processed before the filters needed to be replaced. The filtrate was vacuum distilled at 50 to 10 mm Hg to give an extract product with 390 F melting point containing 0.05 percent ash. The overhead liquid was distilled at atmospheric pressure to give a recycle solvent with a 430 F end point and a residue which was returned to sump phase hydrogenation. The filter cake was coked out in a rotary kiln at 750 F for ultimate oil and tar recovery.

The product was carbonized in conventional slot ovens to give an electrode carbon material for aluminum production. Solvent used was originally a mixture of tetralin and cresols, but operation of the commercial plant was based on a stream of middle oil from an adjacent hydrogenation plant, with recovered solvent returned to that plant.

A plant employing the Pott-Broche process was also in operation in Japan during World War II.

The Solvent Refined Coal Process

Solvent refining was initiated in the United States with the limited objective of producing a low-cost antipollution alternative to desulfurized residual oil and natural gas for use in boilers. Only limited hydrogenation is required since the process is not primarily designed to produce lighter oil products. The hydrogenation step is followed by ash separation and conversion of sulfur to a removable form. The original U.S. laboratory development of the unit operations involved in the process was carried out by Spencer Chemical Corporation (now Pittsburgh and Midway Coal Mining Company) and an economic evaluation of a full-scale plant has been published.(18) More recently Process Research, Incorporated(19) updated this work. Two pilot plants for studying the process are currently being constructed. A 6 ton/day plant for studying the steps in the solvent-refining process is being built at the Southern Electric Company's (SEC) Ernest C. Gaston plant, and is about ready for start-up. Also, a 50 ton/day plant at Tacoma, Washington, is now scheduled for start-up in the spring of 1974. A schematic flow diagram for the pilot plant is shown in Figure 3. The solvent refined coal process can use any rank coal below anthracite, from lignite to low-volatile bituminous.

Using the process, an ashless, low-sulfur fuel having a heating value of about 16,000 Btu/lb can be produced. The fuel product is prepared by dissolving coal in a coal-derived solvent in the presence of H_2 at 1000 psi or greater and 825 F. The coal-solvent solution is then filtered and evaporated to yield a fuel product with ash and sulfur both substantially removed. The fuel product can be utilized as either a liquid or solid.

Initially, coal is crushed to 1/8 inch or less and dried to a moisture content of 3 percent. It is then fed to a slurry mix tank where it is mixed with an anthracene oil at about 300 F to form a slurry. The coal-solvent slurry is then pumped through a line where H_2 is added. In the future, synthesis gas (a mixture of CH_4, H_2, CO and CO_2) may be employed.

The coal-solvent slurry and H_2 are pumped through the dissolver preheater into the dissolver. The coal depolymerization and dissolving process begins in the preheater where the material goes through a gel stage and dissolution is completed to equilibrium in the dissolver.

