COAL LIQUEFACTION: MATERIALS SYSTEMS DESIGN

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INTRODUCTION

The development of viable commercial coal liquefaction methods is a national high priority objective. The Energy Research and Development Administration - Fossil Energy (ERDA-FE) has a prime responsibility for achieving this objective. The Ralph M. Parsons Company is assisting ERDA in its program.

This paper will describe objectives and typical current technology for the coal liquefaction program, with emphasis on the importance of selection and development of adequate construction materials for use in large coal liquefaction plants, which could be in operation in the 1980s.

A prime incentive for development of coal liquefaction technology is the use of coal, our most abundant fossil fuel, to supply our liquid fuel needs. Conversion of coal to liquid form will reduce its sulfur content to make it more acceptable environmentally, while converting it to a form in which it can be more readily used in industrial, residential/commercial, and transportation applications. Since it will be expensive to liquefy coal, a key objective is the development of large, simple, minimum-cost plants.

Economic analysis shows required product selling prices to be highly sensitive to fixed capital investment. It follows that proper selection of economically acceptable materials must be a prime element of a successful liquefaction development program.

Liquid fuels currently dominate U.S. energy consumption. In 1974, approximately 45 percent of U.S. energy was consumed in liquid form.[1] Transportation is heavily dependent on liquids and currently consumes approximately 25 percent of our total energy, and about 55 percent of our liquid fuels.[2] These consumption patterns are important, in view of our increasing dependence on imported crude oil to supply these liquids - and in view of the fact that conversion of a significant percentage of industrial, residential/commercial, and transportation usage from oil to alternate fuel forms represents a time-consuming and expensive operation. As a result, production of usable equivalent <u>liquid</u> fuels from indigenous coal resources deserves consideration, since no conversion of consuming machinery would be needed.

OBJECTIVE

The prime objective of this paper is to define major material problem areas for coal liquefaction plants and to suggest solutions to these problems.

Additonal objectives include: To provide information to assist the materials community to define and develop preferred materials for use in liquefaction plants; also to present recommendations for elements of a development program to assure that economically viable materials are available when large coal liquefaction facilities are required.

PARSONS ROLE

The Ralph M. Parsons Company is actively assisting ERDA in its program to develop viable commercial plants for the conversion of coal to clean fuels. There are two distinct parts involved in this role:

(1) Preliminary design services in which Parsons develops preliminary conceptual designs and economic evaluations for commercial coal

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conversion plants. Examples are (1) a demonstration plant to produce approximately 25,000 barrels per day of clean boiler fuels[3] and (2) a commercial complex to produce approximately 28,000 barrels per day of syncrude plus 830 megawatts of electrical power by COED-based coal conversion.[4] In each of the reports describing these designs, recommended materials for all major equipment items are presented.

Parsons will also develop conceptual designs for a Fischer-Tropsch plant to be responsive to U.S. requirements, an Oil/Gas plant, a coal-oil-gas (COG) multiproduct facility, a commercial solvent refined coal (SRC) facility and a multiunit demonstration facility. Each of these designs will include captive coal mines.

As part of these design services, Parsons does parallel support work to define materials, environmental, and equipment development requirements. The result of these support activities are incorporated into the designs.

(2) Parsons also supplies technical evaluation contractor services to assist ERDA in monitoring certain of the liquefaction development programs.

HISTORY

Coal liquefaction is not new; it has been, and is being practiced industrially. Germany produced most of its aviation gasoline from coal during the later stages of World War II. The major portion of this production was done by coal hydrogenation. The materials available and the knowledge existing then was limited when compared with todays materials availability and accumulated corrosion

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experience. Germany's materials problems were severe, but the plants still produced approximately 80,000 barrels of liquids per day. A summary of their materials experience has been published.[5]

The Fischer-Tropsch indirect liquefaction technology was also used in Germany and has further been used since 1955 in the SASOL Plant in the Republic of South Africa, which is reported to have an 85 percent operational availability record.[6] Question: Why not adopt the liquefaction technologies that have been practiced in other areas of the world? The answer appears to lie in the fact that in the U.S. economy the technology must be economically competitive, and therefore, synfuel plants should be large, efficient, simple, and reliable. If U.S. development program objectives are achieved, the plants will differ significantly from earlier versions and embody modern contributions of all disciplines, including improved materials and materials applications.

PROGRAM ELEMENTS

FUNDING

The importance ascribed to the national coal liquefaction R&D program can be illustrated by the level of expenditures. Figure 1 shows that ERDA expenditures began to rise sharply in fiscal 1974, and are estimated to be of the order of $90 million in fiscal 1976.[7] The sharp acceleration in funding support for this program is therefore quite recent.

FACILITIES

Let's look at the size and number of facilities available for development efforts now, and those conceived for the future. In the order of increasing size, these facilities may be classified as process development units (PDUs),

pilot plants, and demonstration plants, all leading to commercial plant designs. Several PDUs are now operating in the U.S. These include the Clean Coke units located at Monroeville, Pennsylvania, operated by U.S. Steel; and the Project Lignite Unit located at Grand Forks, North Dakota, which is operated by the University of North Dakota. The PDUs are designed to process about a half ton of coal per day and constructed value may be $1-2 million.

Three ERDA pilot plants have been, or are being, operated. These include the Cresap, West Virginia unit to test a donor solvent extraction process, which was operated earlier by Consolidation Coal Company, and which will be operated in the future by Fluor. A second one is the COED pyrolysis pilot plant, which was operated by FMC Corporation from 1970 to early 1975 at Princeton, New Jersey. An ERDA Solvent Refined Coal (SRC) pilot plant is located at Fort Lewis (Tacoma), Washington, operated by the Pittsburg and Midway Coal Mining Company, a Division of Gulf Oil. A smaller SRC pilot unit is located at Wilsonsville, Alabama and funded jointly by the Electric Power Research Institute (EPRI) and Southern Services. The ERDA pilot plants were designed to process from 20 to 50 tons of coal per day and would each have a current constructed value in the range of 15 to 25 million dollars. They are large enough to use equipment considered to be of commercial size for chemical and petrochemical operations. From the pilot plant, the next step will be to a demonstration scale plant. The Coalcon hydropyrolysis demonstration plant will be designed to process 2600 tons of coal per day and is expected to be worth approximately $240 million constructed value. The current concept for commercial coal liquefaction plants is that they will process 10,000 to 40,000 tons per day of coal and be in the billion dollar class. Target dates for startup of the commercial plants are in the 1980s.

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COORDINATION OBJECTIVES

A major liquefaction development program objective is the parallel development of all elements required to assure reliable performance of the commercial scale plants. This includes process, materials, environmental, instrumentation/control, equipment, safety and hygiene, and the many other disciplines required to contribute to the complex technology which can result in coal conversion facilities such as those illustrated in Figure 2. A primary objective is to maintain communications between the separate disciplines as progress is made in each category - and most importantly, to agree on cooperative development objectives.

In the field of materials selection/development, several approaches are apparent. One is to define the hostile environments that exist in coal liquefaction plants and select preferred plant components from available materials. An alternative is to define the materials problems and performance requirements for the materials components required to solve these problems, followed by independent development programs to create improved materials to be available when required. Conceivably, these materials may represent different alloy compositions used in conjunction with revised equipment design approaches. They would therefore require cooperative development efforts between process, equipment, and materials disciplines. Our discussion today is thus an important part of the program to achieve these mutual development goals.

LIQUEFACTION TECHNOLOGY

Current liquefaction processes under development in the U.S. may be somewhat arbitrarily aligned into the four classifications which are shown in Table 1. In the hydroliquefaction process, a slurry of coal in a coal-derived liquid is

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contacted with a hydrogen-rich stream at elevated temperatures and pressures, which effectively increases the hydrogen to carbon ratio of the coal feed stock, and produces liquefaction.[8] The hydroliquefaction can be conducted either with or without an added hydrogenation catalyst. A second type of process is extraction, in which a hydrogenated coal-derived liquid contacts the feed coal at elevated temperature and pressure to extract a major portion of the carbonaceous coal constituents.[9] The hydrogenated coal-derived liquid serves as a hydrogen carrier to the extraction stage, which can be operated at a lower pressure than the hydroliquefaction process.

A third type is pyrolysis in which feed coal is heated to an elevated temperature to produce a gas, a tar, and a char.[10] The char may be gasified to produce a mixture of carbon monoxide and hydrogen, known as syngas, which in turn can be used as a feedstock for SNG, ammonia, methanol, or liquid hydrocarbon production; the gas can also be used as fuel for electric power generation. The tar can be hydrotreated to produce a low sulfur syncrude.

The fourth type is indirect liquefaction in which the feed coal is gasified to produce a syngas, which is purified and then reacted to produce liquid products. This is the Fischer-Tropsch technology.[11]

A key point is that every coal liquefaction plant incorporates a gasification operation. The reverse is not true; i.e., a plant to produce substitute natural gas (SNG) from coal does not necessarily include companion liquefaction operations. In a sense then, liquefaction technology development represents a broader scope challenge to scientific and engineering communities than gasification.

MATERIALS APPLICATION - DEVELOPMENT

Let's next look at representative materials exposure conditions for the liquefaction sections for each process classification, define key problem areas, and summarize how these material selection problems might be handled. Examples of operating conditions for the coal conversion steps for these four classes of processes are shown in Table 2.

HYDROLIQUEFACTION

Key process steps for one version of a hydroliquefaction process are shown in Figure 3. Typically, the dissolving or liquefaction coal conversion step may take place at about 800-850°F and 1500-2000 psig.

A general current problem is erosion/corrosion of equipment when handling coal slurries. This problem can be severe. To illustrate, it has been said by coal conversion plant operators that they have not found a commercially available pump to perform satisfactorily for extended periods when pumping coal slurries.[12] Another problem is pressure letdown valve service for process slurries after the liquefaction step. Here, the experience in the German coal hydrogenation plants, which were operated at higher pressures than the U.S. processes, was that pressure letdown valves had an operating life of 500 to 1500 hours.[13] Current U.S. pilot plant experience also indicates a similar modest life span but with evidence that 2000 hours is currently attainable with proper use of tungsten carbide trim.

With regard to prediction of attack by erosion/corrosion, relatively little is known of the mechanisms of these phenomena. The little data available have been primarily derived from empirical test results, and the analysis of successes or failures of materials in service. For some noncorrosive services,

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the relationship between a substance's size, speed, hardness, etc., and its erosive effects on a particular material have been partially quantified, but there remain differences in opinion in the field. Current expertise does not enable us, from a description of the environmental conditions alone, to predict material loss with reliability from erosion or erosion/corrosion effects. For a reliable design basis, the present state-of-the-art requires materials exposure experience under actual or simulated operating conditions. For example, Figure 4 illustrates damage that can be caused in a coal slurry piping application. Here, only minor erosion has occurred in areas where streamline flow existed; but severe erosion is shown at the turbulent area caused by the internal gap of a socket weld.

A number of materials have been tested in pilot plant pumps handling coal slurries. Materials tried include carbon steel, 300-series stainless steels, Ni-hard, and coated carbon steel. Coatings have included chromium, ceramics, plastics, elastomers, and hard surfacing materials such as the fused coatings containing nickel, chromium, boron and silicon. The pumps have performed moderately well in many cases; for instance, we understand that service lives of the order of 700 to 2000 hours have been achieved. However, none has proven entirely satisfactory.

To illustrate the type of attack that can occur, Figure 5 shows erosion effects in a pump which handles a slurry consisting of 10-15 percent solids.

Proper mating of materials and design considerations is necessary in slurry centrifugal pump applications. A low speed, of the order of 1500 rpm, will tend to reduce erosion as will use of a pump with proper head-volume charac-teristics. Careful attention should be given to impeller and volute geometrical

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design. For longer term development, the desired materials would have the following characteristics: easily castable; weldable; small grain size; capable of maintaining an erosion resistant smooth surface; resistant to high temperature, high pressure H_2S/H_2 environments; immune to stress corrosion cracking; and inherent material toughness and ductility.

An area of original concern in the SRC pilot plants was the slurry preheater, where the feed coal slurry and hydrogen are heated from approximately ambient temperature to 800°F in helical coils. The performance of this three-phase mixture is still being studied. The Wilsonville coil is made of Type 316 stainless steel, and the Tacoma unit is made of Incoloy 800. The current status is that both coils are still successfully in operation; Wilsonville currently has more than 350, and Tacoma more than 300 days of operation on their respective coils. It is important to note that a commercial scale plant will use a design and flow pattern different from the helical coils currently used in the pilot plants, and therefore, will pose new problems for this multiphase slurry preheat application.

There have been erosion problems on the pilot plant scale in check valves for the coal slurry plunger feed pumps to the high pressure dissolver section. The solution has been a combination of materials selection and valve design. It currently appears that use of a spherical, hardened chromium-steel ball on a tungsten carbide seat provides adequate performance. Check valve life was increased from periods as short as four hours to as long as 1600 hours. Of note is that the Black Mesa pipeline has been successfully operating for a number of years while pumping water/coal slurries to pressures in this same range.

There have also been problems in materials in the product recovery section; specifically, in fractionating columns and reboilers. Failures have occured with carbon steel U-tubes in reboilers distilling intermediate coal-derived fractions at temperatures in the range of 400-700°F. The reboiler tubes were replaced with Type 304 SS. Also, fractionating trays made of Type 410 SS failed in about 150 days at temperatures of the order of 600°F. These have been replaced by trays of Type 304 SS construction.

The dissolver, where the coal slurry is hydrogenated, is exposed to a corrosive environment. To date, the Tacoma pilot plant dissolvers of 2-1/4 Cr - 1 Mo material weld overlaid with Type 347 SS have operated sucessfully. The potential troublemakers in dissolvers are sulfur compounds, hydrogen, and such other compounds that may be present as indicated in Table 2. These factors are discussed below.

Sulfur and Sulfur Compounds

Coal, especially that found in the Eastern part of the United States, contains substantial sulfur. During processing, this sulfur is converted to hydrogen sulfide (H_2S) which becomes increasingly corrosive to carbon steel at temperatures greater than 450-550°F. Hydrogen (H_2) is also present. Here we can draw upon the experience of petroleum refineries, which have had extensive experience with H_2S corrosion at temperatures from ambient to about 1000°F, and operating pressures to 3500 psi.

The combination of H_2S and H_2 is particularly troublesome because the 5 Cr-1/2 Mo and 9 Cr-1 Mo steels commonly used to resist moderately high temperature sulfur and sulfur compound corrosion show little improvement over carbon steel in corrosion resistance to H_2S/H_2 atmospheres. A chromium content of at least

12 percent is required. The 300 series of austenitic stainless steels (minimum 18 Cr-8 Ni) have excellent resistance and are normally specified for the H_2S/H_2 environments found in petroleum refineries. Extensive corrosion data and experience have been developed with various stainless steel materials in H_2S/H_2 atmospheres at temperatures to about 1000°F. Figure 6 illustrates corrosion rates of several materials for various H_2S/H_2 conditions.[14]

At temperatures between 800°F and 1550°F, the austenitic stainless steels experience a tendency to precipitate carbides (sensitization) along grain boundaries. In the case of process upsets, it is conceivable that the dissolver temperature could exceed 850°F. This sensitization tendency may be mitigated by reducing the amount of carbon initially present, or by tying up the carbon by adding small amounts of strong carbide-forming elements (stabilization) such as columbium, tantalum, or titanium. Welding and fabricating problems are increased by the alloying additions, and a reduced carbon content, though beneficial, does not eliminate the possibility of polythionic and chloride cracking problems at low temperatures.

