FOREWORD

This monograph was prepared from results of one of several technical studies to help plan the R&D program of the Battelle Energy Program (BEP). BEP is publishing it with the hope that, as a technical survey, it may prove to be of interest to the scientific and engineering community that is involved with fuels and energy broadly, and particularly with liquefaction and chemical refining of coal. Portions of the original work, of interest only for their contributions to the operating procedures of the BEP, were deleted.

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LIQUEFACTION AND CHEMICAL REFINING

INTRODUCTION

Coal can be converted to clean liquid or solid fuels by five different processing operations which have been developed to various stages of feasibility over the past 100 years or so. The first involves treatment with an aqueous solvent to preferentially leach out harmful pollutants, such as sulfur, and leave a relatively clean solid carbonaceous residue. The second is a solvent refining process and consists of heating coal in an organic solvent, usually in the presence of hydrogen, to a temperature level just sufficient to dissolve most of the organic material in the coal. The solvent, dissolved coal, and undissolved residue are filtered, and the dissolved coal precipitated to produce a relatively low-ash and low-sulfur product resembling asphalt in appearance. A third classification involves hydrogenation to liquids by using temperatures, pressures, and contact times sufficiently severe to convert the majority of the coal to a material which is liquid at ambient temperatures. Ash is separated from the liquid by a suitable filtration or centrifugation operation. Hydrogen requirements are higher than for solvent refining, and catalysts are generally employed to accelerate the reaction. The fourth technology is a process wherein hydrogen and carbon monoxide (produced from coal) are recombined over a suitable catalyst at elevated pressures and temperatures to produce liquid fuels by the so-called Fischer-Tropsch or related reactions. Finally, suitable fuels can be produced by a fifth technology involving treatment in an inert atmosphere or in the presence of reactants for selective volatilization of sulfur or other impurities. These are called pyrolytic or carbonization processes.

At present, the problem of utilization of coal for the production by catalytic hydrogenation processes of liquid fuels and chemicals, and especially fuel for utility boilers is being discussed widely in Government, scientific, and technical circles. Governments are beginning to allocate considerable funds for basic and applied research on the use of coal as a raw material for various branches of industry. Investigations are being carried out in the United States, Germany, England, India, Japan, Poland, the USSR, and other countries. Interest has also broadened recently to include less severe noncatalytic hydrogenation processing, or the so-called solvent refining approach, to de-ash and desulfurize coal. In addition, there is widespread interest in chemical leaching to meet the pending air pollution regulations on utilities in the United States.

The information contained in this monograph and the conclusions and recommendations presented below result from an extensive review of this technology by analysis of the available literature; discussions with individuals from Government, industry, and the Battelle staff; and numerous personal visits to pertinent research and development facilities throughout the United States.

Technology Summary

Aqueous Leaching Processes

The major impurities of coal – sulfur and ash – are subject to attack by a variety of leachants and, thus, can be removed from the coal matrix. For example, pyritic sulfur can be extracted with aqueous acidic and alkaline solutions. At the present state of development, a significant portion of the organic sulfur can also be removed with alkaline leachants. The ash content (mineral matter) can be reduced to a low value by leaching with aqueous acidic solutions.

Although chemical leaching (cleaning) of coal is not now practiced commercially, significant effort is being devoted to the cleaning of coal prior to utilization as a fuel and for other applications. Those known to be investigating this avenue to a clean coal are TRW Corporation (TRW), Redondo Beach, California; Kennecott Copper Corporation (KCC), Lexington, Massachusetts; U.S. Bureau of Mines (USBM); Southern Research Institute (SRI), Birmingham, Alabama; Battelle's Columbus Laboratories (BCL), and some of the universities.

Several potential uses exist for the clean coal produced by the hydrothermal process. These include (1) use as a solid fuel and (2) as a raw material for the production of liquid fuels, gaseous fuels, metallurgical coke and specialty products.

Solvent Refining Process

In this process coal is ground and slurried in an initial solvent oil. The slurry is pumped through a heater to elevate the temperature and enhance solubility. A small amount of H_2 is introduced into the slurry prior to preheating to aid the solution process and stabilize the products formed. A portion of the organic sulfur in the coal unites with H_2 to form H_2S, which is later separated as a gas. The unutilized H_2 is recycled back to the preheater.

After the coal has been dissolved, the ash is separated by filtration or centrifugation, the pyritic sulfur leaves the process mixed with the other separated mineral matter, and the solution of coal is flash-evaporated to obtain recycle solvent.

The remaining hot liquid residue is discharged and cooled to form a hard, brittle solid of solvent-refined coal. Various shapes and sizes are possible, depending on the form of the mold. If balanced solvent operation can be maintained, the solvent-refined coal has viscosity characteristics which allow it to be handled as a hot liquid. Thus, if desired, the product could be melted and stored or shipped in heated tanks such as those used for asphalt tars. Another possibility is storage and shipment as a solid and use as either a liquid or solid.

Catalytic Hydrogenation Process

Liquefaction processes were in widespread use in former times and therefore this technology, albeit somewhat antiquated, is available, but needs to be optimized and improved. Many organizations, particularly the oil companies, have been or are becoming involved in planning and pilot-plant studies in this area.

There are several basic problems directly connected with the conversion of coal to liquids. For example, a major effort needs to be expended towards the reduction of the high cost of hydrogen. Also, a search should be made for more active hydrogenation catalysts that are long-lived and specific in their activity. It seems possible that by the choice of a proper catalyst, direct hydrogenation to hydrocarbons or hydration to alcohols can be accomplished. In the case of chemical by-products, it is rapidly being realized that if oil refineries put all of their production into fuels, a severe impact would be felt on the rest of the chemical industry, especially polymers. Since the organic constituents of coal are essentially aromatic, it is an ideal raw material source of chemical intermediates.

