Office of Fossil Energy

Energy Research and
Development Administration

QUARTERLY REPORT

October - December 1975
ERDA 76-33-4

COAL LIQUEFACTION

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OCTOBER-DECEMBER 1975

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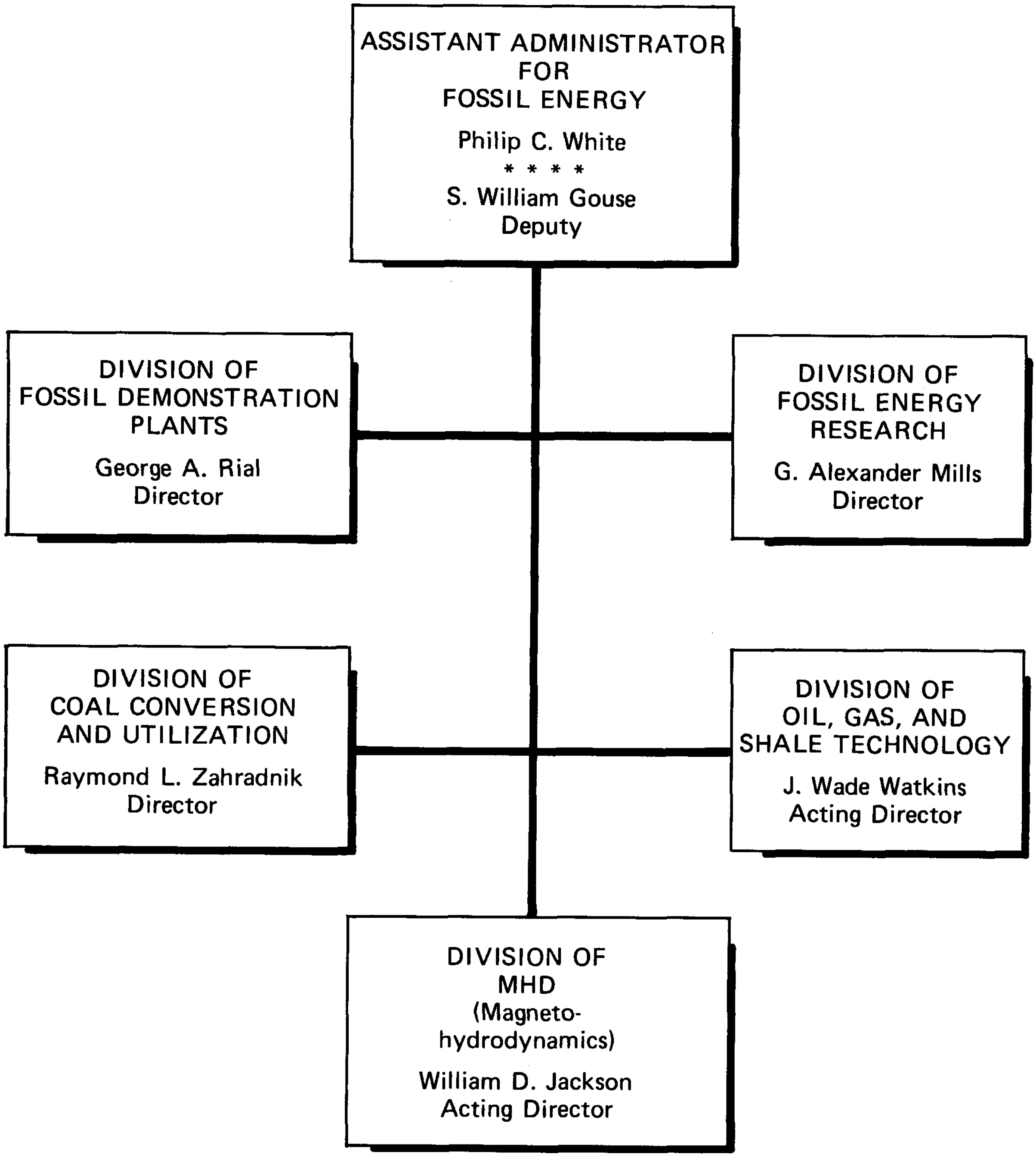
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EXECUTIVE SUMMARY

The United States has more energy available in the form of coal than in the combined resources of petroleum, natural gas, oil shale, and tar sands. Nationwide energy shortages, together with the availability of abundant coal reserves, make the commercial production of synthetic fuels from coal vital to the nation's total supply of clean energy. In response to this need, the Office of Fossil Energy of the Energy Research and Development Administration (ERDA) is conducting a research and development program to provide the technology for rapid commercialization of processes for converting coal to synthetic fuels and for improved direct combustion of coal. These fuels must be suitable for power generation, transportation, storage, and residential and industrial uses. The technologies selected for development (gasification, liquefaction, and combustion) satisfy an urgent need for a particular type of fuel, are potentially feasible both technically and economically (in terms of research and development costs and the costs of the final product) and will not exceed the air, water, and solid pollution standards established by the Environmental Protection Agency (EPA). The emphasis given to each of the technologies varies depending upon factors such as technical complexity, stage of development (laboratory research, including bench-scale tests and experiments with process development units, and pilot plant design, construction, and operation), flexibility of the use of the fuel produced, and the urgency of the energy need that the technology is designed to satisfy.

ERDA's program for the conversion of coal to liquid fuels was started by two of ERDA's predecessor agencies, the Office of Coal Research (OCR) in 1962, and the Bureau of Mines, U.S. Department of the Interior, in the 1930s. Techniques for converting coal to synthetic liquid fuels, originally developed in Germany in the early 1930s, are being improved to increase the supply of nonpolluting liquid fuel and to produce a more easily transportable and usable fuel. Current emphasis is being placed on the development of fuels suitable for firing industrial and electric utility boilers and gas turbines. Modern improvements are providing better catalysts, better reactor designs, and better construction materials, leading to more attractive processing economics and lower capital investment. Coal liquefaction can now be achieved under more moderate processing conditions and more rapidly than was the case in the early 1930s. The advantage of coal liquefaction is that the entire range of liquid products, including fuel oil, gasoline, jet fuel, and diesel oil, can be produced from coal by varying the type of catalysts and other operating conditions. Furthermore, coal-derived liquid fuels have potential for use as chemical feedstocks.

To develop the most efficient utilization of coal resources, ERDA is sponsoring the development of several conversion processes, which are currently in different stages of development. Four are in the pilot plant stage. Responsibility for the design, construction, and operation of pilot plants is assigned to FMC Corporation for the Char-Oil Energy Development pilot plant at Princeton, New Jersey; Pittsburg & Midway Coal Mining Company for the Solvent-Refined Coal plant at Ft. Lewis, Washington; Hydrocarbon Research, Inc., for the H-Coal pilot plant at Catlettsburg, Kentucky; and Fluor Engineers and Constructors, Inc., for reactivating an ERDA-owned facility in Cresap, West Virginia. A process development unit is being designed by Foster Wheeler Energy Corporation to test the Synthoil process, which was originally developed by the U.S. Bureau of Mines; laboratory research is being conducted by the Pittsburgh Energy Research Center (PERC), Sandia Laboratories, Argonne National Laboratory, Battelle Memorial Institute (Columbus Laboratories), Exxon Research and Engineering Company, and Morgantown Energy Research Center (MERC). The Clean Coke process is being developed by USS Engineers and Consultants, Inc., a subsidiary of United States Steel Corporation; the results of laboratory tests and data obtained in a process development unit can be used for eventual pilot plant scale-up. The Rocketdyne Division of Rockwell International is conducting a research program to develop a technology that would permit the liquefaction of coal by direct hydrogenation in an entrained-flow reactor. Research to improve solid-liquid separation using filtration is being conducted by Johns-Manville Sales Corporation. The Dow Chemical Company is conducting a research and development program on the use of coal-derived liquids as chemical feedstocks. R&D engineering services, both those involved in the development and operation of a fluidized-bed hydrocarbonization reactor and those involved in the development of a process to carbonize residue, are being provided by Oak Ridge National Laboratory.

The ***Char-Oil Energy Development*** project has been completed. Arrangements are currently being made to dismantle the pilot plant during the first and second quarters of 1976. The pilot plant equipment will be used at the Pittsburgh Energy Research Center in the Synthoil process development unit.

The ***Solvent-Refined Coal (SRC) Process*** pilot plant operated for a total of 55 days during the quarter; 400 tons of specification-grade solvent-refined coal product were produced. Data from two material balance runs made during this quarter and from previous runs were recalculated to obtain a better indication of the actual operating conditions. The water yield was also revised so that a total mass balance could be obtained. Operational problems occurred in the solvent recovery area and modifications were made. Ten runs were conducted in the laboratory reactor unit, five using the slurry recycle mode and five using the distillate solvent mode.

Synthoil Process efforts concentrated on process development. Aspects of the process being studied include:

- Testing of catalysts, testing the removal of solids by using a rotary-drum pressure filter, conducting hydrodynamic studies using the cold-model reactor, and studying the pyrolysis of residue from the process
- Studying the mechanisms of deactivation and reactivation of catalysts, studying the effects of coal-ash content on liquefaction, and studying the effects of process parameters on the kinetics of hydrodesulfurization and liquefaction
- Determining the heat of reaction of hydrogen with coal slurries, determining the heat transfer coefficients from reactor fluids to heat exchangers, testing the removal of solids from liquids by the use of additives, and the testing of new catalysts
- Testing to measure the viscosity, density, electrical resistivity, and the dielectric constant of the Synthoil liquids
- Determining the chemical properties of Synthoil products and feed
- Conducting an economic analysis of a Synthoil plant that would produce 50,000 barrels of liquid fuel per day.

Site preparation for the process development unit has been completed and the proposal to manage the construction of the process development unit has been approved by ERDA.

The site plan for the ***H-Coal Process*** pilot plant was approved by ERDA. Design and engineering work continued on the coal preparation, coal hydrogenation, and offsites sections of the pilot plant. A test run was conducted in the process development unit to produce fuel oil with a sulfur content ranging from 0.6 to 1.0 weight percent. A ceramic hydroclone, used during the last few days of the test run, removed ash more efficiently than stellited hydroclones used earlier in the run. The solvent precipitation test unit was assembled and operated with a slurry of diluted H-Coal vacuum still bottoms; a clear overflow with less than 0.1 weight percent ash was obtained. Construction continued on the centrifugation test unit and filtration studies were scheduled.

Renovation of the ***Cresap Test Facility*** continued. Construction of several pilot plant items was completed. Delays are still being encountered in obtaining the wastewater permit for the sanitary treatment system from the West Virginia Department of Health. Process sketches and test setups were completed and tests schedules were released for review. The Liquified Coal Development Corporation has been formed and incorporated; the corporation will operate the pilot plant.

Clean Coke Process efforts continued to emphasize the development of the carbonization aspect of the process. Two high-temperature carbonization runs were conducted. The first run produced a low-sulfur char from a first-stage semichar; the second run was the first in a series of runs planned to determine optimum residence time and temperature to produce specification char. Corrosion tests were made from a series of test specimens of various types of steel removed from the unit. In the binder preparation section, a tube heater was installed for use as a recycle heater. A 3-day run of the flash vaporizer was begun; the run was terminated when the recycle pump failed and a larger pump motor was installed. A 4-day run was completed successfully. New heat traces are being added and faulty ones replaced in the slurry oil preparation unit. The hydrogenation process development unit is being structurally revised and the coke preparation process development unit was operated to produce green coke pellets. Problems with the 3-inch continuous carbonizer laboratory unit were corrected and experimental work with the unit will begin next quarter.

Studies of the ***Liquefaction of Coal by Direct Hydrogenation*** included the construction of the cold-flow test unit for the transport and mixing tests. Plugging problems encountered in initial tests were resolved. Transport tests conducted in the cold-flow unit showed that pulverized coal can flow uniformly and consistently from the pressurized feeder without difficulty. Further analysis of void fraction and transport gas requirement data obtained previously indicated that the transport gas requirement is low. Injection elements and the two-phase flow probe for the mixing tests were fabricated. Preliminary design efforts were directed toward definition of the required hardware for the 1-ton-per-hour reactor system.

The ***Filtration Process and Equipment Studies*** laboratory test facility was completed during this quarter to a point that test filtration runs were initiated to develop procedures to be used in the major experimental program. The first set of tests used water and organic media to establish precoating and cake cutting procedures. Difficulties in forming the filter cake resulted in the use of a finer mesh wire on the filter leaf and a filter aid. Tests using coal oil emphasized the need for an effective equipment cleaning agent. In subsequent tests with coal oil, difficulties were encountered with the filter cakes decomposing.

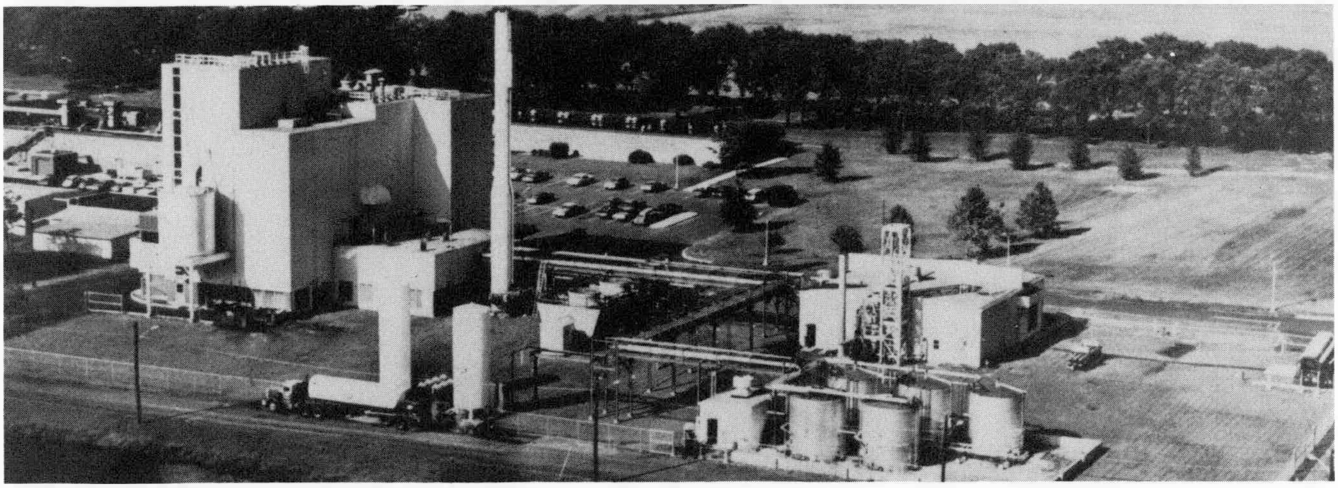
In the ***Chemicals from Coal*** project, the COED naphtha was hydrotreated in two stages to obtain a low-nitrogen and low-sulfur product. The entire Synthoil sample was distilled to obtain a mid-distillate; it was decided not to study the Synthoil light-oil fraction because only a nominal amount is produced. The H-Coal naphtha was further reformed using Aeroform PHF-4 platinum reforming catalyst and hydrocracking of the

H-Coal straight-run vacuum-gas oil was completed. The hydrocracked SRC product was received from the U.S. Bureau of Mines.

In ***R&D Engineering Services–Hydrocarbonization,*** the results of two experimental runs conducted last quarter were reported, and three more experimental runs were conducted. The installation of the bench-scale system was completed and further shakedown tests were made using nitrogen as the feed gas; two tests were run at 5 atm and two at 20 atm. The bench-scale system was prepared for the first scheduled runs with hydrogen.

In ***R&D Engineering Services–Carbonization of Residue,*** literature concerning the design and operation of the Cresap test facility carbonizer was reviewed. Modifications were made to the bench-scale batch reactor to convert it to a continuous-feed-flow fluidized reactor. The only residue for which any data are currently available is that of the H-Coal vacuum tower bottoms. This material, finely ground, can be transported pneumatically to the reactor. A second feed system is being designed in case the one currently planned is not successful.

I. CHAR-OIL ENERGY DEVELOPMENT (COED)



FMC CORPORATION
PRINCETON, NEW JERSEY

Contract No. E(49-18)-1212
Total Funding: $11,160,373

INTRODUCTION

The COED project is being conducted by the FMC Corporation under ERDA sponsorship. The objective of the COED project is to develop a method for converting coal to low-sulfur synthetic crude oil and medium-Btu gas on a commercial scale. Specifically, different types of coal are to be tested in the existing pilot plant in order to select the optimum type for use in a commercial plant. Figure I-1 shows the COED project schedule.

PROCESS DESCRIPTION

The COED process converts coal to gas, oil, and char through heating in multistage fluidized beds, as shown in Figure I-2. In this process, the coal is first crushed and dried, then is pyrolyzed in a series of four fluidized-bed reactors with successively higher temperatures. The temperature of each fluidized-bed reactor is just below the maximum temperature to which the coal can be heated without agglomerating. The number of stages and the operating temperature vary with the agglomerating properties of the coal. Heat for pyrolysis is provided primarily by burning a portion of the char with oxygen in the presence of steam in the fourth stage of pyrolysis. (Nitrogen is used for start-up to fluidize the first stage until enough flue gas is available.) Hot gases from the fourth stage flow countercurrent to the char. These gases, which provide the fluidizing medium for the third and second stages of pyrolysis, are then passed to a product recovery system where the gas and oil are produced.

