboratories are investigating the properties and processability of the SRC product to evaluate its potential for other fuel and feedstock applications. Southern Services, Inc., and Wheelabrator-Frye have announced plans to study the feasibility of construction and operation of a 1,000-ton-per-day plant expandable to 10,000 tons per day.

3. Solvent-Refined Lignite (SRL) Process

The solvent-refined lignite process (University of North Dakota) is a noncatalytic solvent extraction-hydrogenation process being developed by the University of North Dakota Engineering Experiment Station under contract to ERDA. This process is based on technology derived from the PAMCO-SRC program and the studies of the Costeam process in order to produce a low-ash, low-moisture, high-heating-value fuel. The process recovers about 70 percent of the lignite feed as a 150- to 200 °C-melting-point solvent-refined lignite as well as additional quantities of lighter liquids and gases. It is possible the SRL products can be used as boiler fuel or can be catalytically upgraded to lower boiling fuel oils. The primary difference between the SRC and SRL processes is the SRL option of utilizing synthesis gas ($H_2 + CO$) in place of the hydrogen. Synthesis gas is an ideal application since the low-rank, high-moisture coals provide the necessary steam for the in-situ production of hydrogen by the water-gas shift reaction ($CO + H_2 \rightleftharpoons CO + H_2$). A flow plan for the SRL process is shown in Figure 14.

Pulverized lignite with its retained moisture is slurried with recycle solvent at pressures up to 205 atmospheres and at 480 °C in the presence of H_2 or H_2 and CO. Optimum liquefaction was obtained at 400 °C, 171 atmospheres at a liquid hourly space velocity of 1.4 ft³ and a gas space velocity 330 ft³ per cubic foot of reactor space with a 50 percent H_2 and 50 percent CO mixture.²⁶

The products from the dissolver or hydrogenation reactor are subjected to a series of pressure letdowns that first flash off the high-pressure gases, which are purified, then the light condensates, and finally recycle solvent from the SRL product containing unconverted lignite and mineral matter. The final flash separation step is operated under vacuum and recovers the remaining volatile liquids and solvent.

The vacuum tower bottoms are pumped to a surge vessel and mixed with

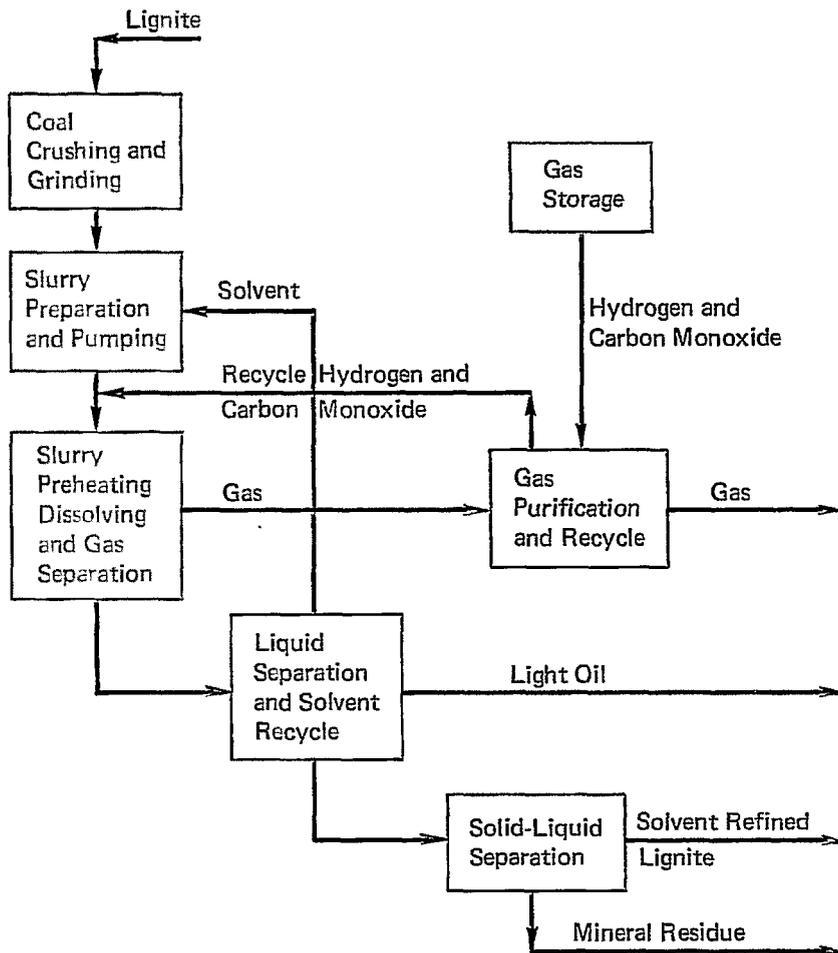


Figure 14 Block flowsheet for solvent-refined lignite process.

benzene or toluene as a deashing solvent. The resulting mixture is pumped to a gravity settling tower that operates above the critical pressure but below the critical temperature of the deashing solvent. The tower is operated countercurrently to recover dissolved SRL and deashing solvent as overhead and unconverted lignite and mineral matter residue as underflow. Deashing solvent is recovered from both streams and recycled to the gravity settling tower. The SRL product after removal of deashing solvent is solidified or maintained in its liquid state. The dried residue can contain up to 40 weight percent unconverted lignite in addition to mineral matter. Table 7 summarizes the results of two typical runs.

At the University of North Dakota, bench-scale laboratory research to determine optimum operating parameters has been completed. A 0.5-ton-per-day production-development unit is in its initial operating phases at Grand Forks, North Dakota. Start-up was in mid-1975, and progress to date has not resulted in solvent-balanced operation. Operation is intended to establish sufficient data to allow specification of conditions for a projected run with lignite in the SRC process at Fort Lewis, Washington.

4. Costeam Process

Coal can be liquefied by treatment with CO and water, probably by way of reaction with hydrogen formed in the water-gas shift reaction,^{27, 28} which appears to be more "reactive" or at least as active as molecular hydrogen. For example, at 380 °C and 100 atmospheres in the presence of phenanthrene- α -naphthol solvent, a CO-water mixture caused liquefaction of coal faster than did hydrogen.²⁷ The ultimate analysis and physical appearance of the product for 140 atmospheres were nearly the same whether hydrogen was used directly or formed from CO and water. These reactions form the basis of the ERDA (U.S. Bureau of Mines) Costeam process.

A slurry of pulverized coal in recycle product oil is pumped with CO or CO-rich synthesis gas into a stirred reactor at about 425 °C and 275 atmospheres (Figure 15). The steam for the reaction is derived from the moisture of the coal. Products from the reactor go to a receiver, where the raw oil is separated from the product gas. Unreacted coal and mineral matter are removed from the product oil by centrifugation or filtration, although flash distillation may be more attractive in the future. The process is specifically designed for coals with high reactivities and high moisture contents, such as lignite, since no catalyst may be required.

The Costeam process has been under development at ERDA in small-scale bench units (2.25 gal) since 1968. Further testing is planned to provide sufficient data for the design and fabrication of a 10-ton-per-day pilot plant.

Table 7 Yields From Solvent Refined Lignite (SRL) Process²⁶

	Run Number	
	M-1C	M-9C
<u>At End of Yield Period</u>		
Hours on Coal During Run	62	43
Cumulative Hours on Coal	62	422
Liquid Hourly Space Velocity	0.90	1.41
Gas Hourly Space Velocity	164	321
Solvent/Coal Ratio	2.30	1.91
Coal Charged, lb/hr/cu ft Reactor	18.6	32.9
Gas Charged, scf/ton Coal	17,700	19,500
H ₂ Equivalent Consumed, Wt % MAF Coal	2.35	1.50
<u>Yields, Wt % MAF Coal</u>		
Net Gas	10.4	15.9
Net Liquefied	69.4	66.8
(Light Oil)	--	(9.5)
(SRL)	(69.4)	(57.3)
Net H ₂ O & Ash	-6.5	-4.4
Unconverted MAF Coal	26.7	21.7
Solvent Recycle, %	85.9	89.2
<u>Conditions</u>		
Temperatures, °C		
Preheater Outlet	370	400
Reactor Exit Temperature	395	410
Vacuum Flash	310	314
Pressures		
Dissolver, atm abs	103	171
Inter. Sept., atm abs	24.8	28.2
Vac. Flash, atm abs	0.013	0.020

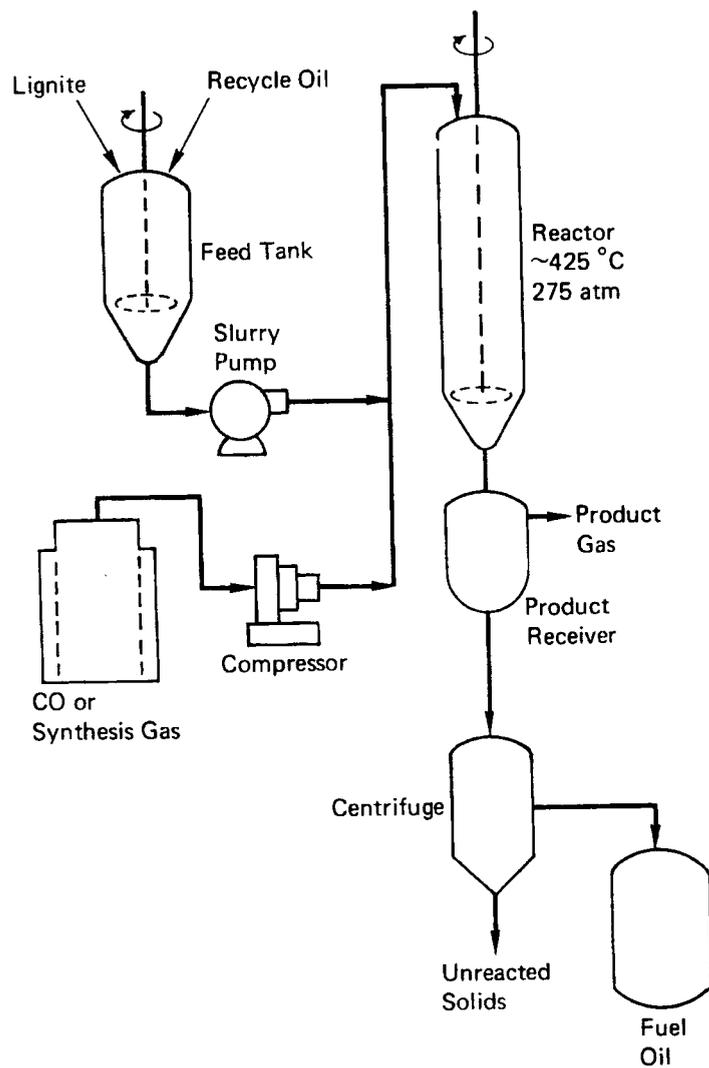


Figure 15 Schematic of the Costeam process.

