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Hydrocarbonization Process Evaluation Report

Volume II

Evaluation of Process Feasibility

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MASTER

OAK RIDGE NATIONAL LABORATORY

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COAL TECHNOLOGY PROGRAM

HYDROCARBONIZATION PROCESS EVALUATION REPORT

VOLUME II

EVALUATION OF PROCESS FEASIBILITY

Prepared by

J. M. Holmes, D. A. Dyslin, M. S. Edwards,
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Prepared for the

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Volume I, ORNL-5212

Volume II, ORNL-5213

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HYDROCARBONIZATION PROCESS
EVALUATION REPORT
VOLUME II
EVALUATION OF PROCESS FEASIBILITY*

by

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ABSTRACT

Volume II of a two-volume study concerning the preliminary design and economic evaluation of a Hydrocarbonization Facility includes: (1) a review of the current status of the major processing units, (2) an assessment of operating problems, (3) considerations of possible process alternatives, (4) an evaluation of the overall process feasibility, and (5) recommendations for future process development. Results of the study emphasize the need for testing the evaluated process, which is based on the Clean Coke Process, in a continuous pilot plant using a wide variety of highly caking bituminous coals as feed material. A program suggested for the pilot plant would encompass: (1) development of improved methods for the prevention of agglomeration of highly caking coals during hydrocarbonization, (2) optimization of the yields of coal liquids, (3) investigation of a single-stage high-temperature hydrocarbonizer optimized for char production, and (4) optimization of beneficiation ratios employed during coal preparation.

1. INTRODUCTION

This report comprises Vol. II of a two-volume study on the preliminary design and economic evaluation of a Hydrocarbonization Facility for the production of clean fuels from high-sulfur coal based on the carbonization technology developed by the United States Steel Corporation in their "Clean Coke" process. Volume I (ORNL-5212) contains the basic design and economic

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analysis for the facility. This volume includes (1) a review of the current status of the major processing units, with emphasis on those systems that are still in the developmental stage; (2) an assessment of operating problems; (3) a consideration of possible process alternatives; (4) an evaluation of the overall process feasibility; and (5) recommendations for future process development.

In the Clean Coke process, coal must be beneficiated to prepare a feed to the hydrocarbonizer reactors; this feed would contain a significantly lower percentage of inorganic sulfur and ash than the raw coal. As a result, char produced by the hydrocarbonizers could comply with the Environmental Protection Agency standards for sulfur emission from power plants. Hydrocarbonization is accomplished in two stages: In the first stage the coal is partially devolatilized, and in the second stage the devolatilization is completed and the char desulfurized. Agglomeration of the coal in the hydrocarbonizers is prevented by pretreatment upstream of the hydrocarbonizers.

High-sulfur high-ash coal resulting from beneficiation will be burned in a fluidized-bed combustor to provide heat for the hydrocarbonizer reactors. Limestone will be added to the combustor for control of sulfur emissions. Sufficient hydrogen will be produced during hydrocarbonization — and from the methane and heavier hydrocarbons evolved during hydrotreating — to provide the feed stream required for hydrotreating the liquids to an acceptable fuel oil product. Cryogenic separation of the methane evolved during hydrocarbonization will result in the production of some pipeline gas for sale. The major products from the hydrocarbonization plant will be clean char and fuel oil that are suitable for use as boiler fuels. The

total product heating value will be nominally equal to the heating value of 100,000 bbl of fuel oil per day.

A summary and recommendations are presented in Sect. 2 of this volume. Sections 3-7 contain the detailed assessments of the major processing units, including beneficiation, hydrocarbonization, the tar hydrotreater, solids-liquid separation, and the fluidized-bed combustor respectively. An analysis of the physical data available for design is discussed in Sect. 8. Section 9 reviews the status of transportation and combustion of the char product.

2. SUMMARY AND RECOMMENDATIONS

2.1 Current Status of Process Development

Table 2.1 lists the current status of the major components selected for the Hydrocarbonization Facility. The development phases of the various components are designated as process development unit (PDU), pilot plant, or commercially available.

The hydrocarbonization system (Unit 12) is currently being developed as part of United States Steel Corporation's "Clean Coke" process in a PDU located in Monroeville, Pennsylvania, and having a capacity of 1/4 ton of coal per day. The carbonizer vessel in this PDU has a 10-in. ID and char bed depths of 15 or 30 in.; these depths are capable of providing up to 2-hr holdup time in the bed. Heated fluidization gas is fed to the bed through a perforated distributor plate, and the gas plus the volatiles released from the coal leave the top of the carbonizer after passing through a 6-in.-diam cyclone. The carbonizer vessel is operated under conditions that simulate both the stage I (840°F) and stage II (up to 1500°F) hydro-

Table 2.1. Current status of major components
of the Hydrocarbonization Facility

Component	Unit No.	Current development status
Beneficiation	11	Commercially available
Hydrocarbonization	12	PDU ^a (1/4 ton of coal per day, at Monroeville, Pa.)
Atmospheric fluidized-bed combustion	26	Pilot plant (30 MW, at Rivesville, W. Va.)
Cryogenic separation	15	Commercially available
Acid gas scrubbing and shift conversion, reforming, methanation	13, 14, 21	Commercially available
Sulfur plant	24	Commercially available
Tar hydrotreater H-Oil process H-Coal process	16	H-Oil commercially available; H-Coal pilot plant under design (600 tons of coal per day, at Catlettsburg, Ky.)
Oil solid-liquid separation (filtration)	19	Pilot plant (50 tons of coal per day, at Ft. Lewis, Wash.)
Sour water treatment	57	Commercially available

^a PDU = process development unit.

carbonizers during sequential periods of operation. Condensation of the coal liquids occurs in an exchanger in the presence of a wash oil, which prevents deposition of the particulates. No major problems have been encountered that limit the operation of the PDU at design conditions, and the program is currently directed toward obtaining experimental information to provide the basis for design of a 240-ton/day pilot plant. A decision to proceed with construction of the pilot plant is scheduled for late 1979.¹

Material-balance data on the liquid yields from the Clean Coke carbonizers were not available at the time when the process design was developed for this study. Therefore, the overall material-balance data utilized for this study contain an estimate of the liquid yields from the two hydrocarbonizer stages. However, actual data for the Clean Coke carbonizers published quite recently² indicate that the estimated liquid yields were in reasonable agreement with the experimental data. For example, the yield of liquids estimated based on MAF feed coal was 17.3% as compared to a total yield of 18.3% obtained from both stages of the Clean Coke PDU.

The design of the atmospheric fluidized-bed combustor (AFBC; Unit 26) was based on test data developed by Pope, Evans and Robbins, Incorporated (PER), in a 9-ft² fluidized bed at their Alexandria, Virginia, laboratory. However, the development of the AFBC has progressed to a 30-MW multicell fluidized-bed boiler pilot plant. This pilot plant has been constructed by PER at the Monongahela Power Company's Rivesville, West Virginia, facility and is currently in the start-up phase of operation.

Selection of an ebullating bed for the tar hydrotreater (Unit 16) was based primarily on the advantages of filtering the oil after hydrotreating instead of separating the solids from the raw oil prior to hydro-

genation. This concept is embodied in the H-Oil process, which is commercially available for hydrotreating heavy petroleum oils with low levels of solids. However, operation with high levels of coal particulates flowing through the bed has been demonstrated by the H-Coal process. Both processes were developed by Hydrocarbon Research, Incorporated, of Trenton, New Jersey. The H-Coal process is currently under development in a 2.5-ton/day PDU, and a 600-ton/day pilot plant is being designed for installation at Catlettsburg, Kentucky.