Gas and oil are recovered from vapors coming off from the second pyrolysis stage. These vapors pass into a cyclone which removes the fines. The vapors leaving the cyclone are then quenched directly with water in a venturi scrubber to condense the oil, and the gases and oils are separated in a decanter.

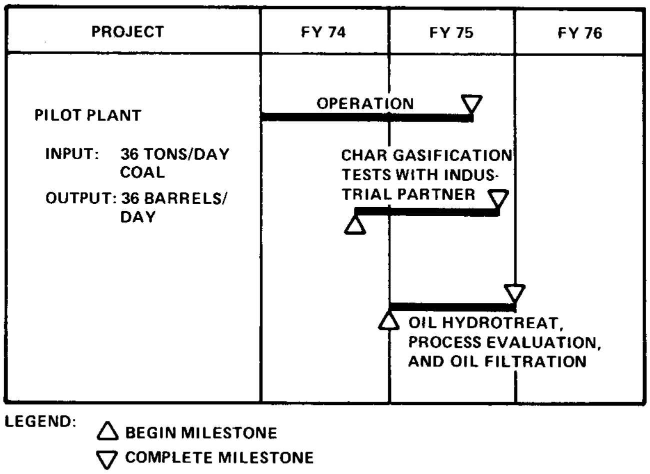


Figure I-1. PROJECT COED PROGRAM SCHEDULE

The gas is desulfurized in the gas cleaning plant, then enriched with steam by a steam reformer. Part of the product gas is converted to hydrogen and used in the process; the balance of the product gas can either be scrubbed and sold as fuel gas or converted to pipeline gas or hydrogen.

The oil from the decanter is dehydrated and filtered in a rotary pressure precoat filter. The solids-free oil is then pressurized and mixed with hydrogen in a fixed-bed catalytic reactor (hydrotreater). The hydrotreater removes nitrogen, sulfur, and oxygen (which are reacted with hydrogen to form ammonia, hydrogen sulfide, and water) and produces a heavy synthetic crude oil with a specific gravity of 0.9.

The char produced by the process is desulfurized in a shaft kiln. In the kiln, hydrogen is added to the char, which produces hydrogen sulfide; the hydrogen sulfide is then absorbed by an acceptor, such as calcined limestone or dolomite. After desulfurization, the char and spent acceptor (which can be regenerated) are separated in a continuous fluidized-bed separator. Product char can be reacted with steam and oxygen in a gasifier to generate low-Btu gas. The rank of coal processed and the marketability of the end product determines the final use of the char and gas.

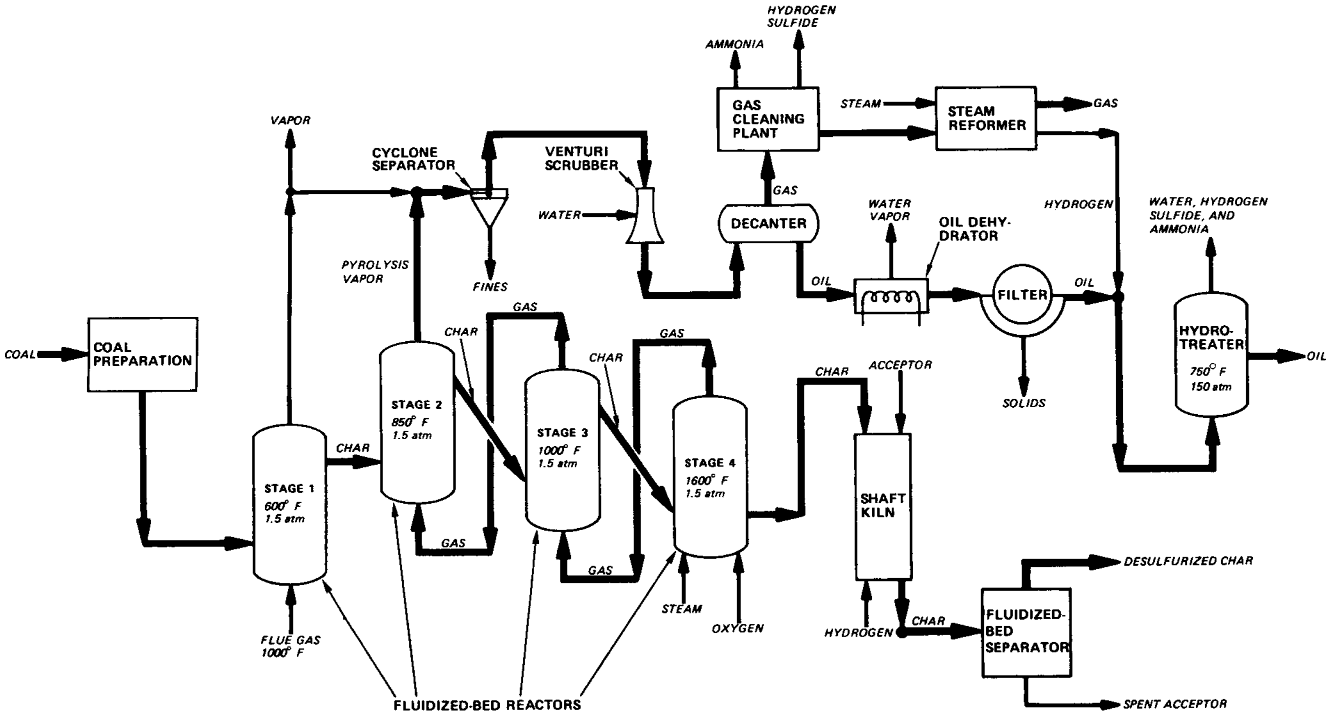


Figure I-2. COED PROCESS SCHEMATIC

HISTORY OF THE PROJECT

The COED project, initiated in 1962 under the auspices of OCR (now a part of ERDA), was tested for several years in bench-scale research studies. In 1965, FMC installed, at its Chemical Research and Development Center in Princeton, New Jersey, a process development unit capable of processing 100 pounds of coal per day. Twelve different kinds of coal were evaluated.

FMC Corporation entered into a second contract with OCR in September 1966. This contract was to (1) continue the investigation of the pyrolysis of coal using the existing process development unit and (2) design, construct, and operate a pilot plant capable of converting 36 tons of coal per day to low-sulfur synthetic crude oil. The plant, located in Princeton, New Jersey, was completed in July 1970. The pyrolysis section of the pilot plant has been in operation since then and the hydrotreating section since June 1971.

FMC entered into its present contract with OCR in 1971. Through 1974, the COED pilot plant processed about 21,000 tons of coal from seven different geographic sources, ranging in rank from lignite to high volatile A bituminous coal. In 1974, high volatile B bituminous coal from western Kentucky and high volatile A bituminous coal from West Virginia were processed. These are the most highly agglomerating coals to be processed in the pilot plant. The circulation of solids between multiple fluidized-bed reactors, the filtration of coal oil, and the upgrading of the coal oil to synthetic crude oil through fixed-bed hydrotreating have been demonstrated successfully. The plant was also operated to test new equipment and provide char and oil for further evaluations. The pilot plant has been operated successfully at design capacity and several 30-day runs have been made.

PROGRESS DURING OCTOBER-DECEMBER 1975

During the final quarter of 1975, all COED project work specified in the contract was completed. Arrangements are currently being made to dismantle the pilot plant (under the existing contract) during the first and second quarters of 1976. The pilot plant equipment will be used at the Pittsburgh Energy Research Center in the Synthoil process development unit and in other liquefaction experimental units. Volume I of the final report on the project, covering August 1971 through June 1975, has been approved by ERDA and printed.

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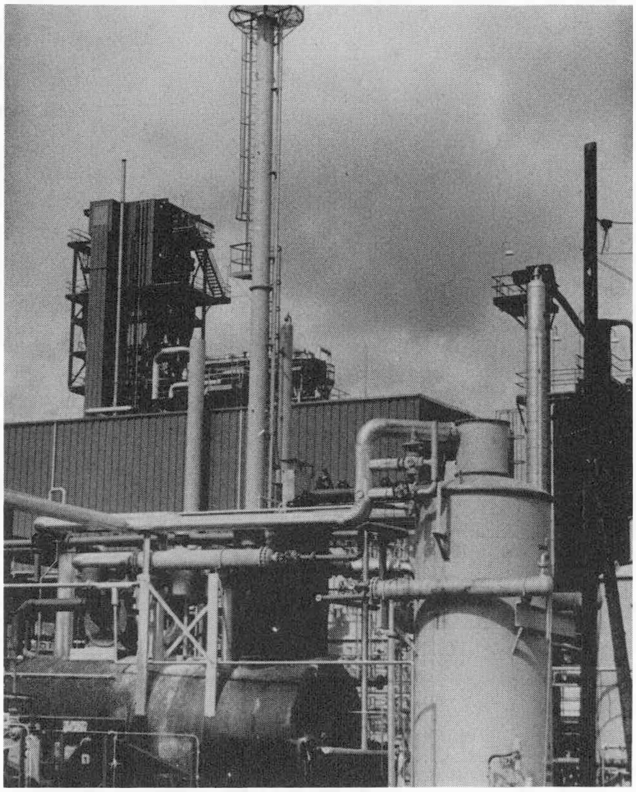
II. SOLVENT-REFINED COAL (SRC) PROCESS



THE PITTSBURG & MIDWAY COAL
MINING COMPANY
MERRIAM, KANSAS

Contract No. E(49-18)-496
Total Funding: $42,002,236

INTRODUCTION

The SRC process is being developed by Pittsburg & Midway Coal Mining Company (P&M), a subsidiary of Gulf Oil Corporation, under the sponsorship of ERDA. The specific objectives of the contract are to (1) continue obtaining technical and economic data from the pilot plant to validate scale-up to commercial production and (2) provide large samples of solvent-refined coal and by-products from the process for market development studies. Figure II-1 provides a schedule for the development of the process.

PROCESS DESCRIPTION

The SRC process converts high-sulfur, high-ash content coals to low-sulfur, low-ash liquid fuel. Figure II-2 shows a schematic of the process. The coal is first pulverized and mixed with a coal-derived solvent in a slurry mix tank. The slurry is mixed with hydrogen, which is produced by other steps in the process, and is then pumped through a fired preheater and passed into a dissolver where about 90 percent of the moisture- and ash-free coal is dissolved. Several other reactions also occur in the dissolver: the coal is depolymerized and hydrogenated, which results in an overall decrease in product molecular weight; the solvent is hydrocracked to form lower-molecular-weight hydrocarbons that range from light oil to methane; and the organic sulfur is removed by hydrogenation in the form of hydrogen sulfide.

From the dissolver, the mixture passes to a separator where the gases are separated from the slurry of undissolved solids and coal solution. The raw gas is sent to a hydrogen recovery and gas desulfurization unit. The hydrogen recovered is recycled with the slurry coming from the slurry mix tank. Hydrocarbon gases are given off and the hydrogen sulfide is converted to elemental sulfur.

The slurry of undissolved solids and the coal solution pass to a filtration unit where the undissolved solids are separated from the coal solution. In the commercial-scale process, the solids are sent to a gasifier-converter where they react with supplemental coal, steam, and oxygen to produce hydrogen for use in the process. The coal solu-

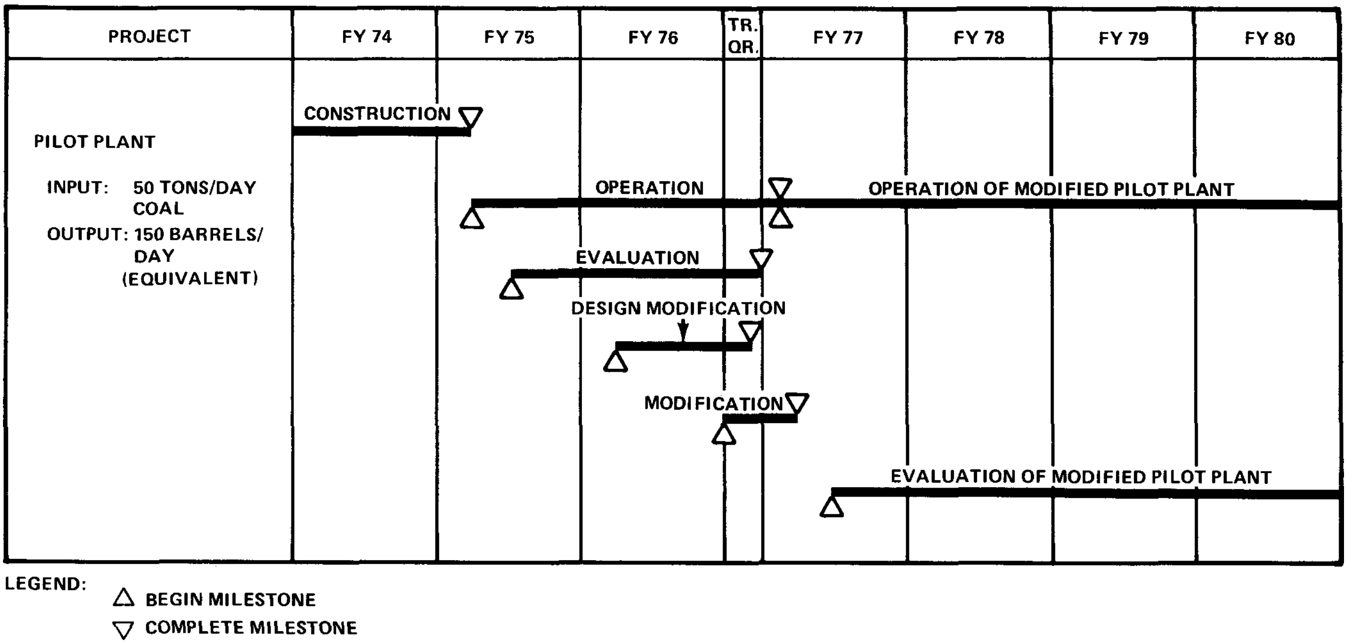


Figure II-1. SOLVENT-REFINED COAL PROGRAM SCHEDULE

tion passes to the solvent recovery unit and the final liquid product, solvent-refined coal, is produced. The solvent-refined coal has a solidification point of 350° F to 400° F and a heating value of about 16,000 Btu per pound.

HISTORY OF THE PROJECT

The SRC project was begun in 1962 when Spencer Chemical Company was awarded a research contract by OCR (now part of ERDA) to study the technical feasibility of a coal deashing process (now called the SRC process). In 1965, the process was successfully demonstrated in a 50-pound-per-hour continuous-flow unit, and the work on the contract was therefore completed. During the term of the contract, Gulf Oil Corporation acquired Spencer Chemical Company. After reorganization, the contract was assigned to the research department of P&M.

To further develop the SRC process, a contract was awarded to P&M to design, construct, and operate a pilot plant that would be capable of processing 50 tons of coal per day. In 1969, Stearns-Roger Corporation completed the design for the pilot plant but funds to begin construction were not available until late 1971. In June 1972, OCR extended its contract with P&M for the construction and operation of the pilot plant. Rust Engineering Company began construction of the pilot plant in July 1972 at Ft. Lewis, Washington. As units were completed, preliminary tests of process equipment and instrumentation were performed. The pilot plant became fully operational in October 1974.

In conjunction with this project, economic studies of the feasibility of the SRC project have been and are continuing to be conducted through an interagency agreement between EPA and ERDA. The interagency agreement also provides for environmental studies, including the removal of sulfur and nitrogen compounds from the coal.

Supporting laboratory work is being conducted by Oklahoma State University and Washington State University as well as by P&M. Work at Oklahoma State University concentrates on the catalytic hydrogenation of coal liquids. Washington State University is conducting experiments on coal mineral residues and trace elements in the SRC process. P&M's research concentrates on providing process engineering data for guidance of the pilot plant operation and for evaluation of promising areas of improvements in the SRC process.