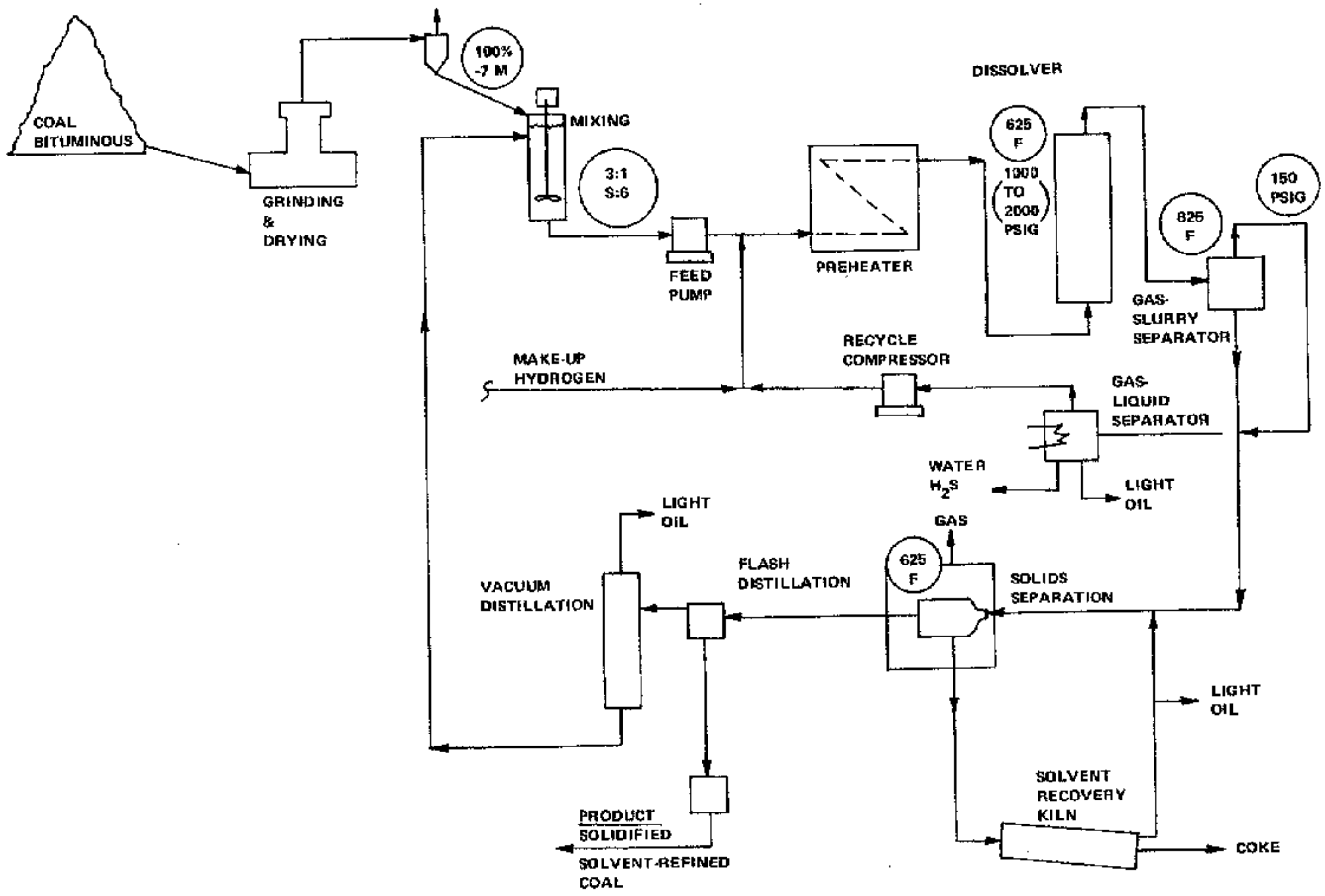

FIGURE 3. "SOLVENT REFINED COAL" PILOT PLANT DISSOLVED COAL PRODUCTION

As a result of the solution and hydrogenation reactions which occur in the dissolver, hydrocarbons, H_2S, heavy oils and CO_2 are formed. The total product stream flows from the dissolver to the high-pressure flash vessel in which vapor and liquid are separated. The vapor stream, containing light hydrocarbons, phenols, cresols, water vapor, H_2S, CO_2, and fuel gas, is fed to the gas-liquid separation section of the plant. After further pressure reduction, the liquid stream is fed to rotary pressure filters.

The filters separate ash and undissolved carbon from the coal-solvent solution. The filter cake is washed with light solvent to remove coal-solvent solution. In commercial operation the remaining mineral residue, containing about 70 percent ash and 30 percent carbon, must then be recycled to the coal gasifier.

The coal-solvent solution is fed to the vacuum flash evaporator where it is flashed at 625 F to separate liquid coal from the anthracene oil and light solvent. Flashed anthracene oil wash solvent, light hydrocarbons, and dissolved gases are condensed and fed to the solvent recovery unit. The liquid coal, with light oil blended back in, is then ready for fuel use. It can be fed as a hot liquid directly to an on-site user or it can be solidified for shipment to a distant use point.

In the acid gas removal system, CO_2 and H_2S are separated from the gas stream and sent to a Claus unit (and tail gas treatment system) where the H_2S is converted to elemental sulfur. The other gases, with 99.9 percent of the H_2S removed, are used for plant fuel.

In the solvent recovery system, the solvent mixture is first fed to the wash solvent splitter column. Here wash solvent and lighter material are boiled off overhead to the light-ends column, leaving anthracene oil for recycle to the coal preparation system.

The wash solvent and other light materials are fed to the light-ends column where light oil is boiled off, leaving the wash solvent for recycle to the rotary pressure filters. The light oil flows to the phenol and cresol separation unit, if economics dictate such a unit. Otherwise only a water-light oil separation unit will be used.

The design basis for the solvent refining process was developed during the period of 1962 to 1965 in the pilot-plant studies of Spencer Chemical Company.(20) Primary variables selected for study were (1) type of coal, (2) type of solvent, (3) temperature, (4) reaction time, and (5) solvent-to-coal ratio. These were initially restricted to Kentucky No. 11 coal, coal-derived solvent, temperature range of 350-450 C, reaction time of 1 to 4 hours, and solvent-to-coal ratio of 4:1 to 1:1. Bench-scale experiments were conducted to support the process pilot plant and were concentrated on the degree of solution (depth of extraction). Autoclave runs made without H_2 confirmed that temperature and residence time were of prime importance in achieving dissolution; however, sulfur removal efficiency was low.

Fifty-seven autoclave runs were made to evaluate the use of H_2 for improving extraction and solvent recovery. Initially it was contemplated that the solvent would be hydrogenated separately, but experimental work indicated that satisfactory results could be obtained by adding the H_2 directly to the dissolver. The beneficial effect of H_2 was attributed to the termination of free radicals which were formed as the coal depolymerized. A decline in solvent efficiency as it was reused in the absence of H_2 was noted and attributed to a transfer of H_2 from the solvent to the coal during the solution process.

The effect of agitation was studied in one run where it was noted that a 20 percent decrease in dissolution occurred without agitation. It was assumed, however, that the presence of H_2 gas in the continuous dissolver would provide satisfactory agitation for dissolution and mass transfer of the H_2.

Sulfur removals were not reported; however, comparative runs on coals with various sulfur content indicated that a higher degree of dissolution could be obtained in the case of high-sulfur coals. It should be noted here that these coals also had a high-ash content.

Electron microscopy was utilized to determine whether the dissolved coal existed as a true solution or as a colloidal suspension as reported by some investigators. Photomicrographs supported the formation of a true solution and indicated that the dissolution process occurred in three stages: (1) solvent absorption, (2) gel formation (swelling of the coal particles), and (3) dissolution.

The batch experiments demonstrated that 70-90 percent of the moisture-ash-free coal could be dissolved in 20 minutes with H_2 gas at 400 C. A bench-scale dissolver was used to test the continuous extraction under these conditions using a 1-inch pipe as a combination preheater and dissolver. Eighty-six to 91.8 percent dissolution was obtained at 385-420 C, solvent-to-coal ratios of 3:1 and 4:1, and residence times of 1/4 to 1 hour. Considerable difficulties were encountered, however, due to the formation of a gel accompanied by an increase in the apparent viscosity of the slurry mixture. The gel disappeared after heating as true solution was attained.

Final studies were carried out in a process pilot plant using different coals (mainly, Kentucky No. 11 and Pittsburgh No. 8 seam coals). In this plant the dissolver consisted of vertically mounted tubes with diameters of 3 to 8 inches. A total of 66 runs was made with a duration of 1 to 89-1/2 hours. Except for four runs all experiments were carried out at 1000 psig pressure. It was found that dissolution could be obtained with solvent-to-coal ratios as low as 2:1; however, the pressure drop across the dissolver increased to 200 psi. The effect of operating variables upon the filterability of the product was studied. A tenfold decrease in the apparent viscosity of the mixture was observed as the dissolver temperature was increased from 425 to 482 C. Coking was observed above 440 C establishing the maximum practicable operating temperature. Hydrogen consumption was found to vary from 0.8 to 1.5 lb H_2/100 lb of coal fuel. No direct relation was found between H_2 consumption and the process variables.

