masked by such limitations. The use of pyrolytic conditions for coal processing is a commonly employed solution in current practice.

Even if transport limitations are removed, the processes for rupture of aromatic platelets to form liquid hydrocarbons require much study. These can be approached through study of asphaltenes and individual hydrocarbons for identification of optimum routes for reaction that can subsequently be applied to coal. Overall, such processes will require the incorporation of large amounts of hydrogen into the coal, but the chemical form in which it is used may not need to be H_2. Hydrogen requirements can be approximated by noting

	H/C Ratio
Bituminous coal	~0.8 to 0.9
Crude oil	~1.4 to 1.6
Gasoline (30% aromatic)	~1.6 to 1.7.

Since coal contains perhaps 7 to 15 percent oxygen and also substantial nitrogen and sulfur, these element concentrations must be reduced substantially. About 1/2 of the sulfur is organic in the form of thiophenes, sulfides, disulfides, and mercaptans. For the nitrogen-containing structures, pyridines, quinolines, amines, and nonbasic structures such as pyrroles and carbazoles have been identified.

Thus, if a new basis for coal processing by catalysis is to be developed, it must be done under conditions where the coal structure is readily available to the catalyst, and consideration must be given to use of reactions that can result in the incorporation of considerable amounts of hydrogen without the need to resort to the prior expense of H_2 generation.

Bergius Catalytic Hydrogenation

As shown in Figure 7, coal was dried in an inert atmosphere, mixed with a plus 325 C process-derived pasting oil and catalyst, then ground to a 40 percent minus 250 mesh, 100 percent minus 100 mesh particle size in a ball mill operated at 225 F.(31) The catalyst for sump phase hydrogenation of German coals was usually 1.5 to 5.0 percent "Bayermasse" or "Roteey" (red mud, an impure iron oxide from purification of aluminum ores), 1.3 percent FeS, and 0.3 percent Na_2S based on dry coal. The final paste, containing 41 percent coal, was fed to the paste presses, which were double-acting, hydraulically driven piston pumps, at a rate of 37 tons per hour to be raised to 10,300 psig for bituminous coals or to a somewhat lower pressure for the brown coals. Downstream from the presses, recycle gas (1,060,000 scfh) was added and the entire mixture heated to 810 F in a three-stage preheater.

The sump phase hydrogenation was carried out in four reactors 3.3 ft in diameter and 59 ft tall. Agitation by the entering feed and reaction products increased the turbulence causing the lighter products to rise and the heavier products to fall. The material gas and liquid passed from one reactor to another in series before entering a gas separator. The highly exothermic reaction was controlled by adding cold hydrogen plus recycle gas (706,000 scfm) to the reactors through a pipe leading from the reactor head to four points in the sump. Hydrogen partial pressure was generally 80 percent.

In the gas separator, approximately 80 percent of the oil boiling at up to 350 C was stripped from the liquid. Gas from the separator was passed countercurrent to the

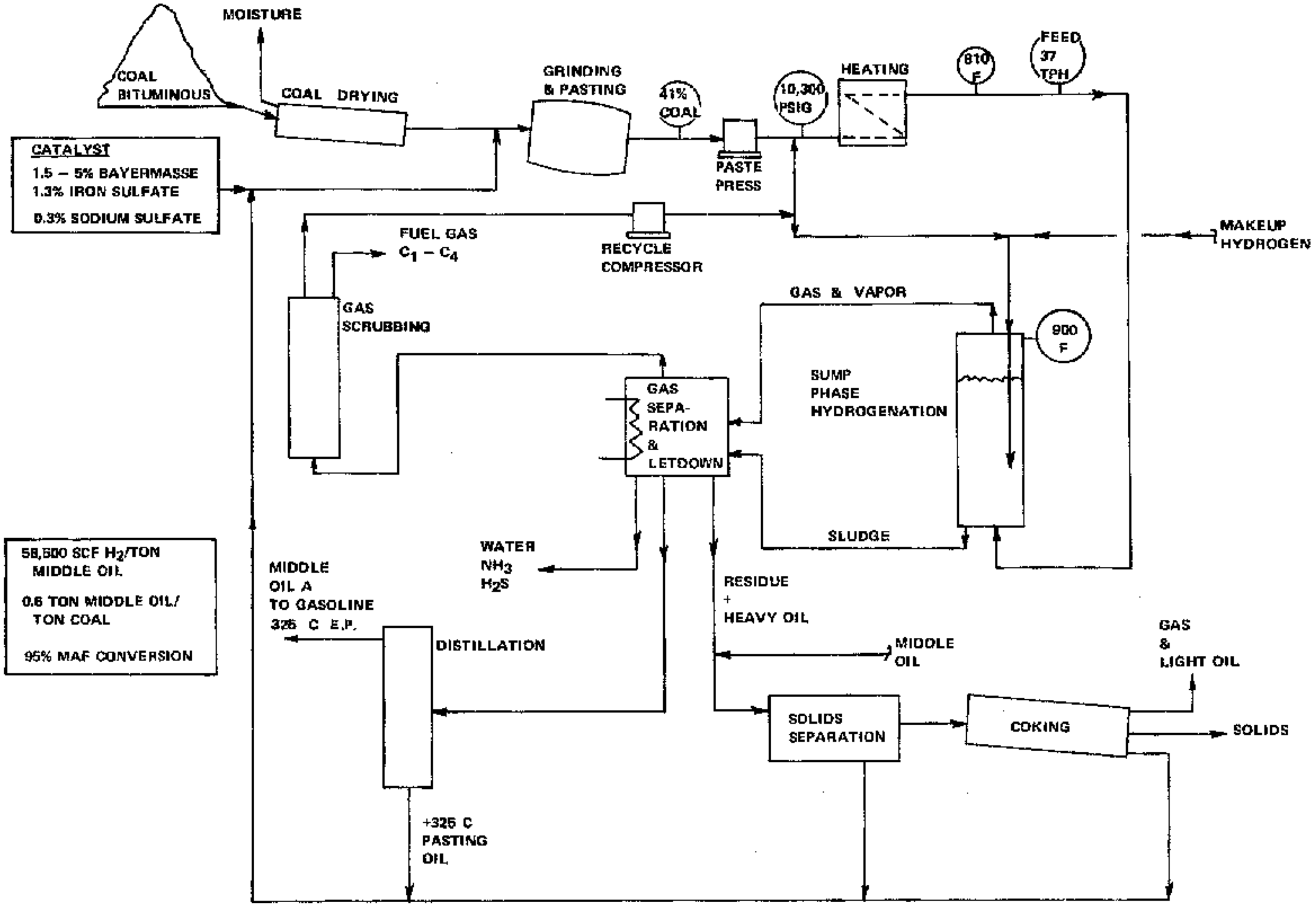


FIGURE 7. BERGIUS CATALYTIC HYDROGENATION GERMAN COMMERCIAL PRACTICE

liquid flow in the first two stages of the preheater. After each stage the condensate was recovered. The gas was then routed to a gas scrubbing section to raise the H_2 content from ~60 percent to 75 percent by removal and recovery of the C_1 through C_4 gases and light hydrocarbons. The lean gas was recompressed (~1100 psi Δp) to be returned to the process.

