Research on catalyst slurry systems was continued in England until June 1961, and the obtained results are summarized in detail by Farley and Ray.(71)

A demonstration plant was built by the USBM at Louisiana, Missouri, with provisions for both oil circulation and slurry-type operation (see summary in Reference 36 and the list of USBM Reports of investigations provided in that review).

The problem of the identity of the activated catalyst has been studied in some detail by Shultz, et al.(72) at the USBM. This study reflects some of the complex phase changes that occur in the modern iron catalyst systems. Catalysts having an initial composition approximating Fe_2C began at higher activities than the corresponding reduced iron catalysts and slowly decreased in activity with time, especially at the higher pressures studied. It was observed that the carbides oxidized gradually during the synthesis operation and it was suggested that these changes might be explained by two processes

1. The reaction of carbide and water vapor to form magnetite and elemental carbon
2. The reaction of hydrogen with carbide or carbon to form CH_4.

Similar oxidation processes were noted for nitride and carbonitride catalysts. X-ray diffraction studies were used to help in identification of the complex phase changes that occurred.

Production of Gaseous Hydrocarbons. At a sufficiently high operating temperature (e.g., about 400 C) hydrocarbon yields above C_6-C_8 become unfavorable (see Figure 12a).(78) Under such conditions, the accumulation of waxes on the Fischer-Tropsch catalyst is not expected, although the alternative process of carbon deposition may continue. If a suitable catalyst is used, the synthesis can be carried out at these higher temperatures to yield CH_4 and low molecular weight hydrocarbons up to about C_8. This concept is currently being reexplored; earlier efforts in this area resulted in the process known as isosynthesis.(73) Isosynthesis was developed during World War II in Germany and in the subsequent years some USA patents were issued on modifications of it. Presently available information does not indicate any commercial use.

In the process, CO and H_2 are passed over difficultly reducible oxides, such as ThO_2, Al_2O_3, WO_3, ZnO, etc., at pressures up to 600 atmospheres and temperatures of about 400 to 500 C. In one such application at 450 to 475 C, and 150 atmospheres using ThO_2 catalyst, mixtures of H_2/CO of about 1.1 gave 40 to 75 percent conversion of the CO to produce yields of 125.7 g products/cu m inert free feed, of which 38 percent were liquids and 26.4 percent was isobutane. Such processes offer an alternative to the conventional Fischer-Tropsch synthesis in which the higher temperatures may be anticipated to simplify the product yield of carbon and production problems can be suitably minimized.

Another alternative mode for operation of the Fischer-Tropsch synthesis is through use of higher pressures to obtain large yields of alcohols. Figure 12b shows that the formation of alcohols other than methanol is favorable thermodynamically for H_2 + CO mixtures that typify the Class A reactions. Alternative methods for production of methanol are covered in another section. The direct synthesis of higher alcohols using Fischer-Tropsch catalysts was called the Synthol process in the early German work, and was carried out under conditions very similar to the isosynthesis but using the alkalized iron oxide catalyst. The product was a mixture of alcohols, aldehydes, ketones, acids and other compounds. A variety of effort has gone into alternative catalyst and process developments,(62) but processes aimed at the higher alcohols have produced mixtures, such as that indicated, that are expensive to handle if separation of the mixture is required. It appears that little concern was given in the earlier work to the possible fuel value of that mixture if used without separation.

Production of Methanol. Among the various novel fuels proposed recently methanol might be an attractive sulfur-free fuel if it could be produced at a reasonable cost. It is clean burning and can be transported and stored readily as a liquid. However, the heating value of methanol is only about 67,000 Btu/gal, compared to about 150,000 Btu/gal for fuel oil so that about twice the volume is required.

Recent consideration has been given to the possibility of producing methanol in large plants from foreign sources of natural gas and shipping it to the U.S. for use as a source of energy to generate electricity.(74) Several utilities have shown an interest in this idea. It has been claimed that the cost of the delivered methanol ($0.70/million Btu) would be less than the cost of delivered liquefied natural gas (0.73/million Btu), assuming availability of foreign natural gas at $0.10/million Btu. Methanol could be used as a fuel for gas turbines as well as for boilers.

Methanol is now produced by reaction of CO with H_2 in the presence of a catalyst. The required mixture containing 2 moles of H_2 and one mole of CO is called synthesis gas. In recent years it has been produced by reforming natural gas, but formerly it was made by reacting steam with incandescent coke to give "blue gas", which was converted through the water-gas shift reaction to increase the hydrogen content. Synthesis gas can be produced directly from coal by reaction with oxygen and superheated steam.

The conventional methanol synthesis process operates at 300-375 C and 270-350 atm. However, in early 1968, Imperial Chemical Industries announced an improved process operating at a lower temperature, 250 C, and substantially lower pressure, 50 atm, and uses a new highly active copper catalyst. Since the lower pressure permits the use of a centrifugal compressor, substantial cost savings over the higher pressure process are realized. Most new methanol plants are using the ICI process. Since the copper catalyst is very sensitive to sulfur poisoning, the synthesis gas must be sulfur free.

The price of methanol has been declining in recent years and is currently about $0.14/gal on the Gulf Coast. A 1970 estimate(75), allowing for a 20 percent return on investment, was about $0.078/gal for either a 200-million-gal/year high-pressure plant or a 100-million-gal/year low-pressure plant. These estimates were based on low-cost natural gas as a source.

Economic Evaluation

Cost estimates were made for Fischer-Tropsch and methanol synthesis. In each case, primary cost data were obtained from the literature(76,77) and the appropriate scaling factors were used to cost a plant having an energy output of 9.6×10^9 Btu/hr. Fischer-Tropsch synthesis produces a synthetic gasoline with a heating value of 22,800 Btu/lb and some waxes. Methanol synthesis produces only methanol which has a heating value of 8,600 Btu/lb. The range of capital and operating cost estimates for these syntheses using various types of coal are listed in Table 16. The lowest costs are for Eastern, low sulfur coal, while the highest costs are for Western lignite.

TABLE 16. EXPECTED RANGE OF COSTS FOR LIQUID SYNTHESIS USING VARIOUS TYPES OF COAL

Process	Capital Cost Range, 10^6 \$	Operating Cost Range[(a)], ¢/10^6 Btu
Fischer-Tropsch Synthesis	423-710	90.9-189
Methanol Synthesis	270-384	64.7-81.6

(a) Does not include cost of coal.

Pyrolytic or Carbonization Processes

Major innovations in the production of coke and valuable by-products, i.e., tars, liquids, and gases, by carbonization of coal were first developed in Germany. In more recent years, the United States has probably been leading in advancing the state of the art. Low-temperature carbonization processes (heat treatment of coal at 450 to 500 C 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 has been limited and the cost of such a desulfurization process has been thought to be relatively high. 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.

The mechanism for pyrolysis for a huge complex molecule such as coal is bound to be complicated while its structure still is not precisely known. In understanding the current state of the art, the behavior of individual hydrocarbons, however, does provide some insight into coal pyrolysis, and assists in the development of new processes to maximize the yield of desired products. Some generalizations can be made.