In summary, the pilot-plant operation confirmed that coal could be dissolved in a continuous reactor in the presence of solvent and H_2 gas. The degree of solution was found to be primarily dependent upon the temperature and liquid residence time. No attempt was made to define a quantitative relationship between the various operating variables and the conversion of coal. These data were then used to build the 50 ton per day Tacoma pilot plant.

Process Research, Inc., performed a conceptual design study on a 222×10^9 Btu/day Solvent Refined Coal Plant,(19) i.e., for a plant large enough to supply fuel to a 950 MW power station. The material balance is shown in Table 2 and on the flow sheet in Figure 4. In this plant, the Btu output is based on producing a single product with phenols, cresols, and light oil included as part of the product. The feed material is bituminous coal having 3.0 percent moisture, 14.5 percent ash, and 3.0 percent sulfur. The fuel product contains 0.6 percent sulfur and 0.05 percent ash. The

TABLE 2. MATERIAL BALANCE INFORMATION-SOLVENT REFINED COAL PROCESS AT 222 x 10^9 BTU/DAY PLANT CAPACITY (950 MW)

	Eastern Coal*
Input, tons/hr	
Coal	514
Energy, BTU/hr	12.35 x 10^9
Output, tons/hr	
Solvent Refined Coal	289
Slag	73.9
Sulfur	13.7
Tail Gas Sulfur	--
Coal Consumed	225
Heat	9.25 x 10^9
Overall Fuel Efficiency, percent	75

* Typical Eastern coal having 3 percent sulfur, 14.4 percent ash and 12,000 Btu/lb.

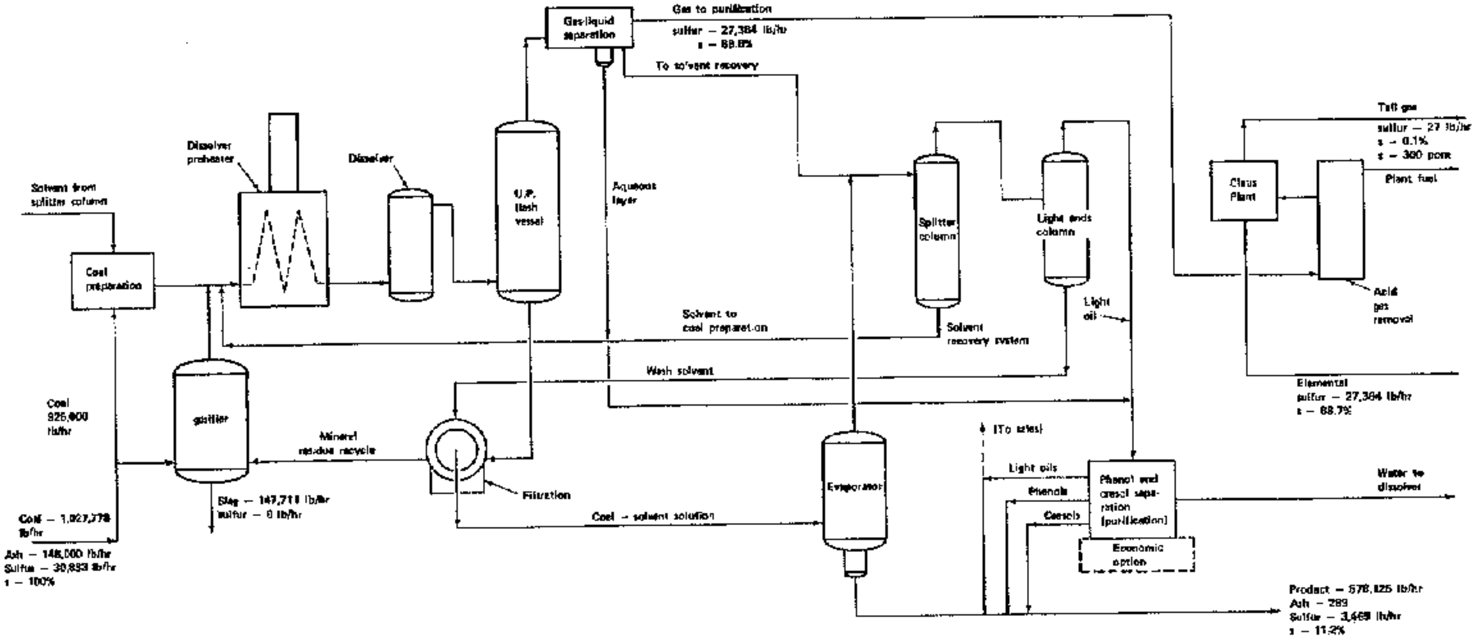

FIGURE 4. SOLVENT REFINED COAL PROCESS

Basis: 222 x 10^9 Btu/day
Coal - 3.0 percent; 1.4 percent
ash; 12,000 Btu/lb

material balance shown in Figure 4 is based on numerous assumptions including two very important ones that must be proven practical in pilot-plant testing: (1) the filtration step, and (2) the use of a gasifier to produce synthesis gas and reduce the char associated with mineral residue leaving the filtration step and entering the gasifier.

Since the process is only now beginning to be pilot tested, it is still speculative whether the 0.6 percent sulfur level can be attained in the product in large quantities on a routine basis. If this can be done, then burning the solvent refined coal product in a power station would achieve a sulfur level of approximately 400 ppm SO_2 in the flue gas with no additional treatment (i.e., assuming 20 percent excess air for combustion). This would be equivalent to about 0.75 lb SO_2/MM Btu burned. Such a level would meet the current EPA standard of 1.2 lb SO_2/MM Btu. If the standard became more stringent, it is conceivable that the sulfur level in the product would have to be decreased. By way of comparison to flue gas desulfurization processes (3 percent sulfur coal with a heating value of 12,000 Btu/lb), the flue gas desulfurization process would have to remove 85 percent of the sulfur to achieve the 0.75 lb SO_2/MM Btu level attainable from burning the solvent refined product (i.e., from about 5 lb SO_2/MM Btu with no control when 3 percent sulfur coal is burned to 0.75 lb SO_2/MM Btu with the product).