The condensed oils and water were separated with most of the H_2S and NH_3 going with the water. The oils were distilled into principal fractions, a middle oil A with a 325 C end point (617 F) and a plus 325 C heavy oil which was recycled as pasting oil. Middle oil A, the more prevalent product, was sent to further processing in a two-step catalytic gas-phase hydrogenation employing a pelleted WS_2 catalyst (No. 5058) and a WS_2 activated clay catalyst (No. 6434). A list of the principal catalysts used by the Germans for tar and oil hydrogenation is given in Table 7.(17) The product was an aviation grade gasoline with an unleaded octane number of 70-75, plus diesel oil.

The residue oil from the gas separator containing 20-22 percent solids was cooled, let down to atmospheric pressure, and diluted with 25 percent thinning oil. This material was centrifuged and the liquid phase filtered. The filtrate was returned to the pasting oil circuit. Filter cake and centrifuge solids were coked at 1200 F to recover additional pasting oil.

Bituminous coal is more difficult to hydrogenate than brown coal or coal tars. It leaves a greater amount of nonhydrogenatable residues and yields a greater proportion of asphalt materials. Adequate destruction of primary asphalts and prevention of formation of secondary asphalts is of great importance. In Germany, two approaches were taken to the problem of destruction of asphalts; one was to use a more active catalyst; the other was to operate at higher pressures.

When the liquid phase was operated at 300 atm, the suitable catalyst was SnC_2O_4. For maximum catalyst activity, acid conditions were desirable, and NH_4Cl was injected. This in turn led to corrosion difficulties. At 300 atm, however, this was serious only when temperatures were below 600 F. Accordingly, an oil suspension of $NaCO_3$ was injected into the upper portion of the last converter to neutralize the products before the temperature was reduced.

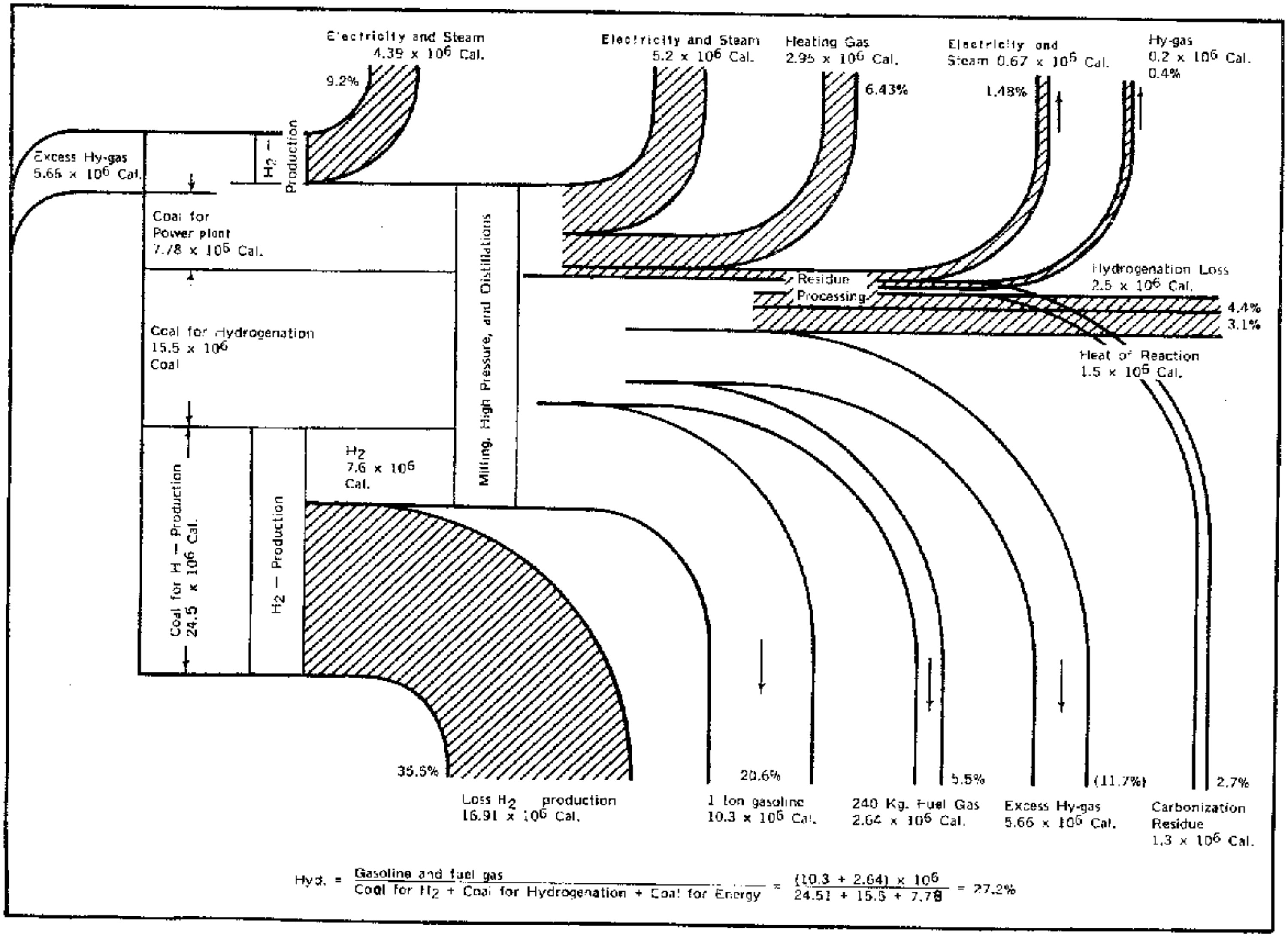
The best catalysts for vapor-phase hydrogenation of middle oil were subject to repression or deterioration by nitrogen and/or oxygen derivatives normally present in the middle oil from liquid-phase hydrogenation of bituminous coal. Customarily, then, these middle oils were partially refined by "presaturation", which was a mild once-through vapor-phase hydrogenation over WS_2 catalyst, designed to eliminate nitrogen and oxygen derivatives. The catalyst was 10 percent WS_2 supported on an activated diatomaceous earth (Terrana). When there was not sufficient sulfur in the feed to maintain the catalyst as sulfide, H_2S was dissolved in the oil feed.

The alternative to the use of active catalysts was higher operating pressures and the slightly higher temperatures this permitted. Operation at 700 atm was adopted at all the later plants in Germany.