2.2 Processing Problems

One major problem that must be solved before the Hydrocarbonization Facility can be considered feasible for all types of bituminous coal is the agglomeration of the coal in the fluidized-bed hydrocarbonizers. An oxidation pretreatment at 350°F for 30 min appears to be adequate for Illinois No. 6 coals; however, the liquid yields will be reduced as a result of the oxidation. Highly caking coals (e.g., Pittsburgh seam coal), on the other hand, will require an extensive heat pretreatment that will be carried out in several stages.

The operating conditions selected for the stage I hydrocarbonizer were established to ensure operation of the bed without agglomeration. An increase of the stage I temperature above 840°F would accelerate agglomeration, but data from similar systems indicate that the production of tars and oils is maximized throughout the temperature range of 985 to 1060°F. Therefore, if an alternative solution to the agglomeration problem can be found, the yields of tars and oils may be significantly improved by increasing the operating temperature of the stage I hydrocarbonizer.

Alternatively, if methods could be developed to feed the dried raw coal directly to the stage II hydrocarbonizer, significant savings in energy and equipment costs could be realized. However, a single-stage system would probably drastically reduce the oil and tar production, with a corresponding increase in light hydrocarbon gases and char. The ultimate choice of process operating conditions will probably be determined by the market demands for the different types of fuel produced by hydrocarbonization; therefore, improvement in the operating flexibility of the system would be very desirable.

Recovery of the heat in the overhead vapors from the hydrocarbonizers in a heat exchanger that would heat the recycled gases would result in a more efficient use of high-temperature thermal energy. Of course, such a heat exchanger would have to be capable of sustained operation in an environment of condensing heavy tars and solids. Operation of the Clean Coke PDU has demonstrated that the addition of a wash oil to the gas-interchanger is necessary to maintain operation without plugging.

Materials problems in several of the major operating units must be resolved before the overall feasibility of the Hydrocarbonization Facility can be ensured. In the coal beneficiation unit, three parallel processing lines are specified; however, only two will be on-line continuously, the third being on standby in the event of equipment failure. Experience with the operation and maintenance of continuous beneficiation systems in future coal conversion plants should reduce the requirement for this standby equipment. In the hydrocarbonizer system, operating experience using high-alumina refractory lining and Inconel 600 weld inlays is needed to establish the feasibility of commercial-scale hydrocarbonizers. Incoloy 800 or

Inconel 601 tubing is specified for the high-temperature gas recycle heating circuit in the fluidized-bed combustor (FBC). Long-term operating experience is needed under conditions where this tubing would be subjected to the corrosive effects of oxidation and reduction (on the fluidized-bed side and the tubeside respectively) as well as to the erosive effects of the fluidized bed.

In the tar hydrotreating unit, data are needed to establish the amounts of hydrogen and catalyst consumed and the overall operating feasibility of the H-Oil system with a coal tar-oil feed. Operation of the H-Coal pilot plant currently under construction will provide information concerning the hydrotreatment of coal liquids in the presence of particulates. Operation of the pressurized precoat filters in the oil solids separation unit using pulverized coal as a precoat and recycle of the coal-char solids to the hydrocarbonizers also need to be demonstrated in commercial-scale equipment.

The selection of an atmospheric FBC over a pressurized FBC was based primarily on the current status of development for the two systems. Suitable recovery turbines and attendant gas cleanup systems for the pressurized system are in an early stage of development, whereas the atmospheric system has progressed to a 30-MW pilot plant that is undergoing start-up. The program planned for this pilot plant will include studies of feed point optimization for large-area fluidized beds, development of light-off procedures, optimization of hot materials handling, and bed removal techniques.

Information concerning the feasibility of transporting the char product via a char-water-slurry pipeline is not available. However, a 273-mile commercial coal-water slurry pipeline is currently in operation

in northern Arizona and southern Nevada. Char-oil slurry pipelines have been studied by the FMC Corporation. Results showed that char-in-oil slurries were similar to coal-in-water slurries except for the effect of the higher internal porosity of the char particles. Since the char absorbed oil from the slurry, a 60 wt % coal-in-oil slurry would have about the same pressure drop as a 40 wt % char-in-oil slurry. A recommendation has been made that an experimental study be performed to determine the feasibility of char-water pipeline slurries, with particular emphasis on possible erosion problems in the pipeline and associated equipment.

Combustion of char from the Clean Coke and Clean Char processes has not been demonstrated. However, commercial-scale tests have been made employing a COED char in a furnace designed for burning anthracite coal. Results of these tests indicate that the COED char can be burned successfully in this type of furnace, and it is quite probable that Clean Coke char would perform in a similar manner.

2.3 Consideration of Process Alternatives

One alternative of the basic hydrocarbonization process considered in this study is the sale of crude coal, tar, and oil prior to the hydrotreating. These coal liquids contain significant levels of sulfur and would have to be further processed to produce a clean fuel, or they might be usable as a petro-chemical feedstock. For this study, it was assumed that the selling price of the coal liquids would be based on their heating value. Results of the evaluation of this alternative indicate that it allows a significant reduction in the capital cost of the facility, which results in a lower overall cost for total plant product mix. The estimated thermal

efficiency of this alternative is somewhat higher than that of the basic process since the fuel gas required for the hydrogen preparation plant is not needed and can be diverted to product gas. However, further study to establish realistic market values for the crude coal liquids is recommended.

A second proposed alternative to the basic process involves optimization of the coal liquids production. The Hydrocarbonization Facility, which uses the Clean Coke process as a basis, produces coal liquid yields that are quite low in comparison with other pyrolysis processes such as Coalcon and COED. The Coalcon process operates under pressure and temperature conditions designed to give optimum tar and oil production. Another process is proposed which would maximize liquids production by operating under similar conditions in the first stage followed by a second, high-temperature stage for the low-sulfur char production of the Clean Coke process. Such a process would produce high liquid yields and a desulfurized char as products; an improvement over the Coalcon and COED processes, which produce a high-sulfur char that must be gasified to produce a clean fuel product.

Additional coal preparation and beneficiation processes considered included chemical comminution as a method for fracturing coal prior to beneficiation and the Battelle Hydrothermal Coal Process (BHCP) as a substitute for the beneficiation system. The chemical comminution processes considered produce a treated coal that has an increased friability, which may result in an increase in the amount of fines generated in the fluidized-bed hydrocarbonizers. The cost for chemical comminution was estimated to be about 35% greater than that for mechanical comminution.

The BHCP is a potentially attractive method for the removal of almost all the pyritic sulfur prior to hydrocarbonization. In addition, coal

produced from highly caking coals by the BHCP has been shown to be non-agglomerating when fed to high-temperature fluidized beds. Thus the oxidation step prior to hydrocarbonization could be eliminated. Further study of BHCP coal to determine the liquid, gaseous, and char yields during hydrocarbonization is recommended.

Other methods for preventing agglomeration during hydrocarbonization were also evaluated. A bed recirculation technique that has been used successfully for low-temperature heavy-oil carbonization in fluid beds is recommended for future investigation. If agglomeration can be prevented in the hydrocarbonizers, operating temperatures can be adjusted to produce optimum product combinations such as increased liquid yields with less char or, alternatively, low liquid and high char yields in a single-stage hydrocarbonizer.

2.4 Overall Process Feasibility and Recommended Future Process Development

Judgmental evaluation of the overall feasibility for this system must be based on the adequacy of the data base currently available for the process units. The Clean Coke process has not yet been operated as a two-stage continuous process, and experimentally based material-balance data for this type of operation are not available. Reasonable estimates for material-balance purposes have been made based on information obtained from United States Steel Corporation's PDU operated in a staged-carbonization mode (operated initially as a first stage followed by later operation as a second stage in the same reactor). Data for the amounts of char and volatile matter produced in each stage, along with the recycle gas analysis were available, but estimates have been made of the coal liquids and water

production in each stage by difference in order to complete the material balance.

The data base for the beneficiation of the coal prior to hydrocarbonization was adequate for the design of the beneficiation system for the Illinois coal selected. However, additional information on higher-sulfur bituminous coals is needed to determine the adequacy of the specified facility under conditions where lower beneficiation ratios (ratio of high- to low-grade coal) will be required.