Petroleum refinery experience has demonstrated that although the austenitic stainless steels are suitable to resist high temperature H_2S during operation, they may be susceptible to stress corrosion cracking when the plant is shut down. Therefore, strict precautionary shut-down procedures, which includes circulation of protective solutions, must be followed during down time to prevent cracking. In large equipment, such as pressure vessels, where such procedures are impractical, the vessels are not made of solid stainless steel, not only because of cost, but also to prevent catastrophic failure of the vessel because of cracking. Clad or weld overlay construction is recommended

because the polythionic and chloride cracking phenomena are not known to propagate into the commonly used ferritic alloy backing materials.

Hydrogen Attack

Hydrogen at temperatures and pressures greater than 450°F and 200 psi, respectively, will cause carbon steel to decarburize, to form methane at internal interstices and the resulting internal pressure to form blisters and failure of the steel. Adding molybdenum and chromium as alloying additives suppresses this tendency because of their strong carbide-forming characteristics and allows these alloys to be used at higher hydrogen pressures and temperatures. Molybdenum is also particularly beneficial in improving creep and stress-rupture strengths.

Figure 7 shows the operating limits of carbon steel, carbon molybdenum steel, and the chromium molybdenum alloys in a hydrogen atmosphere.[15] These materials are commonly used as the pressure retaining material for equipment experiencing metal temperatures to about 1000°F. These empirical curves are based on more than 50 years of experience in cases where failures and successes have occurred. These curves are currently being maintained and updated by the American Petroleum Institute Committee on Refinery Equipment for Corrosion.

All of the above factors will be recognized in selecting commercial scale equipment items, such as the dissolver, in SRC technology.

Chlorides: Stress Corrosion Cracking

Chloride concentrations in the range of 100 parts per million can be expected in the dissolver with a companion moisture content in the range of 1.5 weight percent. To date, there are no reported problems with stress corrosion

cracking in the SRC pilot plants. However, the Project Lignite Process development unit (PDU) located at Grand Forks, N.D. has suffered catastrophic failure of its 316 SS preheater and, general stress corrosion cracking in the high pressure area when processing lignite in an SRC-type process. Chlorinated hydrocarbons had been used to clean some of the equipment prior to failure. Analysis indicated the cause of failure was chlorides. A conclusive explanation of the mode of chloride failure in the PDU is being sought in view of the successful materials performance record of the pilot plants.

EXTRACTION PROCESS

Extraction Step

A brief sketch of the process is shown in Figure 8, with conversion/extraction conditions given in Table 2.

Processes utilizing coal extraction, where hydrogen is transferred to the coal by a donor solvent, experience most of the problems previously described for hydroliquefaction. The fact that initial extraction takes place at a lower pressure; i.e., about 400 psig, reduces the material requirements at that stage for resistance to high pressure/temperature H_2 attack relative to the hydroliquefaction process. Extraction processes do encounter the slurry handling problems, pressure reducing valve erosion, and sulfur compound corrosion; and the potential for chloride stress corrosion cracking of austenitic steels described in the hydroliquefaction section of this paper.

A number of material and engineering problems were defined during operation of the Office of Coal Research (OCR) sponsored Consol Synthetic Fuel (CSF) pilot plant program during the period 1963 to 1970. Illustrations of the results of this program are summarized in the following paragraphs.

Centrifugal pumps handling slurries with an initial service life of 80 to 100 hours were coated with an electrodeposited hard chrome plating; this increased their service lives more than 400 percent. In another case, hard chrome plating was applied to the bottom of hydroclones used for solid liquid separations from a slurry containing approximately 50 percent solids. The objective was to eliminate a spiral wear pattern, which appeared noticeable after approximately 100 hours of operation. After plating, 1800 hours of service were obtained.

Ni-hard pump components have been used with some success in slurry systems, but because of their brittle nature are suspect in case of fire and dousing with water.

No really satisfactory materials/designs were defined to give long maintenance-free life for valves in slurry service. Ball valves are used at lower temperatures and open port construction is preferred. For control valves, tungsten carbide has been the most successful material for seating surfaces. However, for pressure letdown valves, where the pressure drop is several hundred or even thousands of pounds, even tungsten carbide can be destroyed within 500 hours of operation, although, as described earlier, current experience indicates proper materials procedures can give operating lives to 2000 hours. Considerable differences in performance are obtained based on the method of forming the tungsten carbide valve seat. A needle type seat can be used with the flow reversed from normal practice.

Because of the critical nature of valve performance in coal conversion plants, a program to develop improved valves is underway at the ERDA facilities at Morgantown, West Virginia. Additional work to investigate materials for

improving valve performance is underway at Bureau of Mine's units located at College Park, Maryland; Rolla, Missouri; and Albany, Oregon; and also at Battelle Laboratories in Columbus, Ohio, under EPRI sponsorship.

Hydrogenation Step

Hydrogenation of coal extract was designed to operate at pressures up to 4000 psig and temperatures in the range of 775-850°F in the presence of hydrogen and a catalyst. The reaction takes place in a reactor in which the catalyst and coal extract mixture is maintained in a fluidized or ebullient state.

Two equipment items are critical: The reactor and recirculating pumps. Type 347 SS was used for the contact metal for the hydrogenation reactor in the pilot plant. It performed satisfactorily during the very limited operating time it had, which was too short to provide a meaningful test of performance. Here again, the factors described under the hydroliquefaction section of this paper regarding performance in contact with H_2S-H_2 mixtures, plus othe components, would be considered during design of commercial units. Currently, we would suggest 2-1/4 Cr - 1 Mo reactor weld overlays with Type 347 or 308L stainless steel.

For large reactor units; i.e., demonstration or commercial scale plants, the technology for large pressure-retaining reactors; e.g., approximately 10 feet in diameter and 40 feet long, with a wall thickness of about 12 inches and operating at temperatures of 850°F has been fairly well-established for hydrocracking process reactors in the petroleum industry.

On pumps: Although some successful experience was obtained with canned pumps to provide the ebullating bed effect at the Cresap Pilot Plant, it appears that more experience is needed in material performance to assure reliable operation in commercial scale units at 3000 psi and 850°F.

PYROLYSIS

A block flow diagram for a COED-based pyrolysis plant is shown in Figure 9 and reaction conditions have been summarized in Table 2. The results of materials testing in the pilot plant[16] and current recommendations for materials in a commercial plant[4] have been published.

In COED pyrolysis, coal is heated in fluid bed reactors in successive stages over a temperature range of 600 to 1100°F at a pressure of 10 psig. Char gasification can take place at temperatures up to 1800°F. No serious material problems were experienced at the COED Pilot Plant during the course of its operation in 1970-74 at Princeton, New Jersey. For a commercial unit, the higher temperature char gasification vessels would be refractory-lined carbon steel.

The hydrotreating process used for the coal oil produced in pyrolysis is similar to that used for first-stage hydrocracking of petroleum stocks in the petroleum industry, with the exception that the operating conditions are more severe. No serious materials problems occurred in the pilot plant. The potential problems previously discussed concerning sulfide corrosion and hydrogen attack would apply here, and again, a Type 347 SS weld overlay design should be satisfactory.

INDIRECT LIQUEFACTION

A block flow diagram for a version of a Fischer-Tropsch indirect liquefaction plant is shown in Figure 10 and the synthesis, or liquefaction reaction conditions have been summarized in Table 2. The coal gasification section, which is a major part of a Fischer-Tropsch plant, is outside of the scope of this discussion.

Material problems for the liquefaction section of a Fischer-Tropsch plant are not severe, because the feed to this unit is a mixture consisting largely of carbon monoxide and hydrogen, which is produced by gasification and gas purification. The particulate matter and sulfur values have been removed, so it presents characteristics similar to those encountered in petrochemical operations.

In summary, the material technology for the process conditions is considered adequate; greatest experience rests with SASOL in the Republic of South Africa, who has 20 years of experience with Fischer-Tropsch technology.

RECOMMENDATIONS

A great deal of information and experience exists in the field of materials for coal liquefaction plants. Facilities can be designed now which will produce liquid fuels from coal. However, a prime objective remains to further improve the reliability and economics of these capital-intensive plants. The materials community can make significant contributions to these improvements. Recommendations for consideration in shaping future development programs include:

    (1) Establish a priority list of coal liquefaction materials problems, plus explicit objectives for separate materials development program tasks.

(a) This priority list is to result from a careful cost/benefit

analysis of the predicted impacts of design and operation

using existing materials vis-à-vis projected improvements.

(b) Expected high priority objectives, to be confirmed by the

cost/benefit analysis results, are:

- Develop long-life slurry pressure letdown valves.

- Develop high-capacity, long-life centrifugal coal

slurry pumps.

- Develop economical and reliable connections for pipe

and flanges handling high-pressure coal-derived solu-

tion and coal slurries.

- Develop practical nondestructive examination techniques

for determining safety and reliability of operating

liquefaction equipment.

(2) Assure that a materials testing and reporting program is an integral

part of each coal liquefaction process development unit (PDU) or

pilot plant program. Suggested elements include:

(a) Insertion of materials test coupons in each major vessel,

plus periodic analysis and reporting of the test results.

(b) Periodic inspection of each vessel, major pipeline run,

rotating equipment, and other major equipment items for

erosion and/or corrosion attack. Quantitative measure-

ment of rate of attack should be reported.

(c) Establish a separate maintenance and materials performance

record for each major piece of equipment and report this as

an integral part of the development record.

(d) Conduct a failure analysis for those units which fail.

     Report these analyses through a central reporting agency.

(3) For major materials application development program tasks (see
Item 1 above) establish independent supporting programs on laboratory
scale where practical.

(4) For defined problems where existing materials and design procedures
fail to provide satisfactory operating life, define the characteristics
of new materials required, and establish a program to develop and
test them by 1980.

(5) Define and activate multidisciplined equipment development programs,
which pool the knowledge and contributions of materials, process,
project, and equipment specialists. An example is the development
of improved centrifugal pumps for coal slurry service. The improve-
ment can well involve mating a preferred combination of design,
materials, and process parameters.

SUMMARY AND CONCLUSIONS

Ample incentives exist for development of a commercial U.S. coal liquefaction
industry. Coal oil has been produced industrially outside of the U.S.,
proving that it can be done.

A significant coal liquefaction development program is now underway in the
U.S. ERDA-FE has a lead role, and The Ralph M. Parsons Company is assisting
in this program. Selection and development of satisfactory materials are a
key part of this program. Plants can be designed now to liquefy coal. Because
these plants are capital intensive, and the required product selling price is
highly sensitive to required capital investment and plant operating reliability,

there is a strong incentive to select economical materials. In many cases, the best choice will include a combined optimization of materials, equipment design, and process factors.

Examples of four classifications of coal liquefaction processes, as well as materials requirements problems for key coal conversion steps, have been defined. Defined problems include:

o Erosion/corrosion effects when handling and pumping coal slurries.

o Pressure hydrogenation at elevated temperatures in a hostile environment, including the presence of hydrogen, hydrogen sulfide, and other contaminants.

o General erosive problems in slurry piping and handling applications.

o Fabrication and closure problems for large pressure vessels.

o Stress corrosion cracking potential.

Suggested actions regarding these and other problems include:

o Establishment of a priority list of materials problems based on a cost/benefit analysis.

o Establishment of test programs to develop improved coal slurry centrifugal pumps and slurry pressure letdown valves (preferably in conjunction with ongoing pilot plant operations).

o Continuous monitoring of pilot equipment to establish suitability of materials, such as Type 347 SS weld overlays for coal dissolving and coal oil hydrogenation applications.

- Expansion of the program of insertion and analysis of performance of materials, test coupons in major vessels, and product separation/recovery equipment.

- Continuous testing of types of piping design and vessel closures.

We suggest that the overall materials development program be centrally coordinated and the results published frequently. Additional specific recommendations have been made for program elements, to assure the availability of proper materials for use in large plants, which potentially may be built in the 1980s.

LITERATURE CITED

(1) Energy Perspectives, U.S. Department of the Interior, pp. 36, 39, February 1975.

(2) Ibid.

(3) O'Hara, J. B. et al., "Demonstration Plant - Clean Boiler Fuels from Coal - Preliminary Design Details," Vol. I; "Preliminary Design Details," Vol. II; "Preliminary Design/Economic Analysis," Vol. III, R&D Report No. 82, Interim Report No. 1, Prepared for the United States Department of the Interior, Office of Coal Research.

(4) O'Hara J. B., Crawford, C. L., Hincks, H. F., and Mills, E. A., "Commercial Complex, Conceptual Design/Economic Analysis, Oil and Power by COED-Based Coal Conversion," R&D Report No. 114, Interim Report No. 1, Prepared for the Energy Research Development Administration, September 1975.

(5) Wu, W. R. K. and Storch, H. H., "Hydrogenation of Coal and Tar," U.S. Bureau of Mines Bulletin 633, 1968, pp. 157-166.

(6) Tisdall, G. C., "SASOL Operating Experience in Large Scale Pressure Gasification."

(7) Energy Digest, February 5, 1975, p. 480.

(8) Pastor, G. R., "Solvent Refined Coal - A Pilot Plant Report," Presented at 1975 Joint Power Generation Conference, Portland, Oregon, October 1975.

(9) The Ralph M. Parsons Company, "Feasibility Report, Consol Synthetic Fuel Process," Office of Coal Research R&D Report No. 45, 1968.

(10) Scotti, L. J. et al., "Multi-Stage Fluidized-Bed Pyrolysis of Coal at the Project COED Pilot Plant," Presented at the American Institute of Chemical Engineers (AIChE) Meeting, Pittsburgh, Pennsylvania, June 1974.

(11) O'Hara, J. B., Bela, A., Jentz, N. E., and Khaderi, S. K., "Fischer-Tropsch Plant Design Criteria," Presented at the 68th Annual Meeting of the American Institute of Chemical Engineers (AIChE), Los Angeles, California, November 19, 1975.

(12) Roberts, H. L., SASOL, "Oil from Coal, The Engineering Challenge."

(13) Wu, W. R. K. and Storch, H. H., op. cit., p. 185.

(14) Sorell, O. and Hoyt, W. B., "Collection and Correlation of High Temperature Hydrogen Sulfide Corrosion Data," Corrosion, 12, 213t-234t, 1956.

(15) "Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants," API Publication 941, First Edition, July 1970.

(16) Jones, J. F. and McMunn, B. D., "Materials Performance in Coal Pyrolysis and Coal Oil Hydrotreating," paper given at Corrosion/73 Forum, Anaheim, California, March 19-23, 1973.