It is not generally realized that the conversion of coal into liquid fuels was and still is an inefficient process.(32) As shown in Figure 8, only about 30 percent of the total heating values of the coal consumed was recovered in useful form by the catalytic Bergius process. A very high energy price is paid for conversion of coal into a fuel of more convenience or higher purity. The greatest loss was due to hydrogen

TABLE 7. LIST OF PRINCIPAL CATALYSTS(17)

Catalyst Number	Used in	Composition
3510	Saturation, refining, and aromatization	53.5% MoO_3 30 % ZnO 16.5% MgO
5058	Saturation, refining, splitting hydrogenation	100 % WS_2
5615	See 6718	
6434	Splitting hydrogenation, possibly also saturation, aromatization	10 % WS_2 90 % Terrana (fullers' earth)
6525	Phenol reduction, saturation, aromatization	90 % FeS 10 % WS_2
6718	Dehydrogenation, hydrogenation, refining	85 % WS_2 15 % NiS (also called 5615)
6719	Saturation	75 % FeS 22 % WS_2 3 % NiS
7019	Aromatization	15 % Cr_2O_3 5 % V_2O_5 80 % activated coal
7360	Dehydrogenation under hydrogen, pressure, refining	10-12 % MoO_3 90 % Al_2O_3
7846	Saturation, refining	10 % MoO_3 3 % Ni_2O_3 87 % Al_2O_3
7846-W-250	See 8376	
7935	Dehydrogenation under hydrogen	15 % MoO_3 85 % Al_2O_3
8376	Saturation, refining (also called 7846-W-250)	27 % WS_2 3 % NiS 70 % Al_2O_3



$$\text{Hyd.} = \frac{\text{Gasoline and fuel gas}}{\text{Coal for } H_2 + \text{Coal for Hydrogenation} + \text{Coal for Energy}} = \frac{(10.3 + 2.64) \times 10^6}{24.51 + 15.5 + 7.78} = 27.2\%$$

FIGURE 8. EFFICIENCY OF HYDROGENATION INCLUDING HYDROGEN PRODUCTION(32)

manufacture, which was only about 27 percent efficient. It was responsible for a 45 percent loss in heat for the whole process. A 49 percent efficiency was estimated for the balance of the process. It is for this reason that solvent refining to a solid product has continued to attract interest, since it should require less hydrogen than catalytic hydrogenation to a liquid product. It should be noted that the most advanced German technology required 6.7 tons of coal to make one ton of aviation gasoline.

Major improvements in efficiency can be expected.(33) A method was suggested to improve the thermal efficiency for H_2 production by gasifying coal directly in a Koppers powdered-fuel plant and treating the gaseous product, together with cracked hydrogenation gas, in a water-gas-shift reaction plant. The H_2 in the hydrogenation gas would be recovered in a Linde plant, and the remaining gas cracked in a cracking plant. The thermal efficiency of H_2 production by this improved method was estimated to be 62 percent as compared to 27 percent production by the water-gas process in German plants. It might be improved by preheating coal paste in a converter instead of in a tube-type preheater, by hydrogenating the middle oil in vapor phase with the Welheim one-stage process instead of the I. G. Farben two-stage process, and by recovering heavy oil from heavy-oil letdown by flash distillation instead of by combined centrifugation and low-temperature carbonization. The thermal efficiency for producing steam and electricity was estimated to be 40 percent as compared to about 41 for German practice. With the two improved methods, the overall thermal efficiency of hydrogenation of bituminous coal with motor gasoline as the main product was predicted to be about 55 percent as compared to 29 percent for the conventional I. G. Farben process in the German plant. Such an improvement in thermal efficiency depends on more efficient methods, particularly for H_2 production, rather than on increased yield.

Low Temperature Hydrogenation

The equipment for this process is similar to that of the Bergius process.(34) However, the reactor is operated at 570 to 730 F and 4500 psig. The solids-free tar is not mixed with the catalyst during pasting. Rather, the pelleted No. 5058 WS_2 catalyst is placed in the reactor and an ebulliating bed process used. Though throughput is low, low temperature is necessary to carefully refine the high molecular weight substances without cracking them so that they can be recovered as lube oils and waxes.

U.S. Bureau of Mines Adaptation

The USBM(31) also has an extensive background in coal-to-liquid transformation. Immediately following World War II they constructed and operated a pilot plant at Louisiana, Missouri to demonstrate the Bergius process for direct hydrogenation of coal to oil and showed that American coals could be processed to liquid fuels.

Another study demonstrated the feasibility of coal hydrocarbonization to produce either oil or high-Btu gas and a dry char. The primary constitutent of the heating gas was hydrogen. A free-flowing char was produced by heating the coal stepwise to 750 F, 930, 1110, and finally 1290 F. Studies were also made on the catalyzed hydrogenation of vehicle oil at 8000 psig and 1000 F to gasoline. A 32-ft coil of 1/8-inch ID pipe wound in a 4-inch helix was used as the reactor. Coal-oil pastes were subject to the same conditions. Another investigation studied the oil yields of coal when individual coal particles were subject to flash carbonization in the presence of H_2.

The basis for the design of demonstration plants was the 700-atm liquid-phase hydrogenation and 700-atm vapor-phase without presaturation, patterned after the German operations at Lützkendorf and Welheim.

The converters (two in liquid phase, one in vapor phase) were 32 inches in inside diameter and 39 ft long. The internal volume, allowing for the asbestos cement liner, was 130 cu ft. On the basis of German experience with Ruhr coal, this volume would have permitted a charge rate of about 3 tons of coal per hour to the liquid phase. The balance of the plant was not capable of supporting this rate, and the liquid-phase converters were later lined to reduce the volume to 90 cu ft.

Saturation and splitting were performed in one operation over a catalyst of sulfide zinc, chromium, and molybdenum on Terrana. The catalyst was in six baskets with provision for mixing cold H_2 between baskets for temperature control.

The liquid-phase preheater departed from those of German design. Instead of a finned tube heated by forced circulation of hot flue gases, the Louisiana unit used double-walled tubes with superheated steam heated by direct radiant heat from the gas-fired furnace flowing in the annular space. Performance of this unit was satisfactory.

The plant was first operated in the middle of 1949, and before operations were terminated in 1953, 2000-4000 tons of each of four bituminous coals, one subbituminous coal, and one lignite were processed.

From the standpoint of hydrogenation of the coal and the production of gasoline, all the runs were successful, and attention was aimed chiefly at improvements in operability and control, and at reduction in maintenance or replacement of equipment items.

Processing of the heavy-oil letdown to purge solids and asphalts from the system was not completely satisfactory by the time operations were terminated. Two centrifuges were used in parallel and in series, flash distillation was tried, and plans were in process for a delayed-coking unit. Improvement in handling the product slurry through the four years of operation was quite steady and, presumably, if the work had been continued, satisfactory methods would have been developed.

Erosion of all ports through which liquids were let down to lower pressures, particularly if solid particles were present, was also a continuing problem and commanded considerable attention. Here again, there was progress, but probably there would have been no completely satisfactory and still practical solution.

Operating experiences at Louisiana led to the conclusion that flanged joints in high-pressure (700 atm) gas and hot-liquid lines were undesirable and that all-welded flexibly supported piping should be used whenever possible, even though added cost was entailed when maintenance required dismantling.