5. Exxon Donor Solvent Process

The Exxon donor solvent (EDS) process²⁹ involves the liquefaction of coal in a hydrogen-donor solvent with subsequent separation of solids from liquids and hydroprocessing of the liquids to provide regenerated donor solvent and improved quality products. A flow diagram is shown in Figure 16, and operating conditions are summarized in Table 4. Crushed coal in recycle donor solvent is mixed with hot hydrogen at about 100 atmospheres and passed through the liquefaction reactor at 425 to 480 °C and 100 to 140 atmospheres H₂ with a residence time of 0.5 to 1.5 hour to produce gas, raw coal liquids, and heavy bottoms that contains the unreacted coal and mineral matter.

The liquefaction step effluent is separated via flash distillation, and the recycle solvent is catalytically hydrogenated in a trickle-bed reactor over commercially available metal sulfide hydrotreating catalysts at 260 to 450 °C and 80 to 210 atmospheres H₂ pressure with a weight hourly space velocity of 0.2 to 4.9 to produce rejuvenated solvent. The quality of the donor solvent has a major effect on the liquefaction behavior.

The heavy bottoms from the distillation section are further processed by coking or gasification to produce additional liquids and hydrogen or fuel gas for the process. The gas generated from the process can be used as fuel but probably will be used in H₂ manufacture. Depending on the ultimate product utilization, the raw coal liquids may be catalytically hydrotreated.

Solids separation is achieved by vacuum distillation, thus avoiding the problems of other separation techniques. The bottoms from the distillation tower contain all the solid residue from liquefaction and some very high boiling hydrocarbons but very little material boiling below 540 °C.

Liquefaction conditions strongly influence the success of the vacuum distillation step. Table 8 gives typical yield data for an Illinois bituminous coal, and Table 9 gives maximum yields for a self-sufficient plant. The amount of naphtha produced can be varied from 5 percent to at least 25 percent on a dry coal basis. The process utilizes steps that involve engineering and design technology similar to that practiced in the petroleum industry. The processing sequence was designed to allow for feeding different coals and to allow product distribution to be varied based on market demand.

Research, which began in 1966, is now at the 1-ton-per-day pilot-plant stage and has been financed by Exxon. Current operations are 50 percent supported by ERDA. The basic design specifications for a 250-ton-per-day pilot plant, which is sized to provide the critical engineering data to allow scale-up directly to commercial size, have been completed. The next step is preparation of the detailed mechanical design and construction of the unit involving multiparty sponsorship.

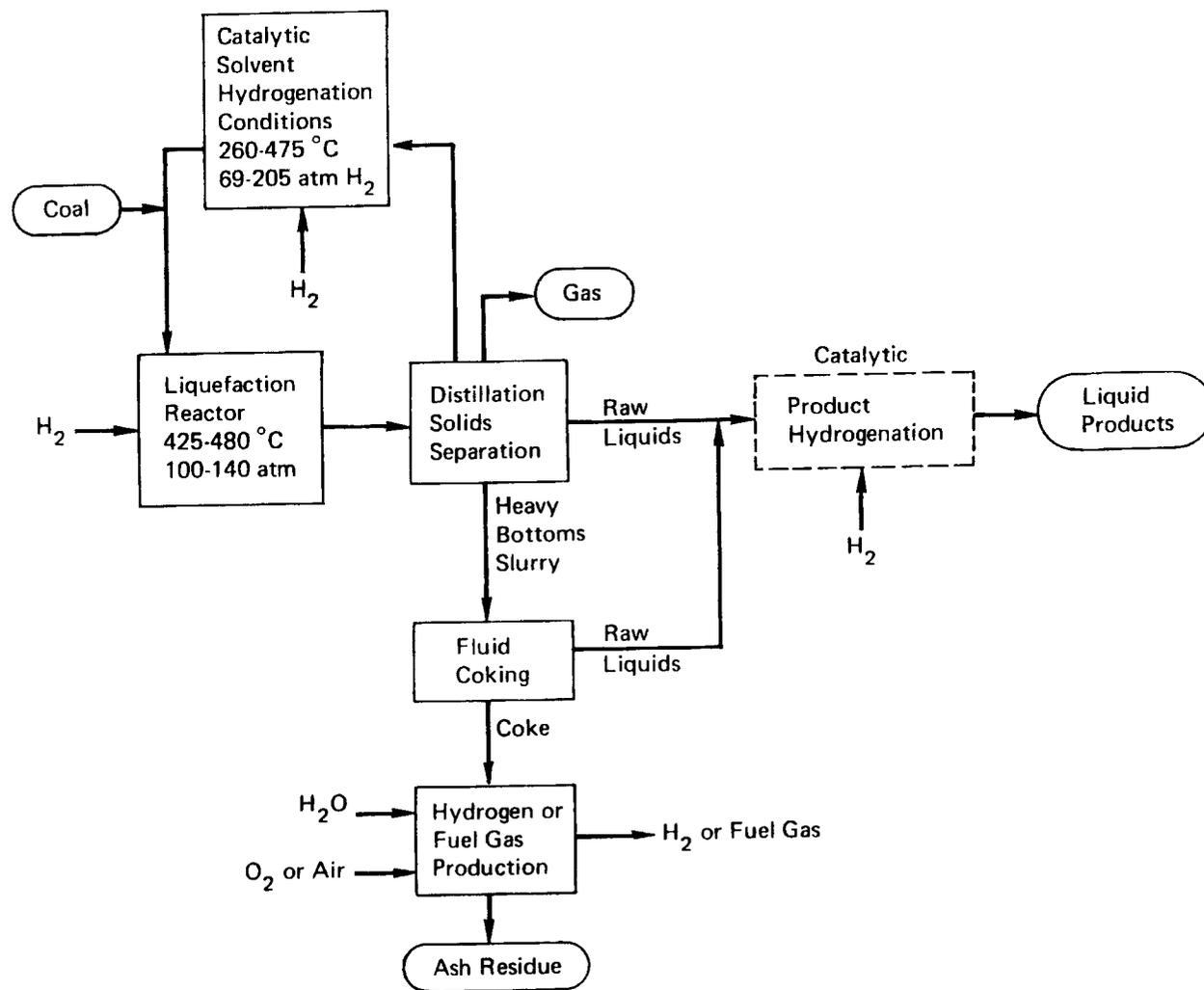


Figure 16 Block diagram of Exxon donor solvent (EDS) process.

Table 8 Typical Yields for Liquefaction of Illinois No. 6 Bituminous Coal in Exxon Donor Solvent Process

<u>Wt % on Dry Coal^a</u>	<u>Liquefaction</u>	<u>Liquefaction Plus Coking</u>	<u>High Naphtha (Liquefaction Plus Coking)</u>
H ₂	-3.1	-3.0	-4.0
H ₂ O, CO ₂ , CO	10	10	11
H ₂ S, NH ₃	4	4	4
C ₁ -C ₃	6	9	12
C ₄ , C ₅	3	4	5
Naphtha (0.455, 0.2N) ^b	15	16	21
Fuel oil (0.455, 0.65N) ^b	17	25	19
Liquefaction Btms.	48	-	-
Coke and ash	-	35	31
	<u>100</u>	<u>100</u>	<u>100</u>

Liquid Yield

wt % on dry coal	35	45	45
bbbl/ton dry coal	2.1	2.6	2.7

H₂ Consumption

scf/bbl liquid	5,600	4,100	5,500 [~] 15,000 scf H ₂ ton coal
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^aBasis of yields is dry coal fed to the integrated self-sufficient EDS plant. Ash content of dry coal was 9.58 wt %.

^bAs received coal was ~4.5 wt % sulfur (about 2.0 wt % organic sulfur) and 1.5 wt % nitrogen: composition, wt % basis; of liquids is indicated.

Table 9 Maximum Practical Yields for Self-Sufficient Liquefaction Plant Using Exxon Donor Solvent Process

	<u>Percent of Dry Coal Feed</u>
Feed coal energy	100
Hydrogen production	10-15
Process heat and power	<u>15-20</u>
Feed energy available for liquids production	65-75
Overall process efficiency, percent	65-75
Maximum practical liquid yield, wt percent	46-54
Barrels/ton of dry coal fed to integrated plant	2.7-3.1

6. Other Processes

a. Extractive Coking Process

Arthur D. Little, Inc., has developed an extractive coking process that is a modification of delayed coking.³⁰ It involves the use of a hydrogen-donor solvent under mild conditions to achieve liquefaction and of delayed coking to separate the product as an overhead vapor from the coal ash and the heavy oils.

Coal is crushed and ground and then added to a coke drum along with mildly hydrogenated recycle solvent whose boiling range is approximately 230 to 400 °C. The coal and solvent react in the drum at about 400 °C for approximately 1 hour under enough pressure to maintain most of the solvent as a liquid (approximately 7 atmospheres). During this period, hot solvent vapor passes through the drum continuously to support heat and agitation. The drum pressure is reduced gradually to flash-off solvent and light ends; incoming hot solvent vapor supplies the latent heat of vaporization. The drum contents are subsequently heated with more hot vapor to about 450 °C and allowed to coke. Coking results in a complete separation of liquids from ash and unreacted coal, which offers advantages over mechanical separation. The drum is cooled and decoked hydraulically while a second drum goes through the extraction-coking cycle.

The vapors from the coke drum are fractionated to separate recycle solvent, which is hydrotreated and stored for use as hydrogen donor solvent. The other portion is revaporized and superheated to provide heat to the coke drum. The fractionation tower further separates the products into gases, light extract (C₄-230 °C), and middle boiling range material (230-400 °C).

The light and middle boiling material would require mild hydrocracking or hydrotreating to qualify as a low-sulfur premium distillate that could be subsequently processed into such typical refinery "white products" as jet fuel, household heating oil, and gasoline. The heavy extract from the fractionation tower probably will require too much hydrogen to justify conversion to suitable feed for further refining; it could go to a fluid coker to produce ash-free coke, be recycled to the delayed coker, or be blended with the lighter fraction to meet the viscosity specifications for residual fuel oil. The process concept is being tested on the bench scale.

b. Extraction by Supercritical Fluids

The Coal Research Establishment in England has been evaluating the use of supercritical fluids to dissolve and remove coal from the mineral matter present.^{5,31,32} Pulverized coal is treated with compressed gases (H₂ and CO) at temperatures of from 175 to 200 °C, causing a portion of the coal to go into solution in the compressed gas. The coal solution

is transferred to a second vessel, leaving the mineral matter (ash) and undissolved coal behind. The pressure on the second vessel is released, precipitating the extract, and the gas is recompressed and recycled to the extraction vessel. The coal extract produced by this process is richer in hydrogen than that produced by liquid-solvent extraction and, thus, is more suitable for the production of hydrocarbon oils and chemicals.

Results have indicated that this process has certain advantages over liquid-solvent extraction in that: (1) filtering to remove insoluble residue may not be necessary, (2) recovery of gaseous solvent is virtually complete, (3) the extraction residue is a porous solid suitable for gasification, and (4) more mobile liquids of higher hydrogen content are obtained. On the other hand, there are some accompanying disadvantages, including the facts that the yield of extract is considerably less than in liquid-solvent extraction and operation at high pressure involves more costly equipment and higher operating costs. This process may be better suited to the production of high-quality special products than to the production of fuels.

