

The results above indicated a need for moderation of the reaction rate, either by use of a less reactive coal or by reduction in catalyst concentration. Autoclave and bench-scale experiments at 500° C. showed that adequate conversion could be achieved with as little as 0.01 percent molybdenum, with considerable decrease in rate of heat release. Consequently, pilot-plant studies were conducted with this catalyst concentration. Temperature control was found comparatively good at 480°, 500°, and 525° C. (896°, 932°, and 977° F.), and no "runaway" temperatures were experienced. "Coking," however, was quite serious at the high temperatures. Use of 0.1 percent molybdenum did not eliminate the tendency toward "coking."

With 0.01 percent molybdenum, conversion to liquid and gases was 93 percent at 480° C. and about 88 percent for the two higher temperatures. The gasoline yield, based on feed, was 3 to 3.5 percent. Boiling ranges of the overhead and the heavy oils produced were approximately the same for the three temperature levels. The asphaltene content of the total product oil was 13 percent at 480° C., 17 percent at 500° C., and 7.2 percent at 525° C. The viscosity of the heavy oil varied from 65 to 82 Saybolt seconds Universal at 180° F. for the three converter temperatures. Hydrocarbon-gas production, based on feed, increased from 14 percent at 480° C. to 23.4 percent at 500° C. and 28.7 percent at 525° C.

Hydrogenation of Topped Low-Temperature Tar

The Bureau of Mines has studied hydrogenation of a topped low-temperature tar from a Pittsburgh-seam coal, in cooperation with the Pittsburgh Consolidation Coal Company. The objective was to determine the feasibility of hydrogenation for converting the material to lower-molecular-weight products containing an appreciable quantity of phenols. Experiments were conducted in high-pressure bench-scale equipment at 3,000 to 7,500 p.s.i. and 450° to 500° C. (842° to 932° F.), without added catalyst. About 92 percent of the topped-tar feed stock boiled above 325° C.; it contained 16 percent benzene-insolubles, 82 percent asphaltenes, and relatively large quantities of nitrogen and sulfur.

At 7,500 p.s.i. and at 4,500 p.s.i., the general effect of higher temperature or increased residence time was to decrease asphaltenes and benzene-insolubles while increasing gasification and cracking. At 7,500 p.s.i., 500° C., and 1 hour residence time, 81 percent of the feed was recovered in the liquid product. This product contained less than 1 percent benzene-insolubles, 12 percent asphaltenes, and 46 weight-percent of oil boiling under 325° C. About 20 percent of the product oil was in the 125° to 230° C. range, with a phenolic content of 3 percent. The amount of alkali-soluble material in this fraction increased with cracking severity.

Product distribution was essentially the same at 4,500 p.s.i. without catalyst as at 7,500 p.s.i., provided residence time was sufficiently increased. However, operation at 3,000 p.s.i. without catalyst was not possible due to severe "coking." Several exploratory runs indicated the feasibility of operating at this pressure provided active catalysts such as molybdenum and tungsten were employed.

Catalyst Development for Vapor-Phase Hydrogenation

Commercial coal hydrogenation for gasoline production was conducted in two basic steps. In the first or liquid-phase step, coal was converted to raw gasoline plus middle oil (325° C. end point). In the second or vapor-phase step, this primary product was hydrogenated to finished gasoline over a fixed-bed catalyst. The vapor-phase step was usually subdivided into a presaturation stage and a splitting-and-hydrogenation stage. Presaturation was conducted on a once-through basis at 3,000 to 4,000 p.s.i. and 400° to 410° C. (752° to 770° F.), using tungsten sulfide catalyst, to remove nitrogen and other compounds that poison the splitting-hydrogenation catalysts. The latter operation was carried out at 3,000 to 4,000 p.s.i. and 450° C. (842° F.) on a recycle basis, using a catalyst consisting of 10 percent tungsten sulfide on activated earth.

Toward the end of World War II, Ruhröl (58) in Germany developed catalyst K-536 for the production of aviation-grade gasoline in a single vapor-phase step at 10,000 p.s.i. and 500° C. (932° F.). This catalyst, which was used by the Bureau of Mines in the Louisiana, Mo., Demonstration Plant, contained 0.6 percent molybdenum, 2 percent chromium, 5 percent zinc, and 5 percent sulfur, supported on Terrana (a Bavarian fuller's earth) activated with hydrofluoric acid.