The FBC design was based on experimental data obtained in PDU-scale steam generators; as yet, process heating applications have not been developed. Consequently, the tubeside temperatures projected for the proposed fluid bed are well above those investigated for steam generators, and the selection of tube materials for this application must be justified operationally. The Modular Integrated Utility System (MIUS) demonstration currently under construction at ORNL will provide information on the use of high-temperature alloys in an AFBC. Other problem areas, such as the optimization of coal feeding, will be studied in the 30-MW FBC pilot plant currently ready for operation at Rivesville, West Virginia.

The overall process evaluated in this report cannot be considered as a viable candidate for scale-up to a demonstration plant until a pilot-scale continuous hydrocarbonization system has been operated over an extended period, feeding a wide variety of highly caking bituminous coals.

The program proposed for a pilot plant would investigate the following aspects of the hydrocarbonization process:

- (1) Demonstration of methods for the prevention of agglomeration of highly caking coals during hydrocarbonization. These methods

would include chemical or oxidative treatment of the feed, bed dilution during hydrocarbonization, and char dilution techniques.

- (2) Optimization of coal liquid yields by investigating a range of temperature and pressure operating conditions in the stage I hydrocarbonizer.
- (3) Operation of the system as a single-stage high-temperature hydrocarbonizer optimized for maximum production of desulfurized char.
- (4) Optimization of the beneficiation ratios employed in the beneficiation system for a wide variety of high-sulfur bituminous coals.

The proposed pilot plant would include beneficiation, hydrocarbonization, and gas treating units. The following design specifications are recommended for the pilot plant:

- (1) Capacity - up to 100 tons of highly caking bituminous coal per day.
- (2) Hydrocarbonizer stages - dryer, stage I and stage II hydrocarbonizers.
- (3) Operating range, stage I hydrocarbonizer: pressure - up to 1000 psia; temperature - 800 to 1200°F; and holdup time - up to 60 min.
- (4) Operating range, stage II hydrocarbonizer; pressure - up to 1000 psia; temperature - 1000 to 1500°F; and holdup time - up to 90 min.
- (5) Quench system - design for rapid quench of liquid products to maximize liquid yields.

- (6) Hydrogen production - includes facility for hydrogen production required for start-up and for makeup when operating in the high-pressure range.

The fluidized-bed combustion and tar hydrotreating units could be installed during a later development phase of the pilot plant, or char and coal liquids from the pilot plant could be shipped to other experimental facilities for developmental tests.

References for Sect. 2

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2. N. S. Boodman, T. F. Johnson, and K. C. Krupinski, "Fluid Bed Carbonization/Desulfurization of Illinois Coal By The Clean Coke Process: PDU Studies," paper presented at the 173rd National Meeting, Amer. Chem. Soc., New Orleans, La., March 21-25, 1977, preprint Vol. 22, No. 2, p. 28.

3. BENEFICIATION

Alternative processes considered for the beneficiation system include a chemical comminution method and the BHCP. Both of these processes are considered developmental at present.

3.1 Chemical Comminution for Coal Fracturing and Impurity Liberation Prior to Beneficiation

Use of chemical comminution as a method for fracturing coal structures to liberate the mineral matter and pyrites, before beneficiation, has been investigated by the Syracuse University Research Corporation¹ (SURC)

in Syracuse, New York, and by Otisca Industries, Limited,² in LaFayette, New York. In the chemical comminution process, a low-molecular-weight liquid (ammonia, anhydrous methanol, sodium hydroxide, etc.) penetrates the naturally occurring fault system of the coal and appears to cause breakage along the fracture plains. The comminuting agent is recovered and reused. The size consist of the coal comminuted by this technique averages about 40 mesh with 75 to 80% +40 mesh. Thus a much lower fraction of fine coal is obtained than when mechanical comminution is employed.

The basic question as to whether or not the chemical comminution technique liberates a greater percentage of the mineral matter and sulfur associated with a coal vs that freed by mechanical comminution has been appropriately addressed by Otisca Industries. Their conclusion is "A distinct advantage for the unique separation of iron pyrites and mineral matter was not observed." Data presented by SURC in comparing utilization of chemical comminution techniques vs employment of mechanical comminution in the liberation of pyrite and mineral matter from coal after sink-float beneficiation in heavy medium, substantiates the conclusions by Otisca Industries in that no significant improvements in separation were observed. This information was developed for two high-sulfur coals (a Pittsburgh seam, and an Illinois No. 6) investigated in several size ranges.

Chemical comminution does improve the grindability of the treated coal. For some applications, such as preparing feed for pulverized coal boilers where a size 70% -200 mesh is required, this can be considered an advantage in lowering grinding costs. However, because of the increased friability of the chemically treated coal, considerable attrition is expected in the beneficiation step and subsequent handling operations, resulting in an increase

in the amount of coal fines. The problem of determining the amount of fines that would be generated has not been addressed by SURC or Otisca Industries. The increase in the coal fines fraction would be a detriment in certain applications such as fluidized-bed applications, where elutriation is a major concern.

In essence, chemical comminution by itself is not a beneficiation process but merely one that serves to reduce coal size and potentially liberate the coal impurities. To determine the comparative operating costs of chemical comminution with the conventional mechanical size reduction, an economic evaluation³ was made on an 880-ton/hr coal chemical comminution operation. The comminuting agent was assumed to be ammonia, and the plant and operating characteristics were based on development data from SURC. The cost analysis considered reactor operation, ammonia liquefaction, cooling tower operation, ammonia distillation, and dewatering of the comminuted coal to recover absorbed ammonia. The total cost of chemically comminuting 880-ton/hr coal was found to be \$2.70/ton.

The estimated cost for mechanically reducing the coal to the same approximate size consist is \$2.00/ton. Thus the cost for chemical comminution is about 35% greater than that for mechanical comminution. However, since chemical comminution is still in laboratory stages of development and since the question of the coal friability still must be resolved, use of this process in the Hydrocarbonization Facility is not considered.

3.2 The Battelle Hydrothermal Coal Process

One potentially attractive method for the removal of almost all the pyritic sulfur from coal prior to hydrocarbonization is the Battelle Hydrothermal Coal Process (BHCP). It involves heating an aqueous slurry of coal (ground to 70% -200 mesh size) and a caustic leachant at temperatures up to 300°C and pressures up to 1000 psig. No loss of volatile matter occurs during the hydrothermal treatment. Desulfurized coal from the reactor is separated from the leachant by filtration, washed with water, and then dried to produce the solid fuel product. Spent leachant is regenerated in a separate system that removes the sulfur as H_2S and recovers the leachant for recycle.

Data published by Battelle Memorial Institute⁴ indicate that the BHCP was successful in removing 87 to 99% of the pyritic sulfur from high-sulfur coals found in Ohio, Kentucky, Pennsylvania, and Illinois. Removal of organic sulfur from these coals was not as complete; extraction efficiencies for organic sulfur removal varied from 30 to 70%. Therefore, it appears that extensive removal of pyritic sulfur prior to hydrocarbonization could be accomplished by the BHCP; in addition, it is possible that sulfur removal could be completed during hydrocarbonization, as demonstrated by the Clean Coke process.

A further advantage of the BHCP is the tendency of the extraction step to reduce agglomeration of highly caking coals. For example, coals having an initial free-swelling index of greater than 6.0 have been shown to have a free-swelling index of less than 1.0 after treatment. Thus the oxidation step prior to hydrocarbonization could be avoided. This should enhance the production of liquid products since oxidation has been known to reduce liquid yields.⁵

Liquid, gas and char yields from the hydrocarbonization of BHCP coal have not been determined. However, based on Battelle's experience where hydrothermal treatment increased the rates of gasification with hydrogen or steam significantly, gas yields would be expected to be comparable to or greater than those for conventional hydrocarbonization. Therefore, substitution of the BHCP process for conventional beneficiation appears to have advantages such as high pyritic sulfur removal, prevention of agglomeration without pretreatment and, possibly, enhanced liquid and gas yields. Therefore, further study of BHCP coal for feedstock to hydrocarbonization systems is recommended.