Table 1 - Process Classification

Classification	Example
(1) Hydroliquefaction	
(a) Noncatalytic	Solvent-refined coal (SRC), Clean Coke
(b) Catalytic	Synthoil, H-coal
(2) Extraction - Donor solvent	CSF (CRESAP), Exxon
(3) Pyrolysis	
(a) Direct	COED, Garrett
(b) Hydropyrolysis	Coalcon, Clean Coke
(4) Indirect Liquefaction	Fischer-Tropsch

Table 2 - Liquefaction Processes

Example Operating Conditions
Coal Conversion Steps

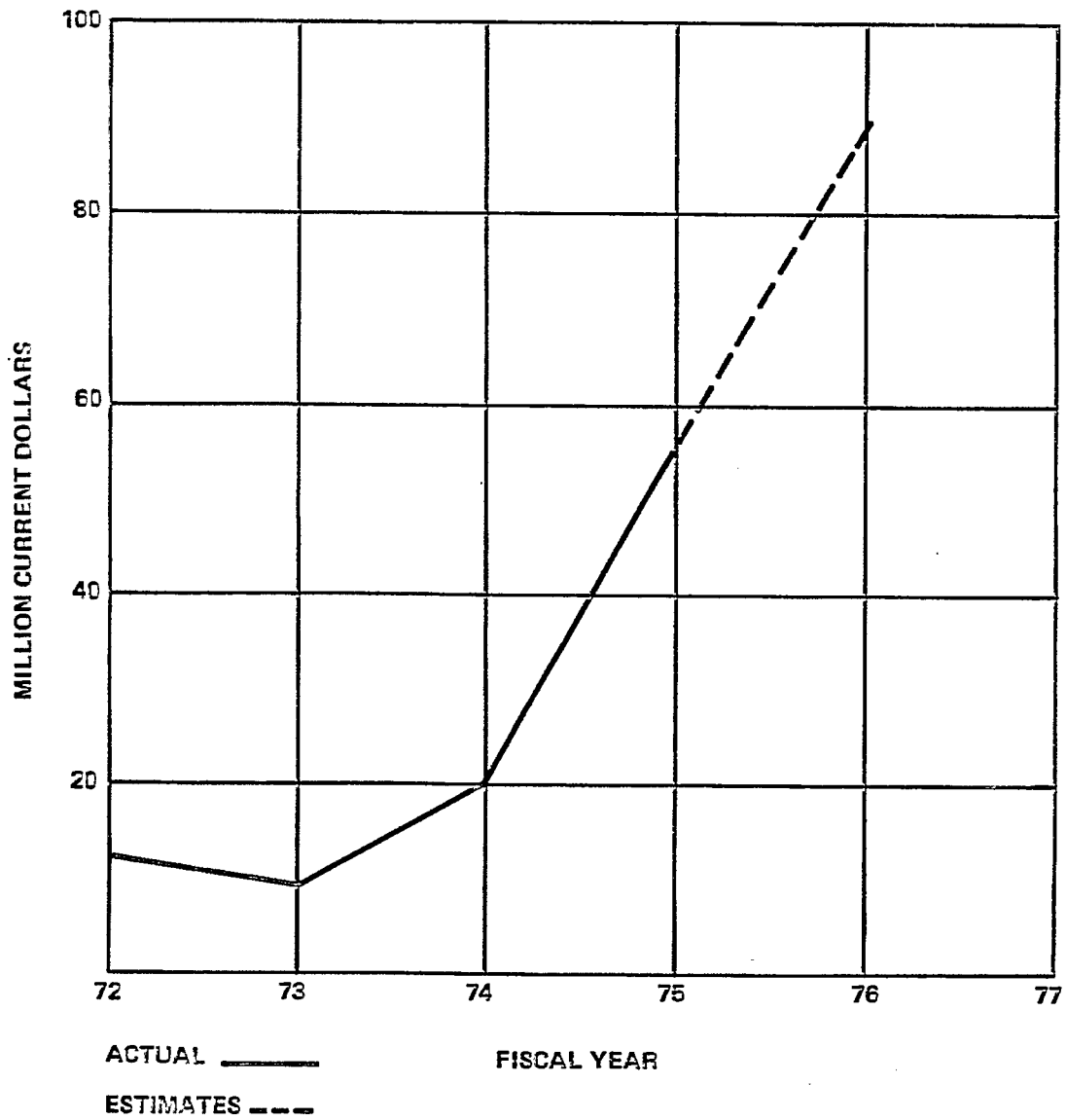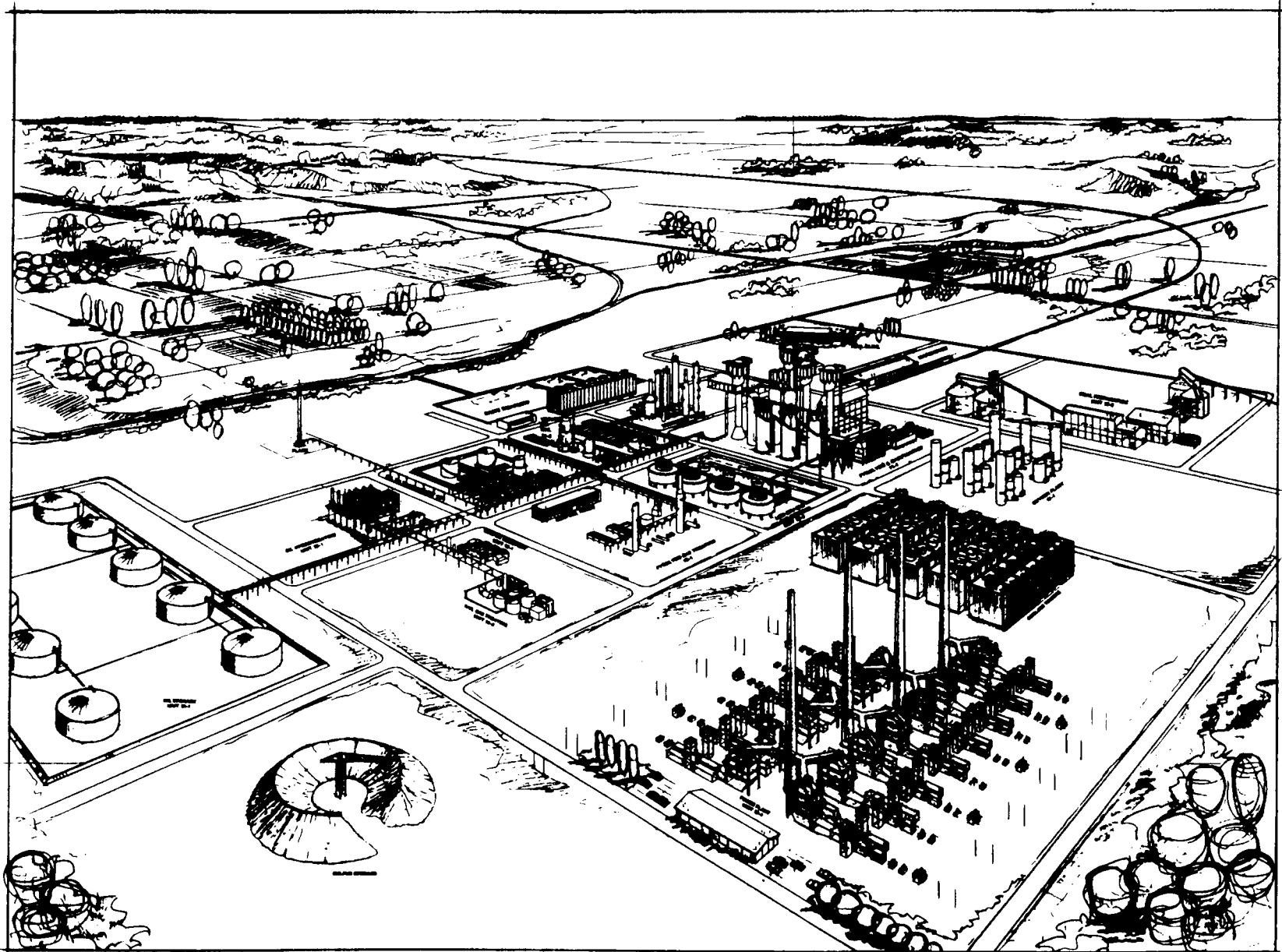| Process	Process Steps	Environment			
		Temp (°F)	Pressure (psig)	Flow/Phase Conditions	Constituents
(1) Hydroliquefaction (a) Noncatalytic - SRC	Coal dissolving	800-900	1000-2000	Three-phase (liquid, gas, and solid) upflow - low linear velocity	Coal fines, coal-derived aromatic solvent of high sulfur and nitrogen content. Gases with H_2, CO, CO_2, H_2S, NH_3, HCN, and H_2O
(b) Catalytic	Coal dissolving Catalytic hydrogenation	800-900	3000-4000	Three-phase (liquid, gas, and solid) upflow through packed catalyst bed	Coal fines, coal-derived solvent with high aromatic, sulfur, and nitrogen content
(2) Extraction - CSF process	Donor solvent Coal dissolving	800-900	400	Oil-coal slurry-agitated	Ground coal, coal-derived solvent which has been enriched with H_2
	Solvent hydrogenation	800+	3000-4000	Three-phase (liquid, hydrogen, and catalyst particles) low velocity, upflow	Hydrogen-rich gas with H_2S, NH_3 and H_2O. Coal-derived aromatic liquid of high sulfur and nitrogen content
(3) Pyrolysis - COED	Pyrolysis	800-1150	10-15	Fluid bed; coal and/or char gas from pyrolysis	Ground coal and/or char. Unsaturated pyrolysis vapors composed of tar, H_2O, unsaturated gas, H_2S, CO_2, NH_3, COS, HCN, and char fines
	Char conversion	1800	5-10	Fluid bed - char Syngas product Steam and oxygen feed	Char fines Syngas composed of H_2, CO, CO_2, H_2O, H_2S, NH_3, COS, CS_2, HCN, and entrained char
(4) Indirect - Fischer-Tropsch	Liquefaction (synthesis)	600	400	Gas phase	Syngas of high purity plus products: paraffin hydrocarbons, oxygenated compounds, CO_2, and H_2O

Figure 1 - ERDA Liquefaction R&D Expenditures

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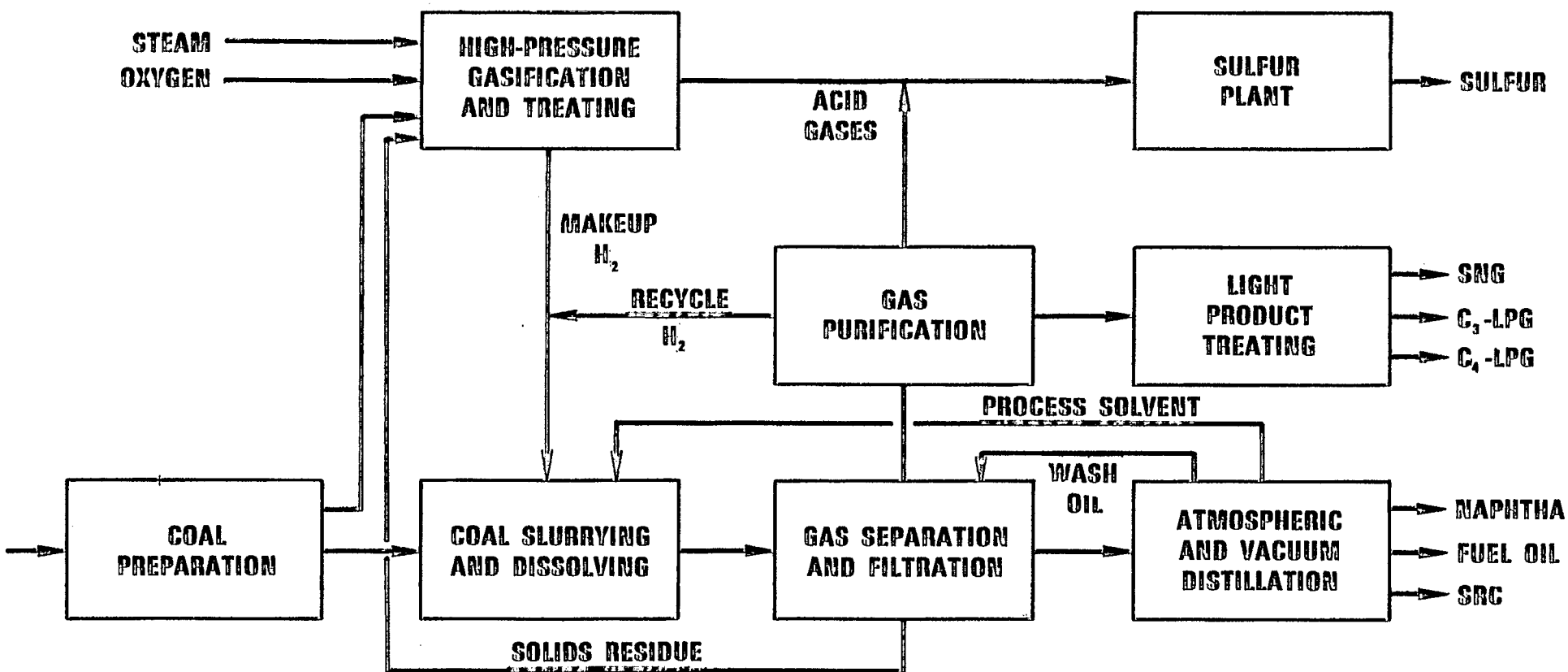Figure 2 - Artist's Conceptual Drawing of COED Plant

STEAM ⟶
OXYGEN ⟶ **HIGH-PRESSURE GASIFICATION AND TREATING** ⟶ ACID GASES ⟶ **SULFUR PLANT** ⟶ SULFUR

MAKEUP H_2

RECYCLE H_2 ⟵ **GAS PURIFICATION** ⟶ **LIGHT PRODUCT TREATING** ⟶ SNG, C_3-LPG, C_4-LPG

PROCESS SOLVENT

WASH OIL

COAL PREPARATION ⟶ **COAL SLURRYING AND DISSOLVING** ⟶ **GAS SEPARATION AND FILTRATION** ⟶ **ATMOSPHERIC AND VACUUM DISTILLATION** ⟶ NAPHTHA, FUEL OIL, SRC