The Bruceton laboratories investigated the feasibility of reproducing K-536 catalyst and its general utility as a single-step catalyst. Base runs were conducted using German-made K-536 at 9,000 p.s.i. and 475° to 500° C. (887° to 932° F.) in the continuous bench-scale unit shown in figure 45. With

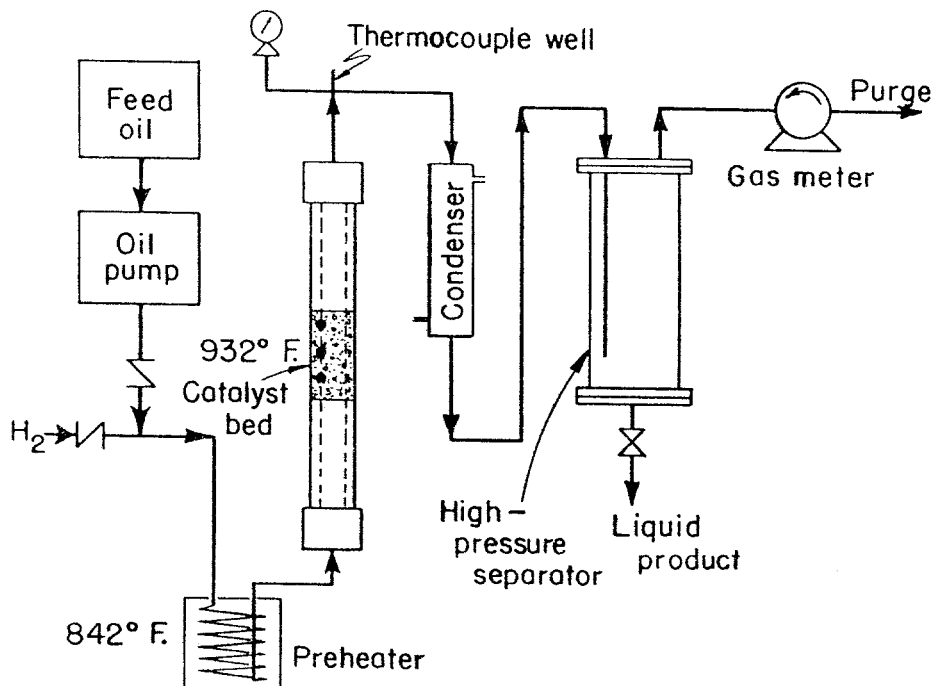


FIGURE 45. - Flowsheet of Bench-Scale Reactor for Vapor-Phase Hydrogenation of Oil Obtained by Coal Hydrogenation.

100 ml. of catalyst, the feed rates were adjusted to provide for space velocities of 0.3 to 1.3 grams of oil per ml. of catalyst per hour. The feed material was a coal-hydrogenation light oil, which contained 0.41 percent nitrogen, 1.32 percent oxygen, and 0.16 percent sulfur, and had an end point of 330° C. with 20 percent distilling below 200° C. In once-through operation at 500° C. and a space velocity of 1.0, 46 percent of the feed was converted to finished gasoline and 4 percent to C₁ to C₃ hydrocarbons. Hydrogen absorption, based on feed, amounted to 3 percent. The gasoline contained 45 to 50 percent aromatics, with only 0.09 percent nitrogen and 0.02 percent sulfur, and had a motor octane rating of 79.8. The effects of space-velocity and temperature variations are shown in figure 46.