Experimental gas extraction units for the preparation and recovery of coal extract have been operated successfully to investigate the processes controlling the rate of extraction and to obtain design data for a pilot plant; another unit has been operated to investigate extraction in the presence of reducing gases such as hydrogen or carbon monoxide and steam.

c. UOP

Universal Oil Products has developed a process similar to the Exxon donor solvent process in which coal undergoes solvent extraction in a flow reactor at 400 to 450 °C and 100 to 200 atmospheres with a liquid hourly space velocity of 0.5 to 2.0. After filtration for solids separation, the entire liquid product stream undergoes hydrotreating to produce a liquid product (200 to 540 °C boiling range) that is low in sulfur (0.15 percent from a 3.8 percent sulfur coal) and accounts for about 70 percent of the coal (moisture and ash-free) fed to the reactor. C₁ to C₄ gases account for about 8 percent and C₅⁺ light oils account for about 5 percent of the coal. The process has been operated for about two years at the pilot-plant scale and is awaiting further investigation. No further details are available.

d. Pott-Broche Process

In the Pott-Broche process,³³ bituminous coal was dissolved in a process-derived solvent at about 150 atmospheres and 450 °C to extract 75 percent of the carbon in the feed coal. Part of the make-up solvent was supplied by hydrocracking to produce a solvent with hydrogen-donor capabilities. Products consisted of light oil, heavy oil, and electrode-grade carbon for the aluminum industry. The process is not under current development although several of the processes described above utilize basic Pott-Broche concepts.

D. CATALYTIC LIQUEFACTION

Catalytic liquefaction covers those hydrogenation processes in which the coal comes into direct contact with a catalyst other than the mineral matter originally present in the coal. It has the advantage of eliminating the need for a catalytic reactor where the hydrogen-donor solvent is re-hydrogenated. Disadvantages of the process are catalyst deactivation caused by action of the mineral matter, tar, and reactive coke-forming fragments from the coal. In some cases, separating the catalyst from the unconverted coal and ash is a problem.

From the beginning of coal liquefaction technology, there has been interest in catalysis by Lewis acids such as $ZnCl_2$, $SnCl_2$, $NiCl_2$, $FeSO_4$, and others.³⁴ The chemistry of the hydrogenation, hydrocracking, and other reactions of coal that these acids catalyze is still not well understood, and the recent literature contains little information to add to what has long been available. Studies have involved almost every material that might show catalytic promise, and attempts recently have been made to apply catalysts that have shown high hydrogenation activity in petroleum refining.³⁴⁻³⁶

To achieve rapid direct hydrogenation of coal, the catalyst and the coal must be in intimate contact or the transfer of hydrogen to the coal must be accomplished with the aid of a hydrogenated solvent. Intimate contact can be achieved by impregnating the coal with the catalyst or by mixing the coal with a catalyst that has sufficient vapor pressure to deposit on the coal surface at the reactor temperature. If the coal and the catalyst are not in intimate contact, as is the case when particulate catalyst is present with coal particles in a liquefaction reactor, the transfer of hydrogen to the coal occurs largely through hydrogenation of solvent molecules on the catalyst and diffusion of these hydrogenated donor solvent molecules to the reacting coal particles where they give up the hydrogen atoms to dissolving coal fragments.

When coal is converted by passing it through a catalyst bed, it is suspended in a heavy oil to form a slurry. In this case, the opportunity for intimate contact between coal and catalyst is much less, and the heavy oil is chosen for its capacity to act as a hydrogen-donor solvent to facilitate the transfer of hydrogen from gas-phase hydrogen to the coal. Examples of processes in which conversion is carried out in a catalyst bed are the H-Coal, Synthoil, Gulf-CCL, and C-E Lummus. Table 10 summarizes the characteristics of these processes.

Processes in which the catalyst is in intimate contact with the coal and in which liquefaction occurs in the presence of hydrogen gas are referred to as solid-gas catalytic liquefaction and also have been called catalytic hydrocarbonization or dry coal hydrogenation. The key features of these processes are rapid heating to temperatures of 450 to 600 °C, short residence times, and quenching of the reactor effluent. For some time it has appeared that gas-solid catalytic liquefaction may have

Table 10 Summary of Catalytic Liquefaction Processes

Process	H-Coal ^a	Synthoil ^d	CCL	Clean Fuel from Coal, CFPC
Developer	Hydrocarbon Research	ERDA--PERC	Gulf Oil Corp.	C. E. Lummus
Coal	Lignite Subbituminous Bituminous	Lignite Subbituminous Bituminous	Lignite Subbituminous Bituminous	Lignite Subbituminous
Catalyst	Co-Mo/Al ₂ O ₃ or similar	Co-Mo/Al ₂ O ₃ or similar	Co-Mo/Al ₂ O ₃ or similar	Co-Mo/Al ₂ O ₃ related
Reactor Type	Ebullated Bed	Fixed Bed	Fixed Bed	Expanded Bed
Reaction Temp. ^a °C	450	450	>400	400-430
Reaction Pressure ^a atm abs	150-205	135-275	135+	68+
<u>Product Yield^{a,b} per ton</u>				
Char	110 lb	140 lb (17,000 Btu/lb)	not available	not available
Oil	1,480 (>4.0 bbl)	1,453 lb (4.0 bbl)	3.0 bbl low sulfur oil	2.5-3.0 bbl oil
Hydrogen Consumption per ton & H ₂ Source	13,000-18,000 scf HRI-developed multi-bed gasifier for H ₂ via steam-oxygen	~15,000 scf, unspecified gasification scheme	consumption not available, reforming of product gas for H ₂ .	not available gasification of residue
Remarks	two operating modes, lower H ₂ consumption yields low-sulfur fuel oil, higher H ₂ figure yields the 15° API syncrude, rapid catalyst deactivation based on H-oil technology	long preheater residence time, very short residence time required in reactor, short catalyst life	reactor design and new catalyst claimed key to process, low catalyst deactivation rates, proprietary technology	solvent deashing for solids separation, staged coal dissolution and hydro-treating of dissolved coal-ash slurry without solids separation
Current Status	successfully tested in 3 TPD plant, Kentucky site selected for construction of 600 TPD demonstration plant	1/4 TPD pilot plant with 1.0 bbl/day oil output in operation, 8 TPD pilot plant is in design and engineering stages	1 TPD pilot unit started up January, 1975.	small pilot plant scale tests, Lummus holds patents on solvent separation technique

^aExact operating conditions and yield will depend on coal being processed and on products desired.

^bYields are typical values observed or ranges reported; yields are based on moisture- and ash-free (MAF) coal fed to the reaction zone. Yields based on coal fed to a self-sufficient integrated plant would be significantly lower, and yields will vary with the coal fed.

^cYields are for an Illinois coal, synthetic crude oil mode of operation.

^dSynthoil yields include gas and liquids obtained from pyrolysis of solids residue and are for a Western Kentucky coal.

significant advantages over liquid-phase hydrogenation.³⁷⁻³⁹ Similar catalysts also may be brought into intimate contact with coal in a liquid-phase environment.

Examples of processes in which coal is mixed or impregnated with catalyst before conversion are the Bergius, University of Utah, Schroeder, and liquid-phase zinc chloride (Conoco). Table 11 summarizes these processes. In the Bergius process, the coal and catalyst are mixed with a heavy recycle oil to form a paste. In the second and third processes, the coal and catalyst are fed into the reactor dry in a stream of hot hydrogen. In the zinc chloride process, a slurry of coal in recycle oil and a stream of molten catalyst are fed simultaneously to the reactor.

1. Bergius Process

The conversion of coal into oil by the action of hydrogen under pressure was first achieved by Bergius in 1913.⁴⁰ The process involved treating a paste of coal, heavy recycle oil, and a small amount of iron oxide catalyst with hydrogen in the liquid phase at 450 to 500 °C and 205 to 680 atmospheres absolute in a stirred autoclave. Later it was developed commercially by I. G. Farbenindustrie A.G. to give good quality gasoline as the chief product. Between 1927 and 1943, 12 plants were built by the Germans, 2 by the British, and 1 by the Koreans, all of which were operated during World War II.⁴¹ The German plants produced almost all of Germany's aviation fuel requirements.

A number of other catalysts were found to be active with various coals (e.g., molybdenum oxide, stannous oxalate, and iodine); however, iron oxide continued to be used because of its low cost. Pressures up to 700 atmospheres gave better yields, especially on high-rank coals. In general, the products were separated into light, middle, and bottom fractions. The middle distillate fraction was treated further over a hydrotreating catalyst in the vapor phase and under relatively mild conditions to produce petroleum-like products. The bottoms fraction was filtered or centrifuged to remove solids (unreacted coal, catalyst, and ash), and the remaining liquid was utilized as recycle oil to mix with fresh coal.

Because a shortage of petroleum was expected in the United States after World War II, a demonstration plant using updated German technology was constructed at Louisiana, Missouri, to hydrogenate 50 tons of coal per day (feed coal to the reactor, hydrogen, and all utilities were supplied from external fuel sources) and was operated from 1949 to 1953. The plant produced 200 barrels of oil per day and permitted testing of various American coals. Cost studies showed that the process was not competitive with products derived from petroleum, and since the increase in imported petroleum cost certainly was not then anticipated, operation was discontinued in 1953. For the same reasons, none of the coal hydrogenation plants in Germany and Great Britain currently are being used.

Table 11 Summary of Direct Catalytic Hydrogenation Processes

Process Developer	Bergius	University of Utah ^d W. Wisser	Schroeder ^d W. Schroeder	Liquid-phase Zinc Chloride ^d Conoco Oil Co.
Coal	subbituminous bituminous	subbituminous bituminous	subbituminous bituminous	subbituminous bituminous
Catalyst	iron oxide, molybdenum oxide, iodine stannous oxalate	ZnCl ₂ , SnCl ₂	ammonium molybdate	zinc chloride
Reactor type ^b	tubular plug flow	tubular entrained flow	tubular entrained flow	liquid phase
Reaction Temp. ^{b, a, c}	480	500-550	500	360-440
Reaction, Pressure ^b atm abs	205-680	100-170	137	100-240
Solid Residence Time	1 hr	5-15 sec	30 sec	--
Product Yield ^{b, c} per ton				
Char	--	600 lb unconverted	100 lb	406 lb
Oil	--	1,200 lb	1,300 lb	1,098 lb
Gas	--	200 lb	600 lb	260 lb
Remarks	iron oxide used because of low cost, severe operating conditions lead to very high costs, conceptual forerunner of current solvent ex- traction and catalytic hydrogenation technology.	dry coal mixed with 3 wt % catalyst is carried through coiled-tube reactor by high-pres- sure high-temperature hydrogen flow, catalyst impregnated coal due to high vapor pressure at reaction temp., short contact times mean small reactor size, catalyst recovery required.	dry coal impregnated with 1 wt % catalyst, catalyst recovery necessary, complete conversion of carbon in 20 sec longer time cracked liquids to gas, entire process at op- erating pressure to reduce costs, small reactor size.	coal slurry and molten ZnCl ₂ catalyst fed to reactor, product is mainly light fuel oil and gasoline (high octane), catalyst recovery by vaporization from residue in fluid-bed combustor.
Current Status	15 plants were operating during World War II, none are now operating	bench scale 50/lb hr process develop- ment unit.	bench scale tests completed	small scale studies done 2-5 lb/hr bench scale unit under design and construction

^aDry coal is fed directly to the process, recycle oil is not used.