Fischer-Tropsch Synthesis

There are a fairly large number of organic and inorganic reaction possibilities in the Fischer-Tropsch and related syntheses. The balance obtained among those reactions that are possible is controlled by choice of reaction conditions and the catalyst used. Experience has shown that alcohol production by the Fischer-Tropsch process increases at the expense of hydrocarbon production as the pressure is increased in the range from about 10 to 150 atmospheres. It is believed that the terminal carbon at the growth end holds an OH group in its surface-complex configuration, and alternative routes for hydrogenation to desorb a hydrocarbon or alcohol are postulated. At a sufficiently high operating temperature (e.g., about 400 C) hydrocarbon yields above C_6-C_8 become unfavorable. If a suitable catalyst is used, the synthesis can be carried out at these higher temperatures to yield methane and low molecular weight hydrocarbons up to C_8. This concept is currently being reexplored; earlier efforts resulted in the process known as the isosynthesis.

Another alternative to be considered is the hydrogenation of CO_2. However, experience with various mixtures of H_2 and CO_2 or $H_2 + CO + CO_2$ indicates that this reaction system for production of hydrocarbons other than methane has a number of serious shortcomings.

The water-gas shift reaction occurs readily:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

over catalysts employed for Fischer-Tropsch and related reactions, and its velocity appears to increase with the concentrations of both H_2O and CO. For this reason CO_2 production is a common result in reaction systems where both reactants are present. However, a second reaction process, that of hydrocarbon synthesis,

$$3CO + H_2O \rightleftharpoons (-CH_2-) + 2CO_2 \quad ,$$

has been readily demonstrated and offers considerable merit for further investigation. The thermodynamic equilibria for this reaction are more favorable than for the Fischer-Tropsch syntheses. Catalyst selectivities for hydrocarbon synthesis versus the water-gas shift are good, especially for cobalt catalysts.

Although the reaction of water vapor with graphite to yield hydrocarbons is unfavorable at all temperatures of interest, the reactions of water vapor with coal may be anticipated to be far more favorable. Experimental evidence for the process is sparse, but a recent patent (USP 3505 204) indicates considerable success in converting carbonaceous materials, such as coal, bitumen, etc., to hydrocarbons and oxygenated materials using steam at 800 to 1200 F. The catalysts are alkali or alkaline earth compounds plus group 8 metal compounds.

Pyrolytic or Carbonization Processes

Major innovations in the production of coke and valuable by-products, i.e., tars, liquids, and gases, from coal by carbonization of coal were first developed in Germany. In more recent years, America has probably been leading in advancing the state of the art. Low temperature carbonization processes (heat treatment of coal at 840 to 930 F in the absence of oxygen) have been in use for more than 120 years. The most recent area of research, flash carbonization, was not mentioned in the literature until the early 1960's.

Numerous chemicals have been added to coal during pyrolysis in an attempt to selectively remove the sulfur, especially as it might relate to low-sulfur coke production. Technical success was limited and the cost of such a desulfurization process has been thought to be relatively expensive. However, because of the significant costs associated with the various means of control of emissions from utility fuels, these processes should be reexamined as a possible solution to the current environmental crises.

COST SUMMARY

The costs of operating the plants involved in the coal-liquefaction and chemical-refining modules were standardized to a total product heat output of 9.6×10^9 Btu/hr which is equivalent to the heat input required for a 1,000 MW power plant. Cost estimates were based on 1973 dollars and the costs were broken down into modular categories required for the computer model. The modules considered include hydrothermal processing, aqueous leaching using the TRW process, solvent refining, two typical coal hydrogenation liquefaction processes, Fischer-Tropsch synthesis, and methanol synthesis. The underlying philosophy in preparing the cost estimates was to make them as consistent as possible so that meaningful comparison between different modules could be made. Table 1 summarizes the expected costs for the liquefaction and chemical-refining modules using high-sulfur Eastern coal.

The purpose of the liquefaction and chemical-refining modules is to produce a clean fuel or synthetic petroleum from coal. These two objectives are somewhat interrelated since synthetic petroleum can be readily processed into clean fuel. The production of clean fuel from coal for firing in power-plant or industrial boilers must compete economically with stack-gas cleaning. The results of the cost estimates for the various modules indicate that solvent refining and liquefaction are more expensive than stack-gas cleaning for a 1000 MW boiler. As the boiler size or load factor decreases, solvent refining and liquefaction become more competitive because the resulting fuel can be divided for shipment to several boilers; on the other hand, a stack-gas cleaning module must be applied directly to the boiler so that economy of scale is lost and the cost is very sensitive to load factor. However, it appears that the boiler size would have to be fairly small, the equivalent of 10 MW or less, or the load factor fairly low, less than 30 percent, before solvent refining and liquefaction could compete with stack-gas cleaning. In the case of aqueous leaching and hydrothermal processing, the break-even point as compared to stack-gas cleaning appears to be considerably higher than the 10 MW boiler size or the 30 percent load factor. In fact, hydrothermal processing may be competitive with stack-gas cleaning on a 1000 MW base-loaded boiler. However, one must bear in mind that chemical refining still leaves a large

TABLE 1. EXPECTED COSTS USING HIGH-SULFUR EASTERN COAL[(a)]

Module	Capital Cost, 10^6 $	Operating Cost, ¢/10^6 Btu output[(b)]	Product
Selective oxidation	10 ± 5	3 ± 2	Low-sulfur coal
TRW process	47 ± 9	12 ± 3	Low-sulfur coal
Solvent refining	110 ± 28	15 ± 8	Low-sulfur, low-ash solid fuel
Hydrogenation process "A"	250 ± 62	37 ± 14	Synthetic crude (low sulfur)
Hydrogenation process "B"	203 ± 51	30 ± 11	Synthetic crude (low sulfur), naphtha, and fuel gas
Methanol synthesis	282 ± 70	66 ± 30	Methanol
Fischer-Tropsch synthesis	453 ± 114	100 ± 36	Gasoline, waxes

(a) Standardized to a total product heat output of 9.6×10^9 Btu/hr.
(b) Does not include cost of coal or cost of capital.

amount of organic sulfur in the coal so that in many cases it may not be possible to meet SO_2-emission regulations by this type of processing.