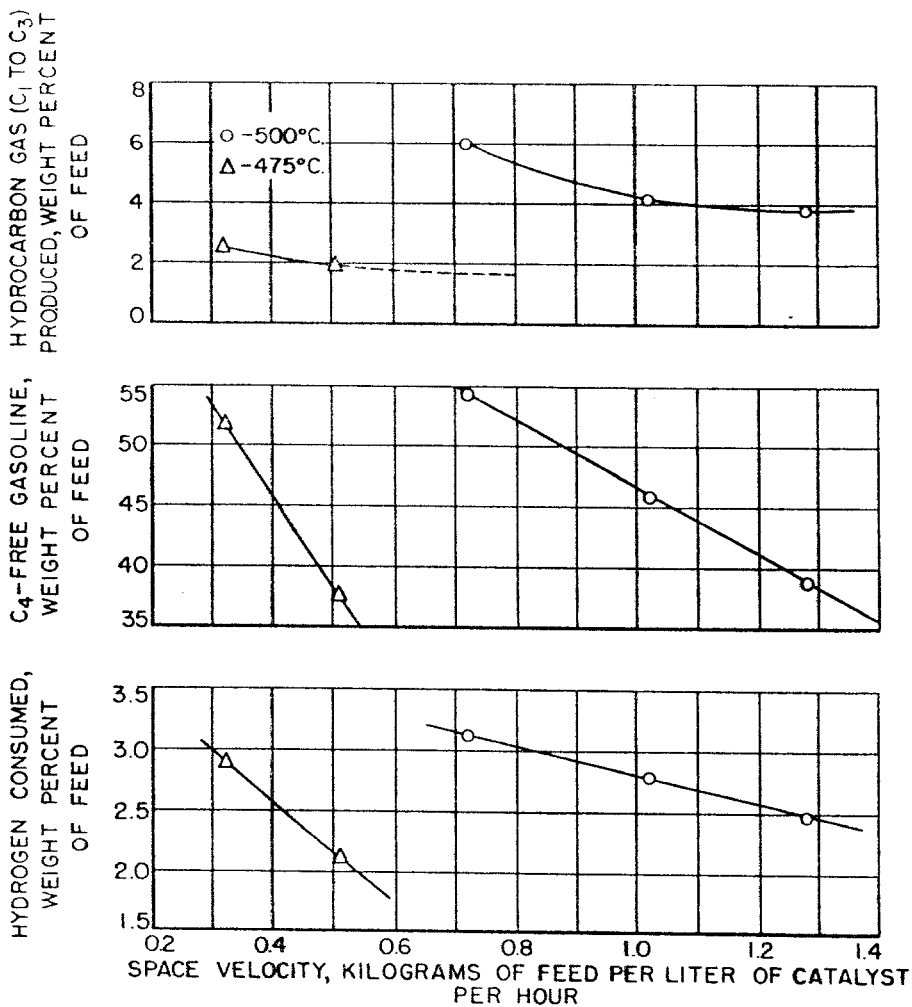


FIGURE 46. - Effects of Temperature and Rate of Oil Flow on Yields of Products and Consumption of Hydrogen in Vapor-Phase Hydrogenation.

Later runs used a Bruceton-made catalyst under identical operating conditions. The catalyst was prepared by impregnating Filtrol-SR (bentonite clay), after hydrofluoric acid treatment, with the required amounts of molybdenum, zinc, and chromium, and then sulfur. The activity (49) of this catalyst was

found equal to that of the German-made K-536. At the end of a 5-week test, activity was maintained and crushing strength had tripled, with no carbon deposition in evidence.

The final phase of this study was directed toward determining the role of each constituent of the K-536-type catalyst. Filtrol-SR, activated alumina, and silica-alumina without added components showed mild cracking ability but no activity with respect to elimination of oxygen, sulfur, or nitrogen. Use of Filtrol-SR resulted in more gasoline production. Tests with molybdenum, zinc, chromium, or sulfur on acid-treated Filtrol-SR indicated that the activity of K-536 was due largely to the presence of molybdenum; the other constituents improved the selectivity of the catalyst.

Hydrogenation of Shale Oil

The feasibility of producing jet and diesel fuels from shale oil by continuous recycle coking and catalytic hydrogenation has been investigated. Continuous recycle coking was explored by the Shale Oil Demonstration group at Rifle, Colo., and hydrogenation of the coker distillate was carried out at the Bruceton laboratories. The objective was to produce oils boiling in the jet- and diesel-fuel range with nitrogen and sulfur eliminated sufficiently to make the oils suitable for such uses. The coker distillate was hydrogenated over a cobalt molybdate catalyst on alumina, as diagramed in figure 47. Preheated hydrogen and feed passed downward through the catalyst bed and the reaction products were led to a conventional high-pressure recovery and scrubbing system.