CONSOL Synthetic Fuel Process

This process differs from solvent refining in that it seeks to produce a gasoline product. The initial extraction step is similar to that of the solvent refining process except that a mixture of the recycle solvent and hydrogenated recycle solvent is used instead of H_2 gas itself being introduced into the reactor. The complete results of the CCC work that relate to the dissolution step are given in the literature(21-23). The process can be modified to produce a solvent refined-type product.

The synthetic fuel dissolved coal plant would use a fixed-bed solvent extraction unit for coal dissolution and hydrogenation which might operate at approximately 1,500 psig and 750 F. An extract cooling and solidification system would also be necessary. No other major changes would be required. A schematic of the equipment is shown and the process steps are described in detail in the next section of this monograph where the process is considered for liquid fuels production.

The dissolved coal product from hydroclone solids separation would contain 0.9-3.2 percent undissolved solids or 0.7 to 1.25 percent ash. Filtration yields a product containing ≈0.2 percent, while filtration plus water washing will reduce the ash level to less than 0.1 percent. Sulfur from a 4.7 percent sulfur coal would be reduced to 1.85 percent. One comparison of solvent refined and synthetic fuel extracts both derived from Pittsburgh No. 8 seam coal, is given below:

Process	Solvent Refined Coal	Synthetic Fuel Process
Temperature, F	800	732
Pressure, psig	1000	400
Extraction Depth, percent moisture-ash-free coal	92.4	78.3
Pilot Plant	Spencer Bench-Scale	Cresap Run 55

Ultimate Analysis	Solvent Refined Coal	Synthetic Fuel Process
Hydrogen	5.21	6.03
Carbon	87.44	84.64
Oxygen	4.30	6.20
Nitrogen	1.83	1.28
Sulfur	1.22	1.85

University of Utah

The solvent extraction and desulfurization of coals by solvents has been studied by Hill and co-workers at the University of Utah as part of the OCR Project Western Coal.(24) This research involved the extraction of high volatile bituminous coal with the hydrogen donor solvent tetralin. Batch autoclave studies were conducted at 350-450 C and dissolution results were correlated with second order kinetics expressions. It was proposed that dissolution occurred after the solvent had diffused into the pores and was therefore initially diffusion limited. Decomposition of the solvent was observed at above 400 C and a mechanism model was proposed wherein thermal decomposition of the coal occurred concurrently with the reaction of the hydrogen donor solvent. Finally, it was proposed that the products from the thermal decomposition were stabilized by hydrogen from the solvent, thereby effecting a depolymerization of the coal.

Underground Liquefaction

The most recent and perhaps most novel approach to coal liquefaction has been proposed by researchers at the University of West Virginia.(25) Underground liquefaction has been suggested to obviate, among other things, many current mining safety problems. Coal solubilization proceeds most rapidly in a solvent that has a high boiling point, the ability to donate hydrogen, a relatively high dipole moment, heterocyclic atoms, and ring stability. Solvents tested have included various cuts of anthracene oil and a commercial motor oil (SAE 30).

Apparently when a solvent is applied to a coal formation, the coal imbibes the solvent and swells. Swelling is accompanied by a close association of coal and solvent, and a transfer of hydrogen to the cohesive structures between the micelles or microplatelets of the coal. The cohesive structure is weakened, the coal forms fragments, and the action of gravity or fluid turbulence removes it from the mine face.

Implications of this proposed mechanism appear significant when it comes to designing a possible remote mining system based on coal liquefaction. The dissolution of coal need not be limited by the programmed use of auxiliary water flooding in the mine. Water-oil liquids would then form the fluidizing medium for transporting coal to the surface where the fluids might be separated by commercial means and then reused.

Economic Evaluation of Solvent Refining. Cost estimates for solvent-refined coal were developed from information presented in the literature.(18) Process components shown in Figure 5 and listed in Table 4 were scaled up in capacity using an exponential power factor of 0.7. The Chemical Engineering plant cost index(26) was