SOLIDS RESIDUE

Figure 3 - Hydroliquefaction Simplified Block Flow Diagram
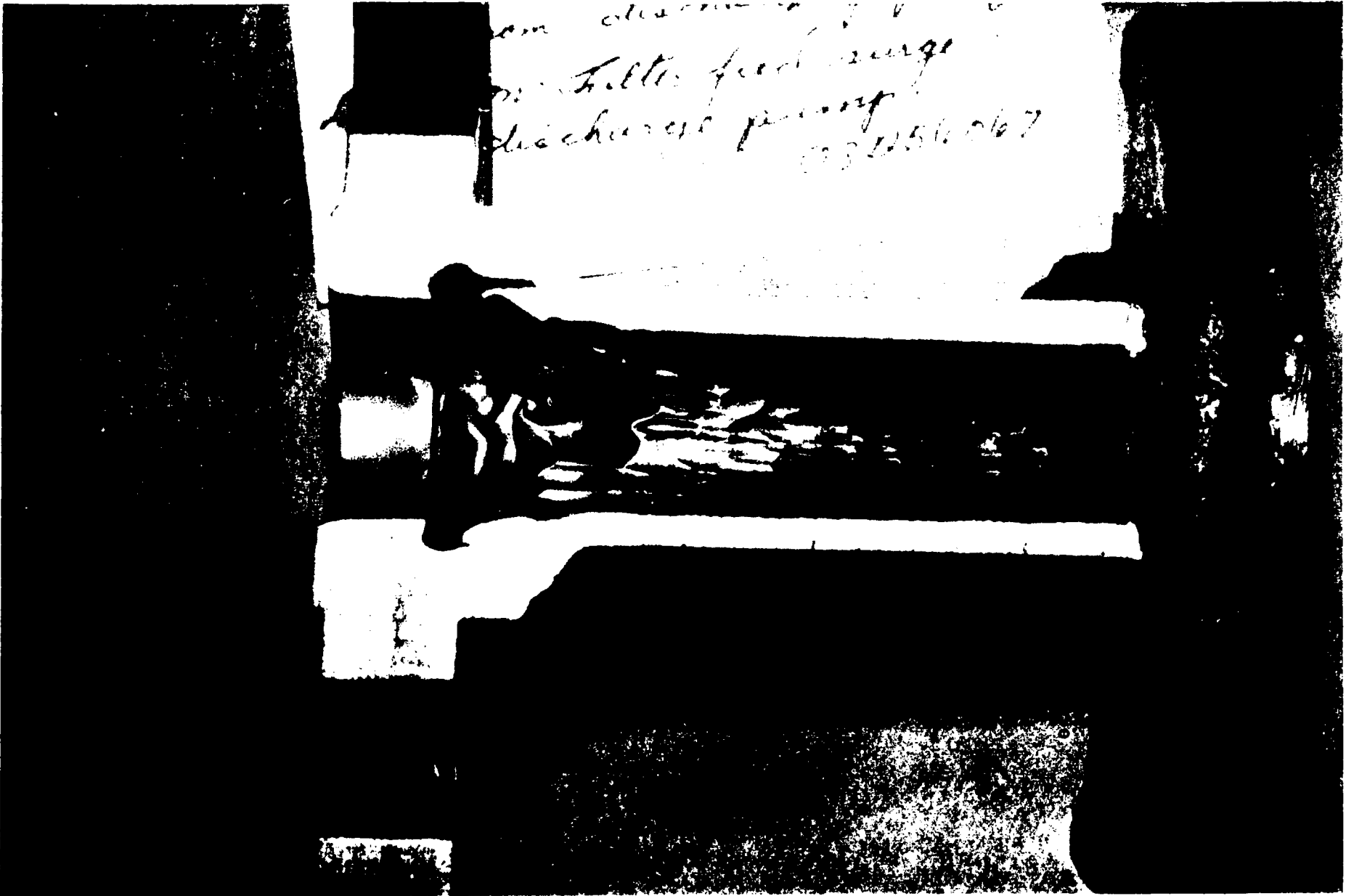
Figure 4 - Illustration of Piping Failure - SRC Pilot Plant
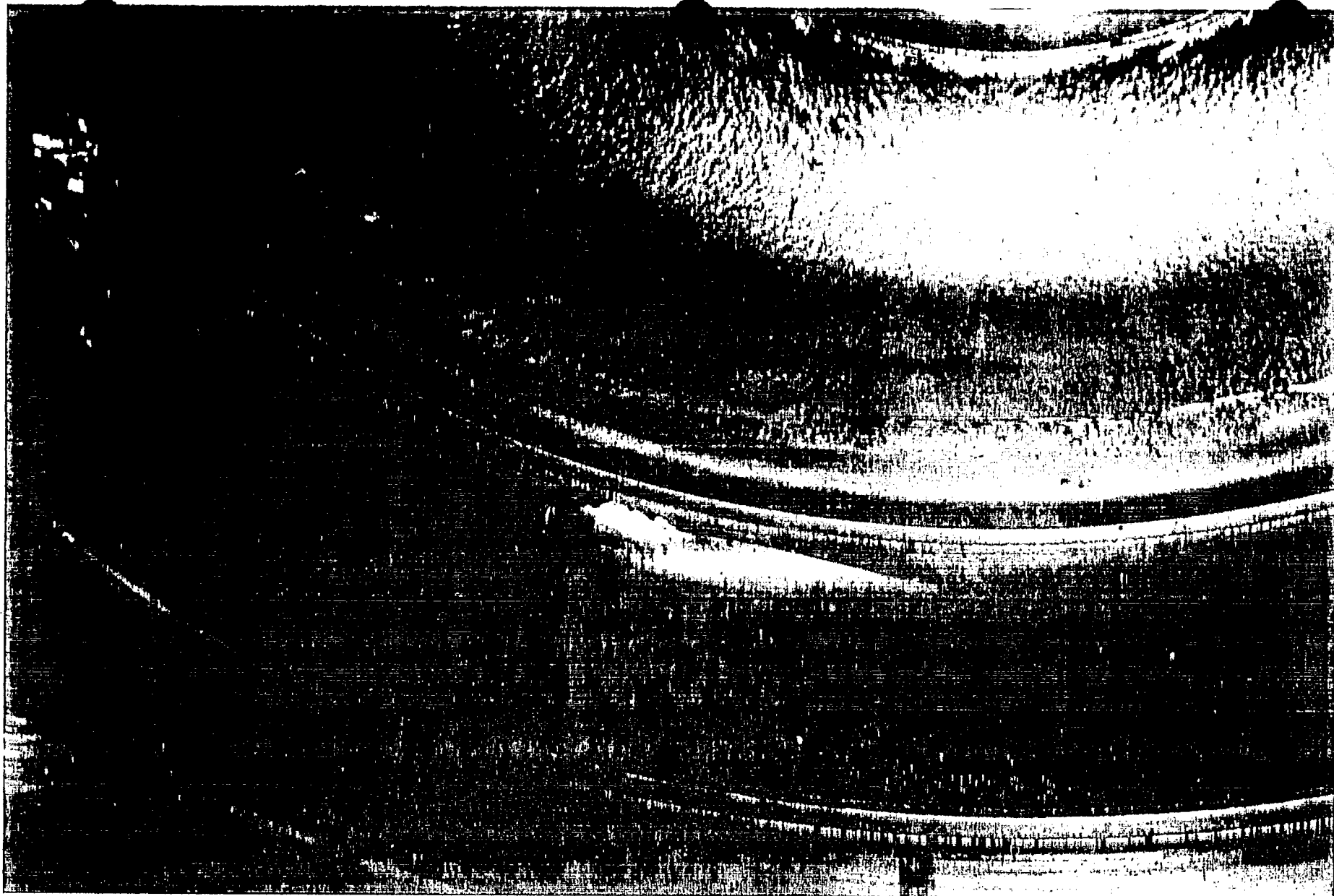
Figure 5 - Illustration of Slurry Pump - SRC Pilot Plant

Figure 6 - Corrosion Rate, H_2S/H_2 Mixtures

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Figure 7 - Operating Limits, Metals in H_2 Atmosphere
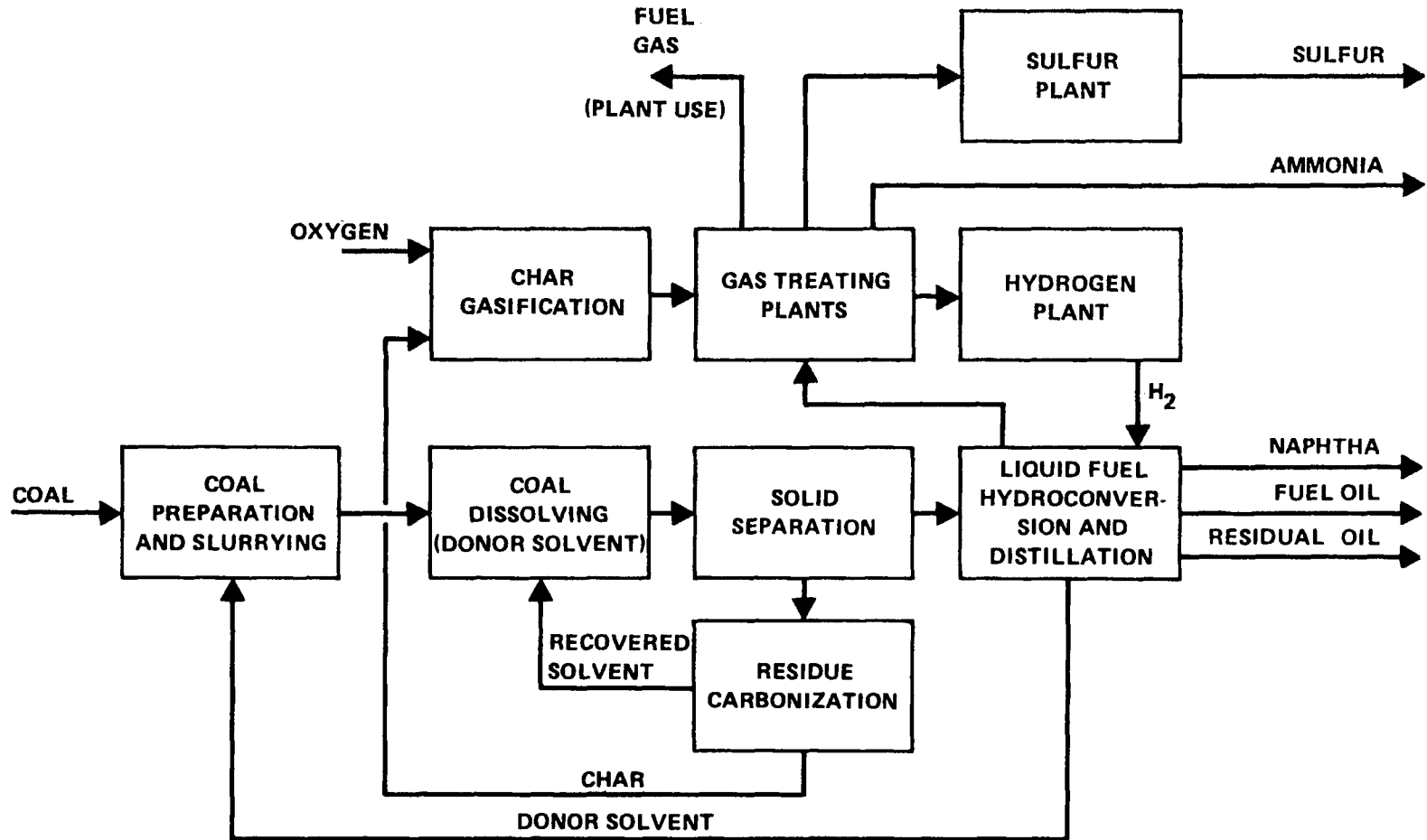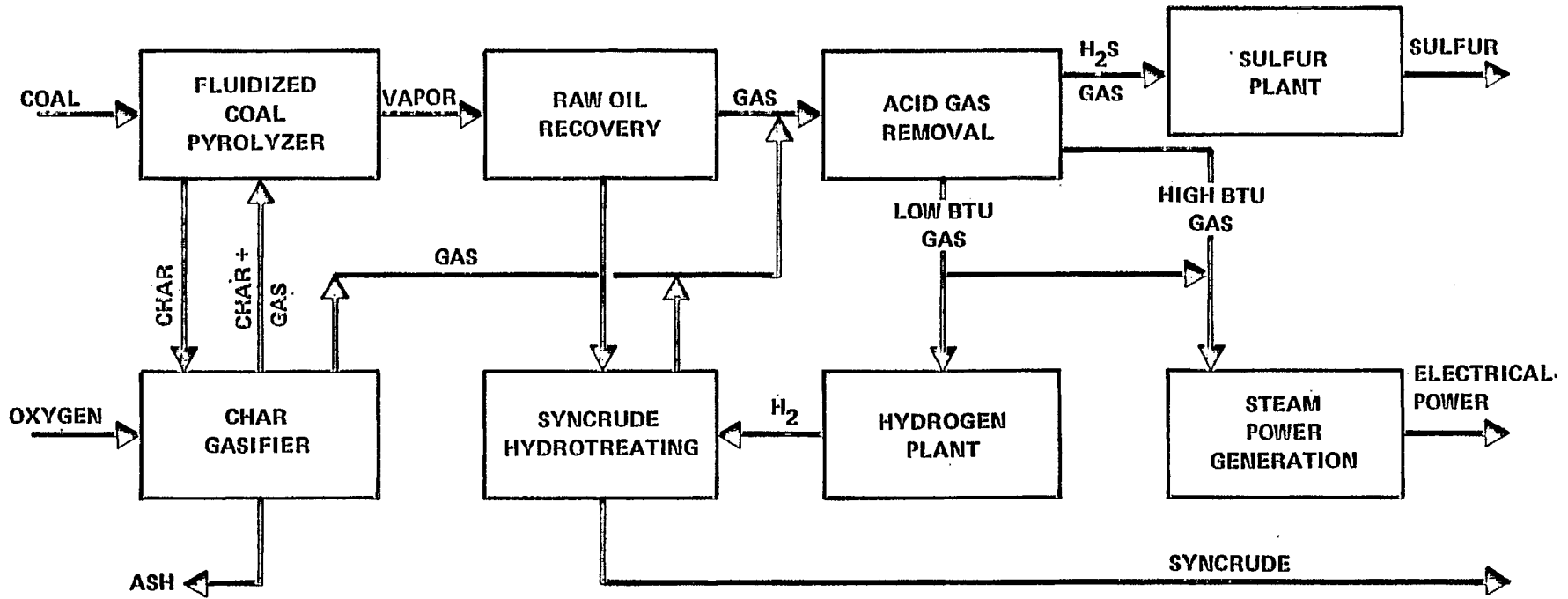
Figure 8 - Extraction Process Simplified Block Flow Diagram