From the heat formation of hydrocarbon bonds, the stability of carbon bonds increases in the order: $C_{al} - C_{al}$, $C_{al} - C_{ar}$, $C_{al} - H$, $C_{ar} - C_{ar}$, $C = C$, $C_{ar} - H$, $H - H$, $C \equiv C$, where C_{al} represents carbon in an aliphatic chain and C_{ar} represents carbon in an aromatic ring. Therefore, upon heating, decomposition of alkanes may be accompanied by dehydrogenation. Since alkenes are more stable, conversion to alkanes is possible but at low rates. Aromatic hydrocarbons with long side chains form condensation products and gaseous hydrocarbons. The cycloalkanes are dehydrogenated or decomposed. Hydrogenation of alkenes formed in the process is possible due to the hydrogen liberated during pyrolysis.

Indirect Heating

C. E. Rolle developed the first furnace for the carbonization of coal by indirect heating. In the Rolle Furnace, a 3-to-5-inch layer of lignite trickled down between two walls of an externally heated retort. The large temperature difference between the external wall (600 C) and the internal wall (300 C) and poor internal mixing produced low tar yields of 65 to 75 percent of Fischer assay yields. Production feed rates were 10-15 tons of pre-dried lignite per day. Despite this, up to 1934 a third (200,000 tons) of the production of German lignite low-temperature tar was being obtained from the Rolle furnace.

The Geissen and Borsig-Beissen furnaces were improvements on the indirect heating process. In the latter furnace, a 1.2-inch layer of lignite moved downward in a helical path in a smooth rotary Sicromal tube while being continuously blended. Heat was introduced from both walls. Tar yields were over 90 percent of Fischer assay yield while throughput was 30 to 35 tons of raw lignite/day.

Direct Heating

Low-temperature carbonization by direct heating is accomplished by passing a hot oxygen-free gas directly through the coal. Furnaces for this process were developed by J. Pinsch, Lurgi, Allgemeine Vergasunsgesellschaft and Deutsche Erdole A. G. (D.E.A.). Of these the Lurgi "Spulgas" process was the most widely used by the German mining industry. For this process the lignite coal was fed into the top of an open shaft. In the drying and preheating (top) zone the lignite was heated to 150 C, losing 30 to 60 percent moisture in the process. The carbonization or second zone heated the dry coal to 600-850 C. The lowest zone cooled the coke and extracted it from the furnace. Heating was accomplished by circulating the waste gas counter to the solids flow. In the cooling zone the gas cooled the coke and was itself heated. The circulating gas was then further heated by the addition of an oxygen-free combustion gas to achieve carbonization temperatures. Hot gas was withdrawn from the top of the carbonization zone, tar vapors condensed, and the waste gas returned to the first and third zones. Hot combustion gas was added to the waste gas and carbonization gas in the first zone for temperature control. Tar yields were 90 to 95 percent of Fischer assay yields while throughput was 250 to 500 metric tons. Carbonization plants consisted of 10 to 50 furnaces.

Process Development

Much recent work on carbonization in the United States has been supported by the OCR at FMC, ARCO and U.S. Steel. Considerable effort has also been expended by the oil companies and the U.S. Bureau of Mines on development of pyrolytic processes for the production of oil from shale deposits. In addition, research has been carried out at many of the major universities, such as the University of Utah, Pennsylvania State University, and others. Some of the major recent industrial efforts are summarized below.

Project COED. Project COED (Char-Oil-Energy-Development)(78) was developed by FMC through a contract with the OCR. COED is essentially a multistaged direct contact carbonization process plus fixed-bed hydrotreating to yield a crude oil. It is intended to maximize gas and oil yields obtainable by coal pyrolysis alone. The temperature staging avoids agglomeration while countercurrent gas and char flow minimize product decomposition. The process gives the same char yield as the standard ASTM proximate analysis plus 1.2 barrels of oil and ~8000-9000 scf of 535 Btu gas/ton of coal. Operation of the 36-ton-per-day pilot plant has been successfully completed. FMC has now obtained partners for private exploitation of a char gasification venture called COGAS. A flow sheet is shown in Figure 14.

Minus 16-mesh coal is fed to the first stage fluid-bed pyrolytic unit operated at 600 F and 5 psig and the coal is heated by inert gas. The off-gas to this unit is circulated through a separate recovery system. Char from stage 1 passes to the stage 2, 800 F fluid bed, then to stage 3 fluid bed at 1800 F, and finally to stage 4 fluid bed at 1600 F. Stage 4 is heated by char combustion with 1000 F oxygen diluted with steam. Off-gas from stage 4 heats stage 3 which in turn heats stage 2. A portion of the product char also acts as a heat carrier and solid diluent to the lower temperature vessels (stages 2 and 3). This undiluted make gas is condensed for hydrocarbon recovery, then flared. In commercial practice it would be cleaned, reformed, and shifted with steam to give a product consisting of 95 percent H_2, 5 percent CH_4.

The recovered tar is filtered in a pressurized rotary filter, then hydrotreated over a fixed-bed catalyst at 775 F and 3100 psig. Crude oil recovery from this operation is 89.6 wt. percent of the feed oil. The catalyst used was American Cyanamide's HDS-3A, a pelleted Ni-Mo on alumina base. Hydrogen in the "syncrude" increased from 8 to 11 percent while nitrogen and sulfur have decreased from 1.1 and 0.4 percent to 0.16 to 0.04 percent. Hydrogen consumption was 2670 scf/bbl of oil feed.

Project Seacoke. Project Seacoke(79) was developed by ARCO in 1970 and supported by the OCR until support was dropped in favor of Project COED. Seacoke differed from COED in that both coal and petroleum residuum were considered feedstock. Project Seacoke was also a multistage (5) direct contact carbonization process using a recycle of char and off-gas to heat the lower temperature fluid beds. It was considered to be, in some respects, more complex than Project COED.

Toscoal Process. The Toscoal process(80) was developed by the Oil Shale Corporation as an alternative to their Tosco II process for retorting oil shale. It is a low-temperature carbonization using direct-heat transfer by ceramic balls. Tar yields correspond to Fischer assay yields. A flow sheet is shown in Figure 15.

Raw coal is preheated by inert hot gas using dilute phase fluid bed techniques. The preheated feed is transported to a rotary kiln where it is contacted with heated ceramic pellets to give an equilibrium temperature of 800 to 970 F. The solid char passes through the trommel screen after leaving the kiln, is then cooled in a second kiln and sent to storage. The cooled ceramic pellets pass over the trommel screen and are returned to the heater. Gas vapors are condensed and fractionated. Noncondensible gas is utilized as a pellet heater fuel or sold.