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4. E. P. Stambaugh et al., "The Battelle Hydrothermal Coal Process," presented at the Second Annual Symposium on Coal Gasification, Liquefaction and Utilization: Best Prospects for Commercialization, the University of Pittsburgh, Pittsburgh, Pa., Aug. 5, 1975.
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4. HYDROCARBONIZATION

4.1 Prevention of Agglomeration

Agglomeration of caking coals during low-temperature carbonization in fluidized beds is a well-known phenomenon that has been observed by many investigators.¹ When caking coals are heated, they begin to soften and then swell, accompanied by decomposition of the volatile matter; finally, they resolidify to form semicoke. Between the temperature at which the softening commences and the temperature where maximum devolatilization occurs, the fluidity of a bed of coal particles (as measured by a rotating viscometer) increases and reaches a maximum close to the temperature where maximum devolatilization occurs. One study² indicated that stickiness and agglomeration of the coal particles in a fluidized bed are related to the fluidity of the coal during swelling; as the fluidity during swelling increases, agglomeration becomes more severe.

During the development of the Clean Coke process, two methods of preventing agglomeration of the Illinois No. 6 seam coal were investigated.³ One method, which involved mixing equal amounts of recycled char with the coal feed, was successful in preventing agglomeration. However, a second method was selected which involved a light preoxidation of the feed coal in a fluidized bed at 340°F for 30 min prior to its admission to the stage I carbonizer. A comparison of the yields for these methods indicated that the unoxidized coal gave more tar and less char during subsequent carbonization. A similar decrease in tar yield was observed by Struck⁴ during low-temperature fluidized-bed carbonization of bituminous coal where a 1% preoxidation of the feed coal at 725°F reduced the tar yields by as much as 8 to 16%.

Recent studies on a very highly caking Pittsburgh seam coal have indicated that preoxidation for about 60 min at 750°F in a fluidized bed will be required to prevent agglomeration during hydrocarbonization.⁵ Although data are not available concerning the yield of tar under these severe oxidation conditions, tar yields will probably be lower based on past experience with preoxidation systems.

Additional methods (i.e., methods other than preoxidation of the feed) which have been investigated include (1) bed recirculation procedures, (2) feed heat treatment, (3) feed dilution procedures, (4) stirred-bed operation, and (5) chemical pretreatment of the feed. Of these, the bed recirculation procedures and chemical pretreatment methods appear to be most promising. Successful experience with bed recirculation techniques for the prevention of agglomeration of heavy oil feed has been observed by several organizations. The British Gas Council developed a system by which the heavy oil was fed to a vertical central riser in the fluid bed where it was mixed with recycled char from an annular downcomer.⁶ The solids in the central riser were in light-phase fluidization (velocity, 30 fps), and the solids in the downcomer were in dense-phase fluidization. Similar observations were made in the low-temperature carbonizer at Cresap, West Virginia, where a mixture of liquid extraction residue and solids was fed to a vertical lift leg where it was mixed with recirculated char particles.⁷ Spraying the oil-solids feed mixture directly into the bed caused a significant increase in mean bed-particle size, whereas spraying the feed into the lift leg minimized agglomeration and permitted stable operation at a smaller mean bed-particle size.

Prevention of agglomeration of chemical treatment of the feed coal has been reported by Battelle Memorial Institute (BMI)⁸ and by Kawa.⁹ The work

at BMI is described in Sect. 3.2; the method used appears to be effective for preventing agglomeration without decreasing the yields of liquid products. However, the costs of chemical pretreatment must be investigated in depth before the overall feasibility of the process can be assessed.

In the proposed Hydrocarbonization Facility, prevention of agglomeration by methods such as bed recirculation or chemical pretreatment of the feed could have the following advantages:

1. An increase in the overall coal liquids yields would probably be possible.
2. The temperature in the stage I hydrocarbonizer could be optimized to increase the coal liquid yield. Stage I conditions that would improve the yields are discussed in Sect. 4.2.
3. More highly caking coals, such as Pittsburgh seam coal, could be carbonized in the plant without requiring extensive feed preoxidation and the attendant losses in liquid yields.

Studies of the central riser and fluidized downcomer concept are currently under way by the Westinghouse Research Laboratories for their fluidized-bed coal gasification process¹⁰ and at Oak Ridge National Laboratory as an adjunct of the hydrocarbonization research program.¹¹ Investigation of chemical pretreatment of the coal feed is currently included in the BHCP development program.

4.2 Improvements of Yields

The goal of the Clean Coke process, which forms the basis for the hydrocarbonization flowsheet, is to produce a low-sulfur char for

manufacture of coke. Liquid and gaseous products are of secondary importance, and a definitive mass balance for their yields in the hydrocarbonization process has not been published. The semichar and char yields are well established, but the relative distribution of the other products are estimates. Table 4.1 summarizes the product structure used in the evaluation study.

Table 4.1 Hydrocarbonization mass balance^a (in percent)

Component	Stage 1	Stage 2	Total
Char	81.48 ^b	64.72	64.72
Tars and oils	11.77	5.51	17.28
Hydrocarbon gases	1.31	4.77	6.08
Other ^c	5.44	6.48	11.92

^aBasis: pound of product per pound of moisture- and ash-free (maf) coal.

^bSemichar not suitable for coke production.

^cIncludes H₂, CO, CO₂, H₂S, NH₃, and H₂O.

The sulfur content of the char is inversely proportional to the temperature and residence time in the reactor. Higher temperature and longer residence times give a lower sulfur content. The conditions of the second-stage reactor, 1380°F and 60 min, are recommended to obtain a sulfur content of 0.5 to 0.6 wt %.

The product structure can be changed by adjusting the operating conditions. Figure 4.1 shows oil yields for a Lake de Smet subbituminous coal^{12,13} which was hydrogenated in a fluidized bed with residence times

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Fig. 4.1. Oil yields as a function of temperature in a fluidized-bed reactor.

varying between 3 and 12 min. Oil and tar yields increase with hydrogen partial pressure but pass through a maximum with respect to temperature. The hydrocarbonization reactor operates at 840°F (449°C) and 1380°F (749°C), which spans the temperature range for maximum production of tars and oils, 985 to 1060°F (530 to 570°C). The effect of residence time is not included in Fig. 4.1. However, Morgan¹⁴ found that tar yields increased as the solids residence time increased for a similar process. As shown in Fig. 4.2, the production of hydrocarbon gases increases with both temperature and pressure.

Two proposed hydrogenation processes, Coalcon and COED, have higher liquid yields than the proposed facility. The Coalcon¹⁴ process, a single-stage process, will operate at 1040°F (560°C) and 405 psig. The COED¹⁵ process, a multistage process, operates at temperatures of 575, 815, and 1050°F in the stages where the tars and oils are recovered. Both processes have operating temperatures in the region of maximum tar and oil production.

It might be interesting to combine the high oil production of the Coalcon process with the low-sulfur char production of the Clean Coke process. This could be accomplished by adding a second stage to the Coalcon process which would operate at approximately 1380°F and at an elevated pressure. No data are available on the effect of elevated hydrogen partial pressure on the rate of sulfur removal from the char. However, we would expect the rate to increase, allowing a corresponding reduction in the residence time.

4.3 Materials Problems

4.3.1 Materials problems in the beneficiation system

The coal beneficiation system proposed by the McNally Pittsburgh

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Fig. 4.2. Total gases produced in a fluidized-bed reactor.