Extensive difficulties were encountered in high-pressure injection pumps. Radical changes in design were required before proper operation was achieved. The final units embodied among other features suction and discharge valve chambers external to the main pump block, compound cylinder construction with centrally located steam drive, and spring-loaded externally lubricated chevron packing. Performance of these units was good.

Two important purposes for the operation of this demonstration plant were the development of domestic manufacturing experience and application of modern engineering techniques to such a demanding process operation. Undoubtedly these purposes were to a large extent fulfilled. In addition there resulted a considerable accumulation of information on the hydrogenation properties and yields of a fairly wide variety of American coals.

This work was terminated in the early 1950's when it was decided that there were ample oil resources still available to the country.

Union Carbide

During the late 1940's and early 1950's, Union Carbide created and operated a 10,000-psig direct-coal-catalytic-hydrogenation pilot plant at Charleston, West Virginia, to explore the feasibility of producing chemical plant feedstocks.(35) While the hydrogenation plant did operate successfully, Union Carbide became discouraged by the economics of separating desirable chemical feed stocks from the hydro product. Apparently no serious effort was made at that time to study high volume products such as boiler fuel, crude oil, gasoline, or jet fuel.

As examples of the rich product streams which could be produced(33), Union Carbide reported the following aromatic-nonaromatic fractions boiling above 175 C:

- Aromatic Indane and Hydroaromatic:
  - Tetrahydronaphthalene
  - Naphthalene
  - 1-Methylnaphthalene
  - 2-Methylnaphthalene
  - 2, 3-Dimethylnaphthalene
  - 2, 6-Dimethylnaphthalene
  - 2, 7-Dimethylnaphthalene
  - Acenaphthene
  - Diphenyl
  - Fluorene
  - 9, 10-Dihydroanthracene
  - Anthracene
  - Phenanthrene
- Aromatic and Hydroaromatic — continued:
  - Chrysene
  - Perylene
  - Picene
  - Aliphatic:
    - *n*-Undecane
    - *n*-Dodecane
    - *n*-Tridecane
    - *n*-Heptadecane
  - Heterocyclic:
    - Dibenzofuran
    - Benzothiophene
    - Dibenzothiophene

and the following bases:

- Pyrrole
- Pyridine
- 2-Methylpyridine
- 3-Methylpyridine
- 4-Methylpyridine
- 2-Ethylpyridine
- 3-Ethylpyridine
- 4-Ethylpyridine
- 2-Methyl-6-ethylpyridine
- 3-Methyl-6-ethylpyridine
- 4-Methyl-2-ethylpyridine
- 2, 3, 4-Trimethylpyridine
- 2, 3, 5-Trimethylpyridine
- 2, 3-Dimethylpyridine
- 2, 4-Dimethylpyridine
- 2, 5-Dimethylpyridine
- 2, 6-Dimethylpyridine
- 3, 4-Dimethylpyridine
- 3, 5-Dimethylpyridine
- 2-*n*-Propylpyridine
- 2-Methyl-4-ethylpyridine
- 2, 5-Dimethylaniline
- 3, 4-Dimethylaniline
- 3, 5-Dimethylaniline
- 1-Naphthylamine
- 2-Naphthylamine

2, 3, 6-Trimethylpyridine
2, 4, 5-Trimethylpyridine
2, 4, 6-Trimethylpyridine
Aniline
2-Methylaniline
3-Methylaniline
4-Methylaniline
2-Ethylaniline
2, 3-Dimethylaniline
2, 4-Dimethylaniline
Indole
2-Methylindole
3-Methylindole
Carbazole
Quinoline
2-Methylquinoline
7-Methylquinoline
Isoquinoline
1-Methylisoquinoline
3-Methylisoquinoline

CONSOL Synthetic Fuel Process

The CONSOL synthetic fuel process was developed by CCC as a means of producing liquid fuels from coal. In August, 1963, the OCR in cooperation with CCC initiated a substantial research and development program involving bench-scale work and eventually the construction and operation of a one-ton-of-coal-per-hour pilot plant at Cresap, West Virginia. In the process a high-sulfur Eastern bituminous coal is used to produce a low-sulfur synthetic crude oil, or a fuel oil suitable for use in utility plants. The coal is processed by extraction with hydrogenated solvents derived from it; unreacted coal and inorganic constitutents are separated from the hydrocarbon extract. Hydrogen for the process can be produced from unextracted coal char. Originally, the pilot plant, which went into operation in 1967, was intended to produce liquid hydrocarbons in the gasoline range. Subsequently, it was decided that a more economically attractive objective was to produce a low-sulfur synthetic crude oil which could serve as a feed to an oil refinery or could be used as a fuel for electric power plants.

Although the process appears to be technically feasible and capable of producing synthetic liquid fuels from coal at reasonable cost during the 1980-1995 time period, the Cresap pilot plant did not achieve satisfactory performance during its 40 months of operation up to the time of its shutdown in April, 1970. Actually, the plant was operating for less than 500 hours during this period and did not provide sufficient data to permit the detailed design of a commercial plant for coal liquefaction. Generally runs were terminated by mechanical and pilot plant failures.(36) A flow sheet of the process is shown in Figure 9, and the various operating steps are described below.

Extraction. Dried coal, having a 99 percent minus 8 mesh particle size, was mixed with a process-derived hydrogen donor solvent (500 x 800 F middle oil) in a ratio of 2.5 parts solvent to 1 part moisture-free coal. This mixture was heated to 800 F, then fed to a stirred staged vessel (extractor) to be held for 30 minutes at an average temperature of 750 F and the vapor pressure of the solvent (150 to 400 psig). This holding period was sufficient to depolymerize and stabilize 70 to 85 percent of the moisture-ash-free coal, requiring that approximately 0.7 weight percent hydrogen transfer takes place. Make gas, make water, and light oil vapors were disengaged from the slurry at pressure then cooled, condensed, and recovered.

Solids Removal. Several alternatives were tested for removing the solids from the extracted coal slurry, including filtration, hydroclones, and centrifuging. Centrifuging work was not completed; filtration was possible process-wise, but not mechanically, while the use of hydroclones produced a reasonable amount of product. In all