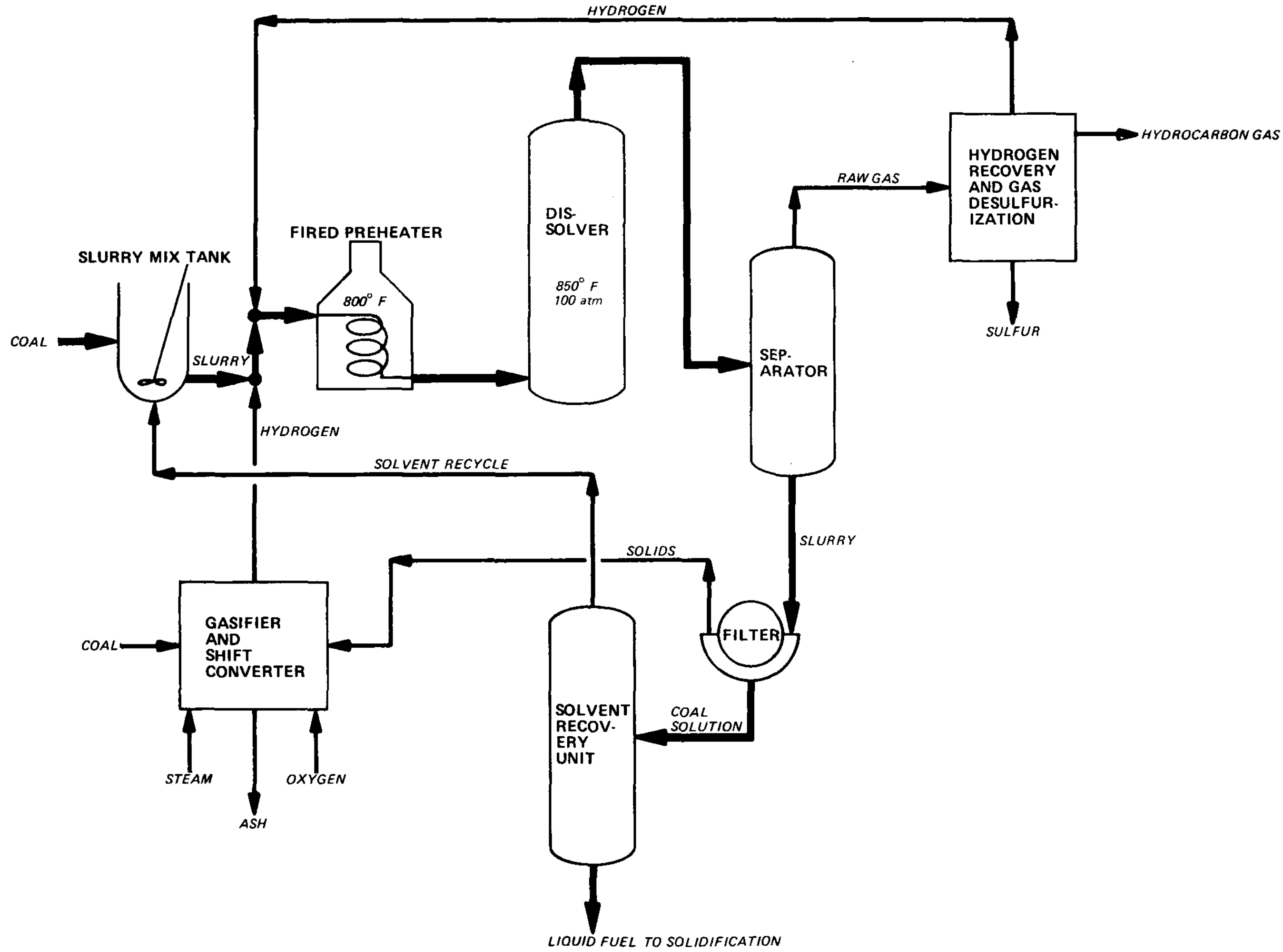


Figure II-2. SRC PROCESS SCHEMATIC

PROGRESS DURING OCTOBER-DECEMBER 1975

Summary

The Fort Lewis SRC pilot plant operated for a total of 55 days during the quarter and produced 400 tons of specification-grade product for full-scale utility boiler combustion tests. The first shipment of the product by open rail car was made to evaluate product handling characteristics. Two material balance runs were made to determine the effect of pressure. The material balances for these runs, and data from previous runs, were recalculated based on redefined distillation cut points. The water yield was also revised so that a total mass balance could be obtained. Major operational problems occurred in the solvent recovery area; several modifications were made, including the addition of a heat exchanger unit to the filter-feed surge vessel and the installation of a pump to recirculate the vacuum bottoms to the flash preheater. Considerable maintenance was required on the distillation columns and on the filters.

Ten runs were conducted in the laboratory reactor unit, five using the slurry recycle mode and five using the distillate solvent mode. The first three slurry recycle runs were conducted to determine if the residence time in the reactor could be decreased, the fourth to simulate operating conditions at the SRC Fort Lewis pilot plant, and the fifth to test another type of coal. Considerable difficulties were encountered in obtaining good steady-state operation in the slurry recycle mode because the viscosities tended to increase and cause termination of the runs. Nevertheless, the data obtained were encouraging.

The first four runs conducted in the distillate solvent mode were made to simulate pilot plant conditions, and the last run was made to correlate the performance of the laboratory reactor with that of the Wilsonville, Alabama pilot plant reactor. In general, a higher level of hydrogenation and also a higher conversion of vacuum bottoms to lighter products were obtained in the laboratory runs.

Pilot Plant Operation

During the quarter, the Fort Lewis SRC pilot plant operated for a total of 55 days, during which 400 tons of specification-grade product were produced. Pilot plant efforts concentrated on producing as much solvent-refined coal product for burning tests as possible. To evaluate product handling characteristics, the first shipment of 85 tons of the product was made in an open coal railroad car.

Two material balance runs (Runs 10 and 11) were made in October. The runs were carried out at 70 atm and 86 atm, respectively, considerably lower than the pressure of 100 atm used for Runs 4 through 9. The dissolver outlet temperatures of 842° F and 848° F, respectively, were approximately the same as those in the previous runs. The marked increase in hydrogen consumption from an average of 2 percent in previous runs to 2.9 percent for Run 10 and 3.6 percent for Run 11 may have resulted from errors in gas measurement. Solvent-refined coal product yields, calculated using a forced ash balance, were within 3 percent of the measured yields; however, calculations on the two runs showed an unaccounted mass loss of 7 percent of the moisture-free coal feed. Mass balances made on the various elements were within 10 percent for all elements except hydrogen and sulfur, for which discrepancies of 15 to 20 percent occurred.

For Run 10, the coal feed rate was 72.6 pounds per hour per cubic foot of reactor and the yield of SRC product was 65.4 percent, roughly the same yield as that of Runs 4 through 9. In Run 11, using a coal feed rate of 73.7 pounds per hour per cubic foot of reactor, the yield was only 61.0 percent, noticeably lower than that of any previous run. The feed rates for both Runs 10 and 11 were lower than those for most of the previous runs.

After distillation cut points were redefined, the material balances for Runs 4 through 9 were recalculated. The water yield was also revised so that a total mass balance could be obtained. The recalculations better reflected the actual operating characteristics of the plant. In general, the revised calculations showed a slightly lower yield of light oil and a slightly higher yield of process solvent. Compared with Runs 4 through 9, Run 10 yielded a smaller amount of light oil and a larger amount of wash solvent and Run 11 yielded a higher amount of light oil and a lower amount of wash solvent.

During stable plant operation, samples of the dried and pulverized coal feed, the mineral residue, the light oil, the wash solvent, the process solvent, and the process product were taken and analyzed on a regular basis. Product analysis showed a near constant value over the entire quarter. Mineral residue analysis showed a drop in the average content of pyridine insolubles, which indicated that the efficiency of the mineral residue dryer had been reduced. Analyses of the light oil, wash solvent, and process solvent appeared constant.

Mechanical problems developed in several areas during the quarter and considerable maintenance was required. The filter-feed surge vessel developed a bulge because of overheating; a Dowtherm heat exchanger unit was installed. Shortly after installation, however, a leak in the unit released Dowtherm into the system, requiring the plant to be shut down so that the leak could be repaired. Another shutdown was caused by coke buildup in the vacuum flash preheater coil. Coking problems continued and are apparently more severe when the feed to the preheater contains substantial quantities of low-boiling material, which causes excessive vaporization in the coil. To correct the coking problems, the solvent recovery area was modified. Considerable corrosion occurred in the Type 410 stainless steel trays in the wash solvent distillation column and the trays were replaced by Type 304 stainless steel trays. The pall rings, which form the packing in the lower part of the column, were replaced with rings made of Type 304 stainless steel.

Other maintenance work was required on the inert gas blower in the coal preparation unit and on both filters. A pump to recirculate the vacuum bottoms to the vacuum flash preheater was installed, but plugging problems required major maintenance work on the system. Various modifications to the system are in progress, including the installation of a larger recirculation line to accommodate the recycle liquid, which is more viscous than previously assessed.

The Stretford sulfur recovery unit was repaired and put back in operation in mid November. A large concrete interceptor box that will direct surface water plant run-off to the waste treatment area and avoid potential contamination of the Hamer Marsh area was 75 percent installed by the end of the quarter.

Process development continued in the hot solvent coal blending area. After two attempts at testing and calibrating the equipment, larger inlet and outlet lines were installed because of plugging problems. Later runs with a solvent-to-coal ratio of approximately 2 and residence times of approximately 20 minutes were made at temperatures varying from 200° F to 500° F. While preliminary results are encouraging, no firm data at the higher temperatures have been obtained. A liquid-level controller was installed in the blend tank, but false level indications and plugging of the mix tank with coal have not been completely eliminated. Some viscosity measurements were made, but accuracy was poor. No foaming problems were encountered.

Five runs were made on the hydroclones during November, two with the 2-inch Cresap hydroclone at 365° F and three on the Doxie-5 hydroclone at 400° F to 414° F. The pyridine insolubles concentration in the overflow from the Doxie hydroclone was appreciably higher than that of the Cresap hydroclone.

Laboratory Research

Ten runs were conducted in the laboratory reactor unit; five runs were made in the slurry recycle mode and five in the distillate solvent mode. The slurry recycle mode is used to produce liquid solvent-refined coal. Using the distillate solvent mode produces a solid product.

The first three runs conducted in the slurry recycle mode attempted to lower residence time from 2 hours, the residence time of a steady-state slurry recycle run of last quarter. The first run, GU 116R, was made with a residence time of 1.5 hours; Runs GU 117R and GU 119R were each made with residence times of 1 hour. Both Runs GU 116R and GU 117R were terminated prematurely because impure hydrogen (73 percent) was mistakenly used, after starting the runs with 90 percent hydrogen. Before the impure hydrogen was introduced, results for Run GU 117R were good: filtrate products were well desulfurized (0.33 percent sulfur content) and moderately well hydrogenated (6.7 percent hydrogen content); filtrate yields averaged about 40 percent, based on coal feed. When the impure hydrogen was used, an abrupt increase in viscosity (too high to be measured at 275° F) and an increase in the nitrogen content from 1.5 percent to 1.9 percent occurred. Run GU 119R, the repeat of Run GU 117R, also had to be terminated early because the slurry pump failed; also, at the time of shutdown, the viscosity of the feed slurry was becoming unmanageable. Data, however, were encouraging; the filtrate contained 0.28 percent to 0.32 percent sulfur and about 7 percent hydrogen.

The fourth recycle mode run, Run GU 121R, was made to simulate the conditions used at the Fort Lewis pilot plant when operating in the slurry recycle mode. The run used low coal concentration (17 percent) in the feed slurry and short retention time per pass (23 minutes). A recorder malfunction caused low temperatures in the early part of the run, but the malfunction was corrected for the final third of the run. Viscosity increased rapidly toward the end of the run and a final filtrate viscosity of about 1,600 centistokes at 210° F was obtained. The primary difference in results between this laboratory run and the Fort Lewis pilot plant runs was that a higher level of solvent to vacuum bottoms ratio was obtained in the pilot plant runs.

The objective of the final slurry recycle run made in the quarter, Run GU 125R, was to apply the conditions developed for partial slurry recycle to Illinois No. 6 high-organic-sulfur coal. The coal swelled, and it was not possible to modify the viscosity of the slurry by raising the operating temperature, as is normally done with Kentucky No. 9 coal. During the run, a progressive failure to maintain a uniform hydrogenation rate resulted in material with gradually less hydrogen content. The run showed that these operating conditions are not satisfactory for Illinois No. 6 coal.

The purpose of the first four runs made in the distillate solvent mode was to simulate the operating conditions of the Fort Lewis pilot plant. The first run, Run GU 118, duplicated pilot plant conditions for a production run made in early September. Conditions were reasonably well matched; however, a higher hydrogen partial pressure occurred in the laboratory run because of the use of pure hydrogen (96 percent hydrogen was used in the pilot plant run). Therefore, the most significant difference in the results of the two runs was the higher level of hydrogenation in the laboratory run, 6.04 percent hydrogen in the laboratory product compared to 5.57 percent hydrogen in the pilot plant product. Also, a higher conversion of vacuum bottoms to lighter products occurred in the laboratory run.

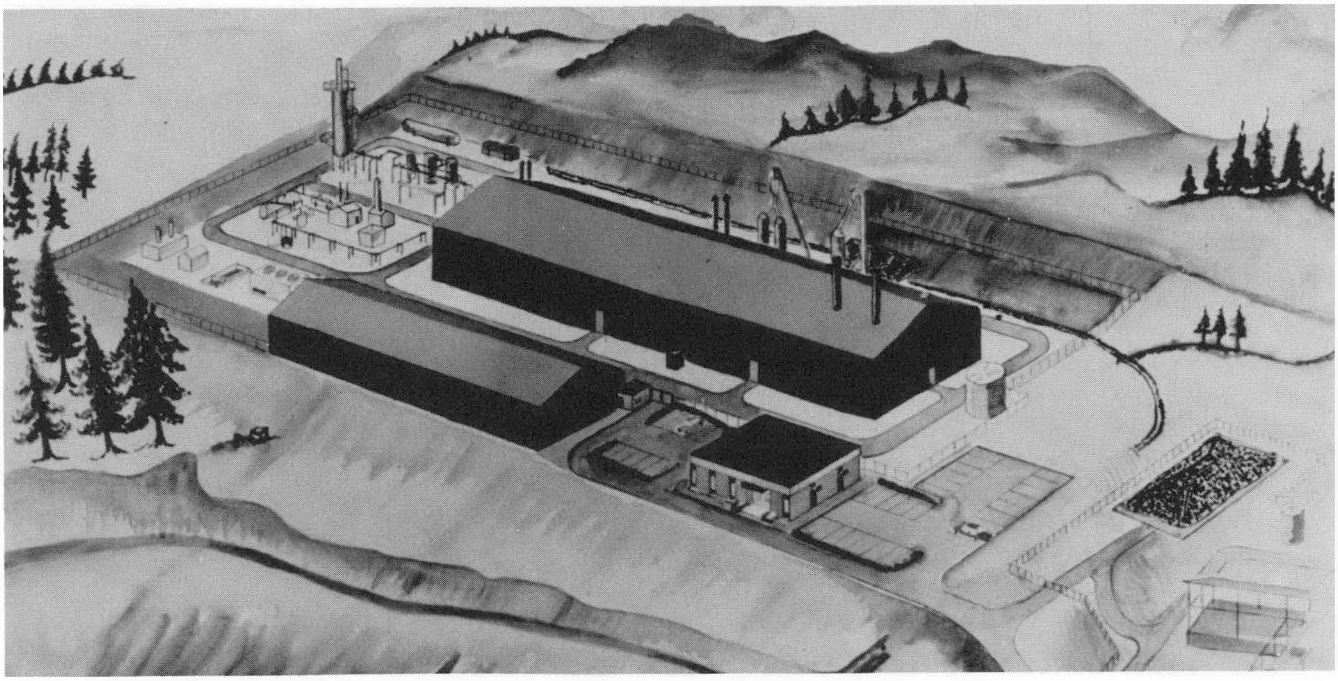
Run GU 120, conducted at a coal feed rate of 76 pounds per hour per cubic foot of reactor was comparable to the pilot plant material balance Run 8. Runs GU 122 and GU 123 both used Kentucky No. 9 coal and were conducted at coal feed rates of 95 to 98 pounds per hour per cubic foot of reactor (comparable to the pilot plant material balance Run 7). However, the iron pyrite content of the coal used in Run GU 123 was lower than usual and thus lowered the hydrogenation level of the recycle solvent and the product yield. In both Runs GU 120 and GU 122, break-even solvent yields were obtained. Variations in desulfurization of the products between the two reactors were not significant.

Run GU 124 was a correlation study to relate the performance of the GU 3 reactor to the performance of the Wilsonville, Alabama SRC pilot plant reactor, using the same type of coal and under the same operating conditions. The laboratory reactor operated at 50° F to 60° F less than the Wilsonville reactor; the large difference in vacuum bottoms yield (51 percent at Wilsonville and 75.7 percent at the laboratory) may have been caused by the temperature difference.

Supporting Research

Mineral residue studies at Washington State University were resumed upon the arrival of new crystalline alumina tubes for the large reactor furnace. After tests for airtightness and control of sampling rates were completed, correct chromatograph results were obtained. Two runs, one at 2,000° F for 2 hours and another at 2,100° F for 2.5 hours, were carried out. Preliminary results showed that only 28 percent of the weight of the material in the coal minerals was reacted. In the trace element/material balance research, the development of instrumental neutron activation analysis procedures for all solvent-refined coal products was completed. Samples from the water streams were freeze-dried to reduce the volume and are currently being analyzed in the same manner as the solid samples. Analysis of samples for all streams are under way. Suitable analytical procedures for beryllium and lead are still being developed.