Manufacturing Corporation, Pittsburg, Kansas, includes three parallel processing lines. The capacity of each line is one-half of the total daily capacity; hence two lines will be operated on a 24-hr/day, seven-day/week basis. The third, or standby, line could be placed into immediate operation in the event of equipment failure.

The proposed method of operation is based on that used in washery plants, which are normally operated two shifts per day, five days per week. Since erosion is severe and equipment breakdowns are frequent, the third shift and weekends are reserved for maintenance operations. However, the Hydrocarbonization Facility requires continuous feed as a processing facility; therefore, the additional line must be available to maintain continuous operation and to permit immediate maintenance on equipment that has been taken out of service for repair.

McNally Pittsburg personnel were consulted concerning the nature of the erosion problems in beneficiation plants. Very little information has been published on the subject, but the prime area of concern is apparently the abrasive character of the coal slurry and its impact on the coal shutes, pumps, screens, etc. However, information from other sources may be applicable to the beneficiation systems. In the operation of the Black Mesa Pipeline in northern Arizona,¹⁶ coal slurry from the pipeline is pumped to a centrifuge for dewatering, fed to a bowl pulverizer where it is swept with hot air to further dry it, and then blown into the boiler. During early operations, problems were experienced with excessive wear of the internal conveyor flights (operating life, ~500 hr) of the centrifuge. Installation of 1/2-in.-thick ceramic (90% Al_2O_3) plates resulted in an increase in life (to ~15,000 hr in March 1976) for an average wear rate of about

0.2 mil/day. At the same installation, centrifugal pump impellers in slurry service last about six months.

The pipeline itself is standard API 5LX welded line pipe with no interior treatment. The nominal outside diameter is 18 in.; the wall thickness varies from 0.219 to 0.469 in., as dictated by internal pressure. The velocity of the slurry at the maximum feed rate (4200 gpm) is 5.8 fps, and the coal concentration varies from 46 to 48 wt % (moisture-free basis) in the water slurry. The current coal size consist is approximately 1% +14 mesh, 80% 14 x 325 mesh, and 19% -325 mesh. Under these conditions, pipe erosion has not appeared to be a problem; internal corrosion, however, is encountered, and sulfite inhibitors are sometimes added to minimize coal- and water-absorbed oxygen. As of March 1976, no pipe failures had occurred over approximately four years of operation. Routine maintenance involves replacing worn cage parts in the Gundlach rotating cage impactors (where coal is crushed to -1/4 in.), adding new rods to the Nordberg rod mills (where the coal is wet-ground to -8 mesh x 0 in.), and replacing piston-pump parts as they wear. In the piston pumps, rod life is about 1000 hr, piston life is about 2000 hr, and valve life is 2500 to 3000 hr.

Extensive experience in pumping coal-oil slurries has been obtained at the Hygas pilot plant at the Institute of Gas Technology.¹⁷ In this system a centrifugal pump is used to feed an oil slurry from a mix tank to a high-pressure reciprocating pump. Initially a high-speed centrifugal pump with a wear-resistant Noroc coating was used, but high wear rates were experienced. Subsequent installation of low-speed (about 1500 rpm) centrifugal pumps with Ni-Hard castings for the pump casing material solved the problem. Operation with flushed mechanical seals on these pumps has also been

successful. Experience with the high-pressure reciprocating piston-pump parts in the Hygas pilot plant led to the use of Stellite-coated valve seats and valves made of slightly softer Colmonoy-6. These valve assemblies are scheduled for change every 1000 hr.

4.3.2 Hydrocarbonization materials

Early United States Steel Corporation studies of corrosion showed significant carburization (carbides of chromium and iron) of the type 316 stainless steel 3-in. carbonizer.³ This vessel was operated as a carbonizer for about 60 hr at temperatures over 1000°F, including 24 hr at over 1300°F. High carburization within the fluid bed and below the gas distributor was attributed to low average H₂S concentrations since the H₂S tends to form protective sulfide coatings on the wall. Above the bed, the carburization was lower because of the inhibiting effect of H₂S picked up by the gas stream through desulfurization of the coal. Subsequent corrosion tests on Incoloy 800; Inconel 600; types 304, 310, and 316 stainless steel; and "Alonized"* 316 stainless steel indicated that carburization was a function of both H₂S concentration and temperature. Type 310 stainless steel and Incoloy 800 showed no carburization when the H₂S concentration was greater than 25 ppm. Inconel 600 and Alonized 316 stainless steel showed no evidence of carburization under all test conditions. Type 316 stainless steel was partially protected by 50 to 100 ppm of H₂S, but type 304 stainless steel was not protected at all by H₂S concentrations up to 100 ppm. Based on these results, subsequent carbonizer vessels were constructed from Incoloy 800, and H₂S concentrations of about 50 to 100 ppm in the

* Process for aluminizing alloy surfaces — Alon Processing Inc., Tarentum, Pa.

process gas were maintained during operation of the PDU to provide inhibition against carburization and subsequent carburization-induced metal dusting.

During subsequent PDU operations, corrosion coupons were exposed at temperatures of 500 to 1410°F in various locations.¹⁸ Highest weight losses were shown by Alonized type 304, 316, and 446 stainless steels and by Alonized Incoloy 800 that had been exposed in the char receivers. Subsurface attack was exhibited by types 304 and 316 stainless steels in the carbonizer. Photomicrographs showed carburization to depths of 6.6 and 5.0 mils, respectively, for these two stainless steels. The Incoloy 800 and Inconel 600 coupons showed no significant subsurface attack after 545 hr at 1300 to 1410°F in the PDU carbonizer.

The choice of construction materials for the Unit 12 hydrocarbonizers was based on consideration of the United States Steel Corporation's PDU results and the requirement for reasonable vessel costs. Type SA387-22 Cl.2 (formerly A387GrD) low-alloy steel (2-1/2 Cr-1 Mo) was chosen for the base material where maximum design wall temperatures of up to 900°F are specified. The addition of chromium in this steel guards against hydrogen corrosion at the elevated temperatures. For additional corrosion protection, a 1/8-in. weld inlay is used over the entire interior surface of all the hydrocarbonizers. The inlay for the stage I hydrocarbonizer is type 316 stainless steel, while an inlay of Inconel 600 was selected for the stage II hydrocarbonizer and the char burner. Consultations with the United States Steel Corporation, Huntington Alloy Products Division of the International Nickel Corporation, and Combustion Engineering, Incorporated, led to the selection of the Inconel 600 as the welded inlay for the high-

temperature service. An Incoloy 800 welded inlay was considered; however, this material is not available in welding rod, and plates of Incoloy 800 are normally welded with other alloy materials. Refractory material is also included for all hydrocarbonizers operating above 900°F in order to reduce the operating wall temperatures below 900°F. A high-alumina refractory material similar to that recommended for coal gasification plants was selected. Aluminosilicate refractories are attacked by steam to form silicic acid and may be extracted by condensate during start-up and shutdown. High-alumina cement-bonded refractory material in which calcium aluminates bind the alumina has been suggested as a better choice for vessel linings.¹⁹

A recommended program for materials development for a demonstration or commercial-scale hydrocarbonizer should include the construction and operation of refractory-lined hydrocarbonizers fabricated with welded inlays from several metals. Operations should also include a number of cycles to simulate the start-up and shutdown of the reactors.

4.3.3 Aqueous corrosion in the tar-oil absorption system

Product gases from the hydrocarbonizers are quenched with oil and then partially condensed in a condenser to remove oils and impurities from the recycle gas stream. The temperatures in the tar-oil absorption tower range between 840 and 315°F, and extensive condensation of water, NH_3 , and H_2S does not occur. However, in the tower condenser, the temperature is reduced to 120°F; as a result, condensation of these impurities plus small quantities of HCN, oils, tar acids, and chlorides (from the coal) takes place. General and pitting corrosion, crevice corrosion, stress corrosion, and weld cracking can occur in such an environment.