^bExact operating conditions and yield will depend on coal being processed and on products desired.

^cYields are typical values observed or ranges reported; yields are based on moisture- and ash-free (MAF) coal fed to the reaction zone. Yields based on coal fed to a self-sufficient integrated plant would be significantly lower, and yields will vary with the coal fed.

^dYield data from "Quarterly Technical Progress Report," May 1-July 31, 1976, ERDA FE-1743-24; August 15, 1976.

Although the Bergius process is obsolete, it represents a milestone in coal conversion technology and many of its concepts are employed in modified form in the coal liquefaction processes under development today.

2. H-Coal Process

The H-Coal process^{4,5,9,42} (Figure 17) being developed by Hydrocarbon Research, Inc. (HRI), is a liquid-phase process in which coal suspended in recycle solvent is contacted with particulate catalyst in a fluidized- or ebullating-bed reactor (Figure 4b). It is a modification of the H-Oil process designed to hydrotreat heavy fuel oils.

The process can be operated to produce a low-sulfur heavy fuel oil or a synthetic crude oil. Coal is dried, pulverized, and slurried with coal-derived recycle oil for charging to the coal hydroprocessing reactor. The slurry is mixed with hydrogen, preheated, and fed to the reactor, where it is contacted with catalyst at about 450 °C and 150 to 205 atmospheres. The ebullating-bed reactor contains the particulate catalyst with the liquid, gaseous, and solid materials passing upward through it. The coal is partly dissolved and both the coal and solvent are hydrogenated. The relative sizes of the catalyst and coal particles are such that only the unconverted coal, ash, liquid, and gaseous products leave the reactor.

Rates of catalyst deactivation are reported to be very rapid, and provision is made to withdraw and add catalyst continuously to maintain constant activity. The reactor provides nearly uniform temperature, effective contact between reacting species and the catalyst, and continuous removal of heavy liquid as well as ash without carrying out the catalyst.

Reactor products are separated in flash drums into gas, distillate, and bottoms, which contain unconverted coal, ash, and heavy oil. The recycle gas stream is scrubbed to remove light hydrocarbons, ammonia, and hydrogen sulfide. The distillate is separated into light and heavy distillates in an atmospheric tower, and the bottoms are processed in a hydroclone from which a clarified recycle stream is returned to the slurry tank; the remaining unconverted coal, ash, and heavy oil are sent to a vacuum tower that yields a heavy distillate and a concentrated slurry. Some of the heavy distillates may also be returned to the slurry tank to control the quality of the recycle stream. The concentrated slurry may be sent to a coker to recover the remaining oil.

As shown in Figure 17, the liquid product from the reactor is a synthetic crude oil that can be converted to gasoline and furnace oil by conventional refining processes. Operating under milder conditions to produce predominantly a low-sulfur heavy fuel oil requires filtration or some other means for separating liquids from unconverted coal and ash. The desired sulfur level in the heavy oil product largely dictates the required operating conditions; this, in turn, determines the relative amounts of desired products and the hydrogen consumption.

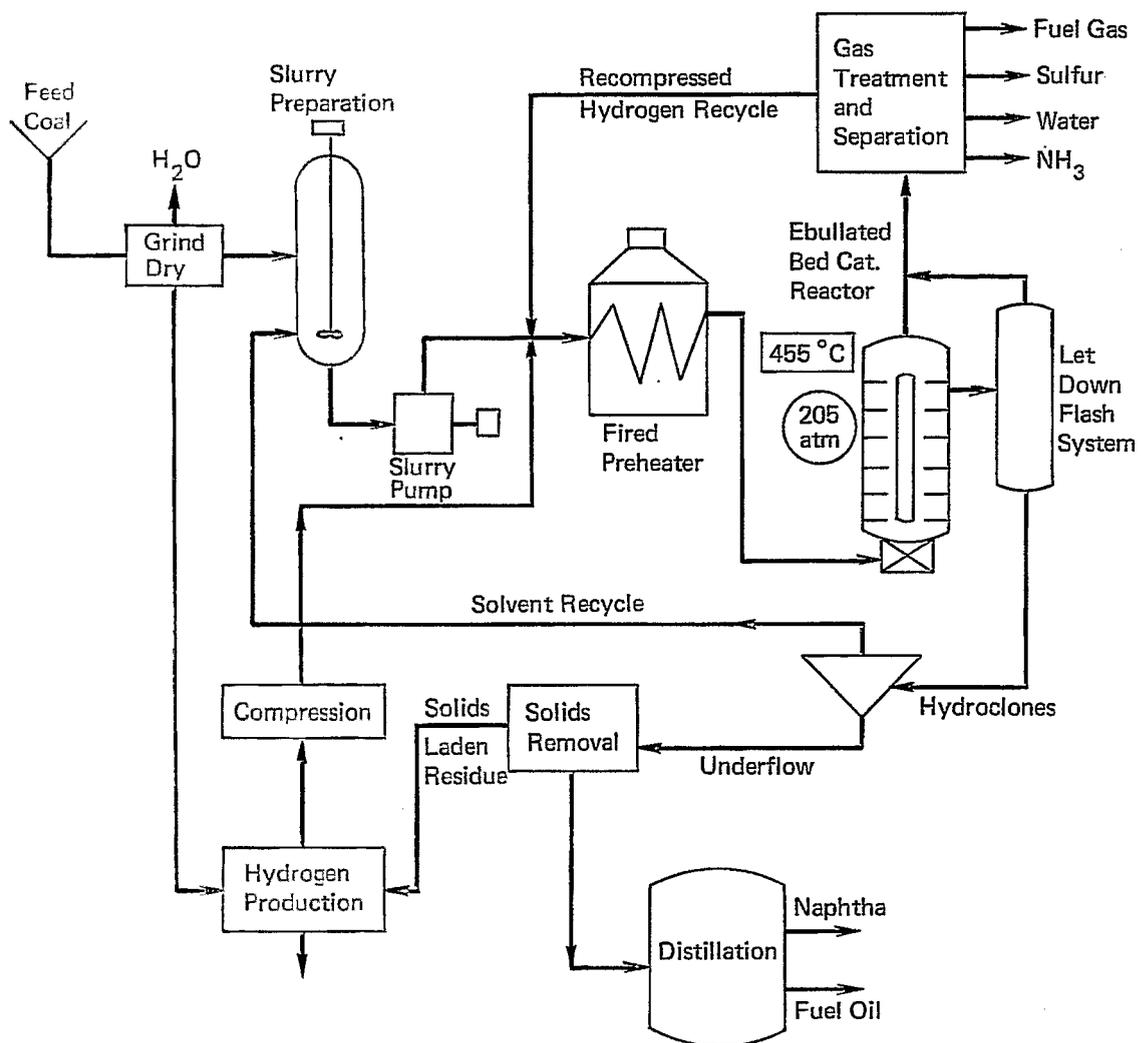


Figure 17 Process flow scheme for H-Coal process operated in the syncrude mode.

Product yields and specifications are given in Table 12. The process produces about 3.5 to 4.0 barrels of liquids per ton of coal (MAF) fed to the reactor. This yield does not take into account process energy and hydrogen that must be supplied (probably by coal or other fuels) and that reduce the overall liquid yield per ton of coal. The overall thermal efficiency of a self-sufficient plant is about 64 percent. Catalyst replacement costs have been reported to be \$1.00 to \$1.50 per ton of coal due to the high deactivation rates encountered.

Table 12 Effect of Processing Mode and Coal on Product Composition from H-Coal Process

Coal Desired Product	Illinois		Wyodak
	Synthetic Crude	Low-sulfur Fuel Oil	Synthetic Crude
Normalized Product Distribution, ^a wt %			
C ₁ -C ₃ Hydrocarbons	10.7	5.4	10.2
C ₄ -200 °C Distillate	17.2	12.1	26.1
200-340 °C Distillate	28.2	19.3	19.8
340-525 °C Distillate	18.6	17.3	6.5
525 °C+ Residual Oil	10.0	29.5	11.1
Unreacted Ash-Free Coal	5.2	6.8	9.8
H ₂ O, NH ₃ , H ₂ S, CO, CO ₂	<u>15.0</u>	<u>12.8</u>	<u>22.7</u>
Total (100.0 + H ₂ reacted)	104.9	103.2	106.2
Conversion, %	94.8	93.2	90.2
Hydrogen Consumption, scf/ton	<u>18,600</u>	<u>12,200</u>	<u>23,600</u>

^aYield based on moisture- and ash-free coal fed to the reactor, yields based on a self-sufficient plant would be significantly lower.

For about 12 years, HRI developed the H-Coal process in a 25-pound-per-day bench-scale unit. This was followed by a process-development unit handling 3 tons of coal per day that was built with support from the Office of Coal Research and a private industry consortium.

In 1974, prior to the formation of ERDA, the Office of Coal Research awarded a 14-month contract to HRI for the engineering portion of a multiphase project for design, construction, and operation of a 600-ton-per-day pilot plant that was to produce low-sulfur fuel oil and synthetic crude suitable for refinery processing into gasoline, kerosene, diesel fuel, fuel oil, and petrochemical feedstocks. It now is planned that this plant be located in Cattlettsburg, Kentucky, and the final design is to be completed by mid-1977. It currently is contemplated that the cost of constructing and operating the pilot plant will be shared by ERDA and an industry team including Ashland Oil Company, Standard Oil of Indiana, the Electric Power Research Institute (EPRI), and possibly others.

3. Synthoil Process

The Synthoil process^{4,5,43,44} being developed by the ERDA Pittsburgh Energy Research Center passes a mixture of coal, recycle liquid, and hydrogen through a fixed bed of catalyst at high velocity (Figure 18). Coal, slurried with process-derived oil, flows concurrently with hydrogen upward through a preheater, reaching a temperature of about 450 °C at a pressure of 135 to 175 atmospheres. The coal particles soften and (except for the inorganic components) are largely liquefied or dispersed in the preheater. The gas-liquid-solid mixture then flows upward through a hydrogenation reactor containing a packed bed of cobalt-molybdate catalyst where the liquids and solids undergo hydrogenation including reduction of sulfur and nitrogen. The flow is highly turbulent, the objective of the design being to prevent plugging of the catalyst bed by deposited inorganic material, coke, or unconverted coal. Thus, the process somewhat resembles a two-stage process involving solvent extraction followed by hydrotreating after a solids separation step between stages.