In short, chemical refining of coal appears to be best suited for non-base-load power-plant boilers or for industrial size boilers, and for coal having a low enough organic sulfur content to allow SO_2-emission regulations to be met. The opportunities for solvent-refined coal appear to be limited since it is more expensive than chemical leaching and is subject to similar limitations with respect to organic sulfur in coal. Solvent-refined coal has most potential for peak-load plants or small furnaces where the available coal supply has a relatively high amount of pyritic sulfur. The potential for coal liquefaction processes lies in the areas of producing fuel oil for residential and commercial space heating, gasoline for transportation use, and a feed stock for petrochemical plants.

One possible method for reducing the cost of removing pyritic sulfur from coal is to use preferential air oxidation at 340 to 450 C in a fluidized bed. The SO_2 concentration in the effluent gases can be increased for sulfuric acid or sulfur manufacture by successive recycling of the effluent gases over fresh charges of coal. It is estimated that if this process were carried out at the site of a new 1000 MW base-load power plant, the capital cost would be about $\$10 \times 10^6$ and the operating cost would be about $\$0.03/10^6$ Btu. These costs represent a large potential savings over the cost of chemical refining. The main problem associated with this process would be to obtain a reducing agent to convert the SO_2 to elemental sulfur. Alternatively, the SO_2 could be reacted with limestone at high temperature to produce gypsum for disposal.

A possible area for cost reduction in the solvent-refining and liquefaction modules is solid-liquid separation. Char solids are separated from coal oil by rotary drum, pressure filtration at temperatures above 150 C. This is a difficult and fairly costly operation so that other feasible separation processes may offer a potential cost savings. Some alternatives to filtration are centrifugation, flotation, and use of hydroclones. In some cases, it may even be feasible to leave the char solids in the fuel product; however, the problems related to further processing or combustion of a mixed solid-liquid product would have to be investigated. In any event, it is estimated that a costs savings of about 10 to 15 percent could be realized by eliminating the filtration step.

An alternative to burning pulverized coal in a boiler is to carbonize the coal to char at 480 to 540 C in a fluidized bed and recover the valuable tars, bitumens, and gases for use as raw materials in the chemical industry. The char would then be burned in the boiler instead of the coal. Since most of the sulfur remains in the char, stack-gas scrubbing would still have to be employed. It is estimated that the capital cost of carbonization is $\$80 \times 10^6$ and the operating cost is $\$0.30/10^6$ Btu based on a heat output of 9.6×10^9 Btu/hr for the char. A credit would be obtained for the chemical feed stock.

The production of methanol from coal appears to be competitive with the production of gasoline or distillate fuel oil from coal. It must be pointed out that hydrogenation liquefaction processes produce a synthetic crude oil which must be further refined to produce gasoline. Therefore, the costs of these modules are not directly comparable with the cost of the methanol module or the Fischer-Tropsch synthesis module. The economics of methanol production are important because it may be easier to produce methanol than CH_4 from synthesis gas and methanol can readily be used in place of gasoline and fuel oil. However, one must consider fuel distribution costs since the heating value of methanol is only 8600 Btu/lb.

An important cost factor in all coal hydrogenation processes is the production of hydrogen. Bituminous and subbituminous coal contains a hydrogen-to-carbon atomic ratio of about 0.8, while liquid and gaseous hydrocarbon fuels contain hydrogen-to-carbon atomic ratios ranging from about 1.4 up to 4. The hydrogen deficit is made up by conversion of steam through a shift reaction with carbon or CO derived from the coal. The economics of coal hydrogenation could be improved considerably if a cheaper method of hydrogen production from H_2O could be developed.

The cost of hydrogen production has important ramifications in the use of hydrogen as a general fuel or energy carrier. In a hydrogen fuel economy, hydrogen would have to be produced by the conversion of water either by reaction with coal or through electrolysis. Although reaction with coal is cheaper than electrolysis, it may be more expensive per 10^6 Btu than methanol production. Therefore, a methanol fuel economy may be more attractive than a hydrogen fuel economy.

TECHNOLOGY DISCUSSION

Coal is the major source of energy for the United States and will continue to be for many years. However, it has high sulfur, nitrogen, and ash content which includes significant quantities of toxic (hazardous) impurities such as mercury, beryllium, and arsenic. These materials find their way into the environment during the combustion of coal and thus constitute a health hazard through atmospheric and food-chain consumption.

Physical separation of these constituents from coal is not adequate since, at best, only a portion of them are removed. Furthermore, flue-gas scrubbing is not yet satisfactory as a means for sulfur and hazardous metals removal at the present stage of development of such systems. Since coal is our major source of energy and the quantity of low-sulfur coal is limited, new or improved technology must be developed for cleaning coal prior to combustion to supply the U.S. with a clean source of energy and, at the same time, reduce the pollution of our environment. This clean coal can be used directly as a solid fuel and as a raw material for producing gaseous and liquid fuels, metallurgical coke, and specialty products.

The three different classes of impurities – sulfur, nitrogen, and metal values – are found in coal in a variety of forms. Sulfur occurs chiefly in three forms: (1) inorganic, (2) sulfate, and (3) organic. A fourth form, elemental sulfur, is rare. Of the inorganic sulfur compounds, iron pyrite (FeS_2 with an isometric crystal form) and marcasite (FeS_2 with the orthorhombic crystal form) are the most common. Other inorganic sulfides, chalcopyrite – $CuFeS_2$, arsenopyrite – FeAsS, and stibnite – Sb_2S_3, have been found, but they are rare.

Of the two major inorganic sulfides, pyrite is the more common. It is found in coal as macroscopic and microscopic particles, as discrete grains, cavity fillings, fiber-bundles, and aggregates. The concentration of pyritic sulfur varies widely even within the same deposit. Normally, it will vary from 0.2 to 3 percent (sulfur basis), depending on the location.