III. SYNTHOIL PROCESS



FOSTER WHEELER ENERGY CORPORATION

Total Funding:	$24,425,776

SANDIA LABORATORIES

Total Funding:	$1,636,000

ARGONNE NATIONAL LABORATORY

Total Funding:	$1,574,000

EXXON RESEARCH AND ENGINEERING COMPANY

Total Funding:	$100,000

BATTELLE MEMORIAL INSTITUTE COLUMBUS LABORATORIES

Total Funding:	$156,000

INTRODUCTION

Development of the Synthoil process, initiated by the U.S. Bureau of Mines, is currently being managed by ERDA through the Pittsburgh Energy Research Center (PERC) in Pennsylvania. The objective of this project is to determine the technical and economic feasibility of the process for scale-up to commercial use. Several contractors are involved with the project. Foster Wheeler Energy Corporation, Livingston, New Jersey, is responsible for the design and construction management of a 10-ton-per-day process development unit to test the Synthoil process. Concurrent with the design of the process development unit, supporting research is being conducted at PERC. In addition, PERC is monitoring laboratory research on various aspects of the Synthoil process being conducted at Sandia Laboratories, Albuquerque, New Mexico, at Argonne National Laboratory, Argonne, Illinois, and at Exxon Research and Engineering Company, Baytown, Texas. The Morgantown Energy

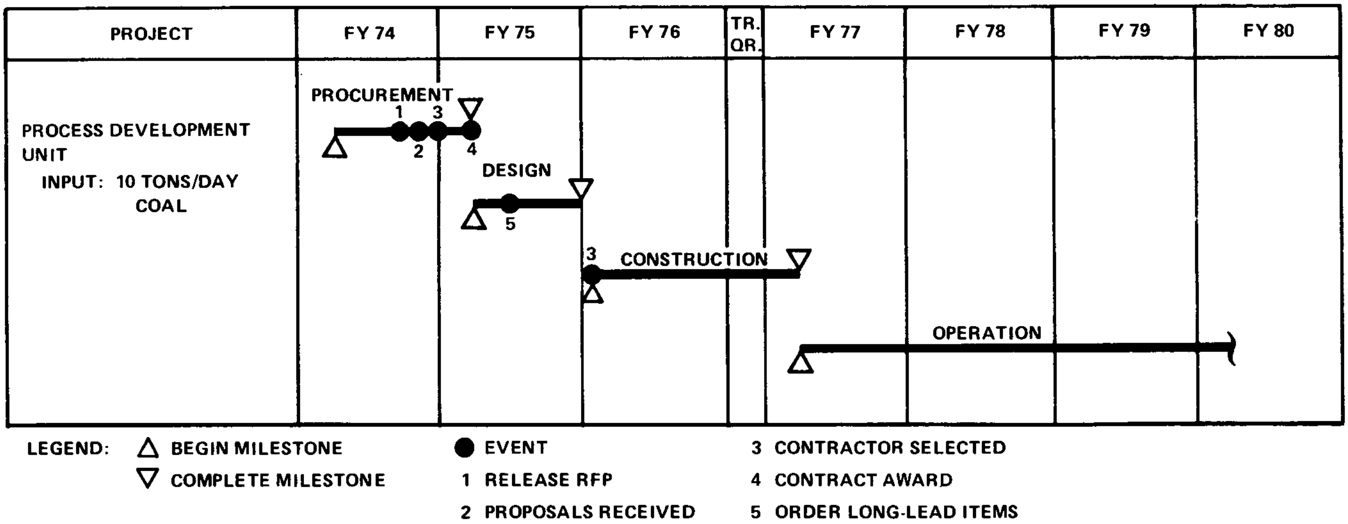


Figure III-1. SYNTHOIL PROGRAM SCHEDULE

Research Center (MERC) in West Virginia is monitoring research being conducted at Battelle Memorial Institute, Columbus Laboratories, Columbus, Ohio. The program plan is shown in Figure III-1.

PROCESS DESCRIPTION

The Synthoil process is a hydrodesulfurization process that converts high-sulfur coal to a low-sulfur, low-ash synthetic fuel oil. A schematic of the process is shown in Figure III-2. The coal is first crushed, ground, and dried; it is then mixed with a portion of the product oil from the process. The slurry produced is combined with hydrogen produced during the process and fed into a fired preheater. From the preheater, the slurry enters a fixed-bed catalytic reactor packed with catalyst pellets of cobalt molybdate on silica-promoted alumina. The mixture is then cooled and passed to a separator where the liquid and unreacted solids are separated from the gases.

The liquids and unreacted solids leave the bottom of the separator and pass into a centrifuge, where the solids are separated and fed into a pyrolyzer. Part of the liquid leaving the centrifuge is recycled to the mixer to continue the process; the remainder is the product oil of the process, a nonpolluting fuel oil. The solids are further pyrolyzed and yield an additional quantity of nonpolluting product oil, as well as an ash residue. This ash residue, which contains some carbonaceous material, is sent to a gasifier and shift converter.

The gases coming off the top of the separator are sent through a gas purification system where they are separated into five product streams. Water and ammonia are withdrawn separately; hydrogen sulfide is sent to a sulfur recovery system that yields elemental sulfur as the product; the hydrocarbon gases are then fed to the gasifier and shift converter where they react with steam and oxygen, together with the ash residue, to form hydrogen for the process; the final product stream from the gas purification system is hydrogen, which is mixed with the hydrogen produced in the gasifier and fed into the slurry stream entering the preheater.

Hydrogen propels the slurry so violently through the fixed-bed catalytic reactor that plugging of the bed by the mineral matter in the coal is prevented as the coal becomes liquified. The turbulence of the slurry promotes mass and heat transfer in the slurry, which in turn promotes hydrodesulfurization and liquefaction.

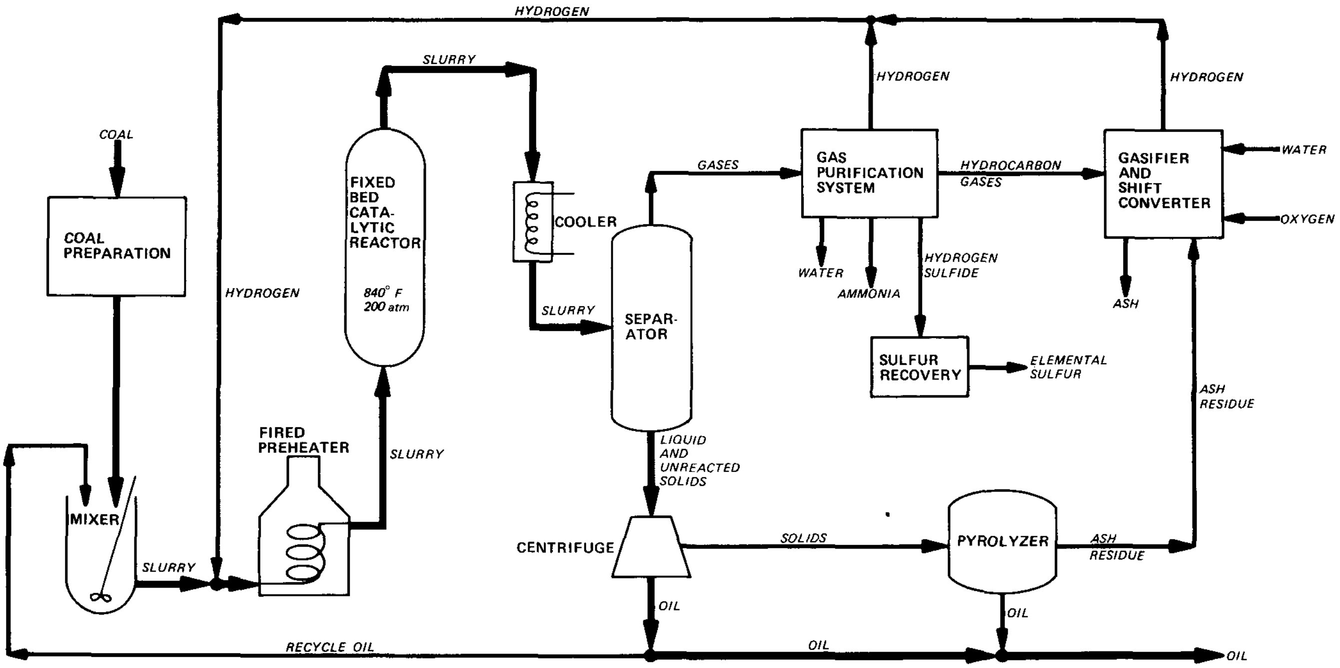


Figure III-2. SYNTHOIL PROCESS SCHEMATIC

HISTORY OF THE PROJECT

Work on this process began in 1969 at PERC. The initial work on the Synthoil process used a reactor with an internal diameter of 5/16 inch in a bench-scale plant that processed 5 pounds of slurry per hour. Experimental work was carried out on various coals, such as Pittsburgh seam, Indiana No. 5, Middle Kittenning Ohio No. 6, and Kentucky strip coal. All of these types of coals were satisfactorily converted to low-sulfur fuel oil with no sensible attrition of the catalyst. Experiments were conducted to study the effect of hydrogen flow rate, the percentage of coal in the feed slurry, the recycle of the product oil, and the effect of hydrogen sulfide in the recycle gas.

To demonstrate the broad applicability of the process, a 1/2-ton-per-day unit was constructed that used a reactor of 1.1-inch internal diameter made of two interconnected stainless steel pipes that were each 14.5 feet long. The operations were carried out on various types of coal at reactor pressures of 140 atm and 280 atm at 840° F. High yields of low-sulfur and low-ash fuel oil were obtained. At the lower reactor pressure (140 atm), the calorific value and yield of product oil were lower; hydrogen consumption was also lower. However, the sulfur and ash content of the product oil was higher than that of the oil produced at 280 atm. Operation at lower pressure would be favorable if the higher sulfur and ash content were environmentally allowable. Research is being conducted on the use of filtration to decrease the ash content of the product oil. Economic analyses will decide the appropriate pressure for this process, considering the cost of filtration, the capital and operating costs for high-pressure and low-pressure operations, and the environmentally allowable sulfur and ash content in the product oil.

PROGRESS DURING OCTOBER-DECEMBER 1975

Summary

The proposal by Foster Wheeler to manage the construction of the 10-ton-per-day process development unit was approved by ERDA during this quarter. Site preparation for the process development unit has also been completed.

At PERC, laboratory research continued to concentrate on testing of catalysts, removing solids by using a sensitive rotary-drum pressure filter, conducting hydrodynamic studies using the 4-inch-internal-diameter cold-model reactor, and pyrolyzing the residue from the Synthoil process. To increase data production, another bench-scale unit will be constructed. Sandia Laboratories are studying the mechanisms of deactivation and reactivation of catalysts, effects of coal-ash content on liquefaction, and the effects of process parameters on the kinetics of hydrodesulfurization and liquefaction. Argonne National Laboratory is investigating four aspects of the Synthoil process: determination of heat of reaction of hydrogen with coal slurries, determination of heat transfer coefficients from reactor fluids to heat exchangers, removal of solids from liquids by the use of additives, and testing of new catalysts. Battelle Memorial Institute continued its program to measure viscosity, density, electrical resistivity, and the dielectric constant of the Synthoil liquids. Studies were recently begun at Exxon Research and Engineering Company to determine the chemical properties of Synthoil products and feed. Also, an economic analysis was conducted by MERC on a Synthoil plant that would produce 50,000 barrels per day of liquid fuel.

Process Development Unit

The Foster Wheeler proposal to manage the construction of the 10-ton-per-day process development unit was approved by the Office of the Administrator, ERDA, and a letter contract was issued to Foster Wheeler during this quarter. Site preparation work for the Synthoil process development unit was completed by Louis M. McMasters, Inc. The 150-day completion period began on October 7, 1975, and actual field construction began at the end of October. Foundations work should be complete by early January 1976 and structural steel erection will begin at that time.

The first of the bid packages to procure construction services on a lump-sum basis for subcontractors under contract to Foster Wheeler is for the process building. This bid package is at the Chicago Operations Office and will be formally advertised early next quarter. Foster Wheeler will hold the bid opening with ERDA personnel present. Ordering of long-lead-time components continued under the prior engineering services contract.

Laboratory Research

Pittsburgh Energy Research Center

A 700-hour uncatalyzed Synthoil run was completed at PERC using the 1/2-ton-per-day bench-scale unit. The 1.1-inch-internal-diameter reactor was charged with 1/8-inch by 1/8-inch glass cylinders instead of cobalt-molybdenum catalyst. The experiment was conducted with Pittsburgh seam coal at 842° F, 273 atm, and a coal feed rate of 25 pounds per hour. The product oil from a previous 200-hour uncatalyzed run conducted under the same conditions was used for start-up. The analytical results will be completed early in the next quarter; however, preliminary data indicated a sulfur content averaging 0.7 percent for the oil product from the run. This run showed that the unit will remain operable even if the catalyst decays completely, except that less sulfur will be removed. When data from this run are complete, comparison with other runs using a catalyst will serve as a basis for quantitative evaluation of catalyst effectiveness.

To remove solids from the overall Synthoil product, a sensitive rotary-drum pressure filter is being used. Two continuous experiments of 86 hours and 273 hours, respectively, were completed using the filter system. The filter precoat for the first experiment was a layer of celite; for the second experiment, a layer of asbestos fibers was placed underneath the celite layer. In the first experiment, significant quantities of celite were found in the filtrate because the celite migrated through the filter support screen. In the second experiment, celite did not appear in the filtrate, and the filtration proceeded smoothly for about 250 hours. Towards the end of the experiment, the ash content in the filtrate was significantly greater than that usually associated with the observed value of pressure drop per unit flow. Disassembly of the filter showed an excessive gap in the rotary valve, which was remachined.

A device for continuous heating at relatively low temperatures to aid in the handling and disposal of the solids residue from the centrifuge or filter was tested. Heating to a weight loss of more than 14 percent removed most of the odorous and adherent properties of the solids residue and most of the weight loss corresponded to a recoverable oil yield. This approach to solids residue disposal will be tested on a larger scale at an equipment manufacturer's laboratory, where specific hardware will be developed.

Liquid hold-up measurements were made using the bench-scale reactor packed with 1/8-inch by 1/8-inch cobalt-molybdate catalyst pellets. One of the methods used to measure liquid hold up was to measure the liquid drained from the column; the results were then compared with results found in literature. The quantity of drained liquid was an order of magnitude less than total liquid hold up in the packed column, indicating that relatively large surface-tension forces were acting on the liquid in the column. The catalyst packing in this run had a void fraction of 0.34 (compared to a void fraction of 0.37 in a previous packing of the same pellets). The liquid hold up decreased more rapidly with increasing gas fluxes in the more tightly packed column, which was attributed to smaller pore openings in the packed bed.

A 10-foot glass column is currently being constructed that will measure residence time distribution of the liquid in a packed bed. A dye injection system has been installed to distribute dye uniformly over the cross-sectional area of the column. Correct residence time distribution can therefore be measured, even though radial liquid velocity varies, by calculating the dye concentration in the liquid after the liquid has passed through the column. Fully developed flow will be ensured by placing 2 feet of packing above the dye injection point. A liquid recirculation system has been constructed to supply liquid to the packed bed. The system is capable of maintaining a liquid to ± 2° F and delivering liquids having a viscosity of 50 centipoise.

Runs using the catalyst life-testing unit were prematurely terminated because of reactor plugging primarily caused by interruptions in the slurry feed. Pump valve malfunctions completely stopped the feed in numerous instances. When feeding was resumed, the pressure difference across the preheater-reactor system increased, indicating that the reactor contained deposits of solids that could not be swept out of the system by the flow of the gaseous and liquid reactants.

Changes were therefore made in the unit to lessen reactor plugging tendencies, which included increasing the internal diameter of the reactor from 1/8 inch to 5/32 inch; increasing the catalyst particle size to 10-by-12 mesh; and increasing the slurry feed rate to 0.75 pounds per hour. The piping in the slurry circulating system was modified to prevent entrainment of nitrogen from the feed tank, which could separate in the high-pressure pump and cause loss of pump prime. In spite of these changes, a run conducted at 273 atm was terminated after 3.5 days because of reactor plugging, which was again caused by several interruptions in the slurry feed.

Laboratory tests continued on pyrolysis of the residue from the Synthoil process. The objectives of this study are to achieve optimum oil recovery while producing a nonpolluting disposable solid residue. Static-bed pyrolysis tests and the analysis of the product yields were completed during this quarter. Proximate and ultimate analyses of the tar, pitch, and char were similar for the tests at various pyrolysis temperatures. Tar component yields did not differ significantly as a result of pyrolysis temperature, except for a test in which 13 percent Synthoil product was added to the charge. The tar yield increased 38 percent to 70.3 gallons per ton and neutral oils increased 87.5 percent to 28.6 gallons per ton. Olefins increased 50 percent; aromatics, 68.6 percent; and paraffins and naphthenes, 268.8 percent.

Characterization studies were made of the centrifuged liquid and solid products from a Synthoil run, using techniques such as high-resolution mass spectrometry, infrared and ultraviolet spectrometry, and gas chromatography. The objective of this study was to identify the similarities and differences in the organic material found in the solids and that found in the liquid product from the process. In addition to the liquid and solid products, a benzene extract of the solid and residue from vacuum pyrolysis of the solid were examined. The data obtained from spectrometric and chromatographic methods of analysis indicated that the liquid product and the organic portion of the solid are similar. The primary inorganic component of the solid was kaolinite. Samples of feed and product materials generated by the Synthoil process were characterized by various analytical techniques and resulted in a total of 2,277 completed analyses being reported.

To increase data production, another 1/2-ton-per-day bench-scale unit similar to the one currently operating will be constructed. The process and instrumentation drawings and layout drawings have been completed and incorporated improvements on process steps, instrumentation, and analyses.