The reactor product is cooled and collected in high-pressure separators. The gas, largely hydrogen, is scrubbed and recycled to the reactor. The liquid-solid product is centrifuged to remove unconverted coal and ash. Other solids separation schemes very likely will require evaluation. The liquid product is in part recycled and mixed with coal to produce the feed slurry; the remaining liquid is the product, a low-sulfur liquid fuel. The process yields as much as 4.0 barrels of oil per ton of coal (MAF) fed to the reactor. Typical processing conditions and product specifications are shown in Table 13. Process yields for a self-sufficient integrated plant will be significantly lower. Projected overall process thermal efficiency of a self-sufficient plant is about 70 percent.

The process has been developed in a 5-pound-per-hour bench-scale unit and a 0.25-ton-per-day pilot plant at the Pittsburgh Energy Research Center. Recent results have shown that the life of the fixed-bed catalyst was considerably shorter than originally anticipated. Foster-Wheeler Corporation has been awarded a contract for the design and engineering services for a 10-ton-per-day pilot plant to be constructed in Bruceton, Pennsylvania. Start-up is scheduled for late 1977, and Bethlehem Steel is scheduled to operate the plant.

4. Gulf Catalytic Coal Liquids (GCL) Process

The catalytic coal liquefaction (GCL) process⁴⁵ is a proprietary coal liquefaction development of the Gulf Oil Corporation. It involves the fixed-bed catalytic hydrogenation of a coal slurry with gaseous hydrogen. A simplified flow diagram is shown in Figure 19.

The process is similar in concept to the Synthoil process. It involves a fixed-bed radial-flow reactor containing a hydrogenation catalyst such as cobalt molybdate. The reactor design involves catalyst

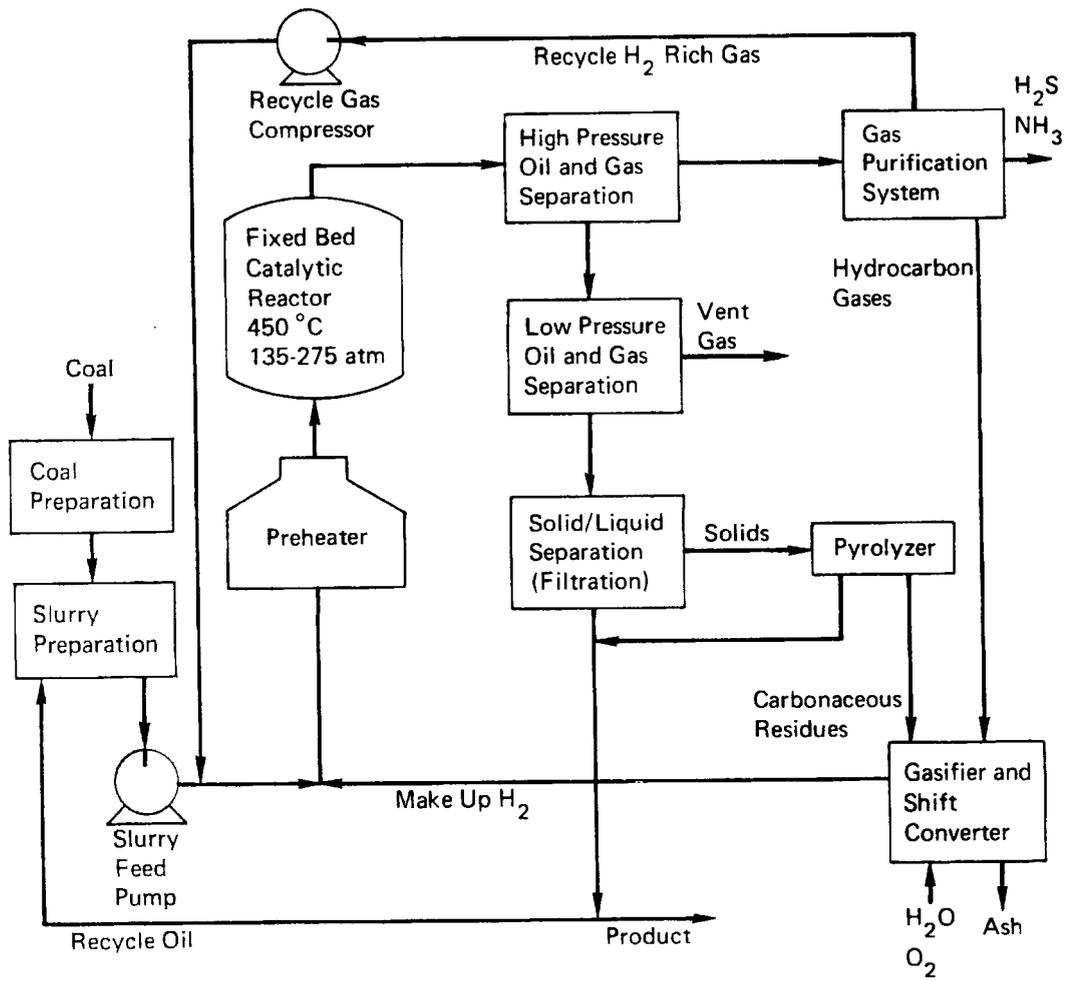


Figure 18 Synthoil process flow scheme.

Table 13 Synthoil Process Data for the Liquefaction of Kentucky Coal

Experimental Conditions:

Liquid Feed Throughout: 140 lb/hr/ft³ reactor volume
Slurry Feed: 45 coal + 55 recycle oil (weight)
Hydrogen Recycle Rate: 125 scf/hr
Pressure: 273 atm abs
Temperature: 450 °C

Sulfur in feed coal, wt %	4.6
Sulfur in recycle oil (product oil), wt %	0.19
Yield: bbl oil/ton coal MAF	3.0 ^a
Solvent analysis of product oil, wt %	
Oil (pentane soluble)	79.5
Asphaltene	17.4
Organic benzene insolubles	2.1
Ash	1.0
Elemental analysis of product oil (ash-free), wt %	
Carbon	89.9
Hydrogen	9.2
Nitrogen	0.6
Sulfur	0.19
Viscosity of product oil, SSF at 82 °C	21.30
Calorific value of product oil, Btu/lb	17,700

^a Oil yield does not take into account the process energy requirements or hydrogen requirements of an independent integrated plant.

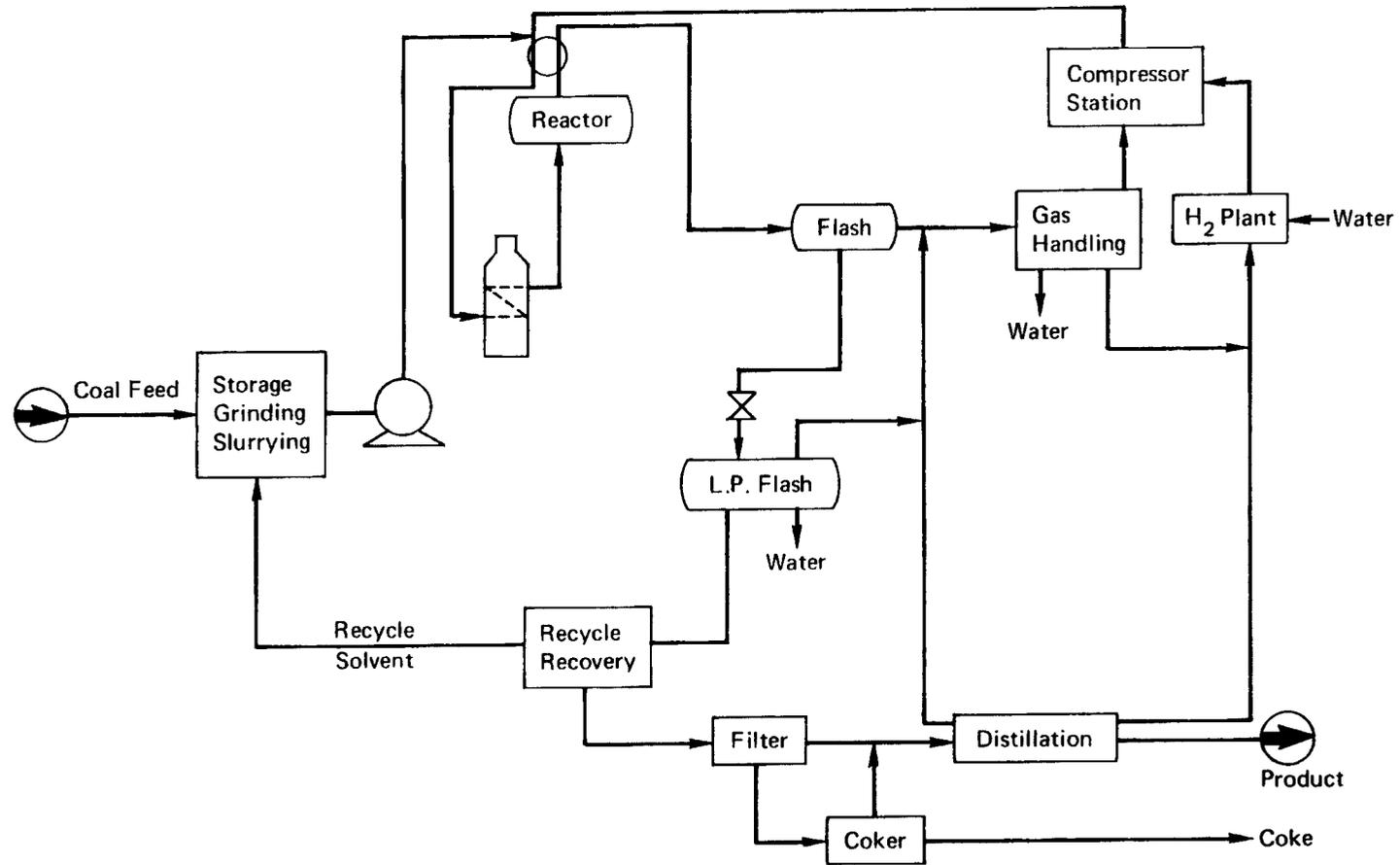


Figure 19 Process schematic of Gulf CCL process.

held in spaced, radially placed baskets. The pilot-plant unit is fed with a 40 percent slurry of coal in oil. The preheater residence time is less than 2 minutes, the average reactor temperature is greater than 400 °C, and the operating pressure is greater than 135 atmospheres. The key to the CCL process is the reactor design and the catalyst, which is claimed to have high resistance to carbon deposition, prolonged high activity, and tolerance to metallic compounds in the coal. Product specifications are probably similar to those for the Synthoil process. Liquid yields have been reported to be 2 to 3 barrels per ton of coal (MAF) fed to a self-sufficient plant depending on operating conditions.

Gulf Research and Development Company has been developing this process for 8 years on an experimental bench-scale level. In January 1975, operation of a 1-ton-per-day pilot plant designed to produce 3 barrels of oil per ton of coal was begun. The pilot plant, located at Harmarville, Pennsylvania, will provide design data for a larger demonstration plant, a conceptual design of which is currently being prepared.