The most prevalent sulfate sulfur is calcium sulfate. Sulfates of iron, copper, and magnesium may also occur, but they are not as common. Normally, coal contains less than 0.1 percent sulfate sulfur, although in heavily weathered coals, it may be as much as 1 percent. Because of its relatively low concentration, it is of little concern in air pollution.

The third most abundant form of sulfur in coal is organic. Since this sulfur is part of and is linked to the coal itself, positive identification of the organic sulfur compounds has not been possible. However, it is usually assumed that organic sulfur is in one of the following forms:

1. Mercaptan or thiol, RSH
2. Sulfide or thio-ether, RSR'
3. Disulfide, RSSR'
4. Aromatic systems containing the thiophene ring.

The sulfur could be present as δ-thiopyrone.

No definite relationship between the organic and pyritic sulfur contents of coal has been established. In U.S. coals, the organic sulfur ranges from 20.8 to 83.6 percent of total sulfur with a mean value of 51.2 percent. The variation of the organic sulfur content of a coal bed from top to bottom is usually small. Pyritic sulfur may vary greatly.

Nitrogen, like organic sulfur, is probably part of and linked to the coal. Eastern coals contain between 0.7 to 2.5 percent and average about 1.4 percent nitrogen.

Metal values make up the part of coal commonly referred to as ash and are generally present as sulfides and oxides. They are found in coal as macroscopic and microscopic particles, discrete particles, cavity fillings, and aggregates. Concentrations range from a few percent to 15 or 20 percent.

An alternative way to combat air pollution resulting from the combustion of coal or coal-derived fuels is to remove the pollutants prior to combustion and thus burn a clean coal or clean fuel. The problem is to produce coal or a clean fuel, i.e., a material containing low sulfur, nitrogen, and ash values. One approach to the problem is to chemically remove the impurities by converting them to a form which will facilitate their separation from the coal matrix. The final product would be a solid material containing essentially carbon, hydrogen, and oxygen. The impurities – sulfur, nitrogen, and ash – would be removed for subsequent use in other applications, stockpiled, or disposed of in an approved landfill.

Aqueous Leaching Processes

In theory, the chemical cleaning of coal appears to be achievable. For example, the pyritic sulfur may be removed from coal as water-soluble ferrous sulfate ($FeSO_4$) and elemental sulfur or water soluble sodium sulfide (Na_2S_2) according to the following reactions:(1)

$$FeS_2 + Fe_2(SO_4)_3 \rightarrow 3\ FeSO_4 + S_2$$

$$FeS_2 + 2NaOH \rightarrow Fe(OH)_2 + Na_2S_2$$

Since pyritic sulfur exists in coal as a phase distinct from the coal matrix, its extraction would be achieved without disturbing the coal structure.

Organic sulfur, believed to be part of the coal molecule, is not readily susceptible to attack by chemical leaching. Organic sulfur compounds such as the thiophenes found in coal are very stable and resistant to attack, while those such as the mercaptans are less stable and subject to attack. Thus, removal of organic sulfur from coal could involve the extraction of that portion of the coal which is combined with the sulfur, for example, the thiophenes. Or extraction of the organic sulfur may be possible by rupturing the carbon-sulfur bond to convert the sulfur to a more readily extractable form.

Ash (mineral matter) like pyritic sulfur exists in coal as a phase distinct from the coal matrix and is therefore subject to removal by a variety of leachants without disruption of the coal structure. However, since the ash is distributed throughout coal as fine particles, it may be necessary to add swelling agents to open the coal structure and make the ash more accessible to the leachant. Also, swelling agents may aid in the extraction of pyritic sulfur and the organic sulfur by making these forms more accessible to the leachant.

While chemical leaching of coal in aqueous media is not yet practiced commercially in the U.S., the use of this technology for producing a clean solid fuel is being studied by several companies. Included in the list of those who are currently studying or who have studied the use of aqueous media for producing a clean coal are

1. Battelle's Columbus Laboratories, Columbus, Ohio (BCL)
2. Systems Group of TRW, Inc., Redondo Beach, California (TRW)
3. Southern Research Institute, Birmingham, Alabama (SRI)
4. Pittsburgh Energy Research Center, U.S. Bureau of Mines, Pittsburgh, Pennsylvania
5. Kennecott Copper Corporation, Lexington, Massachusetts (KCC).

Although each of these companies is using a different approach, the overall objective is to produce a clean coal by removing as much of the sulfur, nitrogen, and ash as possible. A considerable amount of pertinent basic information is also available in the literature.

Chemical cleaning of coal as opposed to physical cleaning involves the separation of the impurities – sulfur, nitrogen, and ash, which includes the toxic or hazardous metal values – by treating or leaching the coal with a reagent to convert the impurities to a soluble form, generally water-soluble. Some of the impurities such as sulfur are removed as a gas, for example, H_2S.

Pyrite (FeS_2) is found in coal as discrete nodules and is, therefore, subject to attack by a wide variety of chemical reagents. These reagents are generally used in conjunction with elevated temperature coal-treatment processes.

Chemical methods for leaching the mineral matter from coal using aqueous solutions of HNO_3, Cl_2, HF and caustic have been reported to be successful.(2) One method employed molten caustic (Na/KOH in a ratio of 1:1) at various temperatures to dissolve pyritic sulfur from conventionally cleaned Pittsburgh steam coal.(3) In this work, complete removal of pyritic sulfur was achieved by treating 1 part coal (minus 40 mesh) with 4 parts of caustic at temperatures between 150 to 250 C. Below 150 C, no removal of sulfur was achieved. At temperatures between 250 to 400 C, the extraction was rapid, requiring approximately 5 minutes. Organic sulfur is not attacked in this system.