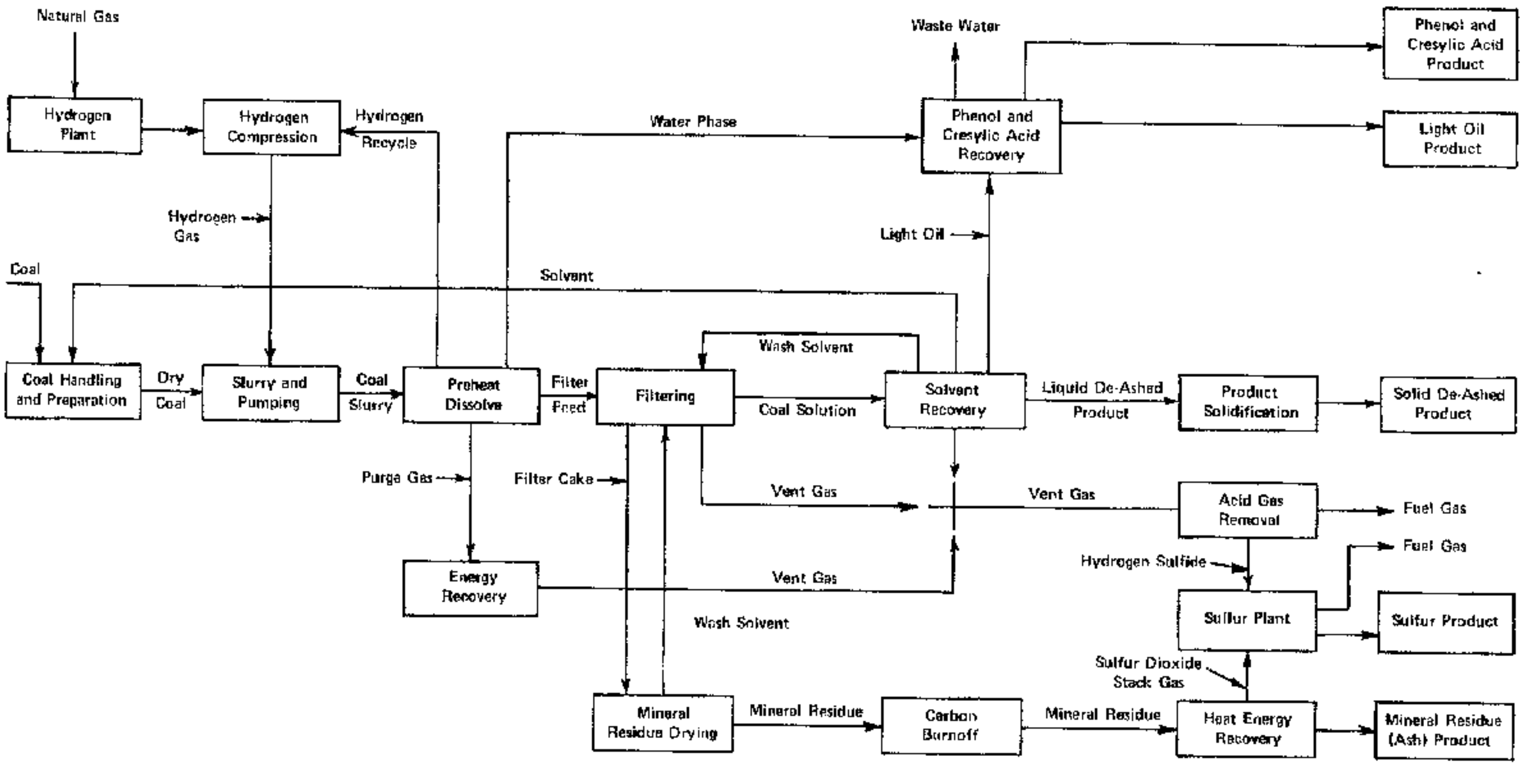

FIGURE 5. PROCESS DIAGRAM: CONCEPTUAL COAL DE-ASHING PLANT

TABLE 3. PARTIAL MATERIAL BALANCE FOR SOLVENT REFINED COAL PROCESS(23)

Coal Type	Coal to Process, lb/hr	Hydrogen[a] Req'd, lb/hr	Ash Produced, lb/hr	Sulfur, LT/day	Fuel Oil[b], lb/hr	Light Oil[c], lb/hr	Cresylic Acid[d], lb/hr	Phenol[e], lb/hr
1. Eastern, medium sulfur	999,381	13,066	89,354	122	75,953	92,942	39,975	9,994
2. Eastern, high sulfur	1,055,347	13,798	104,931	300	80,206	98,147	42,213	10,553
3. Central area, medium sulfur	1,147,116	15,000	102,636	145	87,181	106,682	45,884	11,471
4. Central area, high sulfur	1,199,257	15,682	119,322	347	91,143	111,531	47,970	11,993
5. Western, subbituminous	1,465,759	19,161	145,072	79	111,398	136,316	58,630	14,658

(a) 1.3079 lb hydrogen per pound of coal.
(b) Gas produced is 7.6 percent of coal input.
(c) Light oil produced 9.3 percent of coal input.
(d) Cresylic acids are 4 percent of coal input.
(e) Phenol produced is 1 percent of coal input.

TABLE 4. CAPITAL INVESTMENT FOR SOLVENT REFINING OF FIVE U.S. COALS
(In $ Millions)

	Base Case		1973 by Coal Type[a]				
	Capacity of Unit	1970 Price of Unit	1	2	3	4	5
Coal Handling and Prep.	833,333 lb/hr	6.038	8.18	8.50	9.01	9.30	10.70
Preheaters and Dissolvers	3 x coal rate	16.356	22.17	23.03	24.42	25.20	29.00
Mineral Separation	3 x coal rate	7.256	10.81	11.42	12.41	12.98	15.86
Solvent Recovery	2 x coal rate	7.817	10.59	11.00	11.67	12.04	13.85
Gas Recovery	63,308	0.371	0.50	0.52	0.55	0.57	0.66
Mineral Residue Processing & Storage	60,000 lb/hr (ash rate)	2.097	3.30	3.70	3.64	4.05	4.64
Product Solidification & Storage	488,376 lb/hr	3.873	5.36	5.36	5.36	5.36	5.36
Power Generation	Ash rate	11.897	18.76	21.0	20.67	22.97	26.35
Cooling Water System	--	1.969	2.35	2.35	2.35	2.35	2.35
Waste Water Treatment	--	1.374	1.64	1.64	1.64	1.64	1.64
Tank Farm	--	0.363	0.43	0.43	0.43	0.43	0.43
Hydrogen Plant	10,895 lb/hr	6.30	8.54	8.87	9.4	9.7	11.16
Sulfur Plant	233 LT/day	4.50	--	--	--	--	--
Acid Gas Removal Unit	233 LT/day	2.29	--	--	--	--	--
Phenol and Cresylic	41,650	0.75	5.15	9.67	5.81	10.70	3.8
Acid Recovery			1.02	1.06	1.12	1.15	1.33
Instrument & Service Air	--	0.11	0.13	0.13	0.13	0.13	0.13
Buildings	--	1.383	1.65	1.65	1.65	1.65	1.65
Site Preparation	--	0.360	0.43	0.43	0.43	0.43	0.43
Total		75.11	101.01	110.76	110.69	120.65	129.34

(a) Coal type numbers refer to Table 3.

used to update the costs to 1973. The key consumptions used in obtaining the size for each process unit are

1. The Btu in (coal) per Btu out (product) is fixed at 1.375.(18)
2. As given in Table 3, the production of fuel gas, light oil, phenol, and cresylic acids is a fixed weight percentage of the input coal.
3. The capacities of the base-case process components given in Table 4 and those computed for five coals given in Table 3 were used in scaleup.
4. The capacity of the processing plant for each of the coals is such that 603,000 lb/hr of solvent-refined coal (15,900 Btu/lb) are produced. This assumes that the same quality product is obtained from each of the coals.(18)
5. All light liquid produced was used to satisfy energy requirements.