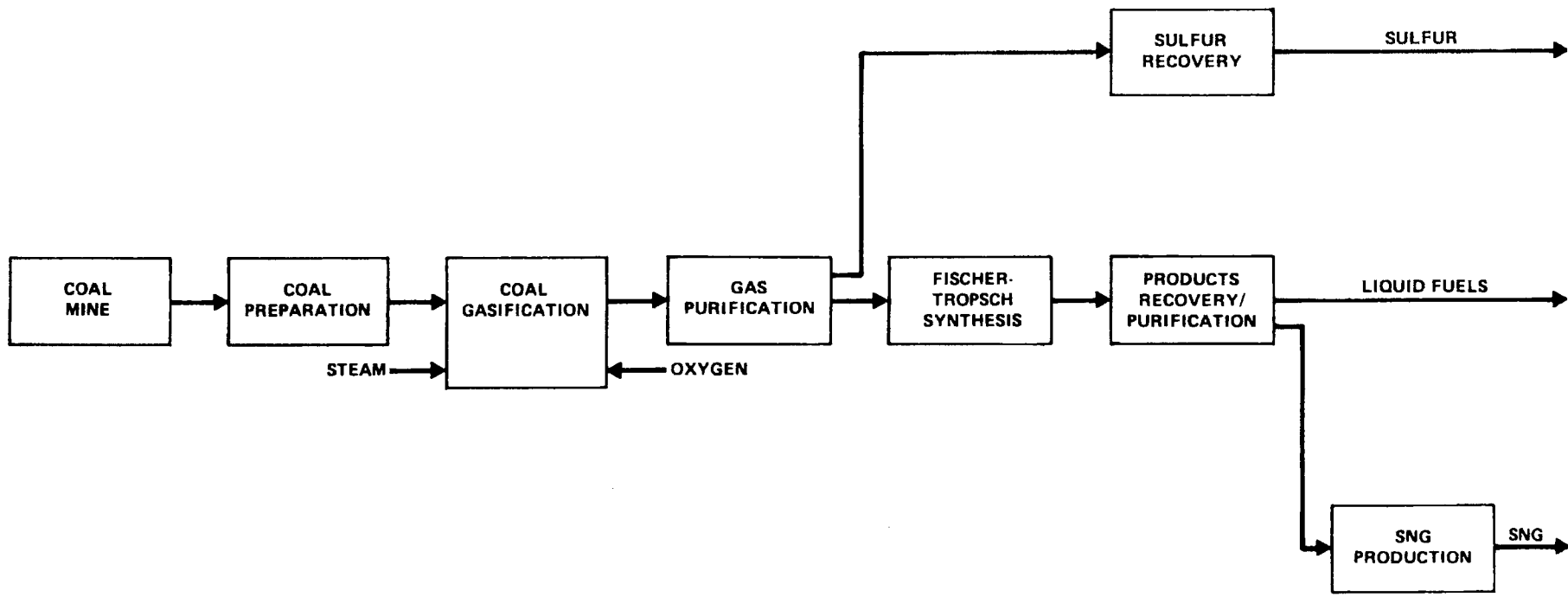Figure 9 - Pyrolysis Process (COED) Simplified Block Flow Diagram

Figure 10 - Indirect Liquefaction Process (Fischer-Tropsch)

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THE MATERIALS PROBLEMS IN

COAL GASIFICATION AND LIQUEFACTION

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ABSTRACT

The Materials Problems in Coal Gasification
and Liquefaction

The conversion of coal to "clean" fuels imposes severe demands on materials
of construction. The operational environments experienced by these materials
may be high temperatures and high pressures and contain substantial quantities
of H_2S, H_2, organic acids, chlorides and particulate matter. Experiences to
date indicate that corrosion and erosion problems will tax materials engineers
and designers.

This paper discusses material problem areas and requirements that have been
identified for coal conversion plants. A summary of critical material selection
areas for coal gasification and liquefaction plants is given.

INTRODUCTION

The conversion of coal into gaseous and liquid fuels is not new. The gasification of coal for lighting streets, homes, and buildings was started commercially in London in 1807. More than 11,000 gasifiers were in operation in the United States by the late 1920's. During World War II, the Germans achieved a production rate of more than 70,000 bbl/day of liquid fuels from 18 hydroliquefaction plants. The Sasol synthetic-fuel plant in South Africa, which has operated for 20 years, converts coal into more than 300 million cubic feet of Syngas per day. Currently, a program is underway to design and construct Sasol II which will be four to five times larger and is scheduled to begin operation in 1980.

Although the basic technologies that are required for coal conversion have been around for half a century or more, they had been little developed in this country, largely because up to now the availability of natural gas as a fuel and the plentiful supply of petroleum has made it uneconomical to do so. However, now this nation is recognizing a limited and decreasing supply of petroleum and natural gas; therefore, a critical review of conserving and prolonging current reserves and of supplementing them with alternate sources is underway. For the past decade or so, the sources of energy in the U.S. have been predominantly oil and gas (44 and 31 percent respectively) with coal accounting

for 21 percent and all other sources, including hydroelectric and nuclear plants, accounting for 4 percent. In contrast, coal accounts for 75-80 percent of the nation's fossil-fuel resources.

The simplest way to obtain energy from coal is to burn it! However, there are incentives to convert coal to "clean" liquid, gas, or solid forms. Coal, because of its content of sulfur and other pollutants, is considered to be a dirty fuel. Removal of the pollutants from stack gases when coal is burned has not yet achieved full commercial acceptance. The principal objective in coal conversion is to transform coal from its "contaminated" solid form to "clean" liquid, gaseous, or low-ash solid products which meet environmental standards.

Conversion of "dirty" coal into "clean" fuels is expensive. In the U.S., a number of advanced processes are under development for more economical conversion of coal to clean burning gaseous, liquid, or solid fuels. Over the last decade, a number of processes have reached the pilot plant stage. The new developments are moving toward three main objectives. As shown in Figure 1, one plan is to replace much of the natural gas, fuel oil, and raw coal now burned in electric power plants with a cheap "power" gas that would have a rather low rating in British thermal units (100-600 BTU/CF) but would be capable of attaining high generating efficiencies. As indicated in Figure 2, another development is to produce a gas of high heat value (900-1000 BTU/CF) to supplement natural gas in the nation's pipelines. Figure 3 shows a third objective which is to produce a range of synthetic-oil products, from crude to gasoline.

The Energy Research and Development Administration in its 1976 plan for "Creating Energy Choices for the Future" estimated 70-140 coal gasification

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or liquefaction plants (50,000 bbl/day oil equivalent) will be potentially
required by the year 2000. Plants of this size cost up to one billion
dollars or more each. Because it is expensive to gasify and liquefy coal,
a key objective is the development of large, simple, minimum-cost plants.
Economic analysis shows required product selling prices to be highly
sensitive to fixed capital investment. It follows that proper selection
of economically acceptable materials of construction must be a major
factor of a successful coal conversion program.

COAL GASIFICATION

A simplified schematic of a gasification process is shown in Figure 4.
The Bi-Gas process consists of a two-stage entrained steam-oxygen gasifi-
cation system in which recycled char is gasified in the lower or first stage
and converted to a mixture of carbon monoxide and hydrogen (SYNGAS), which
in turn is contacted with feed coal in the upper stage. Entrained char is
removed from the overhead and returned to stage one while product gas passes
to purification and methanation facilities.

The chemistry for all coal gasification processes is about the same.
Processes vary on the following three points:

1. Techniques of introducing heat:
    - Heat may be supplied by combustion of coal in air or oxygen or
      by use of a heat transfer medium.
2. Techniques of gas-solids contacting:
    - Extrained
    - Fluid Bed
    - Moving Bed

3. Technique of high-carbon utilization:

- Ash slagging
- Ash non-slagging
- Char for subsequent use or sale

The major problems to be solved for all processes are:

- Feeding solids
- Removing ash (good carbon utilization)
- Control of solids movement
- Materials of construction

COAL LIQUEFACTION

Coal liquefaction is the conversion of coal into liquid products such as chemical feedstocks, distillate heating oil, boiler fuel, and gasoline. The key to liquefaction is to increase the ratio of hydrogen to carbon. The addition of hydrogen to coal results in production of a liquid or near liquid product.

Current liquefaction processes in the U.S. may be somewhat arbitrarily grouped into the four classifications shown in Table 1. A simplified schematic of a coal liquefaction process is shown in Figure 5. In the hydroliquefaction process, a slurry of coal in a coal-derived liquid is contacted with a hydrogen-rich stream at elevated temperatures and pressures, which effectively increases the hydrogen to carbon ratio of the coal feed stock, and produces liquefaction. The hydroliquefaction can be conducted either with or without an added hydrogenation catalyst.

A second type of process is extraction, in which a hydrogenated coal-derived liquid contacts the feed coal at elevated temperature and pressure to extract a major portion of the carbonaceous coal constituents. The hydrogenated coal-derived liquid serves as a hydrogen carrier to the extraction

stage, which can be operated at a lower pressure than the hydroliquefaction process.

A third type is pyrolysis in which feed coal is heated to an elevated temperature to produce gas, liquids, and a char. The char may be gasified to produce a mixture of carbon monoxide and hydrogen, known as syngas, which in turn can be used as a feedstock for SNG, ammonia, methanol, or liquid hydrocarbon production; the gas can also be used as fuel for electric power generation. The liquids can be hydrotreated to produce a low sulfur syncrude.

The fourth type is indirect liquefaction in which the feed coal is gasified to produce a syngas containing primarily carbon monoxide and hydrogen which is purified and then reacted to produce liquid products. This is the Fischer-Tropsch technology.

Examples of operating conditions for these four classes of liquefaction processes are shown in Table 2. A key point is that every coal liquefaction plant incorporates a gasification operation. The reverse is not true; i.e., a plant to produce substitute natural gas (SNG) from coal does not necessarily include companion liquefaction operations. In a sense then, liquefaction technology development represents a broader scope challenge to scientific and engineering communities than gasification.

MATERIAL PROBLEMS IN COAL GASIFICATION AND LIQUEFACTION

A major technological roadblock to large scale coal conversion is the application and fabrication of suitable materials of construction. There are many problem areas. Following are representative environmental conditions experienced by materials in coal conversion processes resulting in materials deterioration and definitions of key equipment material problem areas.

ENVIRONMENTAL MATERIAL PROBLEM AREAS

Sulfur and Sulfur Compounds

Coal, especially that found in the Eastern part of the United States, may contain substantial sulfur. During processing, this sulfur is converted to H_2S which becomes increasingly corrosive to carbon steel at temperatures over 550°F. In the absence of hydrogen, progressively better resistance to H_2S and SO_2 corrosion is obtained by increasing chromium content. The chromium-molybdenum steel alloys and the 300 and 400 series of stainless steels have been extensively used to resist sulfur and sulfur compound corrosion in petroleum refinery applications.

The combination of H_2S and hydrogen is particularly troublesome in that the 5 Cr-1/2 Mo and 9 Cr-1 Mo steels commonly used to resist moderately high temperature sulfur and sulfur compound corrosion show little improvement over carbon steel in corrosion resistance to H_2S/H_2 atmospheres. A chromium content of at least 12% is required. The 300 series of austenitic stainless steels (minimum 18 Cr-8 Ni) have excellent resistance and are normally speci-fied for the H_2S/H_2 environments found in petroleum refineries. Extensive corrosion data and experience have been developed with various stainless steel materials in H_2S/H_2 atmospheres at temperatures to about 1000°F.

Coal liquefaction processes tend to operate in temperature ranges for which substantial corrosion data and material experience has been obtained in petroleum refineries. Recognizing that coal chemistry differs from crude oils, some coal constituents could have serious synergistic effects

in increasing corrosion rates by sulfur and sulfur compounds. Also, the combination of erosive-corrosion resulting from particulate matter in coal could substantially increase corrosion rates currently established for some materials. Therefore, although an extensive data bank of information has been established in this area, programs are currently underway to evaluate materials in pilot plants and process demonstration units (PDU's).

Less corrosion information is available for resistance of materials to sulfur and sulfur corrosion in the higher temperature ranges experienced in gasification plants. Programs are currently underway in laboratories and process plants to evaluate materials in these more severe temperature regimes. An initial approach has been to use iron base alloys containing high chromium with sufficient nickel to produce good mechanical and metallurgical properties. Candidate commercial alloys for this service are Type 310 stainless steel, Alloy 800, HK40 and 50 Cr-50 Ni. Consideration is also being given to provide added protection through aluminum diffusion coatings.

Hydrogen Attack

Hydrogen at temperatures over 450°F and pressure of 200 psi will cause carbon steel to decarburize, to form methane at internal interstices, and the resulting internal pressure to form blisters and failure of the steel.

Adding molybdenum and chromium as alloying additives suppresses this tendency because of their strong carbide forming characteristics and allows these alloys to be used at higher hydrogen pressure and temperatures. Molybdenum is also particularly beneficial in improving creep and stress-

rupture strengths.

In Figure 6 are shown the operating limits of carbon steel, carbon molybdenum steel, and the chromium molybdenum alloys. These materials are commonly used in petroleum refineries as the pressure retaining material for equipment experiencing metal temperatures to about 1000°F. These empirical curves are based on over 50 years experience, indicating where failures have occurred. These curves are currently being maintained and updated by the American Petroleum Institute Committee on Refinery Equipment for Corrosion.

Hydrogen is also of concern in that it can cause embrittlement in metals. This phenomena is more apparent with high strength ferritic materials at ambient or lower temperatures in which hydrogen is present.

Petrochemical experience, e.g., ammonia synthesis and hydrocracking, has not shown hydrogen embrittlement to be a problem. However, programs are currently underway which will indicate whether hydrogen embrittlement is a potential problem in the materials of construction for coal gasification and liquefaction plants.

Erosion, Sliding Wear, and Erosion-Corrosion
Unfortunately, relatively little is known of the mechanisms of these phenomena. What little data that have been developed has been mostly derived from empirical testing and the successes or failures of materials in service. For some non-corrosive services, the relationship between a substance's size, speed, hardness, etc., and its effects on a particular material have been somewhat quantified. However, current expertise does not enable us, from a description of the environmental conditions alone, to

calculate and predict material loss with any great reliability from erosion, sliding wear, or erosion-corrosion. Engineers have relied on experience and empirical factors to design equipment for erosive conditions. In general, equipment has been adequate for the service, but for some cases, the present state-of-the-art requires experience of a materials exposure to actual or simulated operating conditions.

Low Temperature Corrosion (Condensation)

Products produced from coal include inorganic and organic acids, cyanides, chlorides, sulfides, ash, and char. While petroleum refinery corrosion experience can be extrapolated to a great extent, there are potential problem areas in pilot plants that are being observed closely to quantify the different conditions. Some of the complex organic acids from coal do not exist in petroleum refinery operations. These acids can be highly corrosive.

Petrochemical experience has demonstrated that materials such as the austenitic stainless steels that are used to resist moderately high-temperature H_2S during operation may be susceptible to polythionic or chloride stress corrosion cracking when the plant is shut down. Therefore, strict precautionary shutdown procedures, which includes circulation of protective solutions, must be followed during down times to prevent cracking.

In some large equipment, such as pressure vessels, the vessels are not made of solid stainless steel, not only because of cost, but also to prevent catastrophic failure of the vessel because of cracking. Clad or weld overlay construction is used because the polythionic and chloride cracking phenomena are not known to occur in the commonly used ferritic alloy backing materials.

Some coal processing environments contain acidic condensates with unusually high dewpoints. Approximate values range from 212°F to 460°F. Little is

known at this time of their corrosivity, composition, and the materials required to provide economical protection. Programs are currently underway to measure corrosivity for various condensates, and to evaluate suitable materials of construction.

High Temperature Effects in Metallurgical and Mechanical Properties

At increasingly higher temperatures, the following metallurgical and mechanical properties are generally adversely affected.