Two 300-hour tests, at 450° C. (842° F.) and 1,500 p.s.i., used liquid space velocities of 1.1 and 0.9 volume of feed per volume of catalyst per hour at constant gas flow. The liquid product amounted to 96-98 volume-percent (90 weight-percent) of the feed. About 10 percent of the feed was converted to hydrocarbon gases containing 40 volume-percent methane, 21 percent ethane, 18 percent propane, 12 percent butanes, and 6 percent butylenes. Small quantities of propylene, carbon monoxide, and carbon dioxide were also produced. Fractionation of the product oil yielded 60 percent (by volume) jet fuel and 40 percent diesel fuel, both meeting military specifications. The nitrogen content of the jet fuel averaged below 0.02 percent. After each 300-hour test the catalyst contained 5 to 6 percent carbon, indicating the necessity of periodic regeneration. The operation was trouble-free, and no difficulty was experienced with control of the exothermic reaction.

Hydrogenation of raw shale oil was investigated on an exploratory basis to obtain data on general product distribution and process variables. Operations were conducted at 9,000 p.s.i. in bench-scale equipment similar to that shown in figure 45. Cobalt molybdate on alumina, tungsten sulfide, molybdena on Terrana (K-536), and tungsten-nickel sulfide catalysts were used at temperatures from 425° C. to 480° C. (797° to 896° F.), with liquid space velocities of 0.5 to 1.5 volumes of feed per volume of catalyst per hour. Results obtained at 1.0 space velocity are shown in figure 48. With any of the catalysts under test, about 45 weight-percent of the feed could be converted to a low-nitrogen-content diesel fuel.