Garrett Process. The process of Garrett Research and Development(81) is a low-temperature flash-carbonization process with indirect heating. Residence time is reported to be 2 to 5 seconds. Liquid yields are reported to be higher (~double) than those obtained by Fischer assay, and, as shown in Table 17, apparently are higher than any

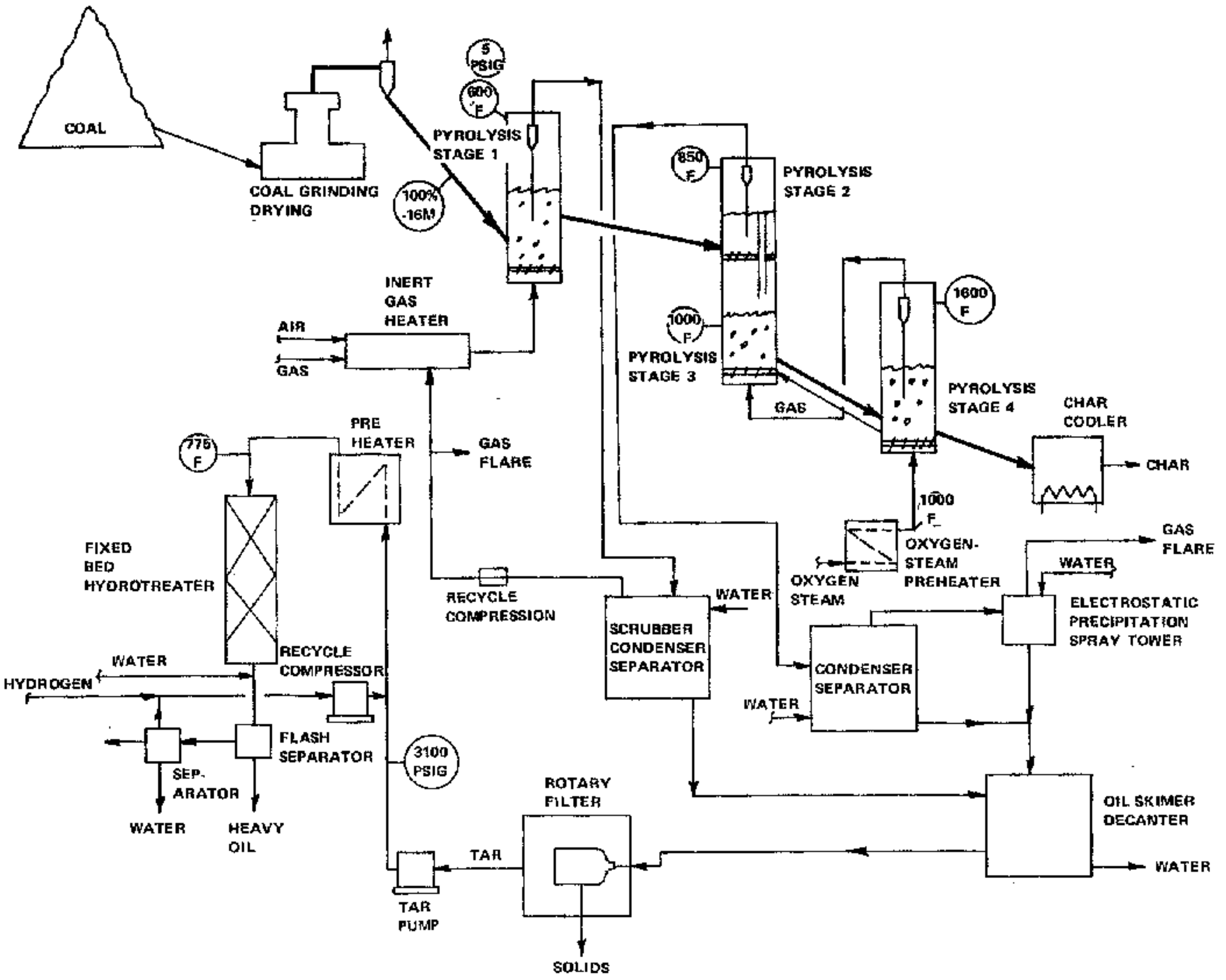

FIGURE 14. (O.C.R.'S PROJECT COED) CRUDE OIL PRODUCTION
36 TPD PILOT PLANT

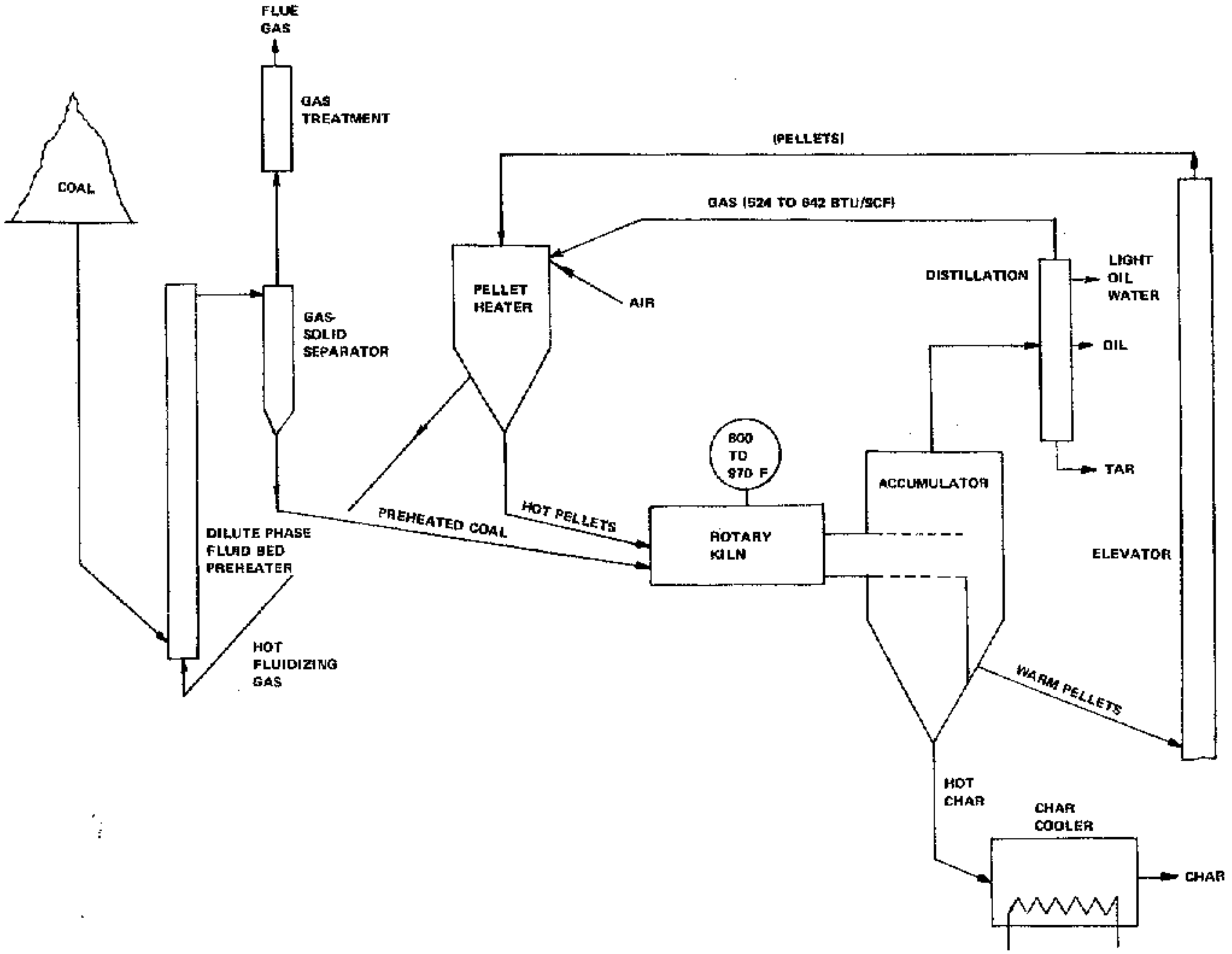

FIGURE 15. THE OIL SHALE CORPORATION TOSCOAL PROCESS 1 TON PER HOUR PILOT PLANT TAR PRODUCTION

other comparative process. Little additional data are available except that a pilot plant has been or is under construction. The literature indicates that Garrett has sought to interest others in the process.