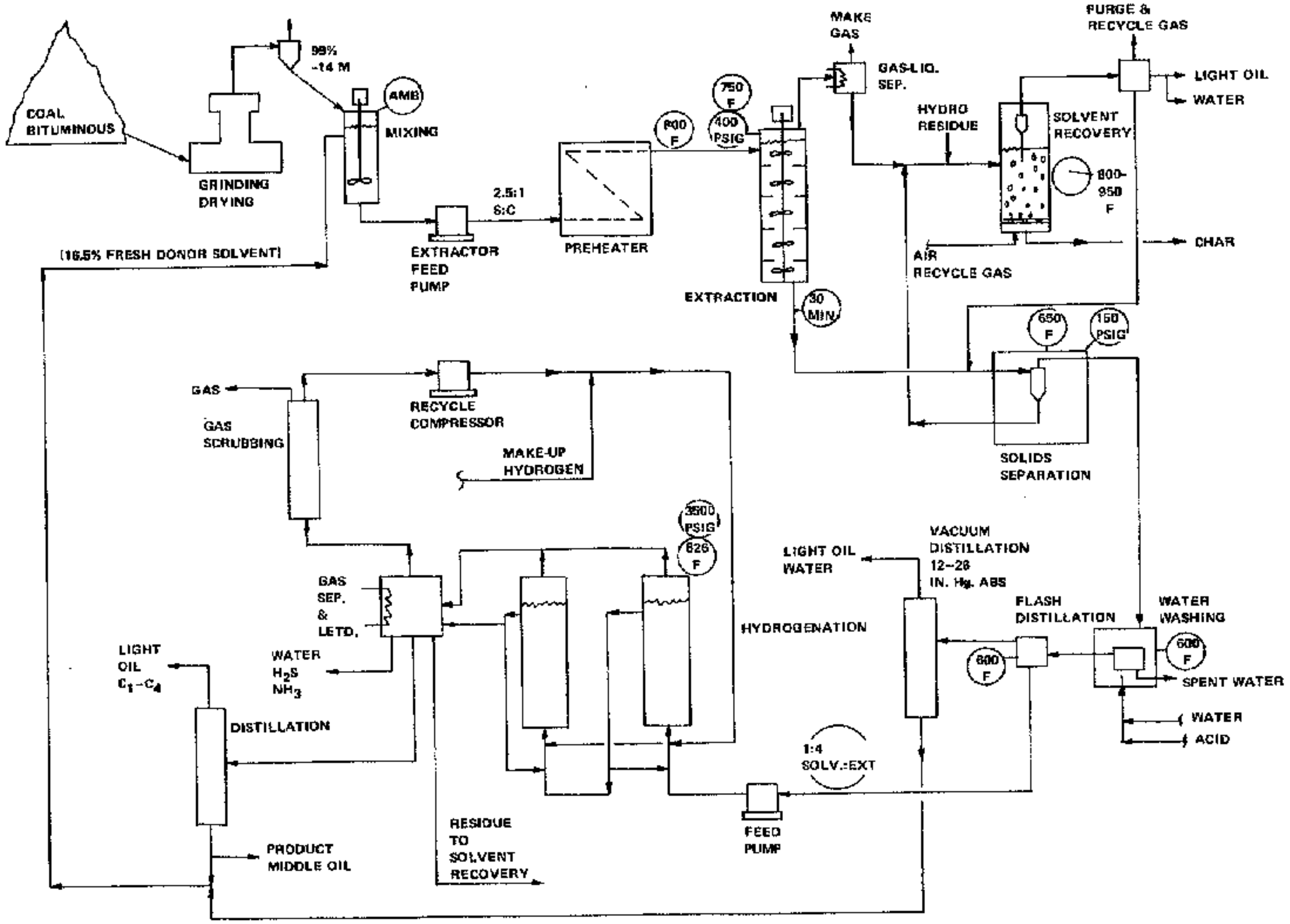


FIGURE 9. CONSOL SYNTHETIC FUEL O.C.R. - "PRODUCT GASOLINE" 1 TON PER HOUR PILOT PLANT CRUDE OIL PRODUCTION

cases the extracted coal slurry was cooled to 625-675 F, depressurized to 150 psig (100 psig at times), and the off-gas collected. The degassed material was fed into a primary and wash hydroclone.

Water Washing. Hydroclone liquid overflow was then partially vacuum distilled and mixed with acidified water at 580 F to remove soluble alkali ash components in the extract which would reduce catalyst activity. Washed extract was recovered by decanting. This portion of the pilot plant was not to be activated until catalyst life tests were imminent; this did not occur.

Distillation. Hydroclone liquid overflow was flash distilled at 12 to 26 in. Hg and abs. 600 F. The overhead vapor was further distilled to light oil and water overheads and hydrogen deficient middle oil, which was recycled to coal mixing.

Hydrogenation. The flash still underflow, containing 15 to 35 percent solvent, was fed to the hydrogenation section which consisted of three reactors in series having a total volume sufficient to give a minimum residence time of 5 hours. The reactors were operated at 800-850 F, 3500 psig total pressure, and 85 percent H_2 partial pressure. Each reactor was filled to 1/3 the liquid volume with spherical 1/16-inch pellet of cobalt, nickel, molybdenum, on alumina gel (UOP-S-6) catalyst. They were operated with sufficient liquid and gas recycle to give a fluid bed expansion of 25 percent. Liquid products were vaporized overhead, cooled, condensed, and separated from the recycle gas. Reactor temperature was maintained by control of the recycle. Liquid feed to the downstream reactors was diverted from the liquid recycle stream. A small purge stream of sludge from the last reactor was recovered and pumped to solvent recover. The condensate was stabilized by removing the gaseous hydrocarbons, then fractionating the oil into a light oil and a heavy or product oil. A portion of the product oil was also recycled to the mixing tanks.

Solvent Recovery. Solvent recovery was obtained with a fluidized bed coker operated at 800 to 950 F. Feed to this unit was hydroclone underflow containing 10 percent extract, 45 percent solids, and the remainder solvent. Bed temperature was maintained by adjusting the air and recycle gas ratios. Recovered solvent and tar, equal to the solvent feed, were returned to the solids separation section. Hot char, containing 20 to 35 percent ash, was slurried with water and stored in a pond.

As in other processes for producing liquid fuels from coal, the cost of production of the required amounts of H_2 was the most expensive part of the process. If desulfurization of the coal extract could be accomplished with less H_2, substantial savings in overall process costs could be realized. What is really needed is a more selective hydrodesulfurization step which will convert the contained sulfur to H_2S and produce sufficient recycle hydrogen donor solvent for the process.

A difficult problem in this and several other processes under consideration for the solvent refining or liquefaction of coal, is the separation of liquid extract from the undissolved coal and inorganic residue. Filters, centrifuges, and hydroclones have been used, but it is not clear at the present time which method or combination of methods will prove to be best.

The Cresap pilot plant was beset with a very large number of mechanical and corrosion problems which seriously interefered with operations. These included pump failures (seals, erosion), plugging of lines with tar, coking in heaters, bearing problems in reactors, filtration problems, breakdowns of the hydrogen compressor, leaks in the hydrogenation section, and loss of catalyst from the hydrogenation reactors.

The catalyst used in the process for extract hydrogenation was a commercial 1/6-inch bead of cobalt-nickel-molybdenum on an alumina base. There were indications that catalyst life was shortened by poisoning from alkali metals present in the coal.

Operation of the Cresap pilot plant was suspended in April, 1970. It is not clear at the present time what action will be taken by OCR with respect to this plant. As the result of an engineering evaluation of the pilot plant research project by Foster Wheeler Corporation in 1970, numerous recommendations were made regarding renovations of the plant and operational changes to obtain the information needed for the process design of a commercial-scale installation.(37) Funds have not yet been provided to carry out these recommendations. It appears that very little work is being done on the process at the present time. It is unfortunate that operation of the pilot plant did not proceed to the point where more meaningful data could be made available for design of a large-scale plant.