The capital costs of solvent-refined coal for a 1000 MW power plant ranges from $\$101 \times 10^6$ to $\$129 \times 10^6$ and the operating cost ranges from $\$0.14/10^6$ Btu to $\$0.17/10^6$ Btu, depending upon coal type as shown in Tables 4, 5, and 6.

Catalytic Hydrogenation Processes

Hydrogenation processes were used in Germany and some other countries in the 1930's and 1940's for the production of liquid fuels from coal and coal tar.(17) At the beginning of the Second World War, Germany had a very large hydrogenation industry. The production of twelve German plants in 1943-1944 totaled 5.5 million tons of fuel, meeting one-third of Germany's petroleum requirements. Hydrogenation plants supplied about 50 percent of the automobile gasoline and diesel fuel and 90 percent of the aviation gasoline.

In Billingham in the United Kingdom, a hydrogenating plant for bituminous coal and coal tar had an annual production of 150,000 tons of liquid fuel. In Italy, two industrial coal-tar hydrogenation plants were built in 1936 with a combined annual production of 240,000 tons of liquid fuel. In 1942, a coal hydrogenation plant that produced 110,000 tons of gasoline and diesel fuel annually was put into operation in Korea. The Fischer-Tropsch process was also used extensively by Germany in World War II, primarily to produce intermediates for subsequent conversion to lubricating oils, soaps, edible fats, waxes, and detergents. At present, the only synthetic liquid-fuels-from-coal plant in commercial operation is the Sasol plant in South Africa. For the past 25 years it has been a prime source of gasoline in that country, but it is subsidized by the South African Government.

Prior to World War II, the principal source of organic chemicals and chemical intermediates was coal tar obtained as a result of producing coke for the steel industry. However, the tremendous growth in the use of aromatic compounds over the past 25 years has created a demand far beyond the production capabilities of known coal tar processes. In fact, at the present time only about 10 percent of the needed volume of aromatics is supplied by the industry. Obviously organizations interested in producing end-use products have had to look elsewhere for their raw materials. Fortunately,

TABLE 5. OPERATING COSTS OF SOLVENT REFINING OF FIVE U.S. COALS

($ Millions Per Year)

	Coal Type(a)				
	1	2	3	4	5
• Operating Labor (155 men and 413,000 man-hr $4.5/man-hr)	1.86	1.86	1.86	1.86	1.86
• Maintenance (3.5% of capital)	3.56	3.88	3.87	4.22	4.53
Labor 40%	--	--	--	--	--
Materials 60%	--	--	--	--	--
• Supervision (15% of labor)	0.49	0.51	0.51	0.53	0.55
• Indirect labor (15% of labor)	0.49	0.51	0.51	0.53	0.55
• Payroll Overhead (35% of payroll)	1.49	1.55	1.55	1.61	1.67
• Taxes and Insurance (2% of capital)	2.02	2.22	2.22	2.42	2.58
• Water Input (0.21 gal/ton coal at 12¢/1000 gal)	0.20	0.21	0.23	0.24	0.29
• Catalysts, Chemical, etc.	0.5	0.5	0.5	0.5	0.5
Total Operating	10.61	11.24	11.25	11.91	12.53
Credits (without sulfur)	(4.53)	(5.03)	(5.20)	(5.74)	(6.99)
Net Operating Cost	6.08	6.21	6.05	6.17	5.54

(a) Coal type numbers refer to Table 3.

TABLE 6. POSSIBLE CREDITS FROM SOLVENT REFINING OF FIVE U.S. COALS

($ Millions Per Year)

	Coal Type(a)				
	1	2	3	4	5
• Phenol (1¢/lb)	0.80	0.844	0.92	0.96	1.17
• Cresylic Acids(c) (0.5¢/lb)	1.6	1.69	1.83	1.92	2.34
• Sulfur(d) ($23/long ton)	0.93	2.3	1.11	2.66	0.61
• Power(e) (6 mills per kwh and 0.5 kwh per lb ash)	2.13	2.50	2.45	2.86	3.48
Total (excluding sulfur)	4.53	5.03	5.20	5.74	6.99
Total (with sulfur)	5.46	7.33	6.31	8.40	7.60

(a) Coal type numbers refer to Table 3.

(b) Chemical Marketing Reporter, October 6, 1973, gives a price of 10¢/lb for phenol. The reported credit, however, assumes a 1¢/lb selling price. This is based on a product coal price of about 63¢/MM Btu.

(c) Assumes that cresylic acids will sell for half the price of phenol or 0.5¢/lb.(18) The Chemical Marketing Reporter gives a selling price of 16¢/lb.

(d) Data from Davy Powergas Co., Lakeland, Florida.

(e) It was assumed that excess power produced is proportional to the amount of ash burned. The base case is 32,000 kwh/hr from a process handling 60,000 lb/hr ash.(18)

the petroleum industry, at least up to the present time, has been able to meet this tremendous demand. Even though crude oil is essentially aliphatic, refineries can produce aromatics by a process known as catalytic hydroforming. This is a complex process but essentially consists of the dehydrogenation of aliphatic crude and converting this intermediate into aromatic cyclic compounds such as benzene, toluene, and xylene. With the current shifts in fuel availability and with the petrochemical industry apparently receiving low or no priority for petroleum feedstocks, there is a possibility of catastrophic results to the plastics industry. It has been estimated that 1.6 million jobs in industries dependent on plastics would be lost if there were a curtailment of only 15 percent in the output of the petrochemical industry. Since only 5 percent of petroleum goes into petrochemicals, this industry is presently extremely vulnerable to small changes in availability of petroleum.

Because of the extreme structural complexity of organic and mineral matter in coal, it is difficult to provide a concise tabulation of the reactions which take place during the conversion of the coal to a refined product under the influence of H_2 and catalytic treatment. Nevertheless, some generalizations can be made with regard to the organic reactions.