Sandia Laboratories

Sandia Laboratories are continuing studies on the mechanisms of deactivation and reactivation of catalysts, the effects of coal-ash content on liquefaction, and the effects of process parameters on the kinetics of hydrodesulfurization and liquefaction. During this quarter, studies to define appropriate analytical techniques for evaluating the physical structure and chemical composition of the catalyst were completed. X-ray photoelectron spectroscopy indicated that the regenerated catalyst investigated was not returned to the original chemical state by regeneration. X-ray photoelectron data will be supplemented with secondary ion mass spectroscopy data as a check of data validity. Also during this quarter, the installation of the equipment and the development of evaluation procedures and preliminary screening tests were completed.

Argonne National Laboratory

The Argonne National Laboratory is investigating four aspects of the Synthoil process: determination of heat of reaction of hydrogen with coal slurries, determination of heat transfer coefficients from reactor fluids to heat exchangers, removal of solids from liquids by the use of additives, and testing of new catalysts.

The specifications of the calorimetric pressure vessel (136 atm to 272 atm, up to 885° F) for the heat of reaction study have been completed, and a contract for fabrication of the vessel is being prepared. Design of the catalyst test unit and of the heat transfer coefficient testing unit has been completed; long-lead-time items have been ordered. The unit configuration and component sizing of the test units were based on slurry and hydrogen flow rates comparable to those in the 1/2-ton-per-day unit. As a preliminary step in the study to investigate the effect of additives in separating solids from liquids, the viscosity of the Synthoil centrifuged product oil was measured at between 122° F and 392° F. Changes in the viscosity of the oil occurred upon exposure to air, as well as non-Newtonian viscosity behavior. The evaluation of new commercially available catalysts will be made on the basis of analyses of coal input and product samples when the catalyst test unit is complete.

Battelle Memorial Institute

Battelle is conducting a program to measure viscosity, density, electrical resistivity, and the dielectric constant of Synthoil liquids, including intermediate liquids and product oils. The measurements will be made, for the most part, in a commercial autoclave modified for use as a viscometer to make possible the measurement of density and electrical properties. The measurements will be made at temperatures from 75° F to 840° F and pressures from 1 atm to 270 atm. The equipment has not yet been mounted in the laboratory, but safety precautions have been taken. A laboratory has been prepared for installation of the apparatus by erecting a steel panel to separate the high-pressure apparatus from the operator. A filtration device of sintered stainless steel filters that is suitable for use at elevated temperatures has been designed for a maximum capacity of 200 cubic centimeters; it is currently being built.

Atmospheric pressure measurement data of density and viscosity have been completed on a few samples. These measurements are exploratory but will also serve as standards and to check the calibration of the high-pressure equipment. In most cases, the results showed a linear relationship between shear stress versus shear rate, indicating that viscosity is independent of shear rate. (When viscosities are high, the data may depart from the linear relationship at high shear rates.) The yield value, which represents the maximum force that can be applied without producing any motion, was low for the liquids tested. The yield value decreased as the temperature increased; however, the rate of temperature increase was less than the rate of viscosity decrease. Therefore, the yield value appears to be of greater significance at higher temperatures. Measurements using two different types of viscometers, a Ferrenti-Shirley and a Weisenberg, were compared. In both instances, the sample was contained between a stationary plane and a rotating cone; the Weisenberg rheogoniometer, however, was capable of measurements at lower shear rates. Minor discrepancies occurred in the results. The results for samples taken from the preheater top were similar to the results for product oils at a temperature of 212° F or lower. A plot of the temperature effect on viscosity showed that the viscosity is approximately an exponential function of the reciprocal of the absolute temperature.

Density measurements of one sample of uncentrifuged product oil were made to verify the anticipated behavior of the product oil and to obtain a sample of known density with which to compare the results of the centrifuged oil from the autoclave. A Westphal balance was used to determine the density as a function of temperature. The viscosity below 104° F was too high for practical use of this method, and at 518° F the liquid began to boil so that data could not be obtained at high temperatures, except by increasing the pressure. The results showed the density to be close to a linear function of temperature.

Exxon Research and Engineering Company

Studies have begun at Exxon Research and Engineering Company to determine the chemical properties of Synthoil products and feed. Techniques such as high-resolution mass spectrometry, gas chromatography, and nuclear magnetic resonance, will be used to analyze the product and feed samples.

Morgantown Energy Research Center

MERC has conducted an economic analysis of a Synthoil plant that would produce 50,000 barrels per day of liquid fuels from two types of coal, Wyodak and western Kentucky. Based on July 1975 price indexes, an estimated $661,366,000 would be required to produce 50,000 barrels per day of heavy low-sulfur-content fuel oil by hydrogenation of Wyodak coal containing 0.7 percent sulfur. The thermal efficiency of the plant is 63.6 percent, based on a gross heating value of 8,051 Btu per pound of coal. A plant of the same capacity that would produce heavy low-sulfur-content fuel oil by hydrogenation of western Kentucky coal containing 4.7 percent sulfur was estimated to require a capital investment of $648,277,300 or $12,966 per daily barrel of capacity (based on July 1975 price indexes). The thermal efficiency of the plant is 67.8 percent, based on a coal heating value of 12,260 Btu per pound and 17,400 Btu per pound for the oil product. Estimated operating and unit costs were also reported for both types of coal.

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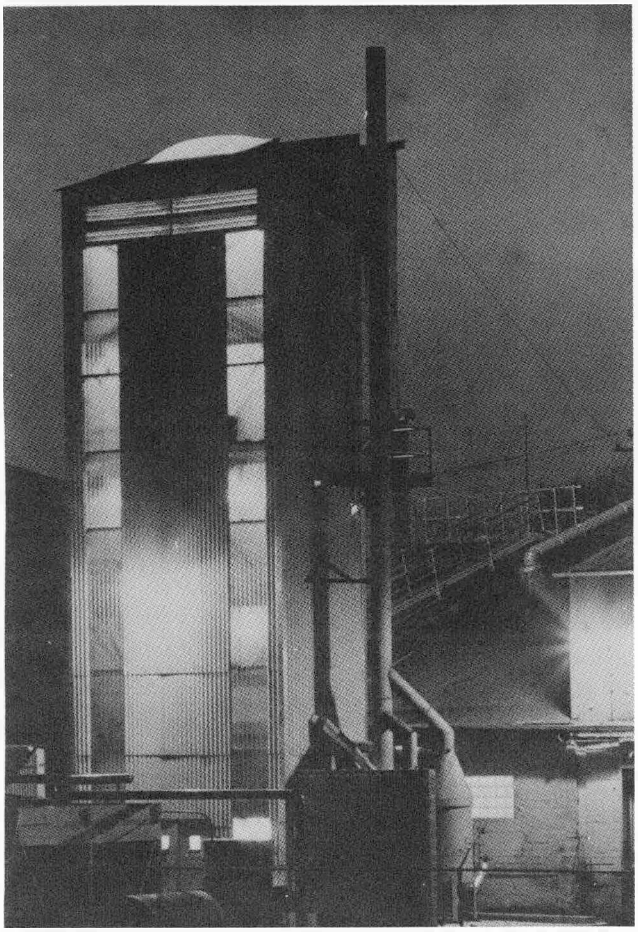
IV. H-COAL PROCESS

HYDROCARBON RESEARCH, INC.
TRENTON, NEW JERSEY

Contract No. E(49-18)-1544
Total Funding: $8,132,596



INTRODUCTION

The H-Coal process is being developed by Hydrocarbon Research, Inc. (HRI), under the joint sponsorship of (1) ERDA; (2) a private industry consortium composed of Electric Power Research Institute, Ashland Oil, Inc., Atlantic Richfield Company, Shell Oil Company, Standard Oil Company (Indiana), and Sun Oil Company; and (3) the state of Kentucky. ERDA is providing two-thirds of the funds and the industry consortium, one-third. The state of Kentucky is also contributing funds. The overall objectives of this project are to further develop the H-Coal process and to demonstrate its technical and economic feasibility on larger scales. The specific objectives are to:

- Perform laboratory research on all phases of the H-Coal process, using the existing bench-scale unit and process development unit to establish design criteria.
- Design a pilot plant capable of converting 600 tons of coal per day to 2,250 barrels per day of low-sulfur boiler fuel.
- Initiate preliminary procurement for the pilot plant.

Ultimately, the pilot plant will be constructed and operated to obtain data for further evaluating the process and designing a full-size commercial plant. The overall program plan is shown in Figure IV-1.

PROCESS DESCRIPTION

The H-Coal process is a catalytic hydroliquefaction process that converts high-sulfur-content coal to boiler fuels that will not exceed emission standards and to syncrude. A schematic of the process is provided in Figure IV-2. Coal is crushed to minus 60 mesh, dried, and then slurried with recycled oil and pumped to a pressure of about 200 atm. Compressed hydrogen is added to the slurry, and the mixture is preheated and charged continuously to the bottom of the ebullient-bed catalytic reactor. The upward passage of the internally recycled reaction mixture maintains the catalyst in a fluidized state.

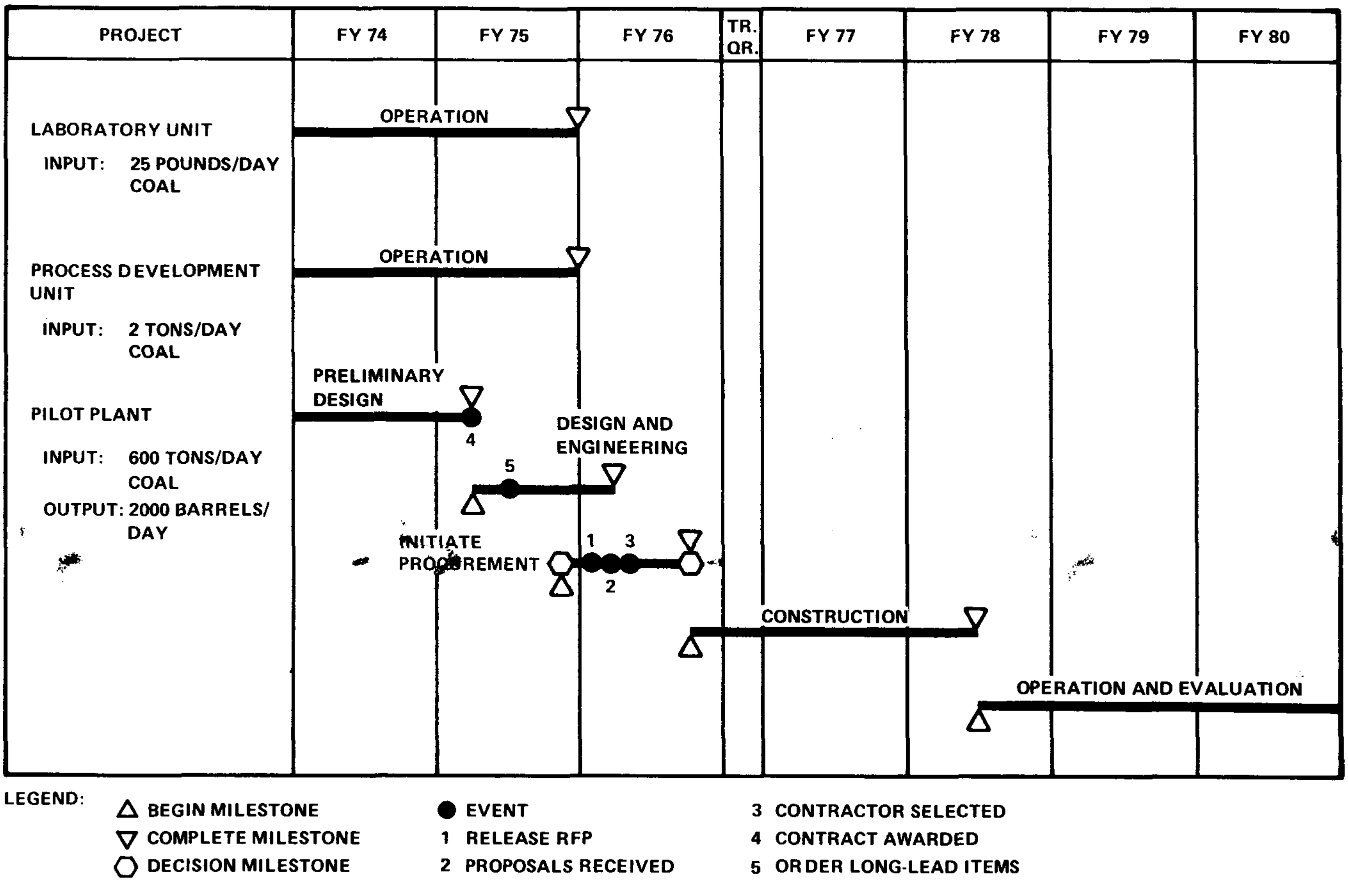


Figure IV-1. H-COAL PROGRAM SCHEDULE

(Catalyst activity is maintained by the semicontinuous addition of fresh catalyst and the withdrawal of spent catalyst.) The temperature of the ebullient-bed catalytic reactor is controlled by adjusting the temperature of the reactants entering from the preheater. Typically, the temperature of the mixture entering the reactor is 650° F to 700° F.

Vapor product leaving the top of the reactor is cooled to separate the heavier components as a liquid. Light hydrocarbons, ammonia, and hydrogen sulfide are absorbed from the gas stream and sent to a separator and a sulfur recovery unit. The remaining hydrogen-rich gas is recompressed and combined with the input slurry. The liquid from the condenser is fed to an atmospheric distillation unit. The liquid-solid product from the reactor, containing unconverted coal, ash, and oil, is fed into a flash separator. The material that boils off is passed to the atmospheric distillation unit that yields light and heavy distillate products. The bottoms product from the flash separator (solids and heavy oil) is further separated with a hydroclone, a liquid-solid separator, and a vacuum still.

The gas and liquid products (hydrogen gas, hydrogen sulfide, ammonia, light distillate, heavy distillate, and residual fuel) may be further refined as necessary. Heavy distillate is recycled as the slurry medium.

The specific operating conditions of the H-Coal process affect the type of fuel produced. Low space velocity (high residence time), high temperature, and high pressure are required in the reactor to produce syncrude as the major product. If residual fuel oil is to be the principal product, a high space velocity and low temperature and pressure are used. Because fuel oil is a less hydrogenated product than syncrude, less hydrogen is required when the process is run in the fuel oil mode.

Features of the H-Coal process are:

- The temperature of the reactor zone is easily maintained at a constant level because the

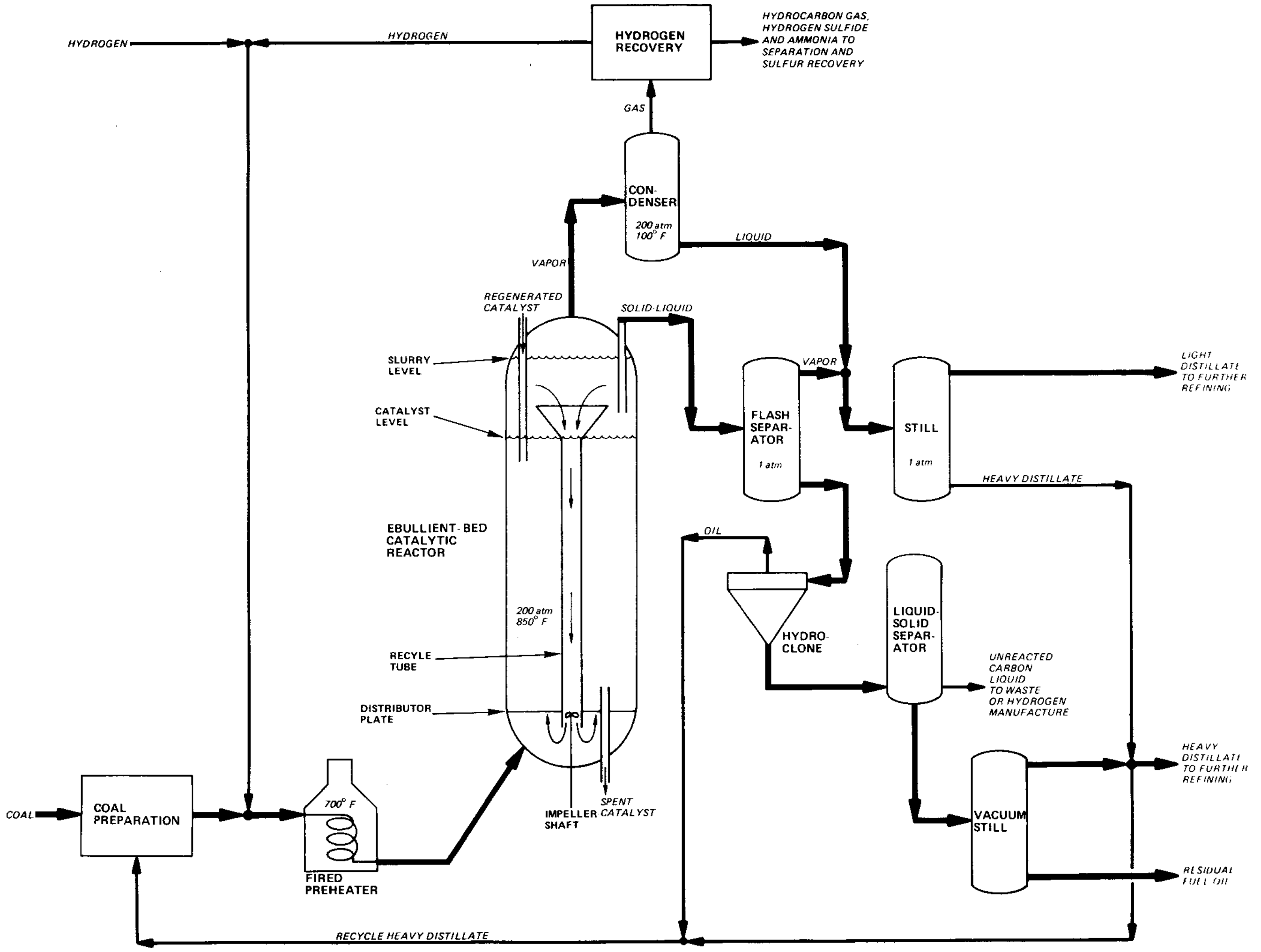


Figure IV-2. H-COAL PROCESS SCHEMATIC

temperature of the incoming slurry can be controlled by adjusting the temperature of the fired preheater. Furthermore, the temperature of the recycled light oils is low enough that additional cooling, using an internal or external cooling system, is not necessary.