Hydrocracking with Zinc Chloride

Under contract with OCR, CCC has also done considerable research and development work on the use of molten $ZnCl_2$ as a catalyst and reaction medium for converting coal extract and coal to liquid hydrocarbons by hydrogenation at elevated temperatures and pressures. Separate reports have described work on the hydrocracking process with $ZnCl_2$(38) and on regeneration of the $ZnCl_2$ catalyst.(39) Molten $ZnCl_2$ is active at lower temperatures and hydrogen pressures than the ordinarily used cobalt-molybdenum-nickel on alumina catalyst, $ZnCl_2$ converts most of the coal extract directly to liquids in the gasoline range. Its disadvantages are that high catalyst-to-extract (or coal) weight ratios are required; the catalyst becomes contaminated with large amounts of sulfur and nitrogen compounds, ash, and carbonaceous residues; and the mixture is quite corrosive. If some of these difficulties can be overcome, the use of $ZnCl_2$ looks promising, particularly for the direct conversion of coal to liquids in the gasoline range.

This process should be considered as a variant of the synthetic fuel process for conversion of coal to liquid hydrocarbons. In one embodiment it involves substitution of a large amount of $ZnCl_2$ for the smaller amount of conventional sulfur-resistant catalyst used in catalytic hydrocracking of coal extract. A second possibility is the direct hydrocracking of coal, thus avoiding the liquid-solid separation problem encountered in the synthetic fuel process but complicating $ZnCl_2$ catalyst recovery. Under similar conditions product yields based on the moisture and ash-free coal are about identical with either coal or coal extract, but when coal is used directly, the mineral components in the coal build up rapidly in the molten $ZnCl_2$.

The $ZnCl_2$ process was studied with coal extract in both batch and continuous units. Only batch studies were made with direct feeding of coal. They were carried out using coal extract in a rocking autoclave under a variety of conditions of temperature, pressure, $ZnCl_2$/extract weight ratio, residence time, etc. Typical operating conditions and results taken from a CCC patent example(40) and from publications(41, 42) describing the work are as follows:

Feed = Coal extract containing 6.14 percent H, 83.73 percent C,
1.46 percent N, 6.87 percent O, and 1.80 percent S.

$ZnCl_2$/extract weight ratio = 1.0
Time = 1 hr
Temperature = 427 C
Hydrogen pressure = 4200 psig

Yields as percent by weight of charged extract:

C_{1-3} = 13.0
n-C_4H_{10} = 1.6
i-C_4H_{10} = 9.6

C_5-200 C distillate = 60.4
200-400 C distillate = 3.1
Total hydrocarbons produced 87.7

In another example(40), 25 g of coal and 75 g of $ZnCl_2$ were heated to 385 C (for 1 hour under 2000 psi hydrogen pressure) to give the following products expressed as percent by weight of coal charged:

CH_4 = 0.9
C_2H_6 = 2.3
C_3H_8 = 7.1
i-C_4H_{10} = 7.5
n-C_4H_{10} = 1.2

boiling range <150 C = 43.8
boiling range 150-200 C = 4.4
boiling range 200-400 C = 4.0
Total hydrocarbons produced = 71.2

In order to maintain fluidity when coal is used directly, a weight ratio of $ZnCl_2$ to coal of about two or more is required for good results.

If the objective of further research is to produce gasoline rather than fuel oil or a synthetic crude oil for refinery feed, then the $ZnCl_2$ hydrocracking process as applied directly to coal appears to deserve additional study. More information is needed on corrosion problems and $ZnCl_2$ catalyst regeneration before a reliable cost estimate of a coal conversion plant based on the process can be made.

Active research and development work by the CCC on the $ZnCl_2$ catalyst for converting coal to gasoline was carried out during the period August 1963 to June 1968, under a contract with OCR. It is not apparent that work is continuing on this process, although CCC may be doing some small-scale studies independently.

The foremost problem in the use of $ZnCl_2$ as a catalyst for hydroconversion of coal or coal extract is catalyst regeneration. The very large amounts of $ZnCl_2$ required (up to 3 times the weight of coal or an equal weight in the case of coal extract) necessitate an economical method of catalyst recovery. Spent catalyst from hydrocracking of coal or extract contains nitrogen and sulfur compounds, ash, and carbonaceous residues which are difficult to convert. According to a recent patent,(43) the amount of $ZnCl_2$ required to react with the 1.5 percent nitrogen and 2 percent sulfur compounds in a feedstock coal extract would be 23 percent of the weight of the feedstock. The following equations indicate some of the reactions which consume $ZnCl_2$:

$$ZnCl_2 + H_2S \rightarrow ZnS + 2HCl$$

$$ZnCl_2 + NH_3 \rightarrow ZnCl_2 \cdot NH_3$$

$$ZnCl_2 \cdot NH_3 + HCl \rightarrow ZnCl_2 \cdot NH_4Cl.$$

A $ZnCl_2$ loss equal to one weight percent of the coal extract feed has been calculated to be equivalent to a make-up cost of about 0.8 cents per gallon of gasoline produced. In the case of direct conversion of coal, the catalyst regeneration problem is further complicated because of the large amounts of ash constituents which end up in the $ZnCl_2$ melt.

A second important problem is concerned with materials of construction for equipment to handle molten $ZnCl_2$ and the corrosive reaction products such as HCl which may be formed.

H-Coal Process

The H-Coal process of Hydrocarbon Research, Inc. (HRI) is not the lineal descendant of preceding coal liquefaction methodology but derives from HRI's prior studies on hydrogenation of petroleum feedstocks. Even though other methods have a longer developmental history, it appears that today the H-Coal process is in the most advanced stages of development among the post-World War II coal liquefaction procedures. The H-Coal studies were begun in 1965 and were initially funded by OCR. Subsequently the sponsorship was expanded to include ARCO, Sun Oil, Gulf Oil, Esso Research and Engineering, Ashland Oil, and CCC. Still later, support was confined to ARCO, Exxon, Ashland Oil, and American Oil. At present activity on H-Coal research is at a very low level. Financial support is being sought by HRI for construction and evaluative operation of a 250 ton/day pilot plant expected to produce about 725 barrels/day of an all-distillate synthetic crude oil containing about 0.2 percent sulfur and no ash or alternatively using 700 tons/day to produce 2250 barrels/day of fuel oil.

The H-Coal process was subjected to an independent evaluation for OCR in 1967 by the staff of American Oil Company.(44) That evaluation essentially confirmed the claim of HRI regarding operating parameters and product yields and properties. Nevertheless, OCR ended its support at that time for budgetary reasons and the industrial sponsors noted above provided subsequent fundings. More recent work appears to have improved the process; higher yields of liquid products than those of 1967 are now claimed by HRI. A schematic of the process in its present form is shown in Figure 10.