Coal with a low degree of carbonization, such as brown coal and some black coal, with an H/C (atomic ratio) >1.08 are suitable for hydrogenation at 200-300 atm and 460-475 C over catalysts. Elevation of pressure up to 650-700 atm and temperature up to 470-490 C in the presence of a catalyst allows coal of a higher degree of carbonization (H/C between 0.78-1.08) to be hydrogenated. With further increases of the pressure up to 1000 atm and more, it will be possible to treat coals with a carbonization degree of H/C <0.78.

In the presence of a catalyst and solvent under high hydrogen pressure, the solid mineral fuel will generally swell with rise in temperature, melt completely, partially, or not at all, and be dispersed in the solvent. At 350-400 C, carbonaceous matter is decomposed with the formation of high-molecular substances having a high asphaltene content. Decomposition of the carbonaceous matter is accompanied by parallel and consecutive reactions of cracking, hydrogenation, depolymerization, and isomerization with the splitting off of the oxygen, nitrogen, and sulfur from the corresponding organic substances in the form of H_2O, NH_3, and H_2S.

With increase in temperature (450-480 C), the hydrogenation process advances with the formation of products of low and medium molecular weight from high molecular weight substances. The coal to be hydrogenated should not contain more than 6 percent ash; however, for brown coal the ash limit may be as high as 13 percent. Tar may be mixed with coal but should contain less than 0.1 percent solid and 0.1 percent H_2O. The higher ash content may have an adverse economic effect, clog, and/or abrade the equipment. No sand should be present in the mineral part of coal going to hydrogenation, as it is resistant to grinding in a ball mill and damages the piping and high-pressure equipment.

Low-temperature catalysts such as Pd, Pt, and Ni are easily poisoned in the presence of sulfur compounds. High-temperature catalysts such as molybdenum and tungsten sulfide are sulfur resistant. Low-temperature catalysts have much lower apparent activation energies but higher heats of adsorption of hydrogen. The concentrations of hydrogen and hydrocarbons on the metal surface decrease sharply as the reaction proceeds. Thus, the reaction rate may decrease at low pressure with rising temperature (250-300 C). For high-temperature catalysts, the concentration of hydrogen on the catalyst surface changes little due to lower heat of adsorption of hydrogen. As the cracking rate of paste oil during hydrogenation is 1.5-1.7 times higher than that of the final product, the control of contact time in the reactor may direct the hydrogenation toward the production of heavy or middle oil.

Although the hydrodesulfurization of petroleum distillates has been carried out industrially for years its chemistry is not well understood. Reaction chains are known for only a few reactants, and results are not easily generalized. Thiophene is desulfurized to butadiene before it is hydrogenated, while benzothiophenes in general are more rapidly hydrogenated than desulfurized. Rates of hydrodesulfurization vary with feed stock. In many feed stocks reactions are first order with respect to reactant concentration and in hydrogen partial pressure; reaction is inhibited by product H_2S and by strongly adsorbed hydrocarbons. Catalysts have been described in terms of two models: the intercalated sulfide model in which the catalytic sites for hydrogenation and possibly hydrodesulfurization involve W^{3+} ions adjacent to vacancies at crystal edges, and the monolayer model with catalytic sites involving Mo^{4+} ions octahedrally coordinated in a surface layer which is stabilized by the presence of promoter Co^{2+} ions located in tetrahedral sites of the underlying support.

Most of the current development activities on high temperature and pressure hydrogenation processes generally represent a combined pyrolysis and random catalytic approach typical of the industrial approach to the problem of petroleum refining prior to World War II. The challenge that remains is to devise more effective catalytic routes that offer better control and variety in the products that can be obtained by a direct dismemberment of the coal hydrocarbon structure. Success in this venture is not assured, but the returns would be great, and the effort must be made.

If one views the conversion of coal to be

$$\text{coal} \rightleftharpoons \text{asphaltent} \rightleftharpoons \text{oils},$$

the problem can be further identified as the slow conversion of asphaltenes. Weller(27) showed that the rate of coal hydrogenation to asphaltene at 400 C was 25 times the rate of hydrogenation of asphaltene. If the processes for coal hydrogenation proceed via production of such asphaltenes, then, clearly, the difficulties encountered in asphaltene hydrogenation (or reaction) must be solved. Defined in this way the problem becomes one of studying the reactions of coal and of asphaltenes.

The chemical constitution of asphaltenes is variable and only generally characterized. In bitumen, for example, extraction with large amounts of n-pentane (40 volumes) leaves a solid insoluble residue that is the asphaltene. Asphaltenes from Athabasca bitumen obtained in this way have a molecular weight in benzene of about 4850 and would represent molecules of at least 400 carbon atoms if other elements are ignored. Their characterization is complicated by the observation that molecular weights are lowered considerably in solvents with a higher dielectric constant (ϵ) than benzene. Thus, for example, in benzene ($\epsilon = 2$) the molecular weight is 4850, in methylene dibromide ($\epsilon = 7.8$) the molecular weight is 3430, and in pyridine ($\epsilon = 12.3$) the molecular weight is 2655. This is an important observation because it reveals the idea that, even if the molecules that make up asphaltene are chemically separate, interactions between them are strong enough in ordinary hydrocarbon media to make the product appear to be of high molecular weight. These interactions shield reactive sites against chemical attack by virtue of the difficulty of penetration of the asphaltene complex.

A similar effect of solvent polarity has been noted for coal dispersion and solvation.(28) Thus the effectiveness of a variety of polar solvents for dispersing and extracting coal species may be the result of hydrogen bonding between the solvent acting as a Lewis base and the acid sites of the coal structure. Interactions between catalyst and coal structures may be expected to have similar dispersing effects on the coal.

The coal structure from which such asphaltenes are derived can be reviewed as a series of laminae each of which is composed of a condensed aromatic ring structure joined by linkages of various sorts. A number of investigators have put considerable effort into a description of that structure (see reviews by Van Krevelan(29), for example). The coal structure envisioned consists of aromatic ring clusters generally no larger than 6 or 7 rings tied together by bridge linkages such as methylene chains of 1 to 4 carbon atoms, ethers, sulfides, disulfides, and biphenyl groups. Details of coal structure differ with the various investigations; the structure shown in Figure 6 is taken from the work of W. Wiser(30).