The Illinois Institute of Technology has initiated a series of autoclave tests to obtain corrosion data in environments comparable to those in gasification systems.²⁰ However, some of the conditions in these tests approximate those in a hydrocarbonization system. Plain and U-bend samples are suspended in the gas-phase gas-liquid interface and immersed in the liquid. Data recorded include weight change, maximum pit depth, stress corrosion susceptibility, etc. Initial tests showed negligible corrosion of types 304, 316, and 329 stainless steel; types 800 and 825 Incoloy; and Hastelloy C and B. Carbon steel, type 410 stainless steel, and Ni Resist showed "noticeable" corrosion in the liquid phase. Based on this experience and the well-known corrosion of carbon steel that has been observed in sour water strippers, austenitic stainless steel was specified for the condenser and heat exchanger tubing downstream of the tar-oil quench tower system.

4.4 Improvement of Energy Balance

From an energy standpoint, the hydrocarbonization process is relatively efficient (i.e., its thermal efficiency is slightly over 70%). However, there are several areas where additional energy savings could be realized.

Hydrocarbonization takes place in three steps: preoxidation, 840°F reaction, and 1380°F reaction. The stagewise approach is required to prevent agglomeration. If a way could be found to feed the dried raw coal directly to the second-stage hydrocarbonizer, significant savings in energy and equipment costs would be realized.

Currently, the recycle gas is split into three fractions: (1) char cooler, 38.3% at 130°F; (2) second-stage hydrocarbonizer, 38.3% at 1450°F;

and (3) first-stage hydrocarbonizer, 23.4% at 768°F. The off-gas from the char cooler and second-stage reactor also forms part of the fluidizing gas for the first stage. If a single-stage process could be developed, a different flow pattern of the recycle gas could be investigated (see Fig. 4.3). The cold gas would pass to the char cooler and then be routed back to the fluidized-bed combustion unit, where a small amount of additional recycle gas would be added and the combined streams would be heated to 1450°F for use in the reactor.

This system has several disadvantages. The product distributions for a single-stage system and a two-stage system would be significantly different. The oil yield would probably be drastically reduced, with a corresponding increase in light hydrocarbon gases and char. However, the oil that is produced will be a lighter oil and might not require hydrotreating. Also, the heat load of the first stage is placed on the second stage where there is a relatively small temperature difference between the fluidizing gas and the bed.

Another area where some additional energy balance improvements could be made is in recovering the sensible heat in the char. After cooling, the char is still at a temperature of 600°F. The hot char is sent to the char recovery and is slurried with water without any further attempt being made to recover heat. The sensible heat in the char is about 6.36×10^9 Btu/day, which, if recovered, would increase the thermal efficiency by approximately 0.7%.

Optimization of the hydrogen production systems could also result in an additional improvement. A portion of the pipeline gas produced is consumed internally (14%) to supply heating requirements and to serve as feed

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Fig. 4.3. Single stage hydrocarbonization.

for the reformer. This amount of gas amounts to 1.3% in the thermal efficiency if it could be recovered.

A heat exchanger rather than a quench tower for the reactor off-gas would result in a more efficient use of high-temperature thermal energy. Part of the exchanger would have to be designed to operate at temperatures above the dew point of the heavy tars in order to prevent plugging of the exchanger with tars and solids. For temperatures below the heavy tar dew point, wash oil could be added to keep the exchanger tubes from fouling. However, separation and recycle of the wash oil from the coal liquids would be required downstream of the exchanger.

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5. TAR HYDROTREATING

Two options are available for hydrotreating coal tars: the ebullating bed and the fixed bed. In the ebullating bed the raw tar and hydrogen are passed upward through the catalyst bed. The velocity of the inlet stream is sufficient to fluidize the catalyst particles. The ebullating bed has several advantages, including isothermal temperature profile, continuous catalyst addition, and the ability to handle solids in the feed stream.

Fluidized beds, with their high degree of turbulence, tend to eliminate axial and radial temperature differences. While the hydrotreating reactions are extremely exothermic (i.e., they release a great deal of heat), the probability of developing localized hot spots is relatively small. Heat removal is a major consideration in fixed-bed design. The same amount of heat has to be removed with either type of bed. However, the fixed bed is analogous to a plug flow reactor, and there will be a definite temperature rise between the inlet and the outlet. The desired reaction temperature will be somewhere between these extremes. Hence only a portion of the fixed bed is maintained at the optimal temperature, while the entire ebullating bed can be controlled at the optimal reaction temperature.

Catalyst removal techniques are significantly different for the two designs. Catalysts can be continuously added and withdrawn from an ebullating bed; thus the activity of the catalyst can be carefully controlled. The fixed bed has to be removed from production and the entire catalyst bed regenerated. In general operation, the activity of the catalyst is high initially but slowly declines, and the hydrotreating reactions are maintained at their proper levels by increasing the severity of the reaction conditions. Eventually the activity of the catalyst diminishes to a point

where the unit must be shut down and the catalyst regenerated or replaced. Very few data concerning catalyst life have been published. In oil refineries, fixed-bed units have operated to well over 100 bbl/lb. However, hydrotreating of coal tars is a different situation, and preliminary indications point to significantly shorter catalyst life.

The third item, the presence of solids in the hydrotreater feed, is a major consideration. The raw tar will contain about 4% solids, which are carried over from the hydrocarbonizer cyclones. Provided that the diameter of the solids is small enough to pass through the distributor plate, the presence of solids should not affect an ebullating-bed reactor. The solids will be removed either with the spent catalyst or with the reactor effluent. Since the entrained solids are much smaller than the catalyst pellets, they will probably pass through the reactor and be separated in the downstream filtration step. However, the regeneration of the catalyst in the presence of semichar needs to be investigated. Solids in the feed stream will probably be a problem in a fixed-bed reactor; the catalyst bed will act as a filter and will eventually become plugged. Therefore, in a fixed-bed design, the solids must be separated prior to hydrotreating.

While the types of reactors and general processing scheme can be determined, experimental data for the coal tar actually produced need to be developed. Hydrotreating characteristics are a function of the feed material, and extrapolating data from a similar process is an approximation.

6. SOLIDS-LIQUID SEPARATION

After coal has been converted to a liquid either through dissolution or destructive distillation (i.e., hydrocarbonization), undissolved or

entrained solids must generally be removed from the coal-derived oil. Solids removal may be required for several reasons, depending on the subsequent downstream treatment of the oil. These include limitations on product sulfur content, erosion of downstream equipment, fouling and poisoning of catalysts in hydrotreating reactors for upgrading the oil, and sludge formation in storage or transportation.

In the process design presented in Vol. I, the difficulty of separating micrometer-sized solids from heavy, viscous tar is avoided by hydrotreating prior to solids-liquid separation. However, this produces an additional problem. For example, in the COED pyrolysis process developed by the FMC Corporation, solids are removed prior to catalytic hydrotreating of the product oil to prevent catalyst poisoning.¹ The particles carried over with the product vapors in carbonization processes tend to be the lightest and smallest char fines; the heavier particles are collected by the overhead cyclones. Char fines carried through the internal cyclones of the COED pyrolyzer (stage II) are in the size range of 0.2 to 2.0 μm . Such small sizes adversely affect the performance of hydrocracking catalysts through obstruction of catalyst pores. To prevent the expected rapid decline in catalyst activity in a conventional fixed-bed hydrotreater, a fluidized-bed catalytic system is presented (design based on the Hydrocarbon Research, Incorporated, H-Oil ebullated-bed reactor).²

The hydrotreated oil has been upgraded sufficiently to allow filtration at somewhat less severe conditions (below 350°F). Alternatives to filtration have been mentioned elsewhere.^{3,4} Vacuum-distillation, centrifugation, agglomeration, or precipitation of solids followed by settling, and a few other techniques have received some attention.