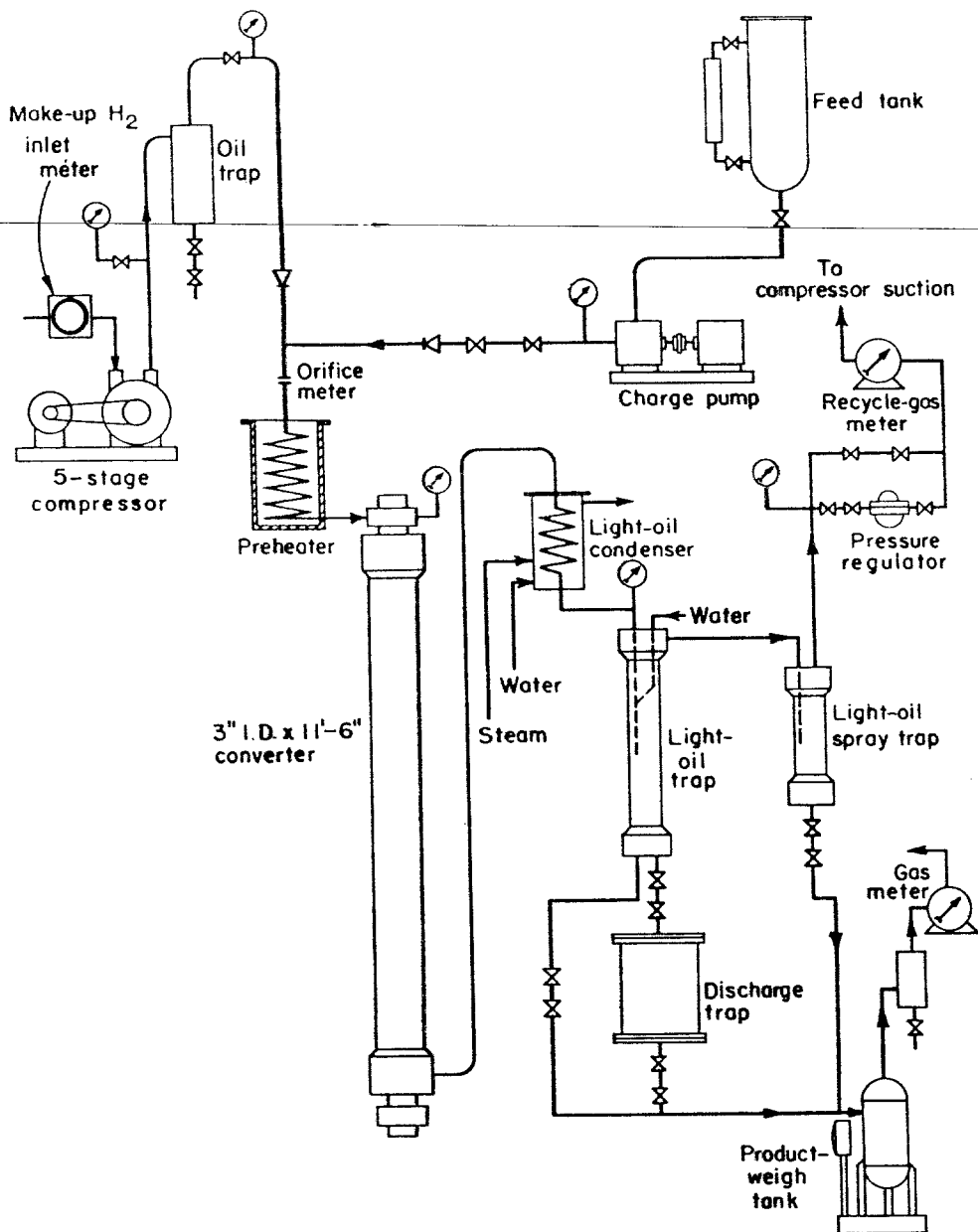


FIGURE 47. - Shale-Oil-Hydrogenation Pilot Plant.

Hydrocarbonization

Hydrocarbonization, the carbonization of coal in hydrogen at moderate pressures, represents the simplest system for converting coal to oil and hydrocarbon gases. Initial experiments were carried out with 100- to 200-mesh Rock Springs coal in a small static system. A slow heating technique gave final temperatures of 500° to 600° C. (932° to 1,112° F.) at 500 p.s.i.g. Without catalyst, 20 to 22 percent of the m.a.f. coal was converted to oil, 50 percent to char, 18 percent to hydrocarbon gases, and the balance to water and carbon dioxide. The char was about 50 percent lower in sulfur content than the original coal and was free flowing. The approximate analysis of the hydrocarbon gas (weight-percent) was 58 percent methane, 26 percent ethane, 11 percent

propane, and 5 percent butane. The oil produced was high in asphaltenes (75 percent) with a moderate amount of material boiling under 325° C. (617° F.). Use of 1 percent tin (chloride) catalyst considerably decreased the asphaltene concentration but produced an agglomerated char.

A pilot plant was erected to carry out the process on a continuous basis at 600° C. (1,112° F.) and 500 p.s.i.g. (fig. 49). The original unit consisted of a 7-foot reactor bed with an inside diameter of 3 inches. Experiments were conducted with 100- to 300-mesh Rock Springs coal at gas velocities