High-temperature steam-air treatment has been reported to be effective in reducing the sulfur concentration. The treatment of Rumanian and Indian coals resulted in sulfur reductions of 30 percent and approximately 57 percent, respectively. The addition of NH_3 along with the steam resulted in the removal of 88 percent of the sulfur from the Indian coals.(3)

The treatment of coal with aqueous solutions is effective for the removal of pyritic sulfur and, depending on the leachant, organic sulfur as well. Leaching of ground coal with aqueous solutions of $FeCl_3$ or $Fe_2(SO_4)_3$ at temperatures up to 130 C has resulted in the extraction of the majority of the pyritic sulfur.(4) By this process, pyritic sulfur is converted to sulfate and elemental sulfur. A continuous countercurrent leaching operation may be employed. The elemental sulfur is separated from the coal by vacuum distillation or extraction with a solvent such as toluene or kerosene. By-products from the process are elemental sulfur, iron oxide and iron sulfate.

Other treatments such as the following are said to decompose pyrites and might be useful in treating coals:(5)

1. Sodium bicarbonate and heavy metal carbonate in a closed system at 185 C
2. Steam at 300 to 400 C
3. Sulfur monochloride vapors at 140 C
4. Moist CO_2 at 250 C
5. Carbon tetrachloride at 250 C.

The use of chemicals in combination with somewhat higher temperatures has been found to be effective in reducing the sulfur content of coal; however, the final product is a "char" rather than coal.(6) For example, when 20- to 40-mesh size coal was treated for four hours at 1000 C in atmospheres of Na, CO_2, CH_4 or C_2H_4, approximately 50 to 60 percent of the sulfur was removed. Treatment with (1) water-gas removed 76 percent, (2) anhydrous NH_3 removed 82 percent, (3) H_2 removed 87 percent, and (4) steam removed 82 percent of the original sulfur present.

Since pyrite and mineral sulfides are not part of the coal matrix, they can, in theory, be considered sulfide ores and, thus, hydrometallurgical technology developed for treating sulfide ores should be applicable for treating the mineral sulfides in coal.

Methods for leaching inorganic sulfide ores can be divided into two groups: (1) in the absence of oxidizing agents and (2) in the presence of oxidizing agents.(1) In the absence of oxidizing agents, dilute acids dissolve some metal sulfides with the liberation of H_2S. For example, FeS_2 is slightly soluble in mineral acids to produce the corresponding iron salt and H_2S. Ferrous sulfide (FeS) is completely soluble in mineral acids. The resulting H_2S can be recovered in principle and converted to elemental sulfur.(7) Other sulfides which are soluble in mineral acids include CoS, ZnS, and NiS.

In the presence of oxidizing agents, pyrite as well as a number of other sulfides react to liberate elemental sulfur or soluble sulfate. For example, FeS reacts quantitatively with $Fe_2(SO_4)_3$ to produce $FeSO_4$ and elemental sulfur(8) whereas NaOCl converts pyrite to the corresponding sulfate. Elemental sulfur is not formed in the latter case. Other oxidizing media include HNO_3, nitrates, and O_2 in the presence of H_2O or other solvents such as aqueous NH_3 solutions.

Organic sulfur in coal is thought to be linked to coal itself and thus a part of the coal structure. It has been observed that the sulfur content of coal extracts is reduced by pressure-leaching of extracts with aqueous NaOH and ZnO at temperatures greater than 150 C.(9) The alkali-soluble material from the extraction of a Pittsburgh seam coal with NaOH contained 1.16 percent sulfur.(10) Leaching Illinois No. 5 and Lower Kittaning coals with p-cresol removed 10 to 50 percent of the organic sulfur.(4)

In addition to the sulfur contaminants, most coals contain a high concentration of ash ranging from a few percent to 20 to 25 percent. This ash is composed of aluminum, silicon, and iron compounds, along with a large number of minor metal compounds containing arsenic, mercury, lead, nickel, cobalt, etc. These materials are found in coal as macroscopic and microscopic particles, as discrete particles, cavity fillings, and aggregates, and they constitute the fly ash and bottom ash from power plants and other facilities using coal as a fuel.

The use of other ferric salts such as $Fe_2(SO_4)_3$ has resulted in the removal of approximately 10 percent of the ash from coal.(4) The USBM further reduced the ash content of an Illinois No. 6 coal which had been leached in caustic from 9.8 to 0.7 weight percent by treating the leached coal with HCl at ambient temperature.(11)

Leaching may also be achieved with other reagents. For example, the mineral (ash) matter was leached from coal using aqueous solutions of HNO_3, Cl_2, and HF.(2) In another study, the ash content of a low-sulfur coking coal was reduced from 0.76 percent to 0.28 percent by heating coal in an aqueous caustic soda paste at 120 atmospheres and 250 C for 20 minutes. Sulfur trioxide content was also reduced from 0.008 to 0.0015 percent.(12)

Nitrogen, like organic sulfur, is believed to be part of and linked to the coal. Therefore, the removal of nitrogen from coal must be achieved by chemical cleaning rather than physical cleaning.

Until recently, little emphasis has been placed on nitrogen removal. However, since there is some evidence that nitrogen oxides (NO_x) may be atmospheric pollutants, efforts are being directed toward the development of methods for the extraction of nitrogen as well as sulfur and ash values from coal. Apparently, nitrogen is subject to extraction from coal with weak organic and strong inorganic acids.(13) In one case, up to 90 percent of the nitrogen was extracted by heating coal in 85 percent H_3PO_4 at 100-150 C.(14)

Biological processes may also be of interest in aqueous treatment systems. Bacteria are divided into two classes: (1) autotrophic – organisms that live on inorganic matter, and (2) heterotrophic – organisms that live on organic matter. Autotrophic bacteria use atmospheric CO_2 as their sole source of the carbon necessary for generation of cellular growth. The organism has adapted itself to live and grow in a strongly acidic environment (pH 1.5-3) and in the presence of many heavy metal ions which are usually extremely toxic to most other forms of life. Some bacteria also convert sulfides to sulfates and sulfates to sulfides; others oxidize H_2S to sulfur and nitrogen to nitrates.