The heart of the process is the unique reactor design. Coal is dried, pulverized, and slurried with coal-derived oil for charging to the hydrogenation unit. The slurry is charged continuously with H_2 to the reactor containing a bed of ebullated catalyst wherein the coal is catalytically hydrogenated and converted to liquid and gaseous products. In the ebullated bed the upward passage of the solid, liquid, and gaseous materials maintains the catalyst in a fluidized state. The relative size of the catalyst and coal particles is such that only the unconverted coal, ash, liquid, and gaseous products leave the reactor while the catalyst is retained. Catalyst can be added and withdrawn continuously so that a constant activity can be maintained.

A simple means of controlling reactor temperature is provided along with effective contact between reacting species and the cobalt molybdate catalyst, permitting a satisfactory degree of reaction at reasonable operating pressure, about 2300 psi.

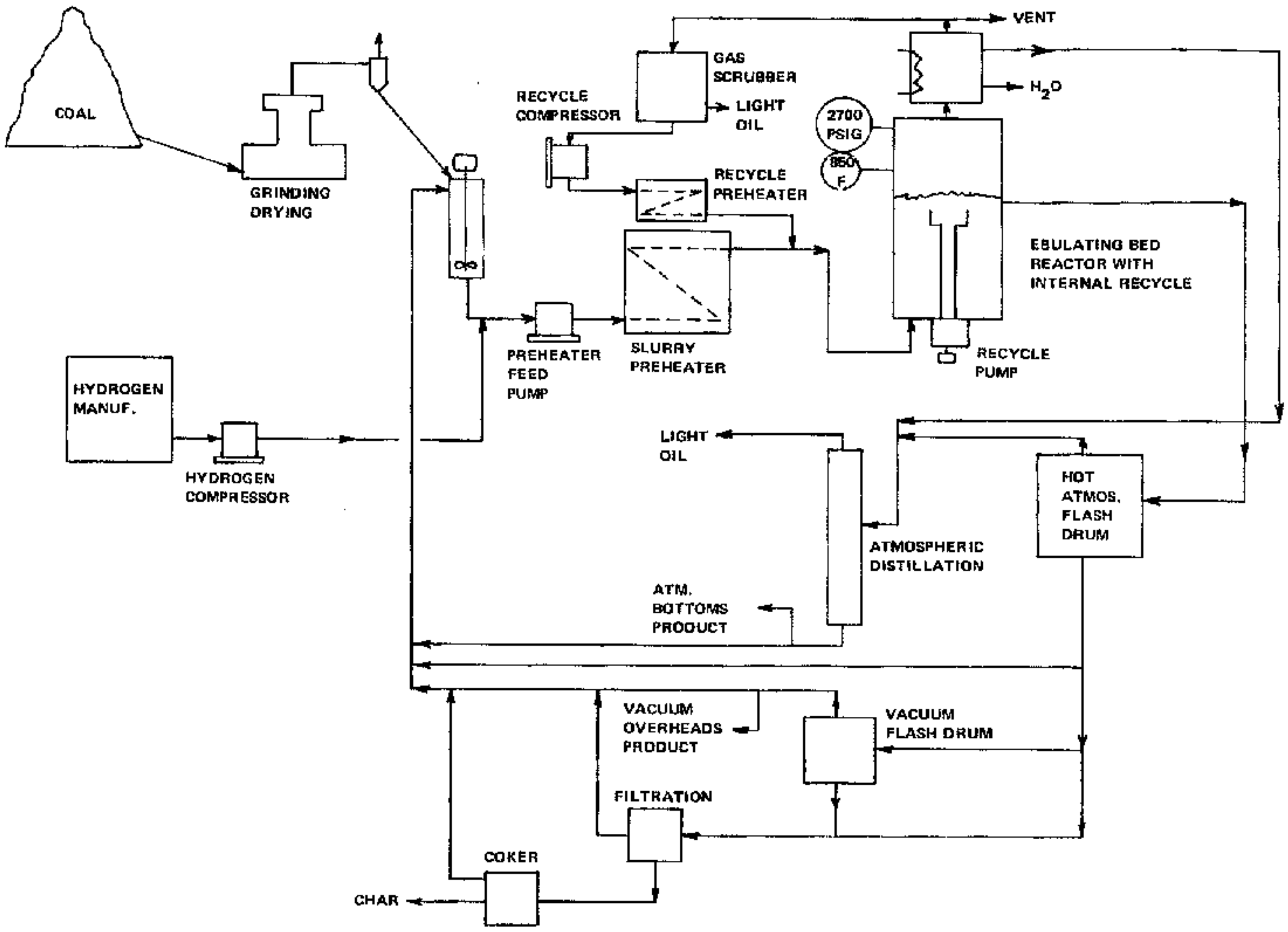


FIGURE 10. HYDROCARBON RESEARCH, INC. – H-COAL PROCESS (INITIAL WORK SPONSORED BY O.C.R.) CRUDE OIL PRODUCTION 250 LB PER HOUR BENCH SCALE

The H-Coal process can produce a synthetic crude which can be refined to gasoline and heating oil by conventional methods or, alternatively, it can be operated under milder conditions to produce low-sulfur fuel oils and fuel gas for power-plant utilization.

Hydrogen can be produced by gasification of the unconverted coal admixed with fresh coal or with a portion of the heavy oil produced from coal admixed with unconverted coal.

Synthetic crude oil from the H-Coal process can be readily processed to yield a gasoline with 100+ octane rating without the addition of lead. The current emphasis on removing lead from gasoline could result in a premium price for gasoline produced from coal for use as a blending stock.

In the process variation to make low-sulfur fuel oil, three products are produced: clean fuel gas of about 100 Btu/cu ft; a light fuel oil; and a heavy fuel oil product (plus NH_3 and sulfur as by-products). The relative amounts of these products depend on the desired sulfur level in the heavy fuel oil. Heavy fuel oil with 0.5 weight percent sulfur has been produced in HRI's process development unit starting with Illinois and Pittsburgh coals containing 3 to 4 percent sulfur. The fuel gas is sulfur free, and the light oil contains less than 0.1 weight percent sulfur.

The performance of the H-Coal process development unit was in the range of the bench-scale results, representing a scale-up factor of over 200. Synthetic crude yield of nearly 4.5 barrels per ton of moisture- and ash-free Illinois coal could theoretically be achieved if a practical method can be developed for recovering the liquids from the unconverted coal and ash. Assuming this could be done, the crude would be about 75 percent distillate which could be refined by conventional methods to produce high-octane, lead-free gasoline. Loss of catalyst by attrition and/or carryover was negligible. Some erosion problems were experienced, but were solved.

It is anticipated that commercial H-Coal reactors will be 10 ft or more in diameter. The next larger unit would be a prototype demonstration plant with a 4.5-ft-diameter reactor, representing a scale-up factor of 100 from the process development unit. Commercial size reactors would represent a scale-up of only 10 from the prototype unit. Therefore, this comparison of results between the bench unit and the process development unit is important and scale-up in the H-Coal process appears promising except for the filtration step.