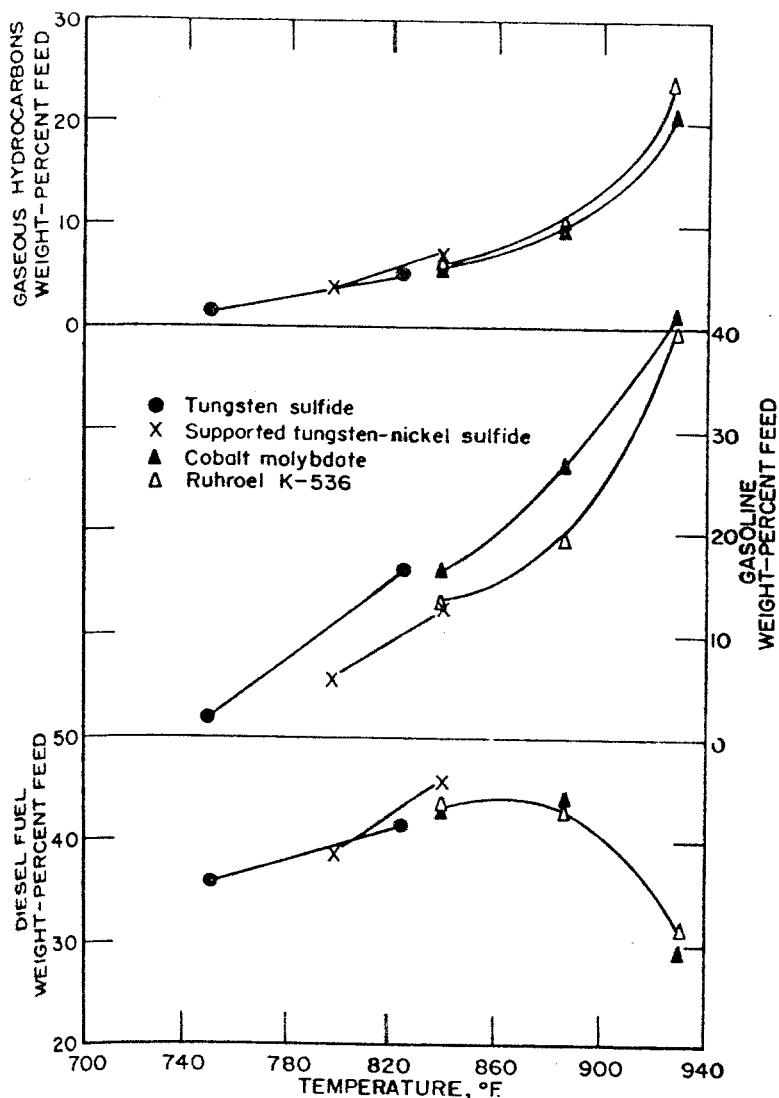


FIGURE 48. - Effects of Temperature and Catalysts on Yields From Hydrogenation of Crude Shale Oil.

ranging from 0.06 to 0.3 f.p.s. The runs were all terminated by agglomeration throughout the bed. Additional studies in a small 1-inch-inside-diameter reactor attempted to avoid or minimize agglomeration by use of high gas velocities. However, agglomeration was not eliminated by an increase of gas velocities from 0.3 to 3.0 f.p.s. Larger coal particles (10- to 20-mesh), dilution of feed with coke, thermal pretreatment of feed, or use of sodium carbonate, did not materially alleviate this problem.

Since a free-flowing char was produced in the initial bench-scale experiments, but not in a continuous unit, agglomeration apparently was associated with rate of heating. During rapid heating sudden flooding of the surfaces of coal and char particles by unstable oils presumably caused particles to agglomerate and to carbonize into a dense mass. With slow heating, the quantity of oils carbonized at any one time was probably insufficient to cause extensive cementation.

For studying the effect of temperature, particle size, and gas velocity on agglomeration of Rock Springs

coal, a bench-scale unit was designed to simulate the heating rate of a continuous unit. A 2-inch-inside-diameter reactor 3 feet long was provided with a pressurized coal hopper to permit instantaneous coal injection. Preheated hydrogen was fed continuously into the bottom of the coal bed at a velocity of 0.06 feet per second. Agglomeration was definitely associated with rate of heating. With slow heating it was possible to hydrocarbonize coal at temperatures as high as 700° C. (1,292° F.) without agglomeration. With rapid heating, mild agglomeration began at 500° C. (932° F.), and severe agglomeration occurred at 600° C. (1,112° F.).