TABLE 17. LIQUID YIELDS FROM VARIOUS COAL CARBONIZATION PROCESSES(81)

Process	Yield, lb/ton of coal
U. S. Bureau of Mines	250-400
FMC Corporation	370-470
Lurgi-Ruhrgas	450-570
Garrett Process	-700

Selective Desulfurization

The most common gaseous reactants used to desulfurize coal have been steam, air, H_2, water gas, N_2, CO, CO_2, CH_4, C_2H_4, town gas, and coke-oven gas. No work was found with halogens.

Steam. Snow(6) carbonized a coal containing 2.51 percent pyritic, 2.63 percent organic, and 0.20 percent sulfate sulfur, crushed to 20 x 40 mesh size, for 4 hours at test temperatures from 300 to 1000 C. A maximum of 2 hours additional time was required for heating the samples to the final temperature. At 600 C, using a steam-to-coal ratio of 0.18 g-moles per g, 65 percent sulfur conversion was obtained with 34 percent organic loss. The results for nitrogen at the same gas-to-coal ratio were 51 percent and 35 percent, respectively, for sulfur and organic gasification. At 1000 C and a gas-to-coal ratio of 0.22, the sulfur gasification was 84 percent for steam and 57 percent for nitrogen. The organic conversion with steam was not measured, but evidently was almost double the value of 43 percent for nitrogen.

Mangelsdorf and Broughton(82) conducted a series of experiments very similar to, but less extensive than those of Snow. They used a coal containing 2.26 percent sulfur, crushed to pass through an 8-mesh screen. They found that at a steam-to-coal ratio of 0.8 g-moles/g during a 5-hour carbonizing treatment at 600 C, 44 percent sulfur elimination was obtained as compared to 33 percent with heat alone. The organic conversion was 40 percent as compared to 28 percent with no added gas.

High-temperature steam-air treatment has been reported by Leonard and Cockrell(3) to be effective in reducing sulfur concentrations. The treatment of Rumanian and Indian coals gave sulfur reductions of 30 and 57 percent, respectively. The addition of NH_3 along with the steam resulted in the removal of 88 percent of the sulfur from Indian coals. Treatment with steam and air at 150 to 200 psi and temperatures up to 120 C resulted in the removal of the pyritic sulfur which made up approximately 50 percent of the total sulfur content.(16)

Air. Campbell concluded that the injection of air into the coking process, as in the beehive oven, gave less sulfur removal than the absence of air, as in the by-product ovens.(83)

However, excellent results were obtained by Postnikov, Kusmin, and Kirillow using air to gasify sulfur from mixtures of carbonaceous pyrites (44 percent sulfur) and premium coal.(84) Using a batch charging technique for the solids, they established that (1) H_2S was first formed and then SO_2 came over in the latter stages, (2) CS_2 formation reached a maximum at 1000 C, where it represents up to 30 percent of the total sulfur, and is favored by an increase in the amount of carbonaceous matter present and a decrease in the air supply, and (3) elemental sulfur formation was extremely favorable with yields up to 80 percent, being favored by moderate temperatures (about 800 C), a minimum amount of carbonaceous matter present, and an optimum oxygen-to-sulfur ratio for each set of conditions.

Oxley(85) used a fluid-bed process to study sulfur gasification rates in the presence of excess air and found highly preferential sulfur oxidation at temperatures of about 550 C. Blum and Cindea(86) have reported good success when carrying out desulfurization at 380 C using an air-steam mixture in a 15:85 ratio. Sinha and Walker(87) have studied sulfur removal from seven U.S. coals at temperatures between 350 and 450 C and consider it a promising approach.

Other Gases. The work of Snow(6) is probably the most extensive. He found the following order of effectiveness for sulfur gasification between 600 and 1000 C, at a gas-to-coal ratio of 0.20 g-moles/g and for a 4 to 6-hour treatment: H_2, NH_3, water-gas, N_2, CO_2, CO, CH_4, and C_2H_4. The efficiency of steam fell between H_2 and NH_3. Steam and water-gas also caused rather appreciable carbon losses, especially at the higher temperatures. Mangelsdorf and Broughton(82) found water-gas to be the most efficient at 600 C of the various gases they tested, with no appreciable carbon loss at a gas-to-coal ratio of 0.8. Their results showed the following order of effectiveness: water, gas, H_2, illuminating gas, and CO. Steam was again just below H_2 in its efficiency for sulfur removal.

Brewer and Ghosh(88, 89) concluded that NH_3 was the most efficient gas they investigated for removing sulfur. Carbonizing a 20 x 30 mesh Illinois coal containing 2.12 percent pyritic, 1.30 percent organic, and 0.13 percent sulfate sulfur at 800 C, they found sulfur gasifications of 52 percent using an NH_3-to-coal ratio of 0.009 g-moles/g, and found no appreciable difference in the effect of ammonia over city gas, and obtained sulfur conversions from 60 to 68 percent at 880 C.

The action of H_2 and hydrogen-rich coke-oven gas on the sulfur contents of coke was determined by Powell.(90) Using a 1.20 percent sulfur coal, he obtained 92 percent sulfur elimination at 1000 C for a hydrogen-to-coal ratio of 0.11. Coke-oven gas at the same conditions gave 71 percent sulfur conversion as compared to 33 percent for ordinary distillation. At 500 C and a gas-to-coal ratio of 0.05, the sulfur gasifications were 60 percent for H_2, 33 percent for by-product gas, and 14 percent for simple distillation.

Vestal and Johnston(91) have recently studied the kinetics of coal desulfurization by H_2 under nonisothermal conditions. They observed that organic and pyritic sulfur in coal can be removed by hydrogen treatment; however, complete removal was possible only at about 1000 C.

Economic Evaluation

The cost of coal carbonization to produce char was estimated from the partial oxidation step of the COED Process. In this step, shown schematically in Figure 16, purified COED process gas is combined with preheated oxygen and steam ahead of the reactor. The overall reaction is exothermic and waste heat is recovered. The synthesis gas, containing soot, is quenched with water to remove the bulk of the carbon. The resulting slurry is exhausted with fuel oil and carbon is recovered in the form of pellets containing 5 percent moisture. The synthesis gas is further processed to produce H_2. A cost estimate was made of scaling data from the literature(92) to a plant having a char output equivalent to 9.6 x 10^9 Btu/hr (10,000 tons/day of char). The capital cost is about \$80 x 10^6 and the operating cost is about \$0.30/10^6 Btu in the char. These costs include the cost of H_2 production from the synthesis gas, but do not include a credit for the heat content of the H_2.

The cost of preferential air oxidation of coal was based on a very preliminary process design as shown in Figure 17 where air at 350 to 460 C is used to fluidize pulverized coal. The assumptions upon which the cost estimate is based are as follows:

1. Coal with a heat content of 12,500 Btu/lb is fed at the rate of 384 tons/hr (high sulfur, Eastern coal)
2. Only 50 percent of the sulfur found in the coal is removed in the process (only pyritic sulfur is removed)
3. The residence time in the fluidized bed is 1 hour
4. The air flow rate into the fluidized bed is twice the stoichiometric requirement for sulfur oxidation and well above the requirement for minimum fluidization velocity
5. The coal particle size is 150 mesh
6. The process is associated with a pulverized-coal-fired boiler.