The reduction of sulfur in coal by the employment of bacterial action to oxidize and remove pyrite represents a specialized form of chemical beneficiation which has been reported in detail in a recent publication.(15) This research demonstrates that by immersing coal in acidified water (pH 3.5) containing Ferrobacillus ferrooxidans bacteria and by raising and maintaining the water at room temperature conditions for four days, considerable pyrite reduction can be achieved. Approximately 50 percent was removed from a Kentucky No. 11 coal while 47.1 to 76.2 percent reduction was achieved (in all but a few tests) with Pittsburgh coal which was treated in a more acidic, bacteria-laden water of pH 2.6. The desulfurization of subbituminous and lignite coals did not respond as well to the preceding treatment as the bituminous coals with the result that modifications to the procedure were necessary. Therefore, these coals were rinsed with acid and washed with water to cleanse the surfaces of acid-consuming carbonates and other basic materials which retarded bacterial action. Next, in order to supplement and restore the leached-out iron content to approximately the same levels that existed in the untreated coal, $Fe_2(SO_4)_3$ was added to the acidic, bacteria-laden water to assist oxidation and desulfurization. Using this procedure, it was possible to bring on substantial pyrite reduction in the problem coals with the result that more than 80 percent of the pyrite was removed in some tests.

This research also showed that desulfurization of coal using bacteria is easiest with bituminous followed by subbituminous and lignite coals. Ease of desulfurization improves as the coal particles being treated become finer.

Ferric Salt Leaching

Two bench-scale experimental programs, one program for the removal of pyritic sulfur and one for the removal of organic sulfur have been conducted by TRW under U.S. Environmental Protection Agency (EPA) sponsorship.(6) Current plans call for piloting of the pyritic sulfur process. Future plans for the organic sulfur removal program are not known.

For pyritic sulfur removal, the process involves leaching of coal with aqueous ferric salt solutions ($Fe_2(SO_4)_3$ or Fe_2Cl_3) at temperatures of 50 to 130 C, pressures of 1 to 10 atmospheres, residence times of 1 to 16 hours, and top coal sizes from 1/4 inch to 100 mesh. Results show approximately 95 percent removal of pyritic sulfur from four coals. In addition, leached coal had a lower ash content and a higher heat content than raw coal. However, in some cases pyritic sulfur was converted to an iron sulfate which was not water soluble and remained with the leached coal product. Removal of this iron sulfate was achieved by leaching the product with dilute H_2SO_4.

The overall TRW process is shown in Figure 1. Basically, it involves leaching of raw coal with an aqueous $Fe_2(SO_4)_3$ solution to remove the pyritic sulfur as a mixture of iron sulfate and elemental sulfur. The majority of the iron sulfate is soluble and is removed in the leach liquor, whereas the elemental sulfur is insoluble and is removed with the leached coal product. The leached coal product is washed to remove any remaining soluble iron sulfate and is then leached with an organic solvent to remove the elemental sulfur, after which the product is washed with water and dried. The leachant is regenerated in situ by conducting the leaching under an overpressure of oxygen or the pregnant liquor is removed from the reactor and regenerated with oxygen in a separate step. By-products from this process are iron sulfates and elemental sulfur.

Products obtained from leaching of lower Kittaning coals were reported to have the following composition range:(4)

Total sulfur, % - 1.26-3.23
Organic sulfur, % - 0.66-0.95
Sulfate sulfur, % - 0.11-1.48
Pyritic sulfur, % - 0.12-2.48 .

The raw coals contained:

Total sulfur, % - 4.32±0.10
Organic sulfur, % - 0.67±0.12
Pyritic sulfur, % - 3.59±0.17
Sulfate sulfur, % - 0.06±0.03 .

On this basis, overall extraction of sulfur ranged from 25 to 70 percent. The highest total sulfur removal of 70 percent was attained at a temperature of 85 to 102 C and an extraction time of 15 hours. At higher temperatures and shorter leaching times, for example 130 C and 2 hours, approximately 50 percent of the total sulfur was extracted to give a product containing approximately 2.5 percent sulfur.