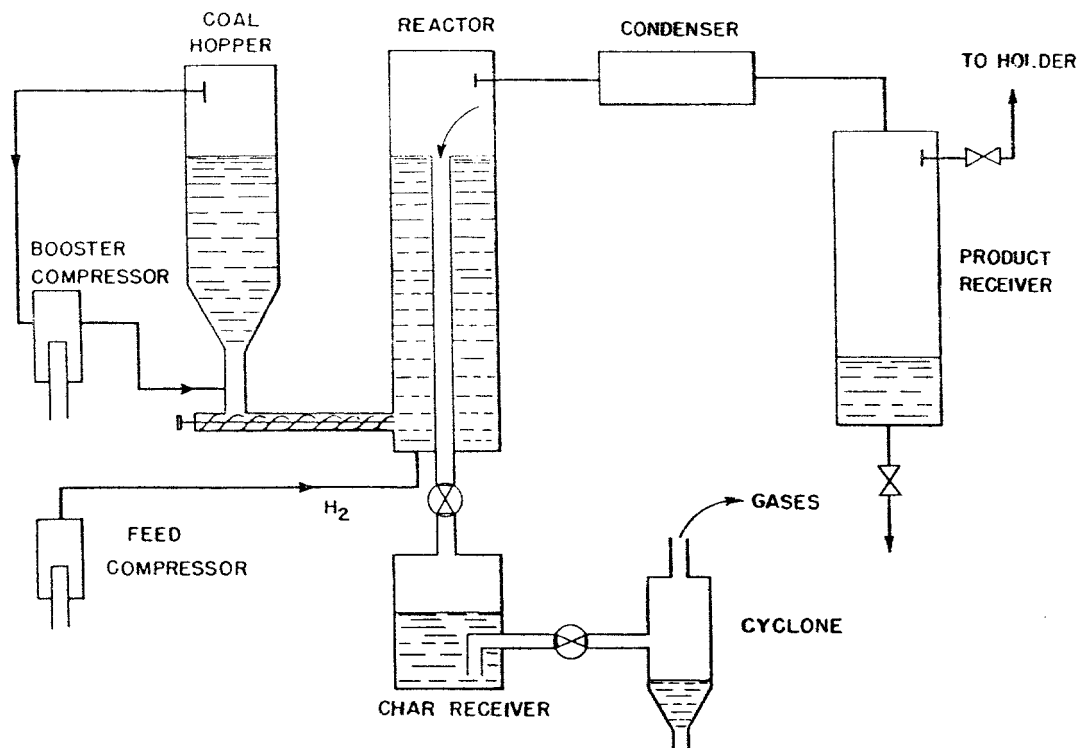


FIGURE 49. - Flowsheet of Pilot Plant for Hydrocarbonization of Coal.

Agglomeration tendencies increased with increasing particle size. The nonagglomerated char produced at 450° C. could be hydrocarbonized at 500° C., with maintenance of free-flowing char product. This char was reprocessed at 600° C., and again at 700° C., without agglomeration. This technique suggested that coal could be hydrocarbonized continuously, if a stepwise heating technique could be employed. Further tests indicated that some of the steps could be eliminated. Pertinent yield data from these experiments follow.

Temperature, °C.	Yields, as weight-percent of m.a.f. feed		
	Organic benzene- insolubles	Benzene- soluble oil	Hydrocarbon gas
400	85	3	0.1
450	73	11	1
500	62	15	6
600	46	20	15
700	33	20	22

In an ASTM-type distillation of the benzene-soluble oil, approximately 5 percent distilled at 90° C., 30 percent at 200° C., and 80 percent at 325° C. Above 325° C. thermal cracking occurred.

Hydrocarbonization of a Texas lignite was feasible at temperatures from 400° to 600° C. (752° to 1,112° F.) without agglomeration regardless of particle size (4- to 300-mesh) and rate of heating.

Solids Removal

The efficient removal of spent catalysts, ash, organic insolubles, and asphaltenes from coal-hydrogenation systems has been difficult. In the primary reaction, the products are mainly heavy oils, with smaller portions of hydrocarbon gases and distillable oils. Further hydrogenation is required for a maximum yield of distillates suitable for processing into gasoline. This has been accomplished by recycling the heavy fractions as a coal carrier. This technique has been successful, provided insolubles and asphaltenes were removed from the recycle stream as rapidly as produced.

Commercially, removal of solids has been accomplished by centrifuging the total recycle stream. This removed the solids in an oil sludge containing as much as 50 percent oil; only about 60 to 70 percent of this oil could be recovered by carbonization. The oil loss was equivalent to 5 to 10 percent of the moisture- and ash-free coal.

Steam stripping at high temperature has been investigated as possibly a more efficient method. Superheated steam was fed into a simple mixing chamber along with a representative feed, and the mixture discharged into a heated separator which served as a disengaging and carbonization section. It was possible to obtain relatively high recoveries of hexane-soluble oil, essentially free of solids. With a stripping temperature of 600° C. (1,112° F.) and a separator temperature of 400° C. (752° F.), 91 percent of the original hexane-soluble oil was recovered; but the total product oil contained about 7 percent asphaltenes, a value close to the original (19 percent). With the same 600° C. stripping temperature, lowering the separator temperature to 80° C. (360° F.) resulted in a total product containing only 7 percent asphaltenes; but the recovery of n-hexane-soluble oil fell to 78 percent. The presence of asphaltenes in the overhead product may be from entrainment. Since this design is capable of almost perfect separation of solids, further development work would be desirable.

Demonstration Plant, Louisiana, Mo.

The coal-hydrogenation demonstration plant (figs. 50 and 51) was built and operated to furnish engineering information for use in the design of commercial-size plants, to foster development of techniques required for fabrication of high-pressure equipment, to test materials of construction, to train engineers and operators, to develop operating procedures, to improve the process against the day when coal hydrogenation may become essential, and to supply data for answer to question, "What is the cost of synthetic motor fuel by the hydrogenation process?"