The cost of coal grinding is charged to the power plant and heat requirements are met by exchange with steam and/or flue gas generated in the power plant. It is estimated that at least 70 percent of the process heat requirements can be recovered in heat exchangers. The coal product is fed to the furnace at 750 F and the tail gas from the fluidized bed is incinerated in the boiler firebox after SO_2 removal. The capital and operating cost estimates are itemized in Tables 18 and 19, respectively. It is anticipated that the capital cost would be about \$10 x 10^6 and the operating cost would be about \$0.03/10^6 Btu.

RESEARCH AND DEVELOPMENT NEEDS

The previous discussion outlines the current state of the art in liquefaction and chemical refining of coal. Based on this information the following R&D needs are presented.

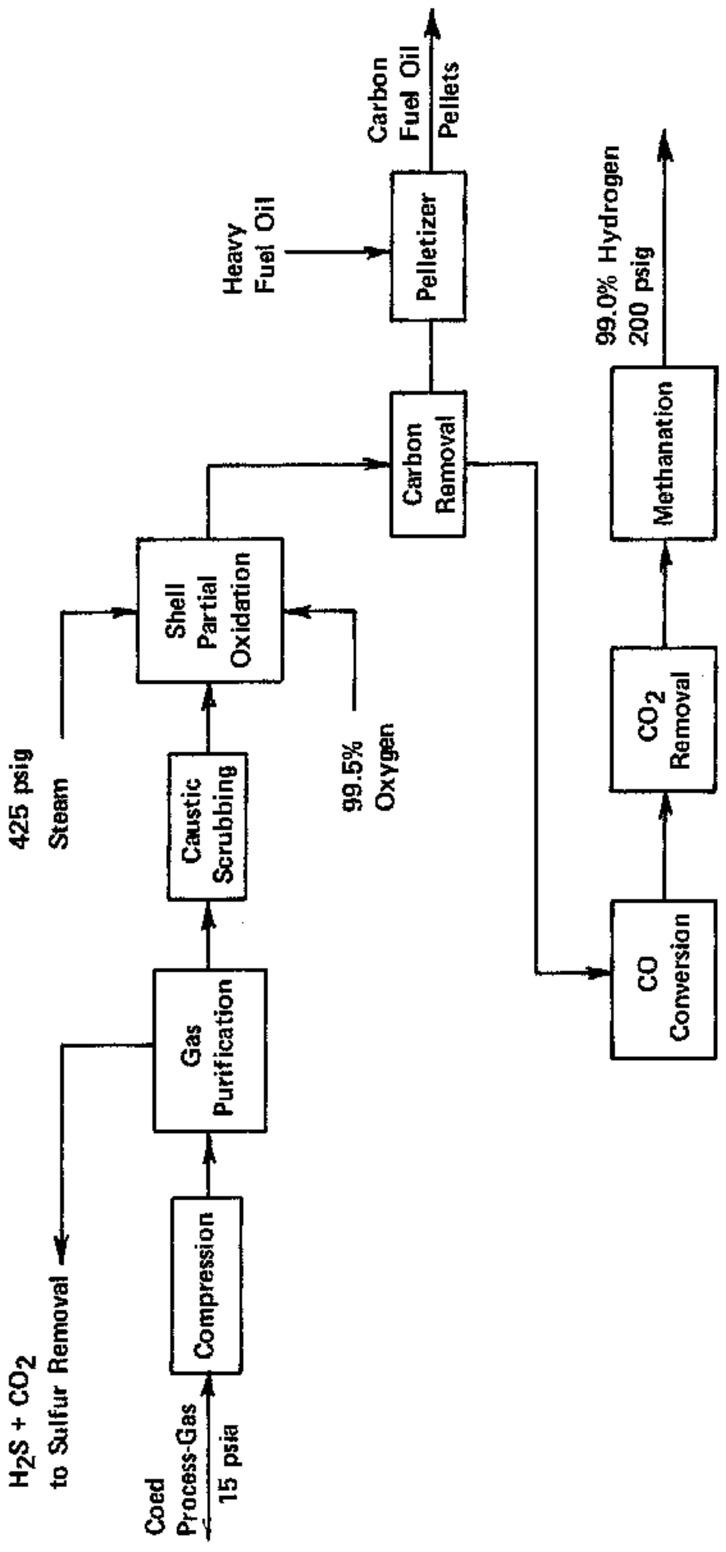

FIGURE 16. BLOCK DIAGRAM FOR PARTIAL OXIDATION PLANT

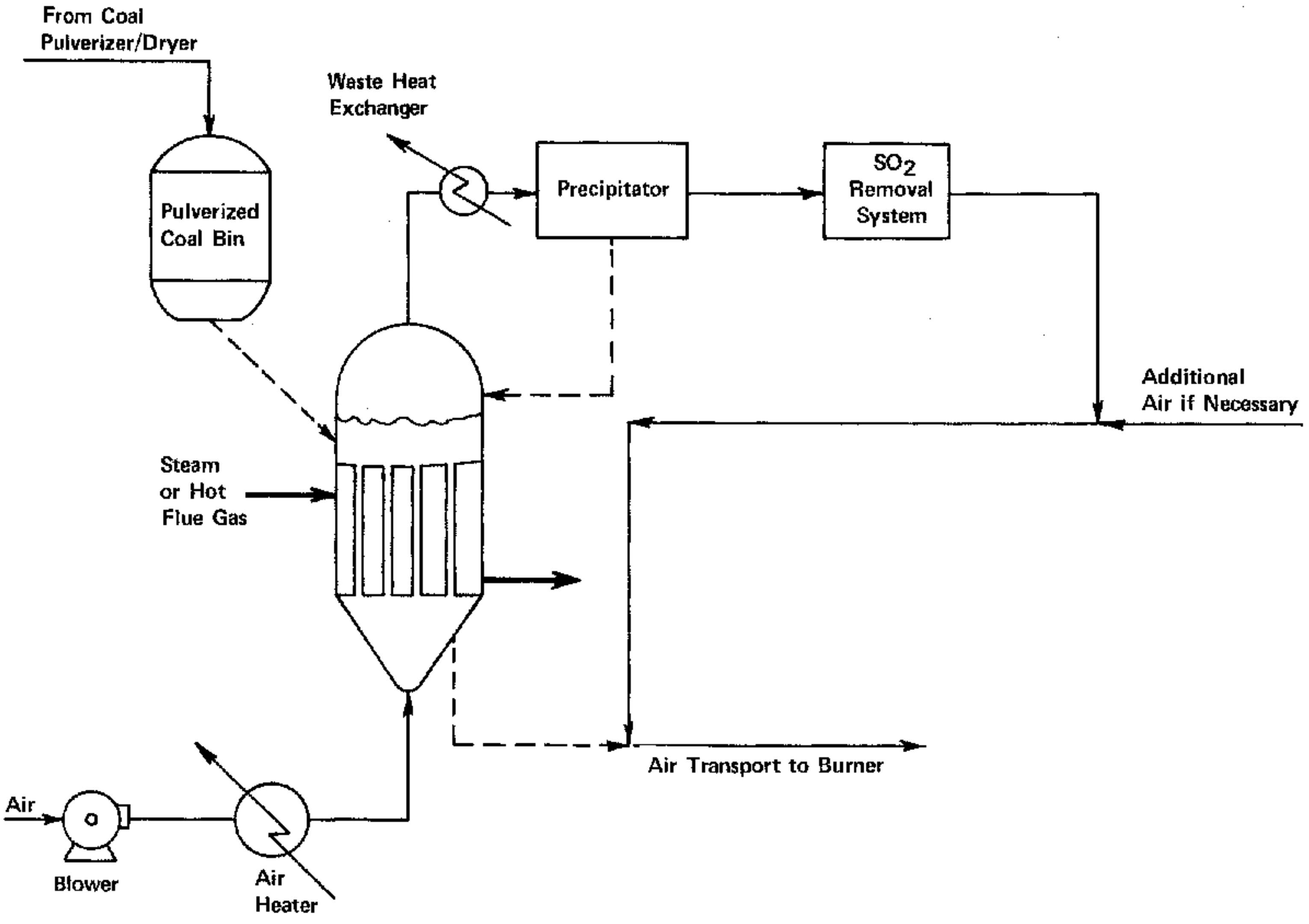

FIGURE 17. PREFERENTIAL OXIDATION OF COAL

TABLE 18. CAPITAL COST FOR PREFERENTIAL OXIDATION OF COAL

Equipment	Capacity	Installed Cost, $
Blower	21,000 fm, 100 hp	250,000
Air Heater	130 ft^2	10,000
Fluidized Bed and Heat Exchanger	21 ft diam by 63 ft high 10,000 ft^2 heat exchange area	2,200,000
Waste Heat Exchanger	130 ft^2	10,000
Precipitator	27,000 fm	60,000
SO_2 Removal System	280 tons SO_2/day	6,000,000
Subtotal		8,530,000
Contingencies @15% of installed cost		1,280,000
Contractor fee @3% of installed cost		260,000
		10,070,000

TABLE 19. OPERATING COST FOR PREFERENTIAL OXIDATION OF COAL

Item	$/yr
Operating Labor	144,000
Supervision	52,000
Maintenance	500,000
Overhead	120,000
Steam	600,000
Electricity	5,000
Raw Materials	650,000
Taxes and Insurance	200,000
	2,271,000

Aqueous Leaching Processes

No major equipment design problems are expected in the crushing-grinding, mixing and leaching and drying steps of aqueous leaching processes. The same equipment as that currently used by chemical companies can be employed. The mixing of solids and liquids and drying of solids are conducted throughout the process industries.

Minor problems may be encountered in pumping the slurry into the reactor, leaching the coal, and removing it from the reactor. For example, erosion of valves and pumps could be a problem. Careful selection of construction materials would be required. Chemical corrosion could be a major problem with ferric salts, especially with ferric chloride which causes chloride pitting. For this reason, ferric sulfate is preferred. Alloys with high-corrosion resistance should be available for construction of equipment.

Washing of residual sulfate from the leached coal and separation of leached coal from aqueous slurries may or may not be a problem. This will depend on such factors as the ultimate particle size of leached coal and the formation of tar-like reaction products.

In addition to the removal of organic sulfur, a major technical problem is the deposition of sulfate sulfur onto the coal from hydrolysis of ferric sulfate and extraction of elemental sulfur from leached coal. Sulfate sulfur can be removed with an acid leach, while elemental sulfur can be extracted with an organic solvent. Solvent losses may be prohibitive.

The feasibility of using aqueous solutions of bacteria to remove sulfur from coal might also be investigated.

Solvent Refining Processes

The principal advantage of solvent refining has been that it represents a viable alternative for stack-gas cleaning, especially for utilities. However, if stack-gas treatment technology proves practical in the next few years the incentive for solvent refining will be less attractive. Solvent refined coal may nevertheless be a very attractive fuel for small industrial and domestic uses. In addition, many of the program elements within a solvent refining research and development effort are applicable to other coal treatment systems as well. After detailed review of previous and ongoing research, the most important areas for further study are