Since centrifugation relies on a difference in density between the liquid and solids to be separated, the earlier removal of the heavier particles by overhead cyclones makes centrifugation more difficult. No data are available on the centrifugation of a hydrotreated pyrolysis oil to permit examination of this possibility at present.

There is a possibility that the solid particles can be adequately separated from the vapor phase prior to condensation. The FMC Corporation, with a similar situation in their COED process, installed an oil absorption column in which solids were absorbed by a heavy oil flowing countercurrent to the vapor.⁵ It is believed possible to design the oil absorption column so that the lighter-oil phase is sufficiently free of solids to meet product specifications. In this case, the heavy-oil phase leaving the bottom of the column is recycled to the top as absorption oil and a slipstream is fed to a rotary drum filtration plant.

Work on the use of an oil-absorption column was conducted at the COED pilot plant. The basic premise was verified in 1972 after installation of the column in the pilot plant. Char fines were preferentially absorbed in the recirculating heavy-oil bottoms, which could then be recycled to the stage III pyrolyzer. The low-solids-content product was withdrawn from the intermediate and top contacting zones of the oil-absorption column. Thus the need for filtration prior to hydrotreating may be reduced or possibly eliminated. Although work directed toward improving the operability of the absorber column was discontinued, the basic approach still looks attractive.

In FMC's examination of antisolvation agents, it was discovered that paraffinic diluents caused particle growth, thus aiding in removal by filtration.⁶ It may be possible to derive a low-aromatic fraction from the

product oil for use as a recycle stream to increase filter rates. However, an economic analysis of the advantages of higher filtration rates vs the added costs of a recycle process has not been performed for this particular system. Work in solvent addition at Oak Ridge National Laboratory has also shown some advantages in more rapid settling and filtration.⁷ Data are preliminary at this time, but the economics show the possibility of significant savings.⁸

Pressurized precoat filtration of COED oil in a rotary-drum filter has been thoroughly studied at FMC. Results at 350°F and 40 psig show on-line filtration rates of 10 gal/hr-ft² when coal-derived oils containing 3 to 10 wt % solids is processed. Filtrate quality of less than 0.1 wt % solids is consistently achievable. Between 20 and 25 consecutive precoats have been applied before a complete dismantling and thorough cleaning of the filter medium are required as a result of blinding of the medium. The design of Unit 19 (fuel oil solids separation) was based on contacts with vendors and operators of current experimental filtration units and others in the field of filtration.^{6,9-13} The design is felt to be conservative because full credit was not taken for the expected increase in filtration rates over that experienced by FMC Corporation. This increase is caused by the decreased viscosity of the fuel oil after hydrotreating. No data are available to permit a good estimate of the expected filtration rate.

Although an effort was made to ascertain the improvements required to decrease the mechanical problems associated with pressure precoat rotary drum filtration, it should be expected that the complexity of filtration will result in substantial downtime. Needed improvements were available from several sources.^{9-11,13,14} No specific amount of overcapacity was

designed into the system to allow for downtime. The design is assumed to be sufficiently conservative because of the low filtration rate used in the design to permit a 90% on-stream factor for Unit 19. In addition to the filters, there is also a lack of high reliability associated with the slurry pumps. High erosion rates in the pumps handling slurries is experienced in present coal conversion pilot plants.¹⁵ Assurance of 90% on-stream capability will be provided by having spare pumps for all pumps handling slurries.

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7. FLUIDIZED-BED COMBUSTOR

In evaluation of alternative systems for supplying the heating and steam requirements for the Hydrocarbonization Facility, three systems were considered: (1) an atomospheric fluidized-bed combustor (AFBC); (2) a pressurized fluidized-bed combustor; and (3) the gasification of coal plus combustion in a gas furnace. The selection of an AFBC over the other alternatives is discussed in the Information Base Report.¹ Since suitable recovery turbines and attendant gas cleanup systems are currently at an early stage of development, the pressurized FBC was rejected. Also, gasification of the coal appeared to be more expensive than the atmospheric FBC system.

Development of the AFBC has proceeded to the stage where a 30-MW FBC pilot plant has been constructed at Rivesville, West Virginia, and is scheduled to begin operation in August 1976.² Design of this pilot plant was based on test data provided by a 9-ft² fluidized bed developed by PER at their Alexandria, Virginia, laboratory. About 9000 hr of service have been accumulated on this system, with no evidence that the erosion or corrosion rates would lead to rapid failure of the boiler tubes.

Industrial-sized demonstration units firing coal have been operated by the National Coal Board in England. Oak Ridge National Laboratory currently has a 1- to 2-MW FBC under design for demonstration as a Modular Integrated Utility System (MIUS) to be used in decentralized power generation plants.³ The unit will heat air for closed-cycle operation of a gas turbine wherein the turbine exhaust will supply heat for a heat recovery system. Several other FBC programs are being funded by ERDA/Fossil Energy and by the Electric Power Research Institute. These programs will provide the additional

development experience required for successful operation of large-scale FBCs.

Potential problem areas that are recommended for further investigation in order to establish the feasibility of the Hydrocarbonizer Facility FBC are identified and discussed in Sects. 7.1-7.6.

7.1 Tube Erosion and Corrosion of Metals in High-Temperature Fluidized-Bed Service

Several zones of the FBC contain heating surface where expected metal temperatures are on the order of 1300 to 1550°F. These zones require expensive alloy material such as Incoloy 800 to possibly Inconel 601. Further investigation into the suitability of these materials is required if maximum cost effectiveness is to be determined.

In particular, the corrosive effects of H_2S on the inner surfaces of various tube materials at various temperatures needs to be examined. The corrosive effects of H_2S should also be examined in conjunction with SO_2 on the outer surfaces of the tubes.

The possibility of using "Alonized" tubing, in which aluminum is diffused into the tube material, should be considered. Alonizing is intended to inhibit corrosion, and preliminary test results appear encouraging. However, the cost impact must also be considered as well as the long-term effects over the design life of the unit.

7.2 Characterization of Limestone

Transportation charges for the limestone are a large portion of the total cost of the limestone. Therefore an evaluation of the combustion characteristics, SO_2 absorption characteristics, and mechanical properties

should be performed on the various limestones that are indigenous to the site. In this manner, trade-off can be established, and a proper economic evaluation can be formulated.

Information from various limestone quarries was obtained by the Fluidized Combustion Company and is detailed in their final report.⁴ The chemical analyses presented reveal that the limestone in the Southern Illinois area is of very high quality. This is confirmed in reports obtainable from the Illinois State Geological Survey (see ref. 4). However, the quarries are reluctant to quote on the 1/8-in. x 16 mesh size specified since they currently do not have the crushing capability or a ready market for the rock dust that would be obtained during the crushing process. Therefore the economic analysis should consider the feasibility of purchasing standard-size limestone, which is readily available, and then crushing and screening it at the plant site.

7.3 Optimization of Coal Feed Points

Fluidized-bed combustors containing heat transfer surface are presently designed with one coal feed point for every 9 ft^2 of bed surface. This design criterion was established in the 1960s by running diffusion experiments in a large coal bed operating at 3 fps and using fine bed material. The data have not been revised since then because no large beds have been made available with suitable facilities for data collection. This design criterion of one feed point for every 9 ft^2 of bed surface imposes an economic penalty on the coal feed system and severely complicates the division and metering of coal. Methods of reducing the number of fuel feed points to a minimum must be investigated if the system is to be optimized.

7.4 Light-Off Procedures

Energy requirements are greater during light-off operation than during normal operation because of the stored energy requirements of the system in the form of sensible heat of the bed and enclosure, the large sensible heat associated with the higher gas mass flow needed to fluidize the bed at low temperature, and the usually inefficient exchange of heat from a supplementary source. These requirements pose no problem for pilot plant operation in which small beds and low orders of magnitude of total heat input are used. With large beds, however, required heat input during start-up is quite significant, and a stepwise procedure must be developed to minimize the supplementary energy requirements during ignition of large beds by operating the bed on the primary fuel source as quickly as possible.