- ° Metallurgical properties

  - Transformation and hardening

  - Sensitization

  - Carburization/Metal dusting

  - Ageing

  - Temper embrittlement

  - Grain growth

- ° Mechanical Properties

  - Tensile and yield strengths

  - Creep/Stress rupture

  - Fatigue strength

These characteristics are well known and understood by the materials community. They receive increased attention in coal conversion plants because for certain applications these properties become the limiting factors for their use.

EQUIPMENT MATERIAL PROBLEM AREAS

Coal Feed Injection and Slurry Pumping

Whether the process is gasification or liquefaction, there must be a method for introducing solid coal into a generally high-pressure, high-temperature system. It is a formidable task in a commercial unit to inject coal at rates of 10,000 tons or more per day into a system such as the Bi-Gas process where the temperature is 1700°F and the pressure is 1000 psi or greater.

One method of coal injection is by use of a lockhopper system. Lockhoppers have the advantage of introducing coal dry and ready for chemical reaction. The major design and material considerations are the suitable performance of sealing valves, the means of solids flow control and the economical pressurizing of the lockhoppers. Lockhopper limitations of pressure differential has been about 400-500 psi. For example, to feed coal into a 1500 psi system could require three lockhoppers in series plus a high pressure feedhopper and a low pressure charge hopper. The timing of valve opening and closing, pumping, and depressurization and pressurization results in a complicated automatic control system. Moreover, the whole string of feed hoppers could be rendered useless if any one of the lockhopper valves fails to function in sealing pressure. Currently, the Bureau of Mines' Synthane pilot plant which is just beginning operations, has a lock-hopper system that uses new valves expected to operate with a 1000 psi pressure differential in a single stage. Experience from this plant can do much to advance the state-of-the-art.

As an alternate means of coal injection, slurry feeding has gained in prominence. Experience has been obtained in use of commercial coal slurry pipelines that have been used to transport coal.

Positive displacement pumps have been and are being used for high pressure slurry systems. Both plunger- and piston-type reciprocating pumps are quite suitable for pumping slurries at high pressures. The pumps should be designed for easy and quick replacement of liquid end parts. Pump check valves have been particularly troublesome.

Attempting to transport slurries at high pressures with centrifugal pumps has been impractical because of the large number of wear parts and close tolerances required. Obtaining high pressures requires high velocities which cause wear parts, impellers, and casings to deteriorate. Currently, studies are underway to develop multi-stage, moderate rpm, high pressure centrifugal pumps.

Centrifugal pumps for transporting slurries at lower pressures have also experienced problems. To reduce wear, wetted parts have been coated or hard-faced. In one pilot plant, various coatings failed within 24 to 48 hours. For abrasive slurries, severe erosion is experienced at the standard 3600 rpm pump speeds. Proper mating of materials and design considerations is necessary in slurry centrifugal pump applications. A low speed, of the order of 1500 rpm, will tend to reduce erosion as will use of a pump with proper head-volume characteristics. Careful attention should be given to impeller and volute geometrical design.

A number of materials have been tested in pilot plant pumps handling coal slurries. Materials tried include carbon steel, 300-series stainless steels,

Ni-hard, and coated carbon steel. Coatings have included chromium, ceramics, plastics, elastomers, and hard surfacing materials such as the fused coatings containing nickel, chromium, boron, and silicon. The pumps have performed moderately well in many cases; for instance, we understand that service lives of the order of 700 to 2000 hours have been achieved. However, none has proven entirely satisfactory.

Coal Gasifiers

Coal gasifier reactors present challenging problems to the design and materials engineers. The process environment is severe. Typical Coal Gasification conditions are shown in Table 3.

Design and material considerations to be resolved are:

- ° Materials to provide a large diameter pressure envelope to withstand pressures up to 1500 psi
- ° Materials to withstand temperatures up to 3200°F
- ° Materials to withstand high temperature corrosive and erosive conditions
- ° Materials to withstand corrosion by condensation of organic and inorganic acids
- ° Materials to withstand degradation by hydrogen at high temperatures and pressures

Material Problems Related to Gasifier Size and Fabrication

If the appropriate operational reliability can be maintained, economics of operation dictate that the largest vessels feasible be fabricated. In

Figure 7 are shown sizes of typical coal gasifier reactor vessels
based on recent studies for coal gasification plants requiring two
reactors capable of producing a total of 250 billon Btu per day.

Experience with the nuclear and petroleum refining industries indicate
shop fabrication is limited by shipping requirements to vessels in the
order of 13 feet in diameter, or 100 feet long or 500 tons in weight.
Depending on the carbon steel or low alloy steel specified, maximum
wall thicknesses are limited to about 14 inches. Plate materials currently
being considered for gasifiers are ASTM A 516, A 204, A 302B, A 533 A,B,C,
and A 387 Gr 22. It is anticipated that thick walled reactor vessels will
be designed to ASME Code Section VIII, Division 2.

Because of the size of gasifiers, it may be necessary to fabricate them in
the field. Concomitant with field fabrication are the associated problems
of maintaining welding preheat, appropriate postweld heat treatment, practi-
cal and efficient nondestructive examination techniques, and more effective
welding methods.

High Temperature Materials ($>1000°F$)
To withstand the high temperatures encountered within the gasifier, to conserve
heat and to increase process efficiency, refractory linings are required.
Both castable and shaped materials are being considered and evaluated.

Problems associated with refractory materials in coal gasifiers are:

-- leaching out of silica materials by steam

-- carbon disintegration of fire clay brick in a CO atmosphere

-- destruction of alumina silica refractories by alkalies

-- corrosion by coal slags

-- erosion and abrasion by particulate matter

-- thermomechanical failures resulting in hot spots at the shell

To resolve these problems, refractory linings of two or more layers are being evaluated. The layer next to the shell is an insulating material over which is a wear or erosion resistant castable or brick refractory. Cooling coils may or may not be used.

To withstand erosion by high velocity particulate matter, dense alumina refractories are recommended. Where slagging is present, it may be necessary to tailor-make the refractory for the ash composition of the coal to be used. Fused cast high-purity alumina, silica carbide, and alumina-chrome and magnesite-chrome brick have been considered for resistance to slag corrosion and erosion.

Other Gasifier Material Problem Areas

Programs are currently underway to evaluate the corrosion resistance, erosion resistance, mechanical, and metallurgical properties of metallic materials for coal gasification environments to temperatures as high as 1850° to 2000°F. Such materials are being considered for use as internal solids transfer lines, valves, cyclones, grid supports, pressure, and temperature probes and refractory anchors. These materials of construction should be suitable for resistance to sulfur corrosion, low temperature corrosion, hydrogen, high temperature, and erosion conditions described previously.

Also of concern in gasifiers is the condensation of acidic components behind the refractory lining causing corrosion of the metallic shell. Keeping temperatures above the dew point results in uneconomical heat losses. Clad or weld overlay materials resistant to the condensates may be required.

Liquefaction Reactors

The maximum temperatures in liquefaction processes does not exceed 1150°F and generally is not over 900°F. However, materials to resist sulfur and sulfur compound corrosion, low temperature corrosion, erosion, and hydrogen attack, as previously described are still required. Pressures up to 2500 to 3000 psi may be experienced requiring thick wall pressure envelopes. For example, in one conceptual design for producing clean boiler fuels from coal, vessel sizes operating at about 1200 psi and 850°F will be in the order of 9 to 12 feet in diameter and 24 to 69 feet long for a plant processing 10,000 tons of coal per day.

Valves

Let-down valves in which pressures are dropped 1000 psi or more have been a particularly troublesome area. The combination of a two-to-three-phase gas-solid-liquid stream, pressure drop and temperature has yet to be solved. While valves have been designed for any one of the above conditions, valve life under the combination of conditions may be only two weeks to 60 days. Material substitution alone, i.e., use of harder, more durable materials, has not been adequate. Increased use of tungsten and cobalt carbide materials has not achieved satisfactory valve life.

Programs are currently underway to develop suitable valves by closer inter-action between valve designers and materials engineers. Also programs are

underway to develop and evaluate single phase materials such as high-purity,

dense, fine-grain oxides, carbides, borides, and nitrides prepared by

sintering or hot-pressing and two-phase cermet type of materials.

Turbines

Power recovery and power generation turbines generally are the two classi-

fications of turbine types for converting energy from coal derived gases.

Power recovery turbines inlet gas temperatures range up to 1200°F while in

power generation turbines the inlet gases are as hot as present design and

materials technology allows which is in the neighborhood of 1900°F.

The limitations of current turbine materials problems are related to the

cleanliness of the inlet gases. Alkali metal impurities, vanadium, sulfur,

char, and ash seriously impair the use of conventional gas turbines. Gas

turbine technology has produced a broad range of sophisticated designs and

alloy materials. Blade materials include advanced nickel, cobalt, and eutec-

tic alloys. Recently, considerable attention has been given to ceramic

materials such as silicon nitride and silicon carbide. Significant gains

have also been made by the application of various cooling techniques to the

hot parts.

Programs are currently underway to resolve coal gas turbine problems by

- removal of impurities in the inlet gases
- modification of operating conditions such as injecting
  deposit-removing materials in gas turbines
- improving equipment design and material of construction
- effective use of additives

SUMMARY AND CONCLUSIONS

Coal occupies a unique position among U.S. energy resources. Although there are extensive reserves, most coal is "dirty" and requires costly conversion processing to satisfy environmental requirements. Sooner or later steps will be taken to utilize more extensively this valuable resource.

Coal conversion works - it has been used industrially. The challenge to the materials community is to improve reliability and decrease costs of process equipment. Many material research and development programs are currently underway. More inter-disciplinary action between the materials community and designers must also be implemented. Especially needed are resolutions to material problem areas where operating conditions are so severe that they exceed satisfactory performance of materials currently available or economical.

LITERATURE CITED

W. G. Dupree, Jr., and J. S. Corsentino, "United States Energy Through the Year 2000 (Revised)", Bureau of Mines, U. S. Department of the Interior, December, 1975.

W. T. Bakker, "Refractories for Coal Conversion Processes: An Engineering Approach", Twelfth Annual Symposium on Refractories, The American Ceramic Society, St. Louis Section, March 26, 1976.

J. B. O'Hara, "Coal Liquefaction", Third International Symposium Large Chemical Plants Design and Operation, Flemish Society of Engineers, Antwerp, Belgium, October 20, 1976.

A. M. Hall, "Coal Gasification Poses Demanding Material Requirements", Materials Engineering, July, 1974.

B. S. Lee, "Slurry Feeding of Coal Gasifiers", Chemical Engineering Progress.

N. B. Cochran, "Oil and Gas from Coal", Scientific American, May, 1976, Volume 234, Number 5, pp. 24-29.

R. E. Dial, "Refractories for Coal Gasification and Liquefaction", Ceramic Bulletin, Vol. 54, No. 711925, pp 640-643.

R. D. Howell, "Mechanical Design Considerations in Commercial Scale Coal Gasification Plants".

R. L. Zahradnik, "Coal Conversion R & D: What the Government is Doing", Chemical Engineering Progress, June, 1976, pp 25-32.

A. J. MacNab, "Corrosion and Erosion of High BTU Gasifier Components-- A Review of Anticipated Requirements for Commercial Plant Development", Symposium on Coal Conversion Systems Design, American Society for Metals, Pittsburg, PA, April 26, 1976.

A. J. Giramonti and W. A. Blecher, "Energy Conservation Through the Use of Combined Cycle Power Systems", Symposium on Environment and Energy Conservation, Sponsored by Environmental Protection Agency and Energy Research and Development Administration, Denver, Colorado, November 4, 1975

The Ralph M. Parsons Company, "Demonstration Plant: Clean Boiler Fuels from Coal", R & D Report No. 82, Interim Report No. 1, for the United States Department of Interior Office of Coal Research.

J. B. O'Hara, W. J. Lochmann, and N. E. Jentz, "Coal Liquefaction: Materials Systems Design," Metals Progress, November, 1976.

W.R.K. Wu, and H. H. Storch, "Hydrogenation of Coal and Tar," U. S. Bureau of Mines, Bulletin 633, 1968, pp 157-166.

G. R. Pastor, "Solvent Refined Coal--A Pilot Plant Report," presented at 1975 Power Generation Conference, Portland, Oregon, October, 1975.

The Ralph M. Parsons Company "Feasibility Report, Consol Synthetic Fuel Process," Office of Coal Research R&D Report, No. 45, 1968.

L. J. Scotti, et al, "Multi-Stage Fluidized-Bed Pyrolysis of Coal at the Project COED Pilot Plant," presented at the American Institute of Chemical Engineers (AIChE) Meeting, Pittsburgh, Pennsylvania, June, 1974.

J. B. O'Hara, A. Bela, N. E. Jentz, and S. K. Khaderi, "Fischer-Tropsch Plant Design Criteria," presented at the 68th Annual Meeting of the American Institute of Chemical Engineers (AIChE), Los Angeles, California, November 19, 1975.

H. L. Roberts, SASOL, "Oil from Coal, The Engineering Challenge."

American Petroleum Institute "Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants," API Publication 941, First Edition, July, 1970.

J. F. Jones, and B. D. McMunn, "Materials Performance in Coal Pyrolysis and Coal Oil."

F. L. Roloson, W. A. Blecher, and A. J. Giramonti, "Combined Cycle Power Systems," Symposium on Environmental Aspects of Fuel Conversion Technology II, Sponsored by Environmental Protection Agency, Hollywood, Florida, December, 1975.

N. S. Bornstein and M. A. De Crescente, "Sulfidation in Gas Turbine Engines" Presented at National Association of Corrosion Engineers, Toronto, Canada, April 14-18, 1975.