As indicated on the flow sheet, the oil used for slurry preparation can be a combination of several streams derived from the H-Coal reactor (the vacuum distillate fraction, the atmospheric bottoms fraction, the atmospheric flashed slurry, or the centrifuge-clarified liquor), depending on the composition desired.

Operating results with Illinois No. 6 coal show a conversion of approximately 90 percent to liquid and gaseous products, with approximately 70 percent conversion to liquid product. The liquid product can be converted to gasoline by conventional refinery processes.

The products obtained from Illinois No. 6 coal in the H-Coal process represent an approximately 90 weight percent conversion of the moisture- and ash-free coal. Yields based on weight percent of dry coal fall in the following ranges.

$C_1 - C_3$ gas	12.3
to 650 F	37.9
above 650 F	23.9.

The hydrocarbon gas product contains the following specific percentage distribution:

Methane	29-36
Ethane	25-34
Propane	33-38.

Less than 0.1 percent of olefin product is generally found. A detailed analysis of the distilled product is given in Table 8.(45)

Research and development activity on the H-Coal process is confined to HRI's efforts which appear at the moment to be at a relatively low level. Even if the funding being sought for a demonstration plant (one-tenth production scale) is forthcoming, work on the process will be chiefly addressed to problems of scale-up rather than process improvement. No work is being done on catalyst improvement although from time to time HRI evaluates catalysts submitted to them from outside. The problem of solids separation is of concern and it appears that some work may be directed toward its solution.

HRI apparently considers the problem of solids separation to be of primary importance. It is not a problem unique to the H-Coal process but applicable to almost every coal conversion scheme. It arises from a very fine ultimate particle size together with a rather viscous liquid phase. Others besides HRI have given attention to the problem but without notable success. Viscosity reduction by addition of a light oil and use of a cyclone separator is claimed by HRI(46) to improve separation. Displacement of liquid having affinity for the residue, e.g., water, followed by separation by centrifugation or other means, has also been suggested.(47) But these and other modifications seem not to have resolved the solids separation problem which is a major cost contributor to those processes which use it, including the H-Coal process when run to produce low-sulfur crude. Thus, any major breakthrough in solids separation technology would have broad applicability and materially improve process economics.

Hydrogen generation and compression are major contributors to the cost of any coal hydrogenation process. In the H-Coal process for example, the H_2 cost is $3.00 or more per barrel of product oil. This is apparently the highest H_2 consumer among the various liquefaction processes. It is now planned to produce H_2 by the water-gas reaction on the bottoms from the product still of the H-Coal process. It has been suggested(48) that these bottoms and possibly other fuels be burned to generate electricity for electrolytic H_2 generation. Credit could be taken for the oxygen produced. However, at first sight, this seems to be an expensive way to make H_2 in view of the low efficiency of the fuel-to-current step. In any event, less costly H_2 or the use of H_2 at lower pressures is an urgent need.

While the cost of catalyst in the H-Coal process is small (ca. $0.35 per barrel of product) compared to the cost of H_2, catalyst improvement could be important for economy and other reasons. If a more active stable catalyst system could be devised which permitted operating the process at lower temperature, higher throughput, and/or lower pressure, the cost of process design requirements could be greatly reduced.

TABLE 8. INSPECTION OF PRODUCTS FROM ILLINOIS NO. 6 COAL(45)

COMPOSITION OF C4-400 F FRACTION

Saturated Compounds

Component	Wt %
nC_4	0.10
iC_5	0.20
nC_5	0.69
C_6	2.48
C_7	2.87
C_8	2.08
C_9	1.59
C_{10}	1.15
C_{11}	0.6[illegible]
C_{12}	0.1[illegible]
	11.99

Saturated Naphthenes

Component	Wt %
Monocycloparaffins	42.64
Dicycloparaffins	8.50
Tricycloparaffins	0.19
	51.33

Unsaturated Naphthenes

Component	Wt %
Monocycloparaffins	5.32
Dicycloparaffins	4.98
Tricycloparaffins	0.90
	11.20

Alkyl Benzenes

Component	Wt %
C_6	0.89
C_7	3.77
C_8	4.76
C_9	4.16
C_{10}	2.58
C_{11}	1.29
C_{12}	0.10
	17.55

Other Compounds

Component	Wt %
Indans	6.44
Naphthalenes	0.59
Phenols (MW)	
108	0.13
122	0.56
136	0.19
150	0.02
	7.93

Total = 100.00 Wt %

TABLE 8. (Continued)

COMPOSITION OF 400-650 F FRACTION

Saturated Compounds

Component	Wt %
n-paraffins	4.8
i-paraffins	1.7
Monocycloparaffins	14.0
Dicycloparaffins	7.9
Tricycloparaffins	2.6
	31.0

Aromatic Compounds

Component	Wt %
Alkyl Benzenes	12.6
Indans & Tetralins	30.8
Indenes	5.7
Naphthalene	0.2
Naphthalenes	3.5
Acenaphthenes (C_nH_{2n-14})	4.0
Acenaphthenes (C_nH_{2n-16})	2.2
Tricyclics (C_nH_{2n-18})	0.4
	59.6

Unsaturated Non-Aromatic

Component	Wt %
Monocycloparaffins	4.3
	4.3

Other Compounds

Component	Wt %
Phenols (MW)	
108	0.04
122	0.52
136	0.98
150	0.38
164	0.07
178	0.01
Other Non-Hydrocarbons	3.10
	5.10

Total = 100.00 Wt %

TABLE 8. (Continued)

COMPOSITION OF 650-919 F FRACTION

Saturated Compounds

Component	Wt %
Paraffins	1.4
Monocycloparaffins	3.1
Bicycloparaffins	0.6
Tricycloparaffins	0.7
Tetracycloparaffins	0.4
Pentacycloparaffins	0.2
Hexacycloparaffins	0.1
Phenyls	0.3
	6.8

Unsaturated Non-Aromatic

Component	Wt %
Paraffins	0.0
Monocycloparaffins	0.5
Bicycloparaffins	0.3
Tricycloparaffins	0.2
Tetracycloparaffins	0.2
Pentacycloparaffins	0.1
Hexacycloparaffins	0.1
Phenyls	0.2
	1.6

Other Compounds

Component	Wt %
Alkyl Benzenes	3.0
Indans &/or Tetralins	0.5
Other Aromatics*	72.8
Phenolic Compounds	1.5
Other Non-Hydrocarbons	13.8
	91.6
Total	100.0 Wt %

* An approximate breakdown of Aromatic-type compounds is given below:

Component Type	Millimoles/100 grams
Naphthalenes	93.4
Phenanthrenes	91.1
Chrysenes	21.9
1-2 Benzanthracenes 3-4 Benzphenanthrenes	14.6
Pyrenes	15.4
5 Ringed Compounds	5.1