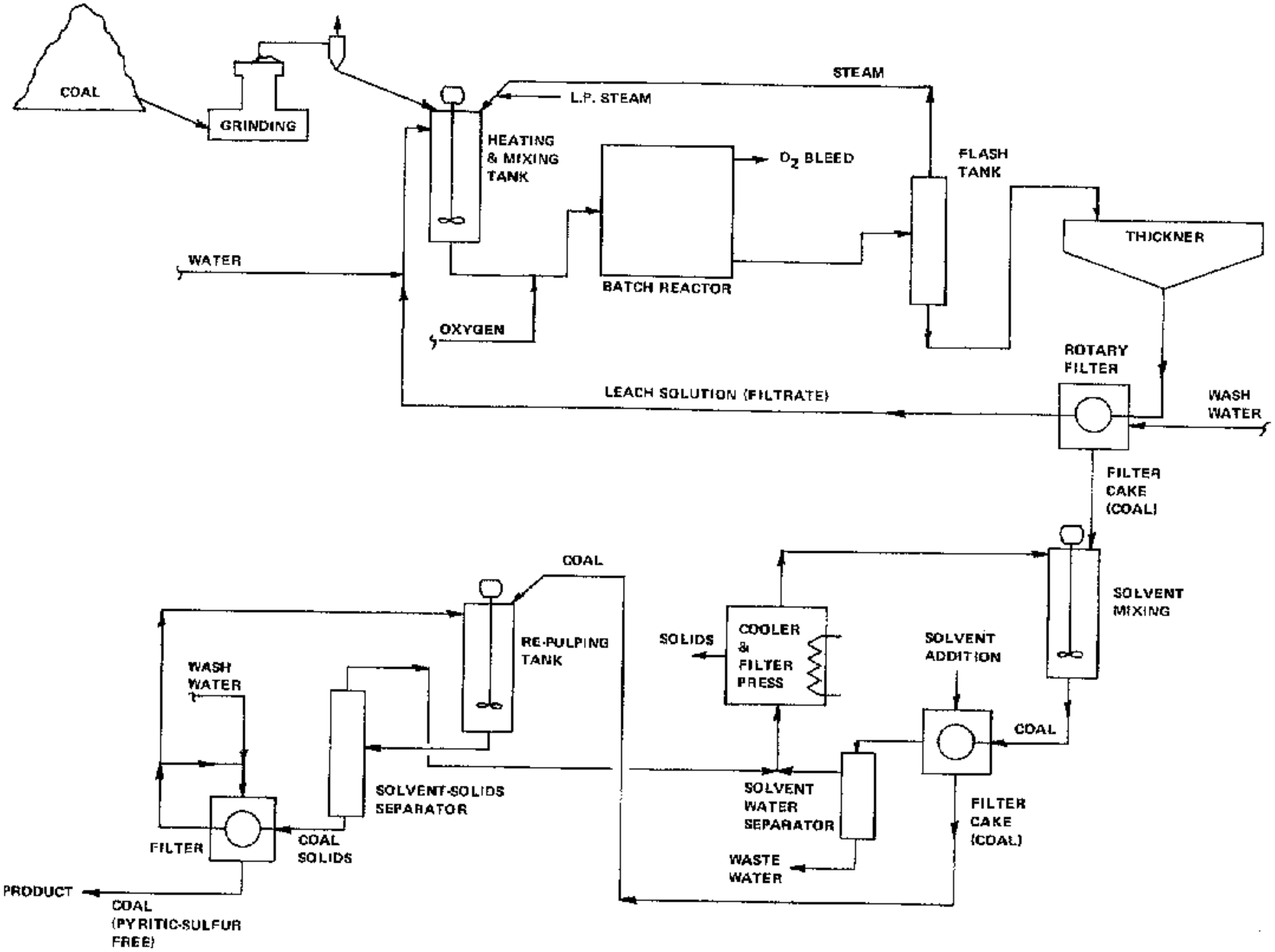

FIGURE 1. CONCEPTUAL PILOT PLANT FOR PYRITIC SULFUR REMOVAL BY THE TRW PROCESS

A limited study has been conducted by TRW on the extraction of organic sulfur. In this study, slurries of the coal and an organic solvent were heated near the boiling point at atmospheric pressure to effect dissolution of the organic sulfur. Of the solvents studied, p-cresol appears to be the most efficient solvent. Approximately 10 to 50 percent of the organic sulfur can be extracted by heating a slurry of coal and p-cresol at 200 C for one hour. Solvent retention appears to be a problem and is dependent on initial coal moisture content and coal-drying conditions. The lowest solvent retention value attained was 2.6 weight percent.(4)

Southern Research Institute Process

This process involves the treatment of coal with steam and air at pressures of 150 to 200 psi and temperatures up to 120 C.(16) This program has resulted in establishing the feasibility of removing the pyritic sulfur as H_2S; the organic sulfur was not removed by this process.

U.S. Bureau of Mines Process

The USBM Pittsburgh Energy Research Center, Pittsburgh, Pennsylvania, has conducted a limited program on hydrothermal processing of three coals Illinois No. 6, Elliot mine coal, and Indiana No. 5. In this program, the coals were treated at 225 C for 2 hours using a 10 percent NaOH aqueous solution as the leachant. In some cases, the hydrothermally leached coal was treated further by an acid leach at ambient temperature.

The USBM reports that the pyritic sulfur is removed by NaOH treatment.(11) Leached coal has a somewhat higher ash content than the original coal. However, if the NaOH treatment is followed by an acid leach, most of the ash is removed. For example, an Illinois No. 6 coal contained 9.7 percent ash and 1.1 percent pyritic sulfur; the leached coal contained 0.7 percent ash and 0.1 percent pyritic sulfur. The yield of coal was 91.5 percent. Similar results were obtained with Indiana No. 5 coal. The depyriting-leaching procedure usually increased the heating values of the coal and the free-swelling index changed only slightly. Little or no organic sulfur was removed.

Kennecott Copper Corporation

No data are available on this process. However, the company may be using metallic oxides as sulfur getters.

Solvent Refining Processes

Coal extraction was studied in Germany even before Pott and Broche pressure-extracted coal with tetralin-cresol mixtures. Early extraction experiments of soluble coal constituents were made at the Reutgerswerke (Teichmann).(17) The anthracene oil fraction of bituminous coal was used as a solvent. Unde and Pfirrmann evaluated this method industrially in 1921, extracted at low pressures 35 to 40 percent as soluble constituents from coarsely crushed bituminous coal and separated the insolubles by centrifuging. They used a specially prepared bituminous coal-tar oil as a solvent.

The dissolved substances were not separated from the solvents which were used commercially for a long time as a cheap newspaper printing ink.

Berl and Schildwaechter were the first to use tetralin as the extraction solvent. M. Pott and H. Broche used similar means in their exhaustive work for a maximum extraction of the coal substance.(17) The younger, oxygen- and bitumen-richer bituminous coals were particularly suitable for extraction. The method is universally applicable to brown coals, which could be extracted more readily and efficiently.

The current U.S. coal liquefaction or extraction processes can be classified either as solvent refining or hydrogenation processes. The solvent refined coal programs of the Office of Coal Research (OCR) and SRI, and the dissolved coal variation of the CCC synthetic fuel process are in this first group; the H-coal, USBM, Gulf and other catalytic processes fall into the second category and are reviewed in the next section of this monograph.