J. B. O'Hara, "Coal Conversion Development: An Overview," Presented at Third Annual Western Regional Conference, Engineering Institute of Canada, Petrochemicals West Calgary, Alberta, May 12, 1976.
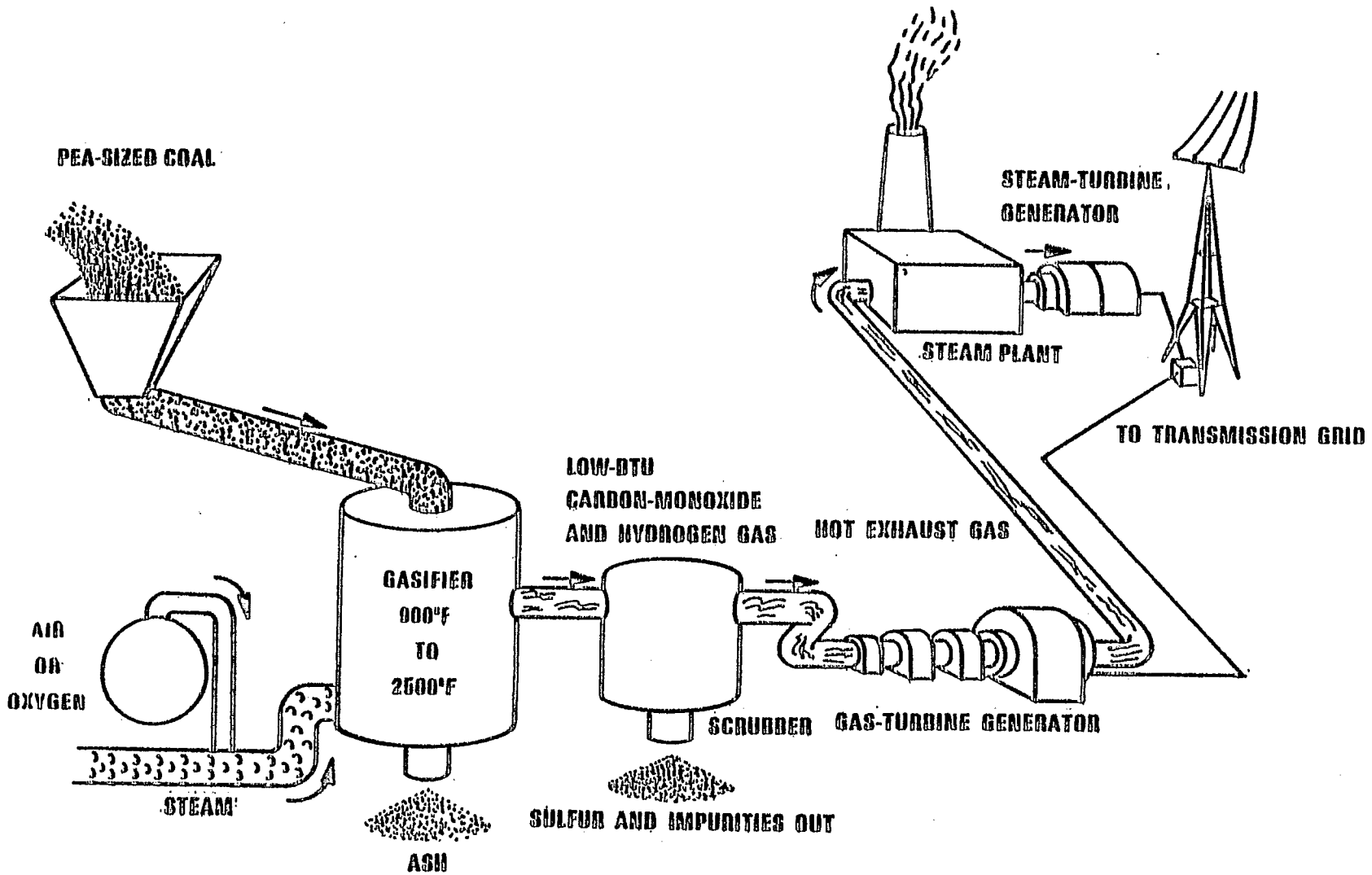
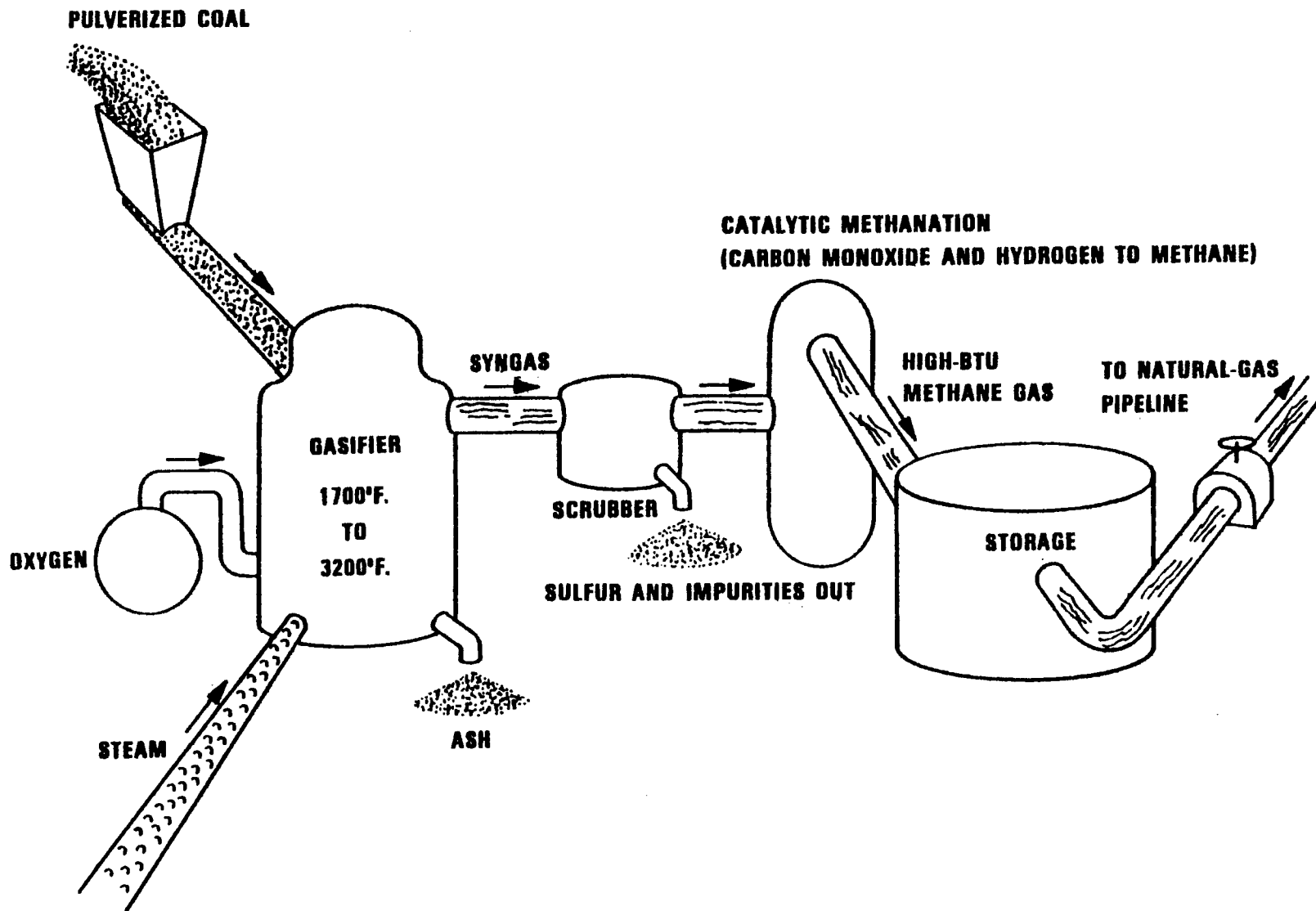# Low-Btu Gas for Electric Power Generation

Figure 1

High-Btu Gas

PULVERIZED COAL

CATALYTIC METHANATION
(CARBON MONOXIDE AND HYDROGEN TO METHANE)

SYNGAS

HIGH-BTU
METHANE GAS

TO NATURAL-GAS
PIPELINE

GASIFIER

1700°F.
TO
3200°F.

SCRUBBER

OXYGEN

SULFUR AND IMPURITIES OUT

STORAGE

STEAM

ASH

Figure 2

Synthetic Oil and Gas

PULVERIZED COAL

SYNTHETIC GAS

VAPORIZED HYDROCARBONS

RE-CYCLED GAS

SCRUBBER

GAS

HOT GAS

HOTTER GAS

000°F.

050°F

1000°F.

1500°F.

COAL

COAL

COAL

COAL

COOLING,
PRODUCT
RECOVERY,
FILTRATION

HYDROGEN

HYDROTREATMENT
IN CATALYTIC REACTOR

SYNTHETIC OIL

HOT, FLUIDIZING GAS

FLUIDIZED-BED REACTORS

RESIDUAL CHAR
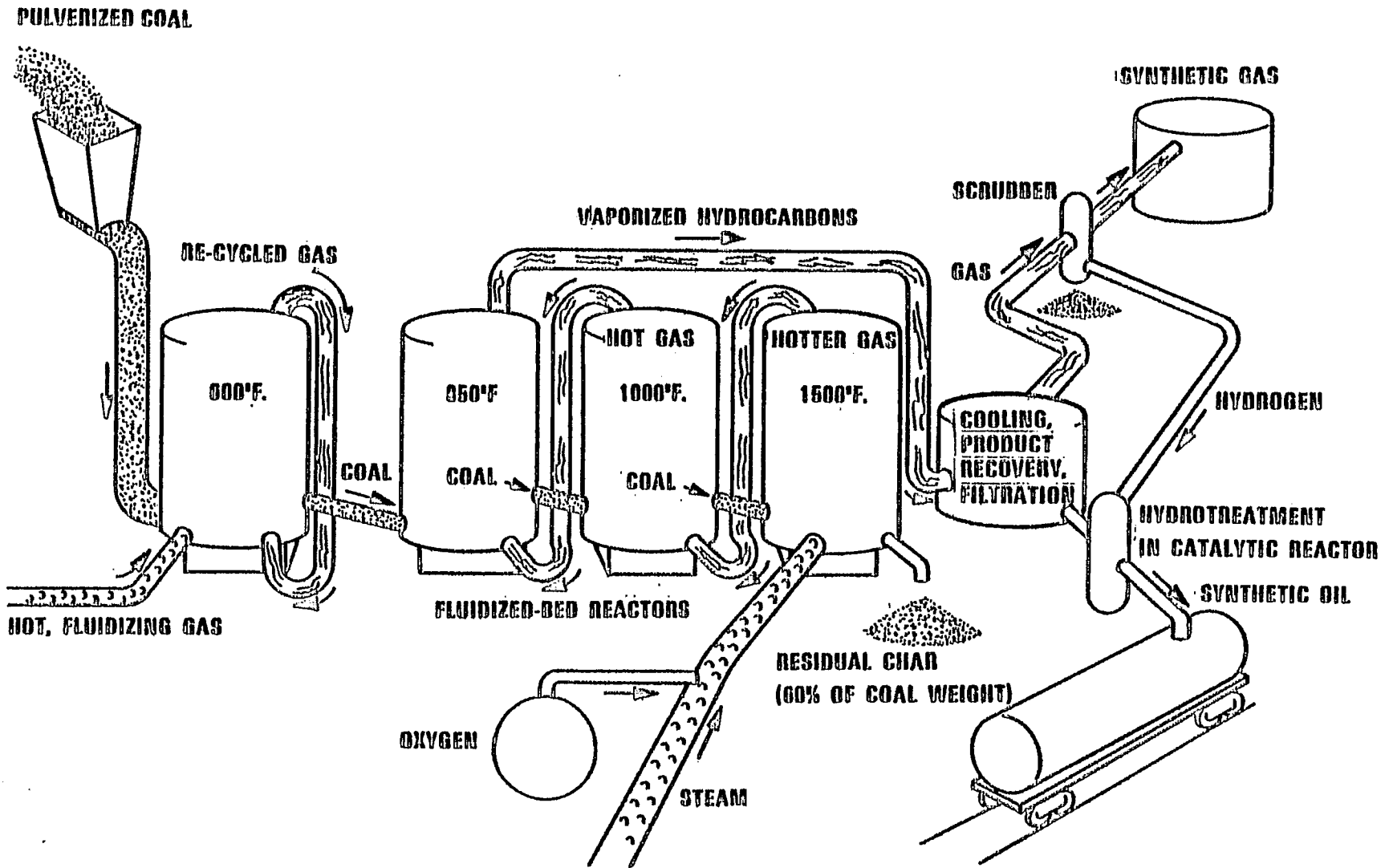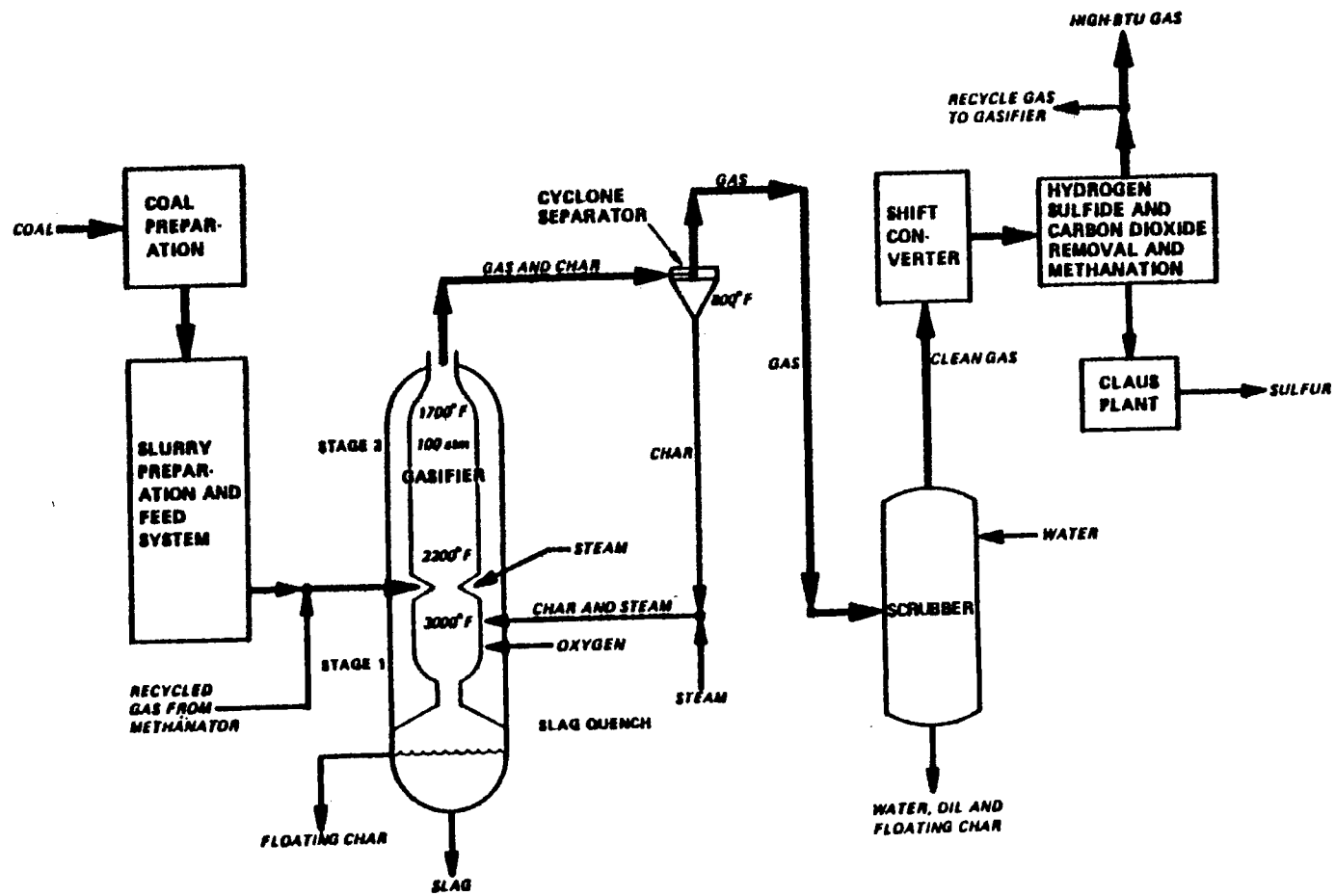(60% OF COAL WEIGHT)