These linkages tend to produce a 2-dimensional structure that in some ways resembles graphite, but the individual aromatic sections are not necessarily co-planar. Objectives in seeking catalytic reactions of coal to produce fuels would appear to be as follows:

1. Rupture linkages to obtain the 6-7 ring structures as individual molecules (e.g., molecular weights of perhaps 300-500). For comparison, the initial product from dissolution and hydrogenation of coal currently has a molcular weight of several thousand.
2. Break the above aromatic clusters into about 2 or 3 fragments, thus obtaining molecules of 1 or 2 rings with a few alkyl groups attached. Rupture has been shown to proceed with model compounds such as anthracene by hydrogenation to form a hydroaromatic (e.g., tetralin-like) followed by hydrocracking of the hydrogenated ring. In such hydrocracking, one wants to hydrogenate and crack the "middle" rings so that benzene derivatives result. Catalysts are needed for these hydrogenation reactions.
3. Apply studies in direct support of process development to provide insight into the rate-controlling mechanisms for the various types of coals. Very little is known about reaction mechanisms of coal hydrodesulfurization or denitrification by catalysis or even in the absence of added catalysts. These studies should involve transport effects, diffusion, coal transformations, and catalytic effects of coal ash.

These envisioned processes are simple in concept and useful, but not readily achievable with the current technology. If one views the problem in the light of what has been presented thus far, the matter would stand approximately as follows.

Coal structures contain a number of reactive linkages which can be broken to produce relatively low molecular weight hydrocarbon fragments. However, because of cross linking between the laminae of that structure, these linkages are accessible to reaction only with difficulty. Indeed, the large amount of pore volume found in coal with diameters <12Å probably represents the narrow passageways between these laminae. These problems are carried over to the asphaltenes derived as primary products of of the hydrogenation of coal. For these reasons, many of the reaction routes for coal are apt to be transport limited and differences in available catalytic activity will be

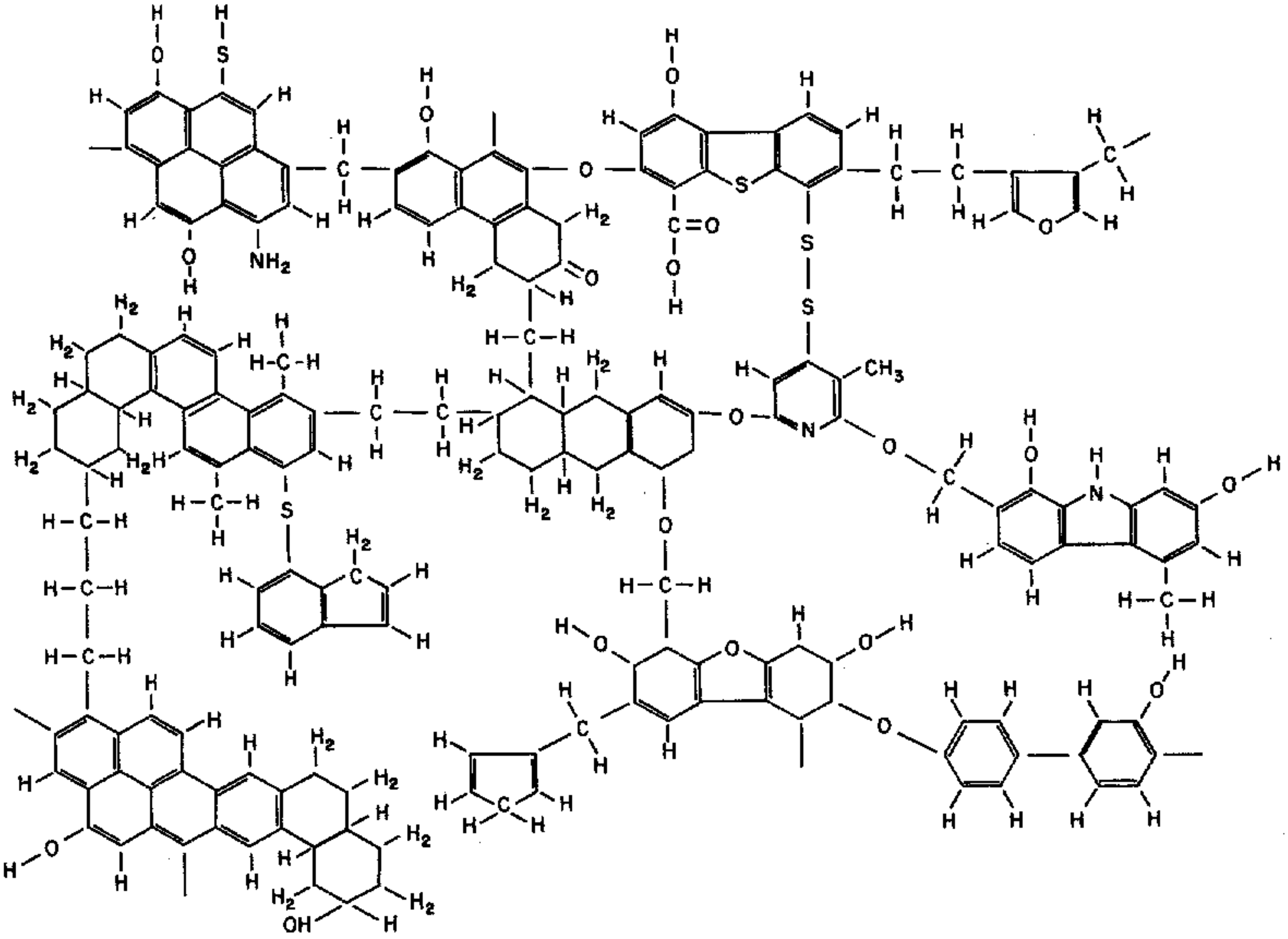

FIGURE 6. A REPRESENTATION OF BITUMINOUS COAL STRUCTURE(30)