The theory for the action of the solvent in the solvent refining process was that the coal is depolymerized by the influence of cresols and heat. The four loosely bound hydrogen atoms in tetralin are available to stabilize the decomposition radicals, preventing them from repolymerizing into higher molecular weight coke. The hydrogen donor action of tetralin provides a means of introducing hydrogen into the system without the presence of gaseous hydrogen. Naphthenic and paraffinic compounds such as decalin or decane are unsuited, as the hydrogen atoms are too tightly bound. Middle oils from the hydrogenation process are good replacements for the more expensive tetralin since they also contain a large percentage of partially hydrogenated aromatics and are more akin to the molecular structure of the parent coal.

A general rule in the extraction of material from solid carbonaceous fuel is that extraction temperature must be below the decomposition temperature of the material. By consecutive stepwise extraction, various residues may be separated. The optimal extraction temperature range is about 390-405 C. Above this temperature, cracking of organic matter of coals begins and the amount dissolved decreases. Solvation increases under hydrogen pressure due to partial hydrogenation.

The use of condensed compounds having aromatic and hydroaromatic rings or hydroaromatic and phenol rings increases the liquefaction of coal. For hydrogenation of coal, the residue of hydrogenation products boiling above 300-320 C makes an excellent solvent.

Pott-Broche Process

In the process initially used by the IGF dried coal was dry ground to 95 percent minus 100 mesh, 65 percent minus 250 mesh in a ball mill, then mixed with a 20 percent cresol-80 percent tetralin solvent in a 2:1 solvent-to-coal ratio.(17) This slurry was then pumped to a preheater where the temperature was raised to ≈800 F at 1460 to 2200 psig. One hour contact time was sufficient to dissolve approximately 75 percent of the moisture-ash-free coal (Ruhr Bituminous - Volatile Matter ≅ 28 percent). Undissolved residue consisted of refractory bitumen, fusain, and inorganic material. A schematic flowsheet is shown in Figure 2.

After dissolving, the solid-coal-solvent slurry was filtered through ceramic cartridge filters 1.3 inches thick in a batch operation. Four thousand batches could be

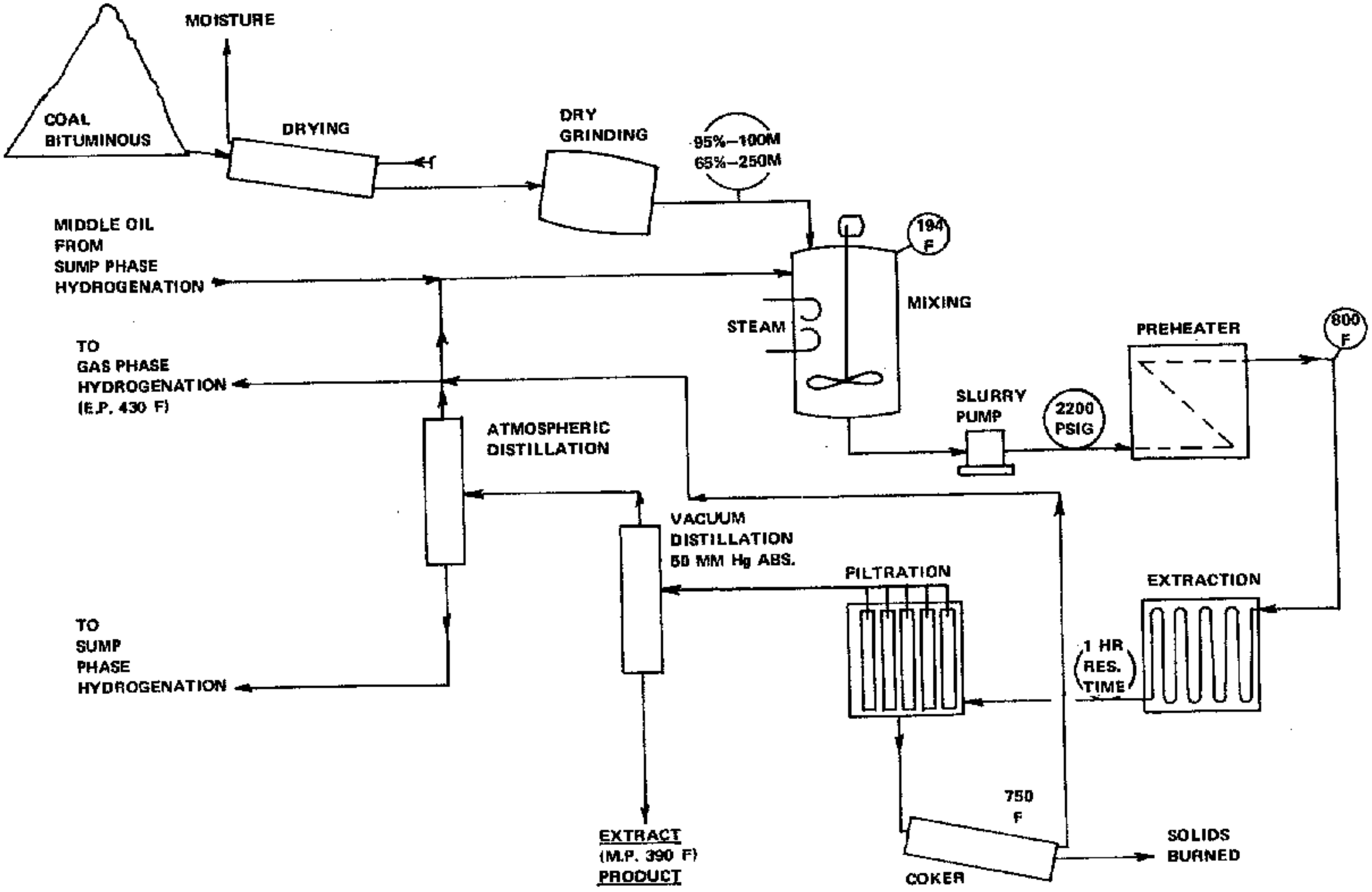

FIGURE 2. POTT-BROCHE PROCESS GERMAN COMMERCIAL PRACTICE