- The activity level of the catalyst is essentially constant because the catalyst can be added and withdrawn as necessary.
- Because the operating temperature of the reactor zone and the catalyst activity level can be controlled, the product quality is consistent.
- Both low-sulfur boiler fuel and refinery feedstock can be produced from the process.

Before the H-Coal process can become commercially and economically competitive an adequate supply of hydrogen must be generated from the process itself. The H-Coal process requires between 14,000 and 20,000 standard cubic feet of hydrogen for each ton of coal processed, depending on the type of oil produced. Some of the hydrogen required is removed from the scrubbed gas from the ebullient-bed reactor and recycled; additional hydrogen is purchased. In the commercial operation, hydrogen will be manufactured. Because the H-Coal process converts about 90 percent of the carbon contained in coal to a liquid, the feed to hydrogen manufacture could be a liquid rather than a solid. This suggests that commercial hydrogen manufacturing processes could be adapted. The solid cake char could also be used to produce hydrogen.

In the H-Coal process, hydroclones have been proven capable of removing about two-thirds of the solids and are useful in partially separating the solids so that the nondistilled liquids can be recycled for slurrying the coal. HRI has also been investigating other methods of separating solids from liquids, such as magnetic separation, filtration, centrifugation, and solvent precipitation. Magnetic separation has shown limited effectiveness. Separation of the solids by filtration has not been conclusive, although filtration rates of 150 pounds per hour per square foot and relatively dry filter cakes have been achieved by using a continuous drum pressure filter.

HISTORY OF THE PROJECT

The H-Coal process was developed by HRI as a further application of the ebullient-bed processing technology originally used to convert heavy oil residues into lighter fractions (H-Oil process). Early development of the H-Coal process, beginning in 1964, involved research with a bench-scale unit and a process development unit and preparation of a conceptual process design. An independent evaluation in 1968 confirmed the technical and economic feasibility of the H-Coal process.

The H-Coal process proved to be highly flexible in bench-scale and process development unit tests. The bench-scale unit can process 25 pounds of coal per day; the process development unit can process 3 tons of coal per day. Many types of coal have been tested satisfactorily on the bench-scale level, including eastern, midwestern, and western bituminous coals, western subbituminous coals, lignite from Texas and North Dakota, and Australian brown coal. The bench-scale unit has also provided information on the effect of process variables (such as temperature, pressure, coal feed rate, slurry oil composition, and catalyst age) on coal conversion and product yield. The process development unit tests demonstrated sustained H-Coal process operation with satisfactory control of the catalyst-bed expansion.

Based on the data obtained from the bench-scale and process development units, design and engineering of the pilot plant was initiated under the current contract in December 1973. During 1974, design of the coal preparation section of the pilot plant was completed to the extent that engineering and plant layout could begin. HRI concentrated, however, on the design and engineering for the ebullient-bed reactor, since the equipment needed for this section requires long-lead times. Engineering for other sections of the pilot plant was started in late 1974. Also during 1974, three possible sites for construction of a pilot plant were evaluated. Based on detailed environmental assessments, it was decided during the second quarter of 1975 to locate the plant on a plot of land adjacent to the Ashland Oil, Inc., refinery in Catlettsburg, Kentucky.

The laboratory research in 1974 concentrated on bench-scale operation, liquid-solid separation, and process development unit modifications. A number of bench-scale runs were conducted to test regenerated, high-density, and aged catalysts. Tests were also conducted to investigate the mechanism of catalyst deactivation and the effects of low-hydrogen partial pressure and high-gas velocities in the reactor. Other tests were directed at minimizing the differences between the bench-scale and process development unit. The process development unit was modified to ensure effective and safe operation, but the unit was not operated until 1975.

PROGRESS DURING OCTOBER-DECEMBER 1975

Summary

During this quarter, ERDA approved the site plan for the entire H-Coal facility. Design and engineering work continued on the coal preparation, coal hydrogenation, and offsites sections of the pilot plant. A test run was conducted in the process development unit using 3,061 pounds of coal per pound of catalyst in a continuous operation to produce fuel oil with a sulfur content ranging from 0.6 to 1.0 weight percent. A ceramic hydroclone, used during the last 4 days of the test run, removed ash more efficiently than stellited hydroclones used earlier in the same run. A second test run in the process development unit was started. The solvent precipitation test unit was assembled and operated with a slurry of diluted H-Coal vacuum still bottoms; a clear overflow with less than 0.1 weight percent ash was obtained. Construction continued on the centrifugation test unit and filtration studies were scheduled. Coal foam studies showed that a moisture-free slurry mixture can be obtained from wet feed coals.

Pilot Plant Design and Engineering

HRI completed preparation of the construction bid package and the capital cost estimate for the H-Coal pilot plant. The site plan for the entire facility was approved by ERDA.

Preparatory Phase II construction activities began following completion of drawings and specifications for the culvert under the plant site access road and the fill over the culvert. The administration building and parking area sites were relocated to firmer soil. Design of the plant access road and the railroad crossing continued.

Design and engineering work on the coal preparation, coal hydrogenation, and offsites sections continued. Design criteria were established for the coal preparation section:

- Coal will be pulverized to 40-to-100 mesh.
- Illinois No. 6 coal will have a final moisture content of 2 weight percent; Wyodak coal will have a final moisture content of 5 weight percent.
- The oxygen content of recirculating gases in the dryer system will be as low as 4 volume percent.

Layout and arrangement drawings were prepared for the railroad spur and crossing in the coal preparation section. Design of the railroad receiving hopper and reclaiming hopper continued. Electrical and piping drawings are being developed.

Process flow diagrams and the plot plan for the coal hydrogenation section were approved by ERDA. Design activities for the coal hydrogenation section involved civil and structural design, piping drawings, and electrical diagrams. A model of the coal hydrogenation section is being constructed to facilitate design development.

Offsites section activities included preparation of detailed utility balances, a detailed steam and condensate balance for each anticipated operating mode, the cooling water system schematic concept, a descriptive analysis of the tank farm design concept, and engineering flow diagrams for the sour water and sour gas scrubbing systems. Design criteria for the flare system are being developed for conditions that would activate the system, such as fire, air failure, and water failure. A consultant to HRI will investigate techniques for treatment of wastewater effluent streams from the pilot plant. A study was initiated to determine a suitable method for disposal of large quantities of H-Coal pilot plant products that do not meet specifications.

Purchasing activities for the quarter were restricted to the coal preparation and coal hydrogenation sections. The purchase of all equipment items for both sections was emphasized.

Laboratory Research

Process Development Unit

One test run, Run 130-73, was conducted in the process development unit and Run 130-74 was started. Run 130-73 was conducted to produce fuel oil with a sulfur content of 0.7 weight percent from coal containing more than 3 weight percent sulfur in an uninterrupted operation processing over 3,000 pounds of coal per pound of catalyst. Prior to Run 130-73, the process development unit was inspected and several changes were made to improve performance.

The source of coal feed and catalyst for Run 130-73 was the same as for Runs 130-65 through 130-72. Fifty pounds of catalyst were charged; the reactor temperature was approximately 850° F and the system pressure was 185 atm. The hydroclone overhead recycle rate was about 1.2 pounds per pound of coal; the ratio of recycle feed slurry oil to solids was maintained below 2 pounds of slurry oil per pound of coal feed. The test run continued for 534 hours and 3,061 pounds of coal per pound of catalyst were processed at a feed rate of 253 to 275 pounds of coal per hour with residual oil recycle and a space velocity of 70 pounds of coal per hour per cubic foot. Conversion of moisture- and ash-free coal ranged from 91 percent to 92 percent. Sulfur content of the product fuel oil is shown in Table IV-1.

Table IV-1. SULFUR CONTENT OF PRODUCT FUEL OIL, RUN 130-73

Sulfur Content (weight percent)	Catalyst Age (pounds of coal per pound of catalyst)
0.6	500
0.7	1,000
0.85	2,000
0.92[a]	2,000-3,000

[a] Overall average determined from erratic results obtained for the specified catalyst age.

A second test run, Run 130-74, was started. The objective of the run was to operate the process development unit using a single batch of catalyst under conditions appropriate to the fuel oil mode, but with full commercial gas velocities in the reactor to measure catalyst breakdown, attrition, carryover, and/or loss associated with the hydrodynamic conditions of commercial-scale operation. Prior to the test run, several significant equipment modifications were made: an external vapor-liquid separator was installed downstream of the reactor, a recycle cup with a larger diameter was installed in the reactor to reduce gas entrainment to the internal recycle pump, and the size of the bubble cap orifice was increased to reduce pressure drop across the cap. During start-up operations, several leaks and malfunctions developed in the system and were corrected. Coal feed operations were started after 97 hours but were interrupted twice because of equipment failures. The process development unit was operated for 179 hours and was shut down because of a restriction in the recycle gas line to the reactor. After inspection and repairs, Run 130-74 will be continued.

Other Research

A ceramic hydroclone, installed in the process development unit prior to Run 130-73, was put on line the last 4 days of Run 130-73. Ash-removal efficiencies of the ceramic hydroclone tended to be better than those of the stellited hydroclones used earlier in the run. Inspection of the ceramic hydroclone after shutdown showed no measurable wear in the cyclone area, whereas the stellited hydroclones showed considerable wear.

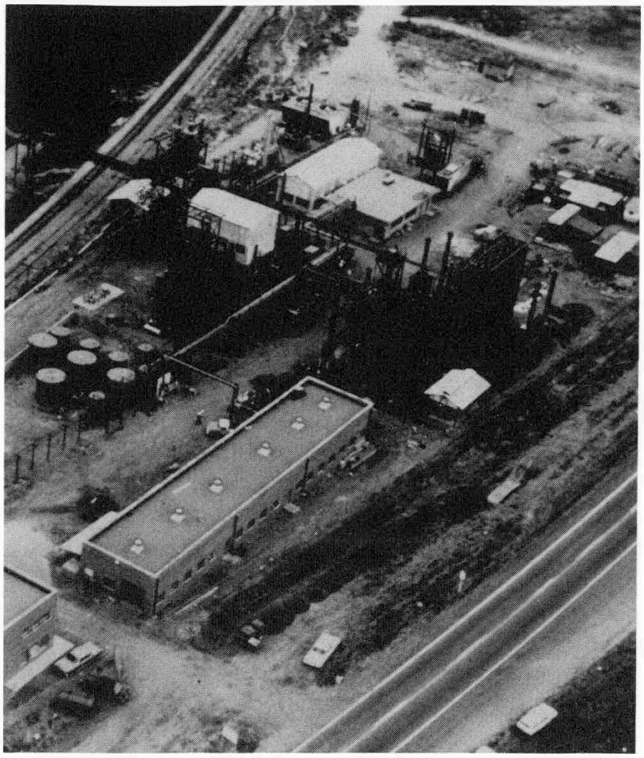
Solvent precipitation studies continued. The continuous solvent precipitation test unit, designed to process 30 pounds of slurry per hour, was assembled during the quarter. The unit was operated using a slurry of H-Coal vacuum still bottoms diluted with Ashland APO oil; a clear overflow with less than 0.1 weight percent ash was obtained readily, but a concentrated overflow stream was difficult to obtain. Batch autoclave precipitation of solids from H-Coal fuel oil products was studied to compare settling rates of solids in fuel oil products with those reported previously for syncrude products. Solids in fuel oil products showed a higher settling rate than solids in syncrude products. The diluent seemed to have a pronounced effect on the solids settling rate.

Construction continued on the centrifugation test unit that will be used to determine the optimum values for process variables that yield no more than 0.1 weight percent ash in the overflow liquid. A nozzle-bowl, disc-type centrifuge was assembled and tested mechanically.

HRI reviewed filtration studies conducted previously with H-Coal fuel oil product and syncrude product; filtration rates at the same viscosity and cake solids loading seemed to be similar for fuel oil product and syncrude material. During the quarter, two types of filtration equipment were selected for further investigation.

Coal foam study experiments, using feed coals containing 6 percent and 9 percent moisture, duplicated a continuous wet coal and slurry oil charging system to produce a moisture-free slurry mixture for charging to H-Coal systems. No operating problems were experienced. The coal moisture, rising to the top of the slurry as a foam that quickly collapsed, was removed to a condenser and collected. Future studies will evaluate the direct feeding of wet, ground coal containing up to 30 percent moisture.

V. CRESAP TEST FACILITY



FLUOR ENGINEERS AND
CONSTRUCTORS, INC.
LOS ANGELES, CALIFORNIA

Contract No. E(49-18)-1517
Total Funding: $13,582,000

INTRODUCTION

Under contract to ERDA, Fluor Engineers and Constructors, Inc., is reactivating an ERDA-owned facility in Cresap, West Virginia. This facility, inactive since 1970, contains much of the equipment required for coal liquefaction. Fluor is to (1) renovate the Cresap facility to test the various critical mechanical components required for coal liquefaction and (2) operate the renovated facility to demonstrate an integrated process for the production of low-sulfur liquid fuel—Consol Synthetic Fuel (CSF) process. Renovation of the Cresap facility, rather than construction of a new facility, will result in earlier operation of the pilot plant and initiation of the test program. The project schedule is provided in Figure V-1.

PROCESS DESCRIPTION

In this process, shown schematically in Figure V-2, coal is converted to low-sulfur liquid fuel. The coal is first pulverized and then combined with aromatic solvent in a mixer. The coal-solvent slurry mixture is pumped to high pressure and heated in a fired preheater. Then, the slurry passes to an extractor where coal liquefaction takes place. The slurry then passes to a liquid-

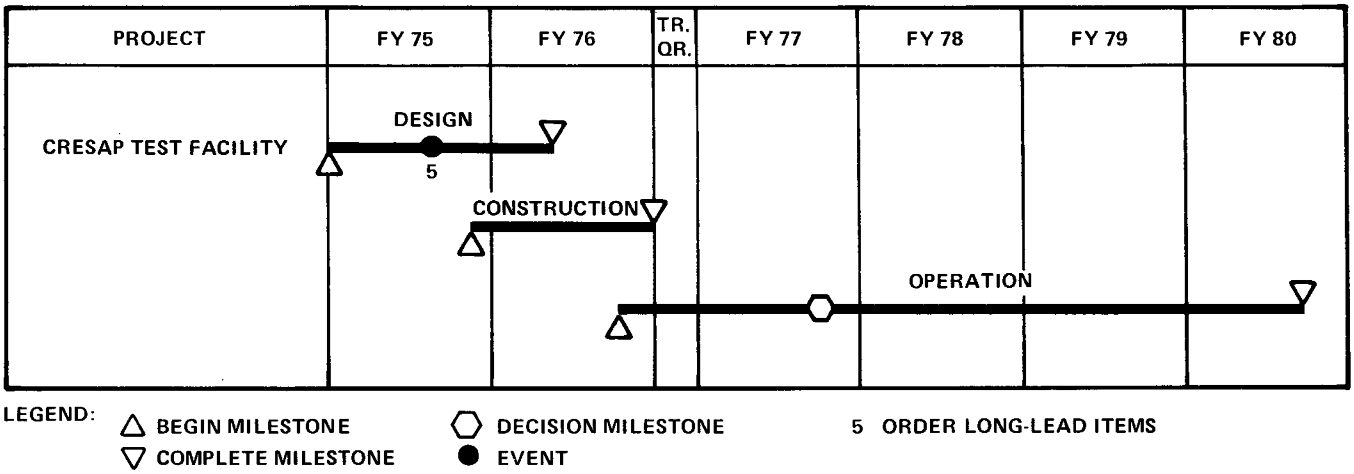


Figure V-1. CRESAP TEST FACILITY PROGRAM SCHEDULE

solid separation system. Forty percent of the feed coal is recovered as char, which can be gasified to provide hydrogen for the process. At the Cresap Test Facility, several methods for achieving this separation process will be tested. One of the most reliable methods for concentrating the solids is a system of hydroclones that was successfully used during prior pilot plant operation. In addition, other separation techniques will be evaluated, including filtration and solids removal by chemical precipitation.