5. C-E Lummus Clean Fuel from Coal (CFFC) Process

The Clean Fuel from Coal (CFFC) process developed by C-E Lummus⁴⁶ is designed to convert coal into a low-sulfur liquid similar in many respects to No. 6 fuel oil. The main features of this process are: (a) catalytic hydrodesulfurization of coal integrated with its dissolution to produce a refined liquid product containing 0.5 percent sulfur or less, and (b) special ash separation to produce a product containing less than 0.1 percent ash. The clean fuel oil would be suited for use in both new and existing power plants and as a feed to a refinery for production of other products. A simplified schematic flow diagram of the C-E Lummus process is shown in Figure 20.

After crushing and drying, coal is slurried and liquefied or dispersed in the presence of an aromatic recycle solvent. The coal slurry is hydrogenated in the presence of a catalyst at elevated pressure and temperature. Sulfur levels of 0.3 weight percent can be achieved even with coals having sulfur contents as high as 3 to 4 weight percent. Concurrent with desulfurization, other constituents of the coal, such as nitrogen and oxygen, also are partially removed, the extent depending on the type of catalyst used and the severity of the treatment. The material leaving the hydrodesulfurization section is processed to remove the ash. The clean fuel product can be produced with an ash content of less than 0.1 percent.

One of the main objectives of the Clean Fuel from Coal program was to develop an improved trouble-free method to separate ash and solids from heavy liquids. An anti-solvent-promoted gravity-settling technique developed by Lummus⁴⁶ is being studied and may offer advantages over the mechanical separation techniques previously considered.

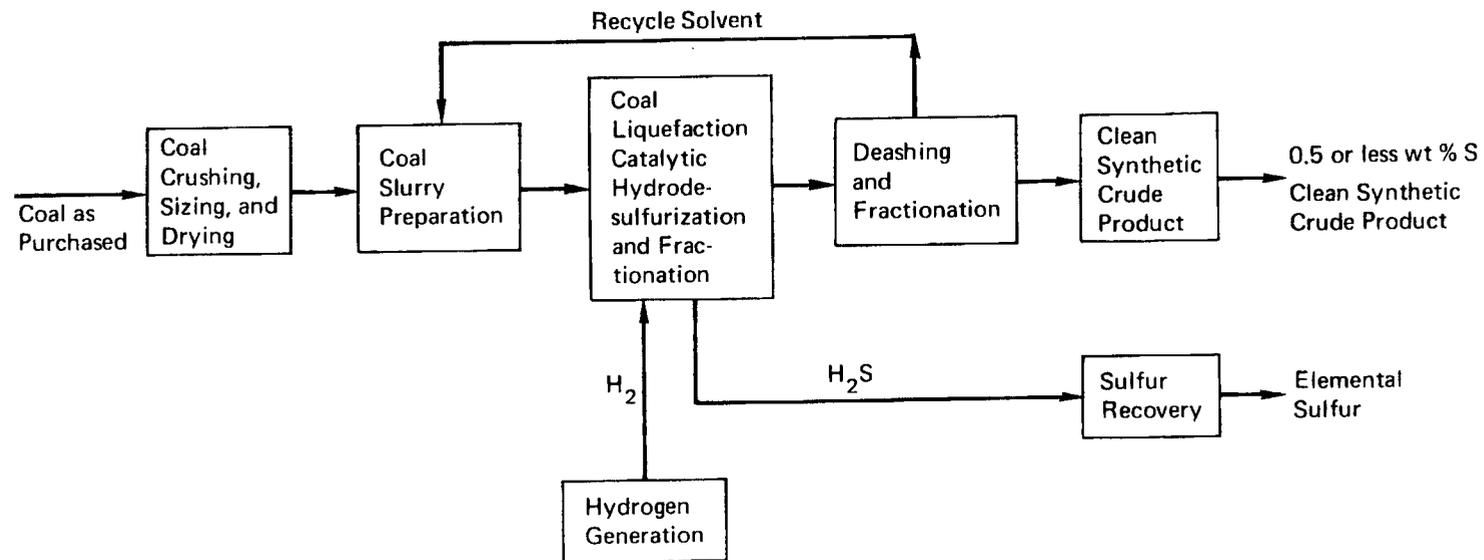


Figure 20 Simplified flow diagram of the C-E Lummus CFFC process.

Prior to deashing, the feedstock solution from the coal hydroprocessing steps is distilled to remove components boiling below 315 °C. This topped feedstock for the deashing process (consisting of recycle solvent, coal liquids, unconverted coal, and ash) is mixed with anti-solvent, and the resulting mixture flows continually to a gravity settler operating in the 150 to 300 °C range and at a pressure sufficient to maintain its contents in liquid state. An overflow stream containing substantially no ash and an ash-enriched underflow stream are simultaneously and continuously withdrawn from the gravity settler. Operating requirements vary somewhat with the feedstock. High-ash bituminous coals, containing as much as 23 weight percent ash, have been successfully processed by the above scheme to yield a fuel containing less than 0.1 weight percent ash.

Both the overflow and underflow streams generated in the deashing process are distilled to recover anti-solvent, slurry solvent, and clean fuel. Ash-containing underflow from the deashing process is vacuum fractionated, and anti-solvent, slurry solvent, and some clean fuel blend components are distilled overhead. An ash-rich residual product is withdrawn as bottoms from the distillation. This material can be gasified with steam and oxygen to produce synthesis gas ($H_2 + CO$).

C-E Lummus holds a number of patents⁴⁷⁻⁴⁹ on the process and has developed it to the small pilot-plant scale. Kerr-McGee and Consol also have carried out precipitation deashing tests of SRC product.

6. University of Utah Process

For about 7 years researchers at the University of Utah have been developing a process (Figure 21) for direct gas-solid hydrogenation of coal.^{50,51} Crushed coal is screened and can be impregnated with the $ZnCl_2$ catalyst to the extent of about 3 pounds of zinc per 100 pounds of coal. The coal then is dried and fed from lock hoppers to a preheater. Alternatively, dry coal and $ZnCl_2$ also can be mixed to provide a uniform mixture leading to equally satisfactory results due to the high vapor pressure of $ZnCl_2$ at reaction conditions. The coal is fed from pressurized lock hoppers by a star feeder into a fast-moving stream of hydrogen that carries it through the preheater and through a coiled-tube reactor at a temperature of 500 to 550 °C and pressure of 110 to 140 atmospheres. The solids residence time in the reactor is regulated by the length of coiled tube and characteristically is under 12 seconds. About 60 percent conversion of coal (MAF) to liquids and 10 percent to gases is achieved. Space utilization rates in excess of 500 pounds of coal per cubic foot per hour are realized.

The zinc is about equally divided between the liquid and solid product phases. About 85 percent of the zinc is recovered by a water wash of the char. An HCl wash is reported to increase zinc recovery to 95 percent and a hot HNO_3 wash to 99 percent.

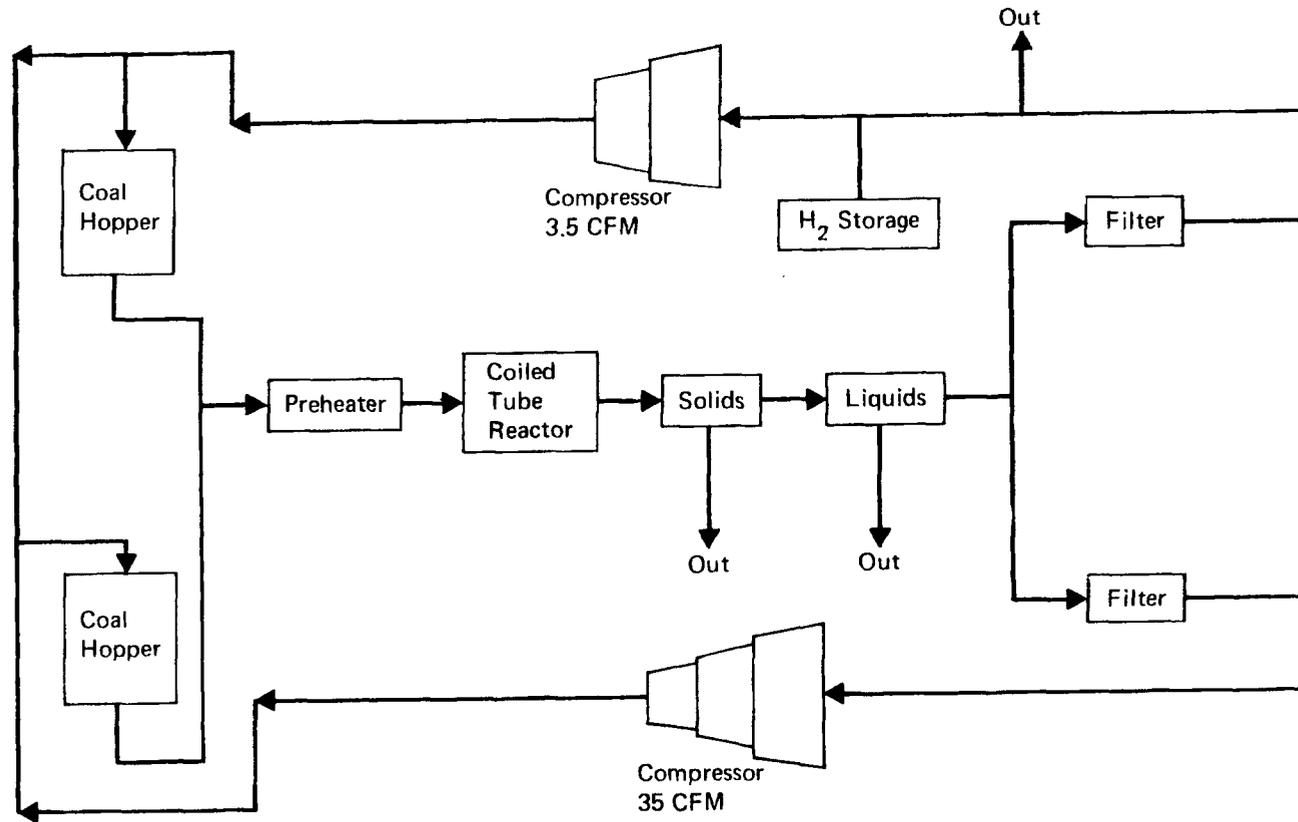


Figure 21 Block diagram of direct gas-solid hydrogenation process being developed at the University of Utah.

The process has been operated with a 5/16-inch I.D. coiled tube reactor, with which the design feed rate of 50 pounds of coal per hour has been achieved. Discussions with potential developers are under way.