7.5 Optimization of Hot-Material Handling System

The fluidized-bed combustion system, using limestone as a means for pollution abatement, requires handling of solids material up to 2000°F. The handling of hot particulates introduces other problems in addition to those encountered in normal solids flow. These problems include material selection, valve design, thermal losses, ignition of unburnt carbon, and heat recovery techniques.

7.6 Optimization of Bed Material Removal Techniques

After a number of hours of operation, the fluidized bed may become contaminated with ash from a large-size fraction of coal. Occasionally, clinkers may form as a result of temporary local overheating of the bed or the presence of a low-melting eutectic formed within the ash. Accumulations of

these impurities in small amounts should not hinder operation. Large amounts however, displace the limestone, causing a reduction in absorption capability of the bed. Cleaning a large bed requires the ability to concentrate the impurities at a single location so that they may be removed with a minimum loss of bed material; otherwise, high thermal losses will result.

Practical experience to date has been limited to small beds, and methods most suitable for application in large beds must be determined.

7.7 Recommended Program

Many of the potential areas discussed above will be investigated in depth during the operation and development of the 30-MW pilot plant in Rivesville, West Virginia, and in the various other FBC programs that are being started in the United States and foreign countries. Probably the most important area to be studied for the application of FBCs to hydrocarbonization is the tube erosion and corrosion problem. Other potential users of FBCs, such as refineries and chemical plants, who utilize high-temperature process heaters extensively, would also benefit from a materials development program. The MIUS also requires high-temperature tubing for its air heating tube banks.

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8. PHYSICAL DATA

The data base for the hydrocarbonization process is not well defined. The major uncertainties are the hydrocarbonization and hydrotreating reactions. Although the other reactions are rather straightforward, the effect of small amounts of coal tars is not completely known.

A complete mass balance for the two-stage hydrocarbonization reaction is not available. The char yields are fairly well known, and a complete analysis of the char is available. Since char is the major product, the uncertainties in the gas and liquid yields are not as significant. Steady-state gas compositions have been estimated for each stage, but the relative amount of gas produced is not known with a high degree of accuracy. Analyses and yields of the oils produced in each stage are lacking. In order to proceed with the evaluation, the oils were assumed to be similar to those produced in the COED process, using the same coal. There are some significant differences between the two processes. The Clean Coke process uses a beneficiated coal, a different temperature, and a higher hydrogen partial pressure. The effects of these variables on the characteristics of the tar products have not been determined.

Determining how to hydrotreat the tars was more difficult. The only reasonable solution was to again assume that the tars produced in the process were identical to those produced by the COED process. Experimental data for hydrotreating COED oils were used to design the hydrotreating section. However, if the hydrocarbonization process generates oils significantly different from COED - and this is not an unrealistic assumption - the hydrotreating design would have to be adjusted. Experimental data for hydrotreating the actual oils produced are needed.

Describing the coal liquids presented another problem. The liquids were divided into four pseudo components: naphtha, light-gas oil, heavy-gas oil, and residue. The relative concentration of these components was estimated from a boiling-point curve for COED oil. The COED oil is a rather heavy oil; thus the most prevalent components were heavy-gas oil and residue.

The physical properties of the oil fractions were evaluated from correlations commonly used in the petroleum industry. An API gravity is required for the correlations. Estimating a gravity for the fractions was not overly difficult. The gravity for the heavier fractions was beyond the range generally used in the petroleum industry, and the correlations were used at their minimum gravity or were extrapolated where possible.

Further improvement in the data base will require much additional information such as that provided by boiling-point curves, density vs boiling point plots, and determinations of molecular weights and relative volatilities of the desired oil fractions.

9. TRANSPORTATION AND COMBUSTION OF CHAR PRODUCT

Information concerning the feasibility of transporting the char product via a char-water slurry pipeline is not available. However, a coal-water slurry pipeline is currently being operated commercially in the Southwest.¹ Black Mesa Pipeline, Incorporated (BMP), owns and operates a coal-water slurry pipeline which transports 660 tons of coal per hour from the Black Mesa coal mine in northern Arizona to the Mohave generating station just below Davis Dam on the Colorado River in southern Nevada. The pipeline traverses elevations of 6500 to 700 ft along its 273-mile length and has a 35-year design life. Coal that is mined in the Black Mesa area is received at the preparation plant by conveyor and crushed to -1/4 in. by rotating-cage impactors. The coal is mixed with water and wet ground to -8 mesh x 0 in. in rod mills. The slurry is delivered from storage tanks by centrifugal pumps to large double-acting, duplex positive-displacement pumps which raise the pressure to 1500 psig for delivery to the pipeline.

The coal slurry in the pipeline has a normal concentration of 46 to 48 wt % (moisture-free basis) and flows at the rate of 3750 to 4200 gpm. The slurry velocity is 5.8 fps at 4200 gpm. Three booster pumping stations equipped with piston pumps are used along the pipeline. The outside diameter of the pipeline is 18 in., except where the inside diameter is reduced to 12 in. over the final 12 miles (where the elevation drops from 4000 to 700 ft). Operating experience with the Black Mesa pipeline has indicated that pipeline erosion has not been a problem. However, internal corrosion is prevented by the addition of sulfite inhibitions (when required) to minimize coal- and water-absorbed oxygen, particularly in the

first mile of pipe. No pipe failures have occurred, and the availability of the system has been approximately 99% during the past four years.

An investigation of a char-oil slurry pipeline for transporting the products from the process to market was made during Project COED.² The products were an oil, whose viscosity had been reduced to render it pumpable, and a calcined char. An experimental system was constructed for continuously circulating a char-oil slurry through about 50 ft of 1-in. pipe. Pressure differentials over a 20-ft section of the pipe were measured over a wide range of velocities for slurries with various char contents. Results showed that char-in-oil slurries were similar to coal-in-oil and coal-in-water slurries except for the effect of the higher internal porosity of the char particle. Since the char was very porous, it readily absorbed oil from the slurry; thus the maximum char concentrations that could be pumped were lower than those observed for coal-in-oil slurries. Similar pressure drops were determined for a 60 wt % coal-in-oil slurry and a 40 wt % char-in-oil slurry. Comparable conditions will probably occur in a char-water slurry pipeline, but data are not available for this effect.

Erosion of the pipeline carrying a char-water slurry will probably be an important consideration because char is more abrasive than coal. The test period for the COED study was too short (200 hr of operation) to obtain significant erosion data. Although slight pitting at the outlet of the pump case was observed, the 1-in. pipeline was in good condition. The COED study concluded that pumping char-in-oil slurries is technically feasible, even up to the highest concentrations of 40 to 45 wt % char-in-oil. Therefore, a recommendation is made that the char-oil studies be

extended to char-water slurries and include the following parameters:

1. effects of char concentration,
2. effects of char particle size,
3. corrosion and erosion effects on the pipeline and its associated equipment, and
4. separation of the char from water after pumping.

Combustion of the char product from the "Clean Coke" and "Clean Char" processes has not been investigated. However, extensive large-scale boiler performance tests have been made with COED char.³ The tests were conducted in an arched, downward-fired, natural circulation furnace designed by the Foster Wheeler Corporation for pulverized anthracite fuel with a steam generating capacity of 175,000 lb/hr. The program was conducted on the Hunloch Creek Unit No. 2 owned by the Luzerne Electric Division of UGI Corporation, Kingston, Pennsylvania. Results of the tests indicated that the COED char can be burned successfully in the type of furnace used. Based on these results, Foster Wheeler Corporation stated that a commercial steam generator could be designed and its performance guaranteed using COED char as fuel. Since Clean Coke char is quite similar to COED char, it would probably perform in a similar manner; however, this assumption can only be confirmed by an experimental test program.

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