OXYGEN

STEAM

Figure 3

Figure 4 - Bi-Gas Process Schematic

Solvent Refined Coal Process

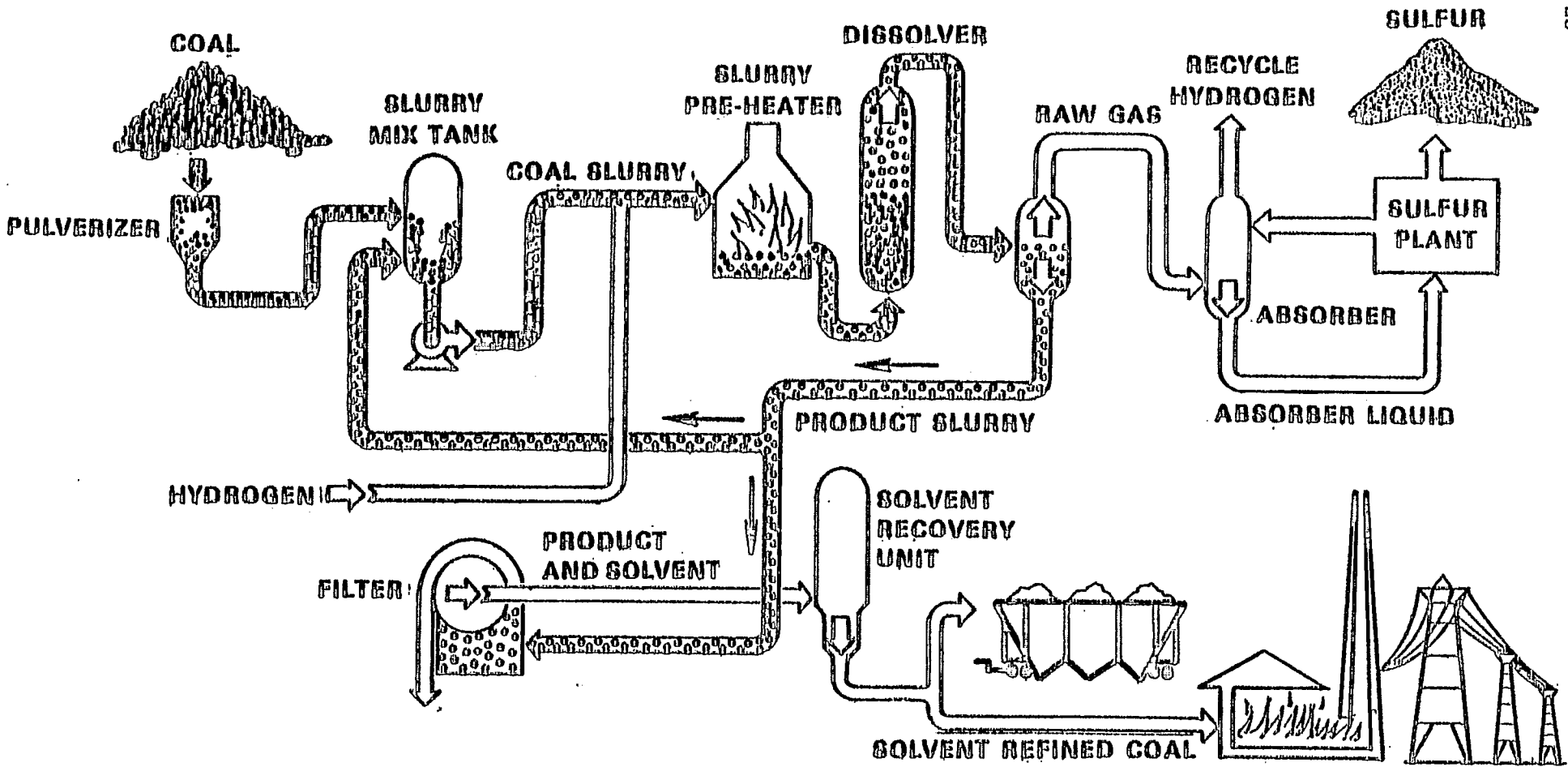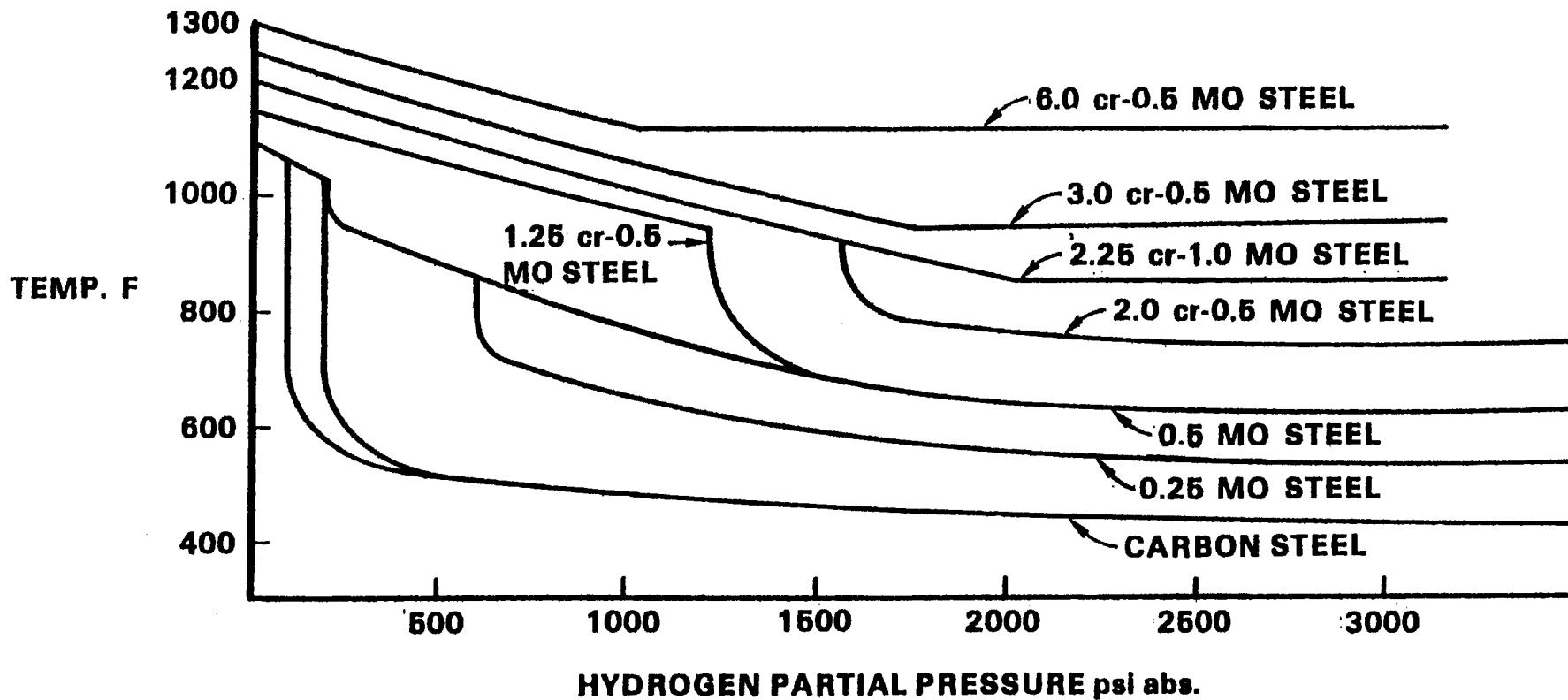Figure 5

Operating Limits, Metals In H$_2$ Atmosphere

Figure 6

Conceptual Commercial Gasifier Requirements
(based on Western Coal Feed)

DIAMETER	THICKNESS
24' 0"	7 1/4"
19' 6"	5 7/8"
10' 0"	3"

218'
T-T

**IGT HYGAS STEAM-IRON
FLUIDIZED BED MULTI-STAGE REACTOR**

DIAMETER	THICKNESS
17' 4"	5 1/4"
24' 0"	7 1/4"
19' 4"	5 11/16"
10' 0"	4"

204'
T-T

**IGT HYGAS STEAM-OXYGEN
FLUIDIZED BED MULTI-STAGE REACTOR**
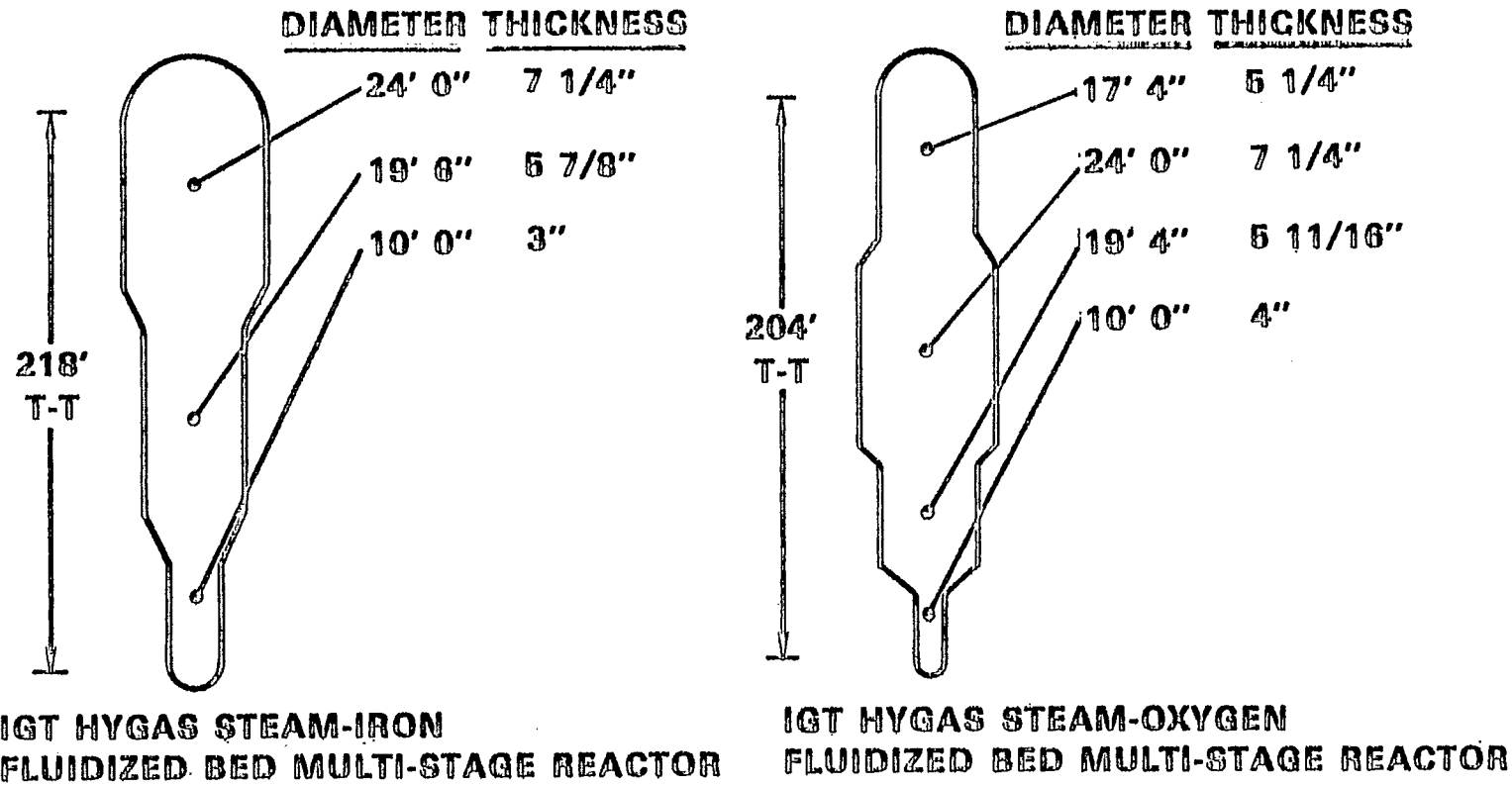
Figure 7

Table 1 - Process Classification

Classification	Example
(1) Hydroliquefaction	
(a) Noncatalytic	Solvent-refined coal (SRC), Clean Coke
(b) Catalytic	Synthoil, H-coal
(2) Extraction - Donor solvent	CSF (CRESAP), Exxon
(3) Pyrolysis	
(a) Direct	COED, Garrett
(b) Hydropyrolysis	Coalcon, Clean Coke
(4) Indirect Liquefaction	Fischer-Tropsch

Table 2 - Liquefaction Processes

Example Operating Conditions
Coal Conversion Steps

Process	Process Steps	Environment			
		Temp (°F)	Pressure (psig)	Flow/Phase Conditions	Constituents
(1) Hydroliquefaction (a) Noncatalytic - SRC	Coal dissolving	800-900	1000-2000	Three-phase (liquid, gas, and solid) upflow - low linear velocity	Coal fines, coal-derived aromatic solvent of high sulfur and nitrogen content. Gases with H_2, CO, CO_2, H_2S, NH_3, HCN, and H_2O
(b) Catalytic	Coal dissolving Catalytic hydrogenation	800-900	3000-4000	Three-phase (liquid, gas, and solid) upflow through packed catalyst bed	Coal fines, coal-derived solvent with high aromatic, sulfur, and nitrogen content
(2) Extraction - CSF process	Donor solvent Coal dissolving	800-900	400	Oil-coal slurry-agitated	Ground coal, coal-derived solvent which has been enriched with H_2
	Solvent hydrogenation	800+	3000-4000	Three-phase (liquid, hydrogen, and catalyst particles) low velocity, upflow	Hydrogen-rich gas with H_2S, NH_3 and H_2O. Coal-derived aromatic liquid of high sulfur and nitrogen content
(3) Pyrolysis - COED	Pyrolysis	800-1150	10-15	Fluid bed; coal and/or char gas from pyrolysis	Ground coal and/or char. Unsaturated pyrolysis vapors composed of tar, H_2O, unsaturated gas, H_2S, CO_2, NH_3, COS, HCN, and char fines
	Char conversion	1800	5-10	Fluid bed - char Syngas product Steam and oxygen feed	Char fines Syngas composed of H_2, CO, CO_2, H_2O, H_2S, NH_3, COS, CS_2, HCN, and entrained char
(4) Indirect - Fischer-Tropsch	Liquefaction (synthesis)	600	400	Gas phase	Syngas of high purity plus products: paraffin hydrocarbons, oxygenated compounds, CO_2, and H_2O

TABLE 3

TYPICAL COAL GASIFIER CONDITIONS

	TEMPERATURE $^\circ F$	PRESSURE psi	GAS/PARTICLE VELOCITY ft/sec
SLAGGING GASIFIER	2800-3200	15-1500	2-10
DRY ASH	900-2500	15-1500	2-60
CYCLONES AND TRANSFER LINES	700-1850	15-1500	40-100

GAS COMPOSITION	CO	CO_2	H_2	H_2O	CH_4	H_2S	MISC. (N_2, etc.)
PERCENT	9-30	5-20	12-44	9-60	4-26	0.1-1.0	1-3