1. Process Economics
    a. Hydrogen Production – Development of an inexpensive source of hydrogen.
    b. Mineral Separation – Development of practical solid separation techniques for recovery of char ash from coal oil.
    c. Dissolution of Coals – Development of design information on rate, material balances, solubilites, etc., to permit less severe conditions to be used in the coal dissolution step, and thus permit more economic processing to be developed.

2. Process Operability
    a. Mechanical Reliability
    b. Materials Problems
        1. Corrosion
        2. Erosion
    c. Process Control

3. Environmental Problems
    a. Control of Emissions and Carcinogenic Residuals
    b. Residual Char/Ash Utilization and/or Disposal.

Active R&D programs are being conducted in several of these areas and are summarized in Table 20. Research programs within Category 1 (Process Economics) involve mainly laboratory and pilot-scale studies. Category 2 (Process Operability) involves pilot-scale programs while Category 3 (Environmental Problems) encompasses laboratory, field and analytical studies. Since most information developed in research on solvent refining should also be directly applicable to liquefaction, considerably larger support of solvent-refining research can be recommended than would otherwise be justified.

A major item, and perhaps the most important factor in the area of liquid fuels technology, is the development of low-cost sources of hydrogen. This is critically important not only for solvent refining, but for liquefaction and Fischer-Tropsch synthesis. Alternatives for hydrogen generation in solvent refining of coal are

1. Use one of the gasifiers being developed for SNG production (may not be suitable for solvent refining)
2. Develop a gasifier that is capable of using the char associated with the mineral residue from the solid/liquid separation step
3. Develop gasifiers especially suited for the needs of solvent refined coal
4. Develop a novel source of hydrogen
5. Perform steam reforming or partial oxidation of the light oil or product gases.

However, in all of the above except 2, disposal of the mineral residue containing about 70 percent ash and 30 percent carbon would then become a serious problem.

There is only one publicly announced major effort at present to produce hydrogen, and that is the steam-iron fluidized bed program in support of gasification programs under OCR sponsorship at the Institute of Gas Technology (IGT). The University of Kentucky has a modest research effort supported by the National Science Foundation (NSF) to consider hydrogen production using electrochemical techniques. Other efforts should also be launched in the near future starting with bench-scale research and development. Although pilot-scale work is possible, it is apparent that few proposed processes are ready for such advanced study. Extensive support of pre-pilot activities is needed.

The solids-liquid separation step is critical to the process and requires considerable R&D to assure high recovery of the wash solvent and efficient solids removal. There are many alternatives:

TABLE 20. ACTIVE R&D PROGRAMS RELATED TO ORGANIC SOLVENT REFINING OF COAL

Organization	Sponsor	Type	Approximate Funding, $ Millions	Duration	Study
Southern Services (SS)	EEI SS	6 ton/day Pilot Plant	6.0	1972-1974	Filtration Process Operability
Pittsburg & Midway	OCR	50 ton/day Pilot Plant	18.0	1972-1975	Filtration Process Operability
Auburn University (AU)	NSF AU	Basic Chemistry	0.7	1974-1976	Solvent Studies
University of Michigan	NSF	Solids Separation	(a)	(a)	Filtration
University of Kentucky	NSF	Solids Separation Hydrogen Sources	0.4	1973-1975	Novel Techniques Novel Techniques
Pittsburgh & Midway	OCR	Bench-Scale Unit	(a)	(a)	(a)
Washington State University	OCR	Residue Utilization	(b)	1971-1972	--
Oklahoma State University	OCR	Environmental Studies	(b)	1971-1972	Desulfurization

(a) Unknown to Battelle staff.