The coal extract and solvent leaving the separation unit are heated and fed into a flash still where the heavy components of the coal extract are separated from the light liquids. The light liquids are further separated in a fractionator into light distillate, and a middle distillate. The middle distillate can be recycled as a component of coal solvent or become a component of the fuel oil product. The heavy components of the coal extract are heated in a fired preheater, hydrogenated and hydrocracked, and then enter a fractionator for separation. The products of the fractionation are light, middle, and heavy distillates. The middle distillate donor solvent becomes a component of the solvent. The heavy distillate becomes a component of the fuel oil product.

HISTORY OF THE PROJECT

Reactivation of the Cresap facility to develop an integrated process test center for producing low-sulfur liquid fuel from coal was initiated in May 1974. Work completed during 1974 included a complete inspection of the mechanical and structural parts of the plant, removal of disintegrated vessel and piping insulation and corroded piping, inspection and testing of all pressure vessels and heat exchangers, and sandblasting and painting of equipment. Overhaul of usable equipment, including pumps, compressors, drivers, pressure vessels, and miscellaneous package units was started. When the renovation work is completed, the plant will meet environmental requirements and current design standards of piping, electrical, and mechanical equipment codes. A task force was established to organize, coordinate, and direct the early testing program.

PROGRESS DURING OCTOBER-DECEMBER 1975

Summary

During this quarter, steps were taken to obtain the remaining equipment required for renovation of the pilot plant. Construction of several pilot plant items was completed. Delays are still being encountered in obtaining the wastewater permit for the sanitary treatment system from the West Virginia Department of Health. Process sketches and test setups were completed and test schedules were released for review. The Liquified Coal Development Corporation has been formed and incorporated; the corporation, which is a wholly

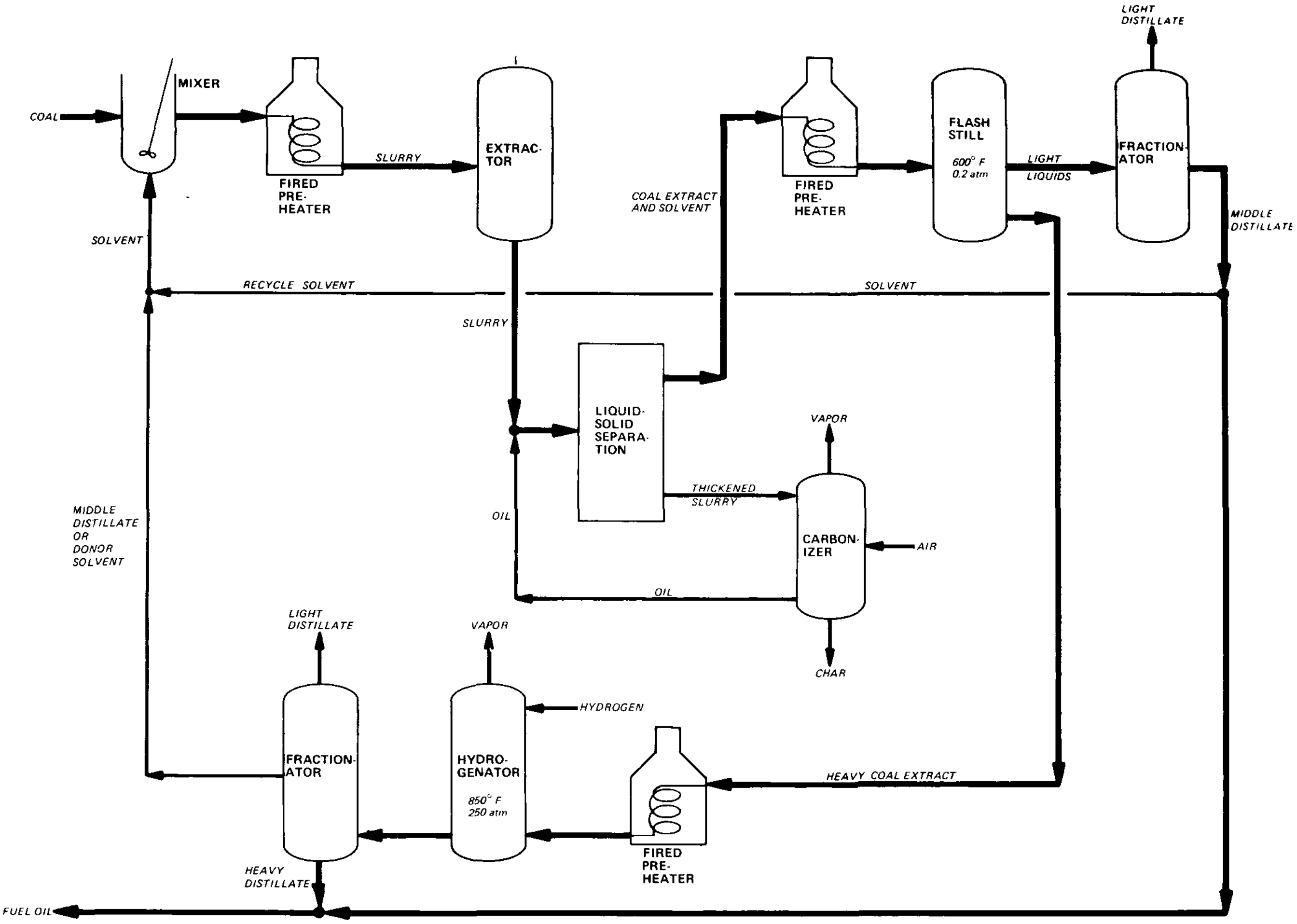


Figure V-2. LIQUID FUEL FROM COAL PROCESS SCHEMATIC

owned subsidiary of Fluor, will operate the pilot plant.

Pilot Plant Design and Engineering

Work on the design and engineering for the renovation of the pilot plant is 80 percent complete. Delays in the issuance of equipment and design drawings affected work progress in other areas. As necessary modifications were made, the changes were incorporated on the drawings, and field work orders were issued. Additional field work orders were also required to correct problems caused by missing or faulty information on the drawings. Structural, electrical, architectural, vessel, and piping drawings were issued, as well as a number of spool sheets. Model reviews of piping are about 50 percent complete. Model reviews were made of the solvent recovery unit, solids separation unit, both the existing and new hydro product fractionation sections, and the low-temperature carbonization unit. Operating manuals have been completed for the coal preparation, extraction, solvent recovery, solids handling, flare system, and sour-water stripper units. Work is continuing on the preparation of the remaining operating manuals.

The West Virginia Department of Health again denied the wastewater permit for the sanitary treatment system. Required design changes are being made and additional information requested by the Department of Health will be supplied.

The test program has reached the design stages; test schedules have been released for review. Process test sketches and setups have been completed. Development of test reports and test procedures is continuing and work has begun on the development of unit test composite flow sheets. Drafts of the justification reports are undergoing review.

Flow sheets were issued for the hydrogenation auxiliary system and the compression section. The solvent deashing flow sheets were released for design. However, the release of the flow sheet incorporating the solvent deashing mechanical flow sheet and the solids separation flow sheet is being held up until changes affecting the renovation of the plant, and therefore the solvent deashing-solids separation area, have been completed.

A single overall process flow sheet representing the major flow scheme of the plant has been prepared. Two separate overall process flow sheets based on high-pressure hydrogenation of coal and coal extract were also prepared. An overall plant materials balance was calculated and adapted to computer logic. The computer program, which encompasses about 25 plant streams, was developed to determine plant material balances. A 10-ton-per-day material balance was prepared for the high-pressure hydroliquefaction process, based on the Synthoil process being developed by the Pittsburgh Energy Research Center. Approval of the cost proposal plan was received from ERDA and a meeting was held with Conoco Coal Development Company to discuss work planned on the solvent deashing concept under the proposed subcontract.

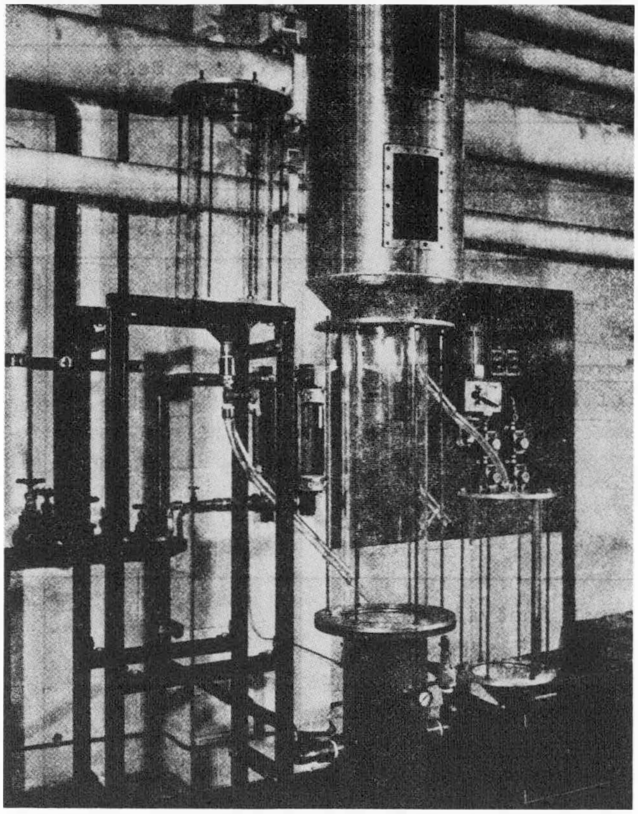
Renovation

Construction completed this quarter included civil work for the tank farm and Stretford unit, erection of tanks, renovation of the existing coal preparation equipment, installation of underground piping in offsites areas, erection of the structural steel for the utilities building extension, and completion of the warehouse. Fuel gas system leaks discovered during pressure tests were located and repaired. A detailed unit-by-unit review indicated that the construction scope of work is more extensive than originally planned, which will require a redefinition and rescheduling of the construction work.

Operations

The Liquified Coal Development Corporation, which has been formed to operate the pilot plant, was incorporated in West Virginia and began functioning as a corporate entity in November. The corporation is a wholly owned subsidiary of Fluor. Working relationships with Fluor have been defined and operating procedures established. Interviewing for key positions is under way, and some offers have been made. However, because of changes in the plant renovation completion schedule, hiring has been reduced below planned levels. Fluor will continue to handle all engineering, procurement, and construction for the plant renovation and the test program.

VI. CLEAN COKE PROCESS



USS ENGINEERS AND
CONSULTANTS, INC.
UNITED STATES STEEL CORPORATION
PITTSBURGH, PENNSYLVANIA

Contract No. E(49-18)-1220
Total Funding: $11,792,329

INTRODUCTION

The Clean Coke process is being developed by USS Engineers and Consultants, Inc., a subsidiary of United States Steel Corporation, under the sponsorship of ERDA. The contract was initiated in 1972 under the auspices of OCR (now a part of ERDA). ERDA is providing approximately 70 percent of the funds and U.S. Steel, 30 percent. The objective of the contract is to convert low-grade, high-sulfur coal to nonpolluting metallurgical (low-sulfur, low-ash) coke, chemical feedstocks, and liquid and gaseous fuels. The process design will be based on the results of laboratory tests and data obtained in process development units. The schedule for developing the process is shown in Figure VI-1.

PROCESS DESCRIPTION

The Clean Coke process, as planned, is shown schematically in Figure VI-2. The process combines carbonization of coal with coal hydrogenation in an environmentally acceptable manner. No external hydrogen and minimal amounts of external energy are planned for use in the process.

After cleaning and sizing, the feed coal is divided into two portions. One portion of the feed coal is sent to the carbonizer. Here pyrolysis takes place in a fluidized bed, producing char, liquid, and a hydrogen-rich gas that is cleaned and recycled to fluidize the bed. The hydrogen-rich atmosphere of the bed provides a hydrodesulfurization environment that reduces high-sulfur coal to low-sulfur char. The char is then pelletized using process-derived heavy oil, and the pellets are cured and calcined in a continuous kiln in an oxygen-free atmosphere to produce low-sulfur metallurgical coke and a hydrogen-rich gas.

The second portion of the coal is sent to a hydrogenation unit where the coal is slurried with a medium oil recycled from the liquid processing section and reacted with hydrogen recovered from the gas treatment section. The hydrogena-

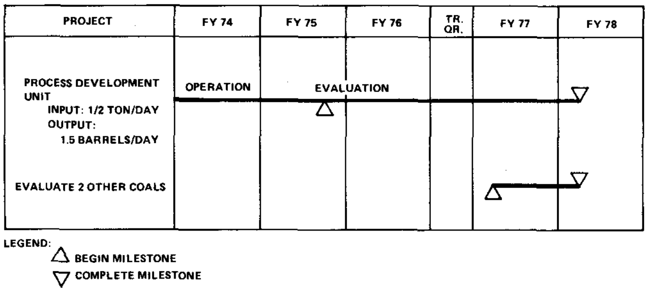


Figure VI-I. CLEAN COKE PROGRAM SCHEDULE

tion process is carried out without a catalyst at elevated temperatures and high pressures. In a novel part of the process, vaporizable material is stripped from the slurry by hot process gas, leaving ash that is removed from the stripper and dryer using a lock system. The vapor from the slurry and the hot gas, which flows countercurrent to the slurry and supplies the heat for the stripping action, combine to form the vapor feed to the condenser. Liquid condensed from the vapor goes to the liquid processing section; uncondensed gas is sent to the gas treatment section. Gases from all operations are processed in a common gas treatment section. This section includes ammonia and acid gas removal systems, a Claus plant, an ethylene plant, and a cryogenic gas separation system. Ethylene and propylene from the gas treatment section are used as chemical feedstocks. Fuel gas is also produced.

Liquids from all the operations of the process are passed into a common liquids processing section. Light oil that contains mostly chemical feedstocks and fuel, a medium oil, and a heavy oil are produced. The light oil is further processed to produce gas, gasoline, benzene and naphthalene (which can be used as chemical feedstocks), and residual tars. The medium oil is recycled to the hydrogenator. The heavy oil is used principally as a binder in the pelletizer unit.

The advantages of the Clean Coke process are that no external hydrogen is required and that metallurgical-grade coke can be produced from high-sulfur, high-ash coal.

HISTORY OF THE PROJECT

Following evaluation of several potential processes for converting high-sulfur, high-ash coal to metallurgical-grade coke, U.S. Steel determined that the most feasible was a process combining low-temperature carbonization and coal hydrogenation. The criteria governing selection of this process, designated the Clean Coke process, were the quality of coal available, the need for economy of raw materials, energy considerations, and value of products obtained.

To establish the technical feasibility of the Clean Coke process, laboratory and bench-scale development studies were performed by U.S. Steel, beginning in 1969, using Illinois No. 6 seam coal. In the bench-scale phase, emphasis was placed on coal preparation, carbonization-desulfurization of coal in fluidized beds, and high-pressure hydrogenation of coal. The purpose of the coal preparation studies was to evaluate techniques for the beneficiation of the raw coal to provide feed suitable for both the carbonization and hydrogenation reactions. Carbonization studies were performed to determine the efficiency of removing sulfur from the coal. The effects of temperature, pressure, reaction time, and type of feed on the carbonization reaction were also studied. The purpose of the bench-scale hydrogenation reaction studies was to determine the effects of reaction time, temperature, and pressure on the conversion of coal to liquid and gaseous products. Some preliminary studies of coke making were also undertaken.

Under contract to ERDA, U.S. Steel is continuing bench-scale studies. Process development units have been built and are operating. The carbonization process development unit is currently in operation, and the process variables affecting carbonization are being tested. The construction of the hydrogenation process development unit has been completed and initial testing begun.