7. Schroeder Process

Prior to 1964, Schroeder^{39,52,53} reported that pulverized dry coal is hydrogenated at pressures and temperatures of about 135 atmospheres and 500 °C entrained in a hydrogen stream with less than 1 minute reactor residence time to produce as much as 30 percent distillable liquid, 35 percent residual liquids, 5 percent char, and 30 percent gas based on MAF Coal (Figure 22). Residence time affects only product composition after about 20 to 30 seconds (Figure 23) since essentially all carbon is converted by this time. The reaction is accelerated by use of an ammonium molybdate catalyst impregnated on the coal to the extent of 1 percent.

Dry coal is fed from pressurized feeders to the hydrogenation reactor along with hot hydrogen from the reformer to bring the coal feed to the reaction temperature. Products from the reactor are cooled and separated; heavy oil is further hydrotreated to distillable oils and gas. Hydrotreated products from heavy oil hydrogenation are separated in a cyclone separator to remove ash and unreacted coal. Distillable oils are combined and cooled before removal of oil from the pressurized system. This two-step hydrogenation produces distillable products directly. Hydrogen, methane, and higher hydrocarbon gases are purified under pressure and are reformed with oxygen and steam to make hydrogen. The entire cycle including operation of the reformer is conducted without pressure letdown, and compression is necessary only to overcome system pressure drop.

The process was evaluated in small bench-scale studies in 1962, and a preliminary economic evaluation based on these data indicates that it may offer lower capital and operating costs than other processes now being considered.

8. Liquid-Phase Zinc Chloride Processes

The liquid-phase $ZnCl_2$ catalyst processes being studied by Continental Oil Company are designed to convert bituminous and subbituminous coal into distillates (in the gasoline range) by severe catalytic cracking under hydrogen pressure (Figure 24). The process may be applied either to coal in a one-step operation or to coal and coal extract in a two-step operation. The process configuration will be set by economic considerations related primarily to the extent of catalyst recovery.

Coal is dried and pulverized before introduction to a feed tank where it is slurried with a process-derived recycle oil. In the reactor the slurry feed is mixed with hydrogen and the $ZnCl_2$ catalyst at 360 to 400 °C and 100 to 240 atmospheres. The products are distillates in the

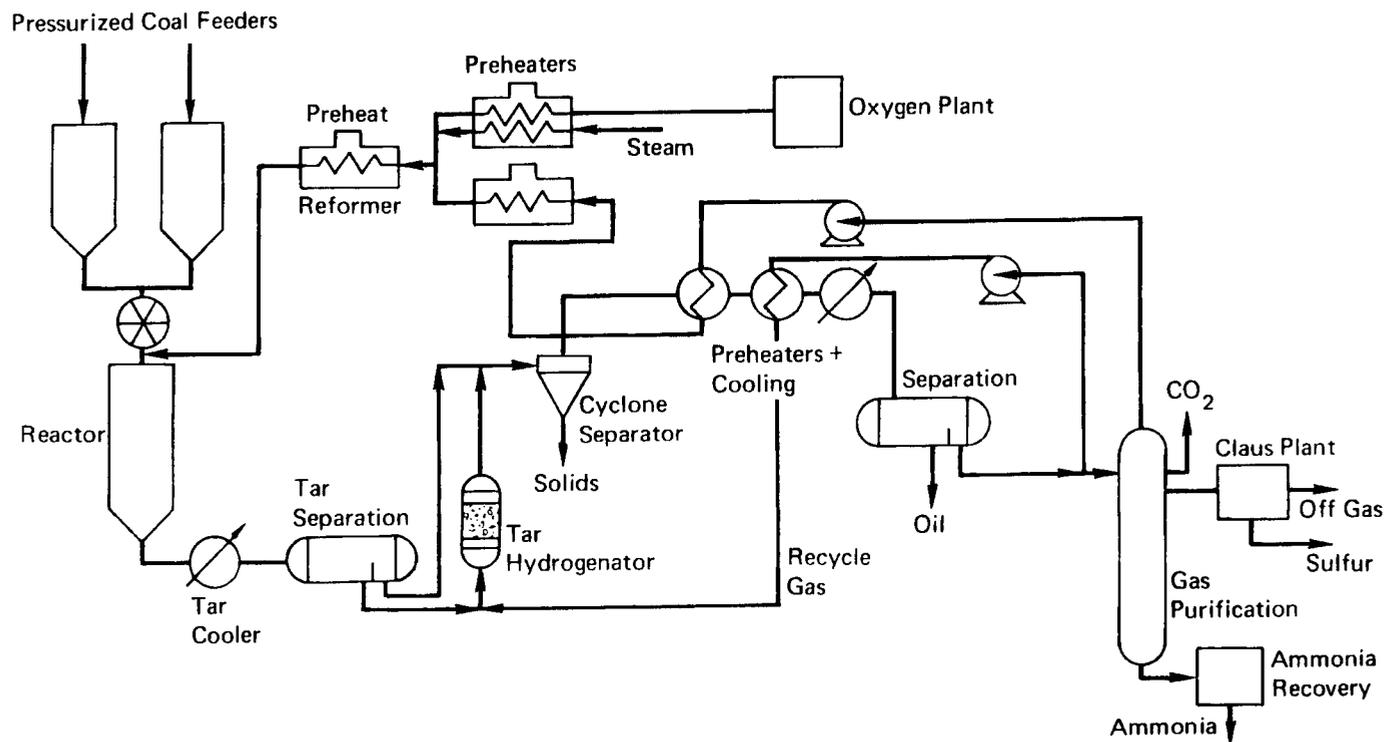


Figure 22 Flow scheme for solid phase hydrogenation of coal to syncrude by Schroeder process.

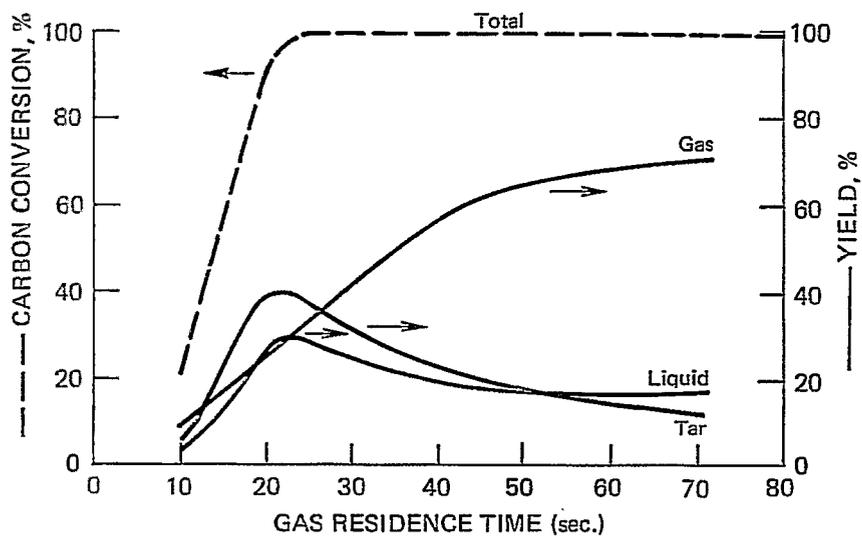


Figure 23 Reaction time is rapid as evidenced by the carbon conversion and product yield for hydrogenation at 137 atm abs and 500 °C.

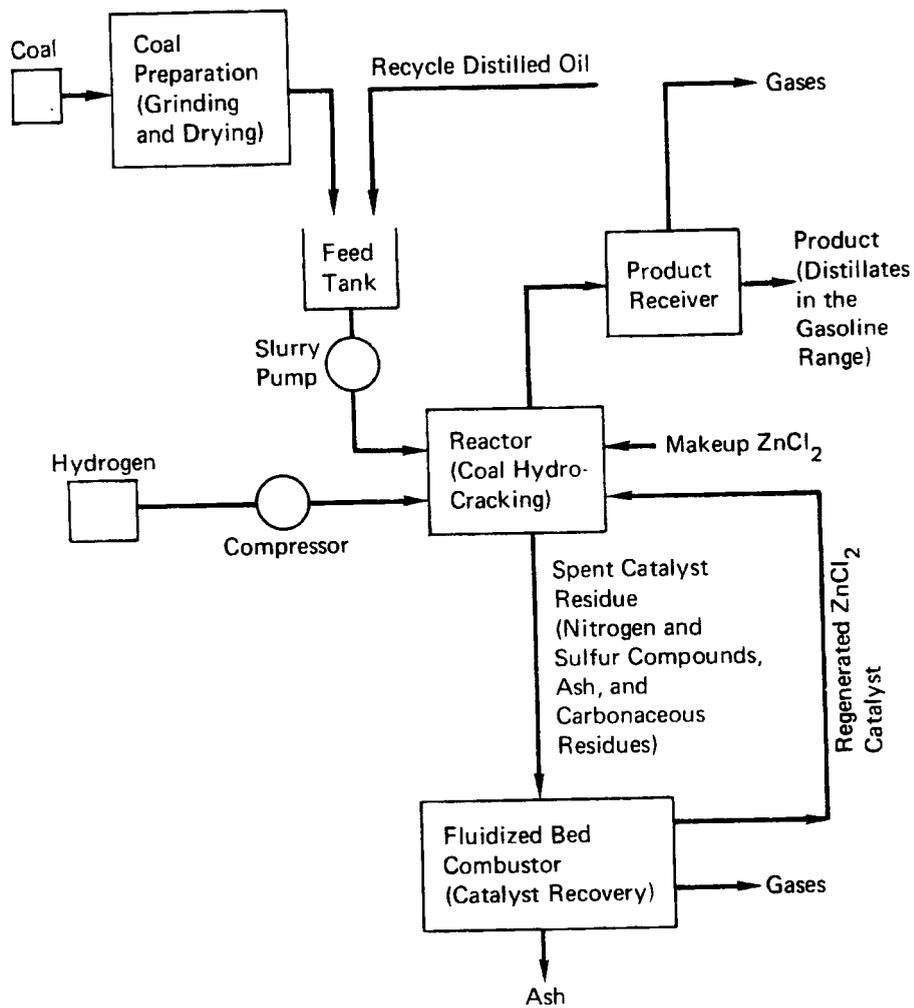


Figure 24 Flow diagram of liquid-phase zinc chloride process being studied by Conoco.

gasoline and light fuel oil range and go to a receiver, where gas is separated from the liquid and the solids are settled out. Typical results with Colstrip subbituminous coal indicate a 55 to 65 weight $C_4 +$ distillate yield (MAF) containing about 0.02 percent nitrogen and 0.02 percent sulfur. The gasoline fraction of this product is 75 to 80 percent of the total and has a research octane number of about 90.

Spent catalyst residue that contains nitrogen and sulfur compounds, ash, and carbonaceous residue is fed to a fluidized-bed combustor that operates at 980 °C and 1.1 atmospheres for recovery. The $ZnCl_2$ is separated from the residue as a vapor, is condensed, and is recycled back to the reactor section. Supplementary $ZnCl_2$ is added to the reactor as required.