(b) Funding level unknown but thought to be modest (i.e., <$25,000 per year).

1. Filtration
2. Centrifugation
3. Gasification
4. Solvent precipitation
5. Hydroclones
6. Electrophoresis
7. Evaporation, etc.

Only the first is being studied adequately, and a major effort in solids liquid separation is recommended.

There is a lack of fundamental data on coal dissolution, transport, and chemistry. Reaction rate kinetics and solvent action on different types of coals are poorly defined. Only a few coal types are currently being studied, and only one is being studied in recycled solvent systems. In contrast to the German experience, lignite and subbituminous coals are reported difficult to refine, while anthracite has not been successfully refined at all. Adaptability of the process to these other coals could be critical to its widespread use. In addition to the work at Auburn, there should be similar programs at other research centers. Considerable attention needs to be given to the factors affecting the fate of coal sulfur and nitrogen as a result of processing, solvent, and coal variations. Impurity removal is the critical step in the process and an almost forgotten item in current research.

Process operability is of major concern both to solvent refining processes and liquefaction processes. The pioneering pilot facility that SEC and Edison Electric Institute (EEI) have launched at Wilsonville for evaluating a variety of processing equipment appears especially suited for component evaluation. Present efforts are being devoted to solids separation and product solidification, but even if these problems are solved, many other needs exist. Use of the facility for a number of years will probably be required for determination of the reliability of equipment, the testing of suitable control devices, process optimization, and sample preparation. Further studies, probably in this facility, on solvent material balances and hydrogen requirements are also needed. Additional component design and development prior to pilot testing appears highly desirable. There is a general feeling by many of the people having some experience in this area of technology, that feeding of solids to the reactor and pressure reduction of the effluent may give rise to serious reliability problems. The adequacy of the materials of construction for each vessel and component in the process should be determined prior to piloting. Current estimated capital costs for a commercial scale plant are based on the use of carbon steel and low-alloy steel in most parts of the plant. If studies show that these materials are inadequate from a corrosion standpoint, then the initial plant investment could be significantly increased. Materials problems in the preheater may be especially difficult to solve.

Environmental problems associated with coal liquefaction may involve significant health problems. It is well known that sufficient exposure to a variety of chemicals can cause cancer in man. Since 1900, it has been recognized that workers handling coal tars, certain aromatic amines, and some heavy metal compounds have increased incidences of carcinoma of the skin, bladder, and lungs respectively. Likewise, other coal-derived products such as benzo(α)pyrene, dibenz(α, ι) anthracene, 7, 12-dimethylbenz(α)-anthracene and 3-methylchol-anthrene are known to be strong carcinogens.

Therefore, prompt attention to conversion of waste to environmentally acceptable materials, hopefully at an economic advantage, is very important. Currently, a modest research effort in this area is being conducted at the University of Washington. Work of this type should be expanded at other locations and considerable emphasis placed on developing several practical solutions in the near future.

Catalytic Hydrogenation Processes

Since many of the R&D needs of hydrogenation technology to produce liquids from coal are the same as those for solvent refining, only those technologies particularly pertinent to severe hydrogenation processing of coal will be delineated in this section. Filtration, hydrogen generation, materials of construction and equipment component developments of general utility were treated in the preceding section. However, it must be emphasized that improvement in hydrogen generation procedures would be of critical importance in the liquefaction of coal. In the H-Coal process, for example, hydrogen production is the major cost item when the all-distillate method is practiced. Any marked reduction in hydrogen cost would be reflected in significant reduction of product costs. Materials of construction and process equipment design common to both technologies also merit attention. The slurries handled are abrasive so that combating equipment wear, particularly at high temperature and pressure, is both a mechanical and a metallurgical problem.

Development of improved hydrogenation catalysts is probably the most important factor needing attention in the synthetic liquid fuels picture. More active, physically rugged, and regeneratable catalysts could improve the processes by lowering catalyst costs, increasing throughput by diminishing reaction time, selectively removing sulfur and nitrogen, and maximizing primary conversion of coal to liquid. With the exception of the German efforts, the selection of catalysts to date has apparently been based on the experience of the petroleum industry rather than the specific nature of the molecular structure of coal. Furthermore, improved activity could reduce the requirements for hydrogen gas pressure. Cost savings would be reflected in lower costs for compression and the simpler design of vessels needed to withstand the pressure. Operating temperatures might also be diminished. Taken together, these benefits would also enhance safety.

The second most critical area needing attention is the support of a developmental effort to carry out process research studies in facilities which permit direct and independent comparisons of the various processes and equipment under study in this country. These include the H-Coal process and the U.S. Bureau of Mines processes, as well as those under study at the University of Utah, Consolidation Coal Company, and elsewhere. Such integrated facilities should probably be sized at a 1/4 or 1/2 ton/hour level, similar to the solvent-refined coal pilot facility of the Southern Company, but perhaps designed with a little more flexibility since variations of the hydrogenation processes are considerably more diverse than with the solvent refining processes. These facilities should be considerably smaller than the demonstration plants being proposed by the U.S. Atomic Energy Commission and others, as demonstration plants have a tendency to freeze design concepts.

The third item needing attention is to select several of the more advanced and less risky coal liquefaction processes and bring them quickly along to the demonstration plant level. Most oil companies and many other organizations have such technology available, but heretofore have not wanted to risk the capital invested in a demonstration plant without some assurance as to the future of synthetic fuels in relation to the volatile political situation in the world fuel market.

The entire area of coal-based petrochemicals needs to be examined before the energy crisis becomes a chemical crisis. Carbon blacks should probably be produced from coal rather than from the diminishing supplies of natural gas. Ammonia, hydrogen, acetylene, vinyl chloride, polyethylene, low-molecular-weight alcohols, aldehydes, propane and a host of other chemicals basic to everyday life are also currently made from natural gas. With liquid fuels also running short, benzene, toluene, xylene, styrene, etc., all also basic to our industrial structure, will be affected in the future. Since production of coal-tar chemicals is a direct function of the need for coke, a viable plan for a massive alternative source needs to be started.

New equipment design and development, and material studies for application of direct interest to catalytic processes should also be supported. These might include high-pressure solid feeding devices, letdown values, process control items, and the like. There is a serious need for an adequate testing procedure and equipment to compare performance of new materials and equipment with previous systems employed in earlier times.

Support of novel process variations to improve the chances for commercial success of liquefaction processes is recommended. New reactor designs, development of an economical process based on a mixed CO-H_2 feed, methods to preactivate the coal, electrolytic reduction, and distillation of all organic materials from the ash residue are examples of work that should be supported at the bench- and laboratory-scale level.

Adequate analytic techniques for determination of various components in coal and coal products have still not been worked out. This is true even in the case of organic sulfur. This situation can be explained by the fact that in combustion processes, only total sulfur has been important. However, the particular form of the sulfur in the coal matrix may be critical since sulfur readily poisons most catalysts. At the present time, total sulfur can be obtained with a high degree of accuracy. This is also true of inorganic or pyritic sulfur. However, organic sulfur is obtained by difference and the value is meaningless for catalyst research since the organic sulfur is in four forms: thiophenes, ethers, sulfides, and disulfides. Means to quantitatively detect each of these must be developed to assist in catalyst development. Similar problems exist with many other components of coal.