The research and development program is being conducted by Continental Oil Company's subsidiary, Conoco Coal Development Division, at Library, Pennsylvania, utilizing a bench-scale continuous hydrocracking unit and a fluidized-bed combustion unit for regeneration of the zinc chloride catalyst in the first stage of the program. The second phase of the program will involve construction and operation of a 1.2-ton-per-day process-demonstration unit. Conoco, Shell Development Corporation, and ERDA are funding the work.

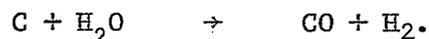
9. Other Processes

Many other concepts similar to those discussed here are undoubtedly under study in the private sector and at the preliminary small bench scale in universities and in the nation's energy laboratories. Much of this work is in support of the processes discussed or has not been reported quantitatively enough to allow evaluation.

E. INDIRECT LIQUEFACTION

Processes for indirect liquefaction of coal involve the selective catalytic production of hydrocarbons and oxygenated compounds from synthesis gas composed of CO and H_2 produced via coal gasification. Historically, the concept of catalytically combining CO and H_2 dates back to 1902 when Sabatier and Senderens⁵⁴ synthesized methane using a nickel catalyst.

Coal initially is gasified with steam and oxygen at temperatures above 800 °C and at moderate pressures to produce a synthesis gas composed primarily of hydrogen and carbon monoxide:



The gasification may be carried out in one of the several existing gasification processes or those being developed or it may be carried out in the future by underground processes. The synthesis gas then is shift-converted to adjust the hydrogen/carbon monoxide ratio to the

desired level utilizing the water gas shift reaction:

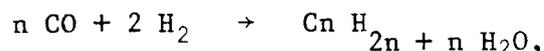


This step is followed by the removal of acid gases such as H_2S and CO_2 as well as other impurities. Then, depending on the selection of catalyst and operating conditions, the mixture can be converted into a wide variety of hydrocarbon liquids or methane.

In the conventional Fischer-Tropsch synthesis route, the reactions:



and



result primarily in low and medium boiling aliphatic compounds. Thermodynamic considerations drive both reactions to the right and release a large amount of heat. Reactor engineering for the process is largely concerned with removal of this heat. Operating conditions generally are set to emphasize the production of gasoline or light hydrocarbons.

Of current interest are the successful commercial applications that produce straight chain paraffinic, olefinic, and oxygenated hydrocarbons. These efforts have been directed primarily toward production of light and heavy hydrocarbons ranging from gasoline to heavy oils and waxes.

1. Fischer-Tropsch Process

In the Fischer-Tropsch process for coal liquefaction, a synthesis gas is initially produced via the steam and oxygen gasification of coal. Gasification can be accomplished in commercially available reactors (e.g., Lurgi, Winkler, Koppers-Totzek, or Wellman-Galusha types) or in any of the various coal gasification reactor configurations being developed for low-, medium-, and high-Btu gasification processes. It possibly can be accomplished in situ, assuming that a gas of consistent composition and purity can ultimately be produced.

The synthesis gas ($\text{CO} + \text{H}_2$) then is converted to liquid hydrocarbons, waxes, and smaller quantities (5 to 15 volume percent) of alcohols and ketones over an iron or a cobalt catalyst. The reaction may be carried out in fixed- or entrained-bed reactors. Total process thermal efficiencies including gasification have been in the range of 40 percent, which is considered a major disadvantage of the Fischer-Tropsch process. Table 14 gives a typical product slate.

Table 14 Typical Product Composition from Fischer-Tropsch Process at SASOL

	Composition, vol %	
	Fixed-bed Reactor ^a	Entrained-bed Reactor ^b
Liquefied petroleum gas (C ₃ - C ₄)	5.6	7.7
Petrol (C ₅ - C ₁₁)	33.4	72.3
Middle oils (diesel, furnace, etc.)	16.6	3.4
Waxy oil or gatsch	10.3	3.0
Medium wax, mp 90-99 °C	11.8	--
Hard wax, mp 90-99 °C	18.0	--
Alcohols and ketones	4.3	12.6
Organic acids	traces	1.0

^aOperating conditions of fixed-bed reactors: iron catalyst, 25.5 atm abs, 220-255 °C, H₂/CO ratio = 2.0.

^bOperating conditions of entrained-bed reactor: iron catalyst, 25.2 atm abs, 315-330 °C, H₂/CO ratio = 3.0.

The fixed-bed reactor system developed by Lurgi-Ruhrchemie requires many small tubes filled with catalyst to achieve the required heat removal. The reactors are essentially large multi-tube heat exchangers with a coolant on the outside. The product from the reactors consists primarily of aliphatic, high boiling hydrocarbons, medium boiling oils, diesel oil, and liquid petroleum gas. The system may use a pelletized, iron-base catalyst in vertical tube reactors operating at 25.5 atmospheres and 220 to 255 °C. The ratio of H₂ to CO is maintained at 2.0 with a recycle gas ratio of 2.4. The maximum production achieved* is 550 barrels per day per reactor of this type. This production rate is not of practical interest, and since such reactors cannot be easily scaled to much larger sizes, the fixed-bed synthesis is probably not of further engineering interest.

The entrained-bed catalytic reactor (Figure 4c) operates at 25.5 atmospheres and 315 to 330 °C. A cyclone separates the catalyst from the off-gas, which is recycled to the reactor. The gas is combined with a recycle gas stream so that the feed to the entrained-bed reactors enters at a 3:1 ratio of H₂ to CO. Products from this unit are mainly olefinic gasoline fractions, with the remainder divided between low boiling aliphatic hydrocarbons, aromatics, and oxygenated compounds. Production of about 2,000 barrels per day is achieved from the entrained-bed reactor currently being operated at SASOL. The unit can be scaled to larger sizes, making this reactor one of primary engineering interest.

The process was operated successfully in Germany during World War II and has been operated commercially by SASOL in South Africa since 1956.

*At SASOL, an operating plant 30 miles south of Johannesburg, South Africa.

Current production is 2.5 million tons per year of petrochemicals and 1.68 million tons per year of gasoline. A new facility is under construction and will increase capacity for gasoline and fuel oil to the point of supplying 40,000 barrels per day of gasoline and fuel oil. This represents about 30 percent of South Africa's automotive fuels market.

Immediately following World War II there was a period of interest in the Fischer-Tropsch process in the United States because of declining availability of crude oil and large discoveries of natural gas. The Bureau of Mines built a demonstration plant at Louisiana, Missouri, which produced 50 to 55 barrels per day of liquid product from coal using a Koppers-Totzek gasification process. The synthesis process used a fixed bed of alkali-promoted iron oxide catalyst with oil circulation for heat removal. Although operating problems were encountered, progress toward satisfactory solutions had been made when cost studies showed that synthetic fuels were not then competitive with petroleum, and operations were discontinued.⁵⁵

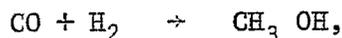
A commercial plant using a fixed fluidized-bed reactor producing 7,000 barrels per day of hydrocarbon liquids was developed by Hydrocarbon Research, Inc., and built at Brownsville, Texas, for a consortium of companies under the name of Carthage Hydrocol, Inc.⁵⁶ Synthesis gas produced by partial combustion of natural gas with oxygen and steam was introduced through distributors into a fluidized bed containing a catalyst prepared by impregnating mill scale with alkali (K_2CO_3) followed by reduction with hydrogen. The heat of reaction was removed by steam tubes placed vertically in the reactor. Operating conditions were 24 to 30 atmospheres and 300 to 330 °C, with a H_2 to CO ratio of 1.8:2.1. Products were intermediate between those listed in Table 14 and consisted of about 50 to 60 percent gasoline and about 10 percent oxygenated chemical.⁵⁷

When crude oil became more abundant and the cost of natural gas increased because of increased demand, the process became uneconomic and the plant was shut down. Recently, however, there has been a renewed interest in the United States in the Fischer-Tropsch process in connection with current schemes for coal liquefaction. The process economics were dictated to a large extent by the gasification system; therefore, improvements in synthesis gas production or development of viable underground gasification schemes and improved efficiency of subsequent conversion steps could substantially improve the overall process economics and the overall thermal efficiency of the process.

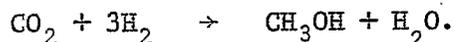
Improvements of this nature are currently under investigation. For example, in a Fischer-Tropsch conceptual design developed by Parsons⁵⁸ for ERDA, the use of a medium-pressure entrained slagging gasifier is proposed. Also under ERDA sponsorship, Exxon Research and Engineering Company has undertaken development of improved Fischer-Tropsch catalysts.⁵⁹ The specific objective of the program is to investigate the effects of sulfur on Fischer-Tropsch catalysts and to establish the existence of any sulfur promotional effects leading to increased liquid yields in the synthesis reaction.

2. Methanol Synthesis

Methanol synthesis occurs according to either of the following reactions:



or



Conversion is thermodynamically favored by relatively low temperatures and high pressures and early commercial processes have operated at 300 to 375 °C and 270 to 350 atmospheres; however, with improved catalysts, it has been possible to operate at pressures as low as 35 to 100 atmospheres.

While numerous metals and their oxides as well as salts have been claimed as catalysts for this reaction, those that appear to be most satisfactory are based on mixed oxides of zinc and chromium⁵⁷ or on copper stabilized by oxides of aluminum and zinc. The methods of preparing the improved catalysts are proprietary.

Methanol has been produced from coal in several commercial-scale plants mainly abroad.⁶⁰ Synthesis gas is produced from various steam-carbon-oxygen gasification processes, purified, and then converted to crude methanol. Even though the process is highly selective, the crude methanol must be purified by distillation or other techniques to remove dimethyl ether, methyl formate, water, and higher alcohols. The commercial catalysts employed, particularly those based on copper, are very vulnerable to sulfur poisoning; therefore, an efficient synthesis gas purification step is essential. The exothermic heat of reaction liberated during methanol conversion is controlled by recycling cooled conversion gases.

More efficient coal gasification processes producing high-purity synthesis gas could reduce the cost of producing methanol substantially. Improved synthesis catalysts, which are more tolerant to sulfur concentrations in the synthesis gas, also would have a favorable impact on the overall economics.

Methanol synthesis technology is readily available and may be considered off-the-shelf technology. However, work has recently been carried out on a liquid-phase process that simplifies the problem of heat removal and reduces the size of the equipment required.⁶¹

3. Methanol to Gasoline

Mobil Oil Corporation is working on a process for the conversion of methanol to aromatic gasoline.^{62,63} The chemistry involves dehydration

of methanol over a zeolite catalyst to form hydrocarbons that are highly aromatic in character. Operating temperatures are from 280 to 450 °C and pressures from 0 to several atmospheres. Because the reaction is highly exothermic, reactor design must be somewhat similar to that of Fischer-Tropsch reactors.

A more recent patent⁶⁴ claims the conversion of synthesis gas (CO + H₂) to gasoline in one step by use of a mixture of methanol synthesis catalyst and a zeolite dehydration catalyst. Operating temperature is probably similar to that above (280 to 450 °C), but operating pressures could be expected to be higher (e.g., 50 atmospheres). These processes are being evaluated at the process-development-unit scale by Mobil with ERDA support.

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