Fischer-Tropsch and Related Syntheses

In 1964, Farley(71) pointed out that "the main cost of the oil-from-coal process is in the production of the actual synthesis gas, and not in transforming the gas into oil". Thus he reported that the cost of the gas was more than 70 percent of the process and felt that technological work on the Fischer-Tropsch method should be stopped until such time as gas could be produced more cheaply. It now appears that a reevaluation of this cost estimate should be undertaken in terms of the current and projected costs for synthesis gas production.

For the Fischer-Tropsch process itself the most important difficulties are identified with the catalyst properties and performance. Improvements in catalyst stability and specificity, and in the methods used for maintaining and regenerating activity would have important impact on the future process design. In view of the lack of emphasis on Fischer-Tropsch processes in the last decade, a detailed study of the state of the art of the surface chemistry of pertinent catalyst systems should be undertaken to determine whether modern surface study methods and results have changed any of the important conclusions reached in the earlier catalyst studies. These two recommendations represent information and literature study programs that would be excellent support for the experimental programs listed below.

The large fraction of the total cost credited to synthesis gas production for the Fischer-Tropsch process is largely a reflection of the cost of H_2 production for the $2H_2 + 1CO$ mixtures required. This realization leads to greater interest in those processes where substantially lower H_2/CO ratios are required or where the direct use of water in the syntheses can replace much of the investment in water-gas and shift technology. Further, the shift in present interest toward liquid fuel production, rather than gasoline production as formerly, leads to interest in a greater range of fuel hydrocarbons. The following have been identified as the most promising areas for further investigation.

1. Study of the direct reaction of CO with H_2O to determine the optimum catalyst, and the processing conditions, that would permit use of available gas mixtures, such as producer gas, blast furnace gases, etc., in hydrocarbon synthesis.
2. Study of catalyst and process development for production of low molecular weight hydrocarbons at temperatures above about 400 C.
3. The direct reaction of coal and derived carbonaceous materials with H_2O, and mixtures of H_2O, CO, and H_2, is a large and promising research area that has been covered in a separate section (see Catalytic Hydrogenation Process).
4. Somewhat less promising but worthy of examination would be the use of the higher alcohol synthesis to generate a partially oxidized product stream having substantial fuel value and convenient transportation characteristics.

Each of these four systems can be studied conventionally in a bench-scale flow system designed for ease of survey of the various parameters and catalyst choice. The basic construction would be the same for each so that a common laboratory might be used for the programs. In view of the survey aspects of catalyst choice indicated for each program, more than one reactor system probably would be required to expedite the studies. Facilities for catalyst preparation and product analysis also would be needed.

The direct reaction of CO and H_2O has produced high product yields and deserves emphasis in further work. The effect of this process is to combine the shift and synthesis reactors of the conventional Fischer-Tropsch, but more information is needed on the effect of other gas components, especially hydrogen, on the course of the intended reaction and the nature of the products. The favorable free energy changes for reaction of CO and water vapor extend the useful temperature range at least to 500 C and offer a wide range for survey of catalyst and reaction conditions. Similarly, the high-temperature production of low molecular weight hydrocarbons offers a wide range of applicability. Previous trials have shown considerable success.

In the 50 years of commercialization that have elapsed, the research and engineering attention to details of the $H_2 + CO$ process has been extensive so that methanol plants based on natural gas as a raw material are essentially standard items. In consideration of the future research and development requirements with respect to the use of coal as the raw material, the following items are noteworthy.

The production of synthesis gas from coal requires consideration of problems in purification of the gas that are significantly worse than exist for natural gas sources. The need for effective and inexpensive gas purification methods for synthesis gas applies to all catalytic liquefaction processes based on carbon oxides and H_2 if coal is the raw material. The current commercial experience with cryogenic processing should be examined to determine if it can replace the more conventional gas separation methods used for gas purification.

The activities of catalysts available for the methanol synthesis are not at all as good as desired, but the intensive effort that appears to have gone into the subject implies that further improvements may be difficult to find.

Current methanol processes are carried out under high pressure, moderate temperature, and high recycle conditions that are chosen as compromises among the limitations that arise due to the stringent need to control catalyst temperature during this exothermic reaction process and the large number of competing reactions that can occur. Part of this problem is taken care of by control of catalyst selectivity, but some consideration might be given to unconventional reactor arrangements that can offer improved temperature control under pressures of 200-400 atmospheres.

Among the alternative methods for methanol production is a commercialized method for direct oxidation of hydrocarbons or coal itself to methanol. The direct oxidation method results in a mixture of products that may have more value as fuel than as a methanol source. The possibility that future coal processing may produce a variety of gaseous hydrocarbon streams may present the opportunity either to use such streams as gas, or convert them to liquid fuels in the form of this crude methanol mixture.

Before initiating experimental work, more reliable estimates than those reported in this study are needed for the cost of producing oxygenated hydrocarbons from coal. A crude methanol product would be satisfactory for fuel use. A cost comparison should be made between production of crude methanol and production of hydrocarbons by the Fischer-Tropsch synthesis, since both processes require a mixture of carbon monoxide and hydrogen of approximately the same composition. If projected costs for production of crude methanol from coal are favorable, experimental work will be needed to determine whether synthesis gas from coal can be satisfactorily desulfurized to prevent catalyst poisoning. Methods to produce methanol, and other partially oxidized fuels directly from coal, in order to eliminate the cost of gasification, should also be considered.

Pyrolytic or Carbonization Processes

There are obviously very substantial R&D needs in this area. In the case of pyrolysis of coal, the yields of liquids have been too low to be an economically attractive venture without an adequate market for the large amounts of relatively high-sulfur char or coke produced. The recent work with flash carbonization appears promising, and should be pursued.

A concentrated long-range effort in carbonization technology would appear to be an important national objective. In the long run, devolatilization of boiler coal feeds and use of the char with stack-gas cleanup may be the optimum environmental compromise to the country's energy crisis for large users of fossil power.

Selective volatilization is believed to offer considerable promise to desulfurizing coals and substantial effort in this area is recommended. Further work on air/steam systems is needed. The use of halides should be investigated, and further work on hydrogenation should not be neglected. The use of catalysts or preactivation techniques also seems potentially of interest. This approach is believed to have important short-range implications and it may be the optimum long-range environmental compromise to the country's energy crisis for small industrial users of power.

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APPENDIX

LIST OF ACRONYMS

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AEC	U.S. Atomic Energy Commission
ARCO	Atlantic Refining Company
BCL	Battelle Columbus Laboratories
CCC	Consolidation Coal Company
COED	Char-Oil-Energy-Development
EEI	Edison Electric Institute
EPA	U.S. Environmental Protection Agency
FMC	FMC Corporation
HRI	Hydrocarbon Research Inc.
IGF	I. G. Farbenindustrie
IGT	Institute of Gas Technology
KCC	Kennecott Copper Corporation
NSF	National Science Foundation
OCR	U.S. Office of Coal Research
RANN	Research Applied to National Needs
SEC	The Southern Company
SRI	Southern Research Institute
TRW	TRW Corporation
USBM	U.S. Bureau of Mines