PROGRESS DURING OCTOBER-DECEMBER 1975

Summary

During the beginning of this quarter, work on the carbonization process development unit was primarily maintenance. During November, two high-temperature carbonization runs were successfully completed. The first run produced a low-sulfur char from a first-stage semichar; the second run was the first in a series of runs planned to

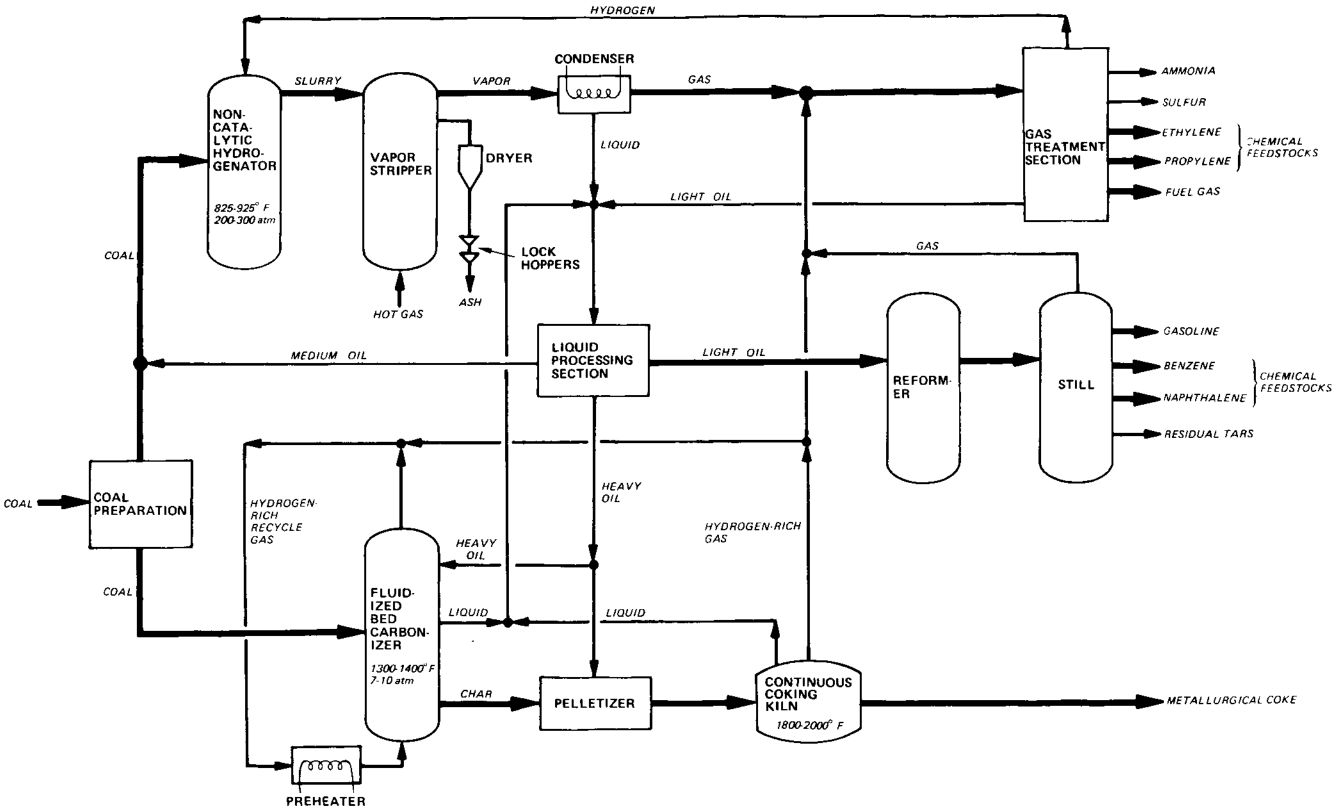


Figure VI-2. CLEAN COKE PROCESS SCHEMATIC

determine optimum residence time and temperature to produce specification char. A complete series of corrosion test specimens of various types of steel were removed from the unit. Also, the damaged heater element subassembly of the recycle-gas heater, which was removed and replaced last quarter, was examined and analyzed to determine the cause of failure; carbon buildup had occurred in many areas.

In the binder preparation section, a tube heater was installed for use as a recycle heater. A 3-day run of the flash vaporizer was begun; the run was terminated when the recycle pump failed. The pump required a larger motor. Another 4-day run was completed. The flash vaporizer was operated to process blow-down wash oil from the carbonization process development unit. Work continued on the construction of a continuous distillation column to separate naphthalene and light ends from the flash-distilled wash oil.

New heat traces are being added and faulty ones replaced in the slurry oil preparation unit. Tests were conducted in the unit with naphthalene column bottoms. Vapor stripper operations data were analyzed. The hydrogenation process development unit is being revised. The coke preparation process development unit was operated to produce green coke pellets. Problems with the 3-inch continuous carbonizer laboratory unit were corrected and experimental work with the unit will begin next quarter.

Process Development Units

Work on the carbonization process development unit during the beginning of this quarter consisted primarily of maintenance. The carbon in the recycle-gas heater was removed by heating the elements to temperatures in the range of 1,300° F to 1,400° F in steam to which gradually increased amounts of air were added. Final clean out of the heater was effected by shutting off the steam and heating with air for 3 additional hours. Other work included the installation of a new transformer to supply power exclusively to the recycle-gas heater, the installation of strip heaters on the interchanger shell-side gas inlet line to ensure vaporization of the water injected into the recycle gas, and modification of the wash-oil spray/quench system to facilitate control of liquid levels in the interchanger and gas cooler pots.

After the carbon removal and modifications were completed, the carbonization process development unit was pressurized to check the performance of the equipment. The recycle-gas heater and the new transformer operated satisfactorily. The revised system for wash-oil level control in the gas cooler and interchanger required an additional piping change to make better use of an automatic control valve.

A 10-day 1,375° F carbonization process development unit run, with a system pressure of 8 atm and a residence time of 90 minutes, was initiated. The run was started at 1,400° F, but the bed temperature was reduced to protect the heater element sheath. This run was interrupted when the feed line plugged because feed with an excess of volatile matter was inadvertently fed into the system.

Two high-temperature carbonization process development unit runs were successfully completed during November. The first run consisted of two tests at residence times of 90 minutes and 103 minutes, respectively. A char containing 0.4 percent sulfur was produced at a bed temperature of 1,410° F, and a pressure of 10 atm. Char production for the two tests was 312 pounds with a sulfur content of 0.5 percent, and 202 pounds with a sulfur content of 0.4 percent, respectively. The volatile matter content of the char produced at the longer residence time was 0.57 weight percent. Because the run was relatively short, no attempt was made to obtain a weight balance and gas production was not measured because of a malfunction in the volumetric flow meter. The significant result of the run was that low-sulfur char was produced from a first-stage semichar containing more than 2 percent sulfur. Because the gas-heater elements were subjected to a temperature of 1,700° F to provide a bed temperature of 1,410° F, a small quantity of carbon formed on the elements.

The second run, at 1,300° F bed temperature, was the first of a series planned to determine the optimum residence time and temperature required to produce a specification char without forming carbon deposits. The run consisted of two tests at residence times of 202 minutes and 146 minutes, and a pressure of 11 atm. The results indicated that higher temperatures will be required to produce a low-sulfur char at residence times shorter than 240 minutes. No carbon deposits were formed. The lower element temperature and injection of 8 mole percent water vapor into the recycle gas apparently prevented carbon deposition. A weight balance for this run was not obtained. The yields of char were 73.5 percent and 74.8 percent; the shorter residence time giving, as expected, the higher char yield. Gas production rate was higher for the shorter residence time (higher feed rate).

A third carbonization run was begun but not completed because of leaks in the flanges of the reactor. The leaks are being repaired. A new set of seals for the compressor alleviated the problem of gas leaks at the compressor shaft. The change in configuration provided greater face pressure and effected a positive seal.

Corrosion tests were made from a complete series of test specimens of various types of steel removed from the carbonization process development unit. The specimens were exposed in the process development unit during operation at both low and high bed temperatures. Upon removal, the specimens were cleaned and evaluated. The results corroborated previous tests: in low-temperature areas, only the carbon steel specimens were corroded, with rates varying from 1.6 to 64.1 mils per year; in high-temperature areas, the specimens showed low corrosion rates, 3.0 mils or less per year. Specimens taken from the heater outlet and carbonizer side and top locations showed a slight weight gain, most likely caused by carbon deposits.

Incoloy Alloy 800 specimens from high-temperature areas showed no significant change in microstructure, except for a minor amount of carbon deposits. The high-temperature areas of the carbonization process development unit are constructed of Incoloy Alloy 800, which should not have deteriorated during the test runs. The failure of the heater-element bundle, made of Incoloy Alloy 800 was evidently caused by extraordinary conditions in that region. Specimens of other alloys tested in the carbonization unit showed minimal carbon deposits or other microstructural changes.

The damaged heater element subassembly of the carbonization unit recycle-gas heater, which was removed and replaced last quarter, was subjected to examination and analysis. Most of the damage occurred in the lower third of the subassembly, the hottest area, where the elements had split and broken. Analysis of a representative sample of the deposits showed that the composition was mainly carbon and ash. Metallographic examination of the removed sections of the elements showed areas of severe carbon buildup and pitting. Grain growth, which is indicative of overheating, was observed in the hairpin area of the element. The most obvious example of overheating occurred higher up in the element bundle.

Microprobe analysis of the heater subassembly showed that the cause of the damage was metal dusting—the formation at elevated temperatures in a carbonaceous atmosphere of carbon mixed with metal carbides and metal oxides in powder form. To inhibit metal dusting, hydrogen sulfide levels of 50 to 100 parts per million were maintained in the fluidizing gas; to inhibit carbon deposition, 6 percent to 8 percent water was injected into the recycle gas.

The water injection resulted in 30 percent to 40 percent water in the used wash oil. A method was developed and is now being used to remove the water before reprocessing the oil in the flash vaporizer. Installation and inspection of a tube heater for use as a recycle heater in the binder preparation section was completed.

Work continued on the flash vaporizer used to reclaim wash oil. In a 3-day run, problems with the feed and recycle pumps resulted in the replacement of the feed pump and the installation of a larger motor on the recycle pump. A 4-day run was then made. Except for minor temperature control problems solved by controlling the steam rate manually, the feed pump operated satisfactorily. The next group of runs processed 3 drums of oil daily for a week through dehydration followed by flash distillation to recover wash oil and carbonization tars. The tar contained char fines that damaged the tar pump. When the pump was rebuilt, fresh oil rather than tar came in contact with bearing surfaces. Work continued on construction of a continuous distillation column to separate naphthalene and light ends from the flash distilled wash oil.

Operation of the hydrogenation process development unit was hampered by leaks in the high pressure fittings and solidification of process fluids in cold weather. Fittings of the same material throughout were installed, which eliminated the cause of the leaks, thermal expansion differences. Remote access fittings were replaced with welded joints. Winterization of the unit (completion of roof enclosure, installation of heat tracings and insulation) solved the cold weather problems.

Heat loss problems encountered in preliminary operation of the slurry oil preparation unit were solved by adding new heat traces to the distillation columns and transfer lines. A mixture containing 16 percent naphthalene and 41 percent methylnaphthalene was fed to the atmospheric distillation unit. About 72 percent of the naphthalene was removed.

Data collected during vapor stripper operations representing steady-state operation for 5 or more hours were analyzed. At an operating pressure of about 137 atm, little additional stripping was accomplished by increasing the stripping gas beyond about 120 standard cubic feet per pound of oil.

A project review meeting with ERDA representatives during December resulted in modification of the hydrogenation process development unit. Revisions were made so that the unit could be maintained from three sides: the blast wall separating Cells 1 and 2 was eliminated; the recycle-gas secondary oil trap was removed; and the stripping column was moved into the open Cell 1 area. The relocation of the stripping column required extensive piping and wiring changes that have not yet been completed. Many of the high-pressure tubing connections were eliminated, particularly in the hot lines where leaks have been occurring.

Modifications in the coke preparation unit included the installation of an insulated, electrically heated enclosure around the pelletizing disc. Because the enclosure around the disc prevents easy access for cleaning the spray nozzles, an automatic cleaning system was installed.

In the coke preparation process development unit, several 16-hour pelletization runs were successfully completed to produce about 770 pounds of green coke pellets from pulverized high-temperature char and a simulated binder. The pellets were of satisfactory quality with solids contents of about 70 percent.

The pellets produced were cured with a support medium (3/4-inch by 1/2-inch coke). The cured pellets and support medium were cooled to ambient temperature in 1 hour, using nitrogen as the quenching gas. These pellets showed very little surface cracking. Only one batch showed any tendency toward bleeding and subsequent sticking, and this batch contained pellets that were more wet with binder. Tests to determine whether the green pellets could be satisfactorily cured without using a support medium were unsatisfactory; the pellets agglomerated.

About 960 pounds of cured pellets were calcined during this period. The temperatures in the hot zone of the coking kiln ranged from 1,610° F to 1,960° F. To prevent mechanical bridging of the pellets during calcining the pellets were mixed with a support medium of 1/4-inch by 1/2-inch coke. No agglomeration or bridging occurred, but tars entrained in the kiln off-gases could not be collected because of difficulties with the scrubbing system. Pellets prepared with the binder made from pitch and bottom flash tars were stronger than those produced with binders made from pitch and heavy creosote oil. Good control of binder properties is necessary for high-strength pellets.

About 3,000 pounds of high-temperature char was pulverized to 98 percent minus 100 mesh for use in future pelletization runs in the coke preparation process development unit. The seventh shipment of Illinois No. 6 seam coal for the process development unit program has been received at the U.S. Steel Research Laboratory; the preliminary crushing, table washing, and analysis have been completed. About 15 tons of clean coal was delivered to the coal preparation area of the laboratory and will be used as needed for coal feed.

Laboratory Research

The major problem encountered in the shakedown tests conducted in the 3-inch continuous carbonizer unit was the persistent burnout of the heating elements of the recycle-gas heater. The elements were redesigned and the problem was solved.

During the shakedown test at the end of this quarter, the semichar from the process development unit was carbonized at temperatures of 1,270° F to 1,370° F, a pressure of 8 atm, and a residence time of 150 minutes. Some problems occurred in the hydrogen sulfide removal system but were easily corrected. The major problem during the test was the burnout of the heaters in the fluidized-bed area; higher capacity heaters have been installed. The unit is now operational, and experimental work with the unit will begin next quarter.

VII. LIQUEFACTION OF COAL BY DIRECT HYDROGENATION

ROCKETDYNE DIVISION
ROCKWELL INTERNATIONAL CORPORATION
CANOGA PARK, CALIFORNIA

Contract No. E(49-18)-2044
Total Funding: $994,375

INTRODUCTION

Under contract to ERDA, starting in August 1975, the Rocketdyne Division of Rockwell International is conducting a research program to develop a technology that would permit the liquefaction of coal by direct hydrogenation by rapid mixing, reaction, and quenching of a gaseous hydrogen and pulverized coal mixture. The specific objective of the program is to evaluate the feasibility of reacting pulverized coal with heated hydrogen to form hydrocarbon liquids suitable for conversion to oil or chemical feedstocks, while preventing subsequent cracking and tar formation.

The program is divided into two phases. Phase I involves the design and fabrication of cold-flow equipment and the operation of the equipment in a series of tests to (1) determine the most effective methods of transporting coal to the point of injection into the reactor; (2) evaluate details of the feed reservoir and the effect of variations in design concepts; (3) evaluate the effectiveness of several injection configurations (coaxial or impingement type), including the influence of various design parameters on mixing and flow uniformity and the possibility and effects of wall impingement and recirculating flow; (4) consider critical areas and rates of erosion; and (5) test flow uniformity and the tendency for irregularities caused by dense-phase flow to define the effect of pressure drop on flow rate. Upon completion of Phase I, the results of the cold-flow tests will be submitted to ERDA to determine if Phase II should be initiated. If Phase II is authorized, a small-scale reactor with a coal feed rate of about 1 ton per hour will be designed, built, and tested. This reactor will be used to evaluate the effects of reactor configuration and operating conditions. Based on these results, a larger reactor, with diverse injection methods and a coal feed rate of about 10 tons per hour, will be built and tested. Test results and analyses will be evaluated to determine the feasibility of the process. The schedule for the development of this process is shown in Figure VII-1.

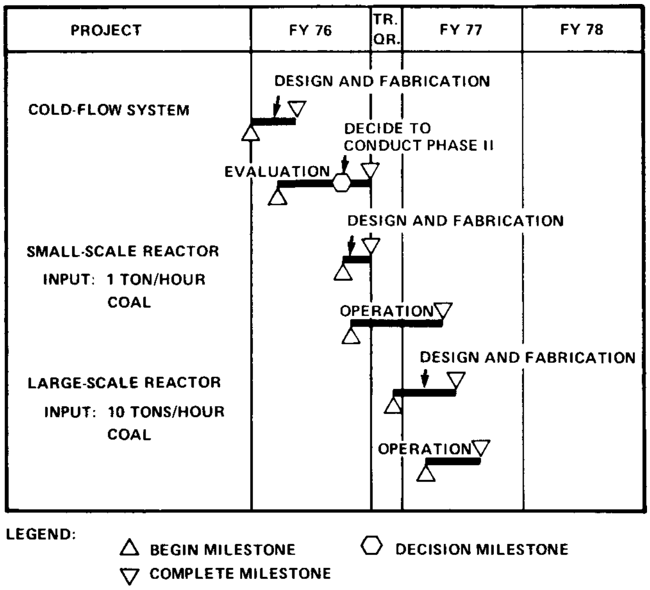


Figure VII-1. PROGRAM SCHEDULE FOR LIQUEFACTION OF COAL BY DIRECT HYDROGENATION

In addition to the contractually funded effort, Rockwell International is sponsoring a corollary effort to provide supporting information and the necessary facilities, including the equipment required for the major portion of the cold-flow tests.

PROCESS DESCRIPTION

The basic concept of this process for the liquefaction of coal by direct hydrogenation is that high liquid yields are favored by rapid mixing, reaction, and quenching of a mixture of pulverized coal and hot gaseous hydrogen. In this process, shown as currently planned in Figure VII-2, pulverized coal is fed into the coal feeder from a batch feeder, with nitrogen used as the transport gas. The coal passes through the feeder, is partially fluidized with hydrogen at the conical exit from the feeder, and then passes to the entrained-flow reactor where it is mixed rapidly with heated hydrogen. (Preliminary design studies indicate that a fired heat exchanger can be used to heat the hydrogen to about 1,500° F.) The pulverized coal and hydrogen react for about 10 to 100 milliseconds in the reactor. The reactor is expected to be operated over a pressure range of 35 to 100 atm and at a temperature of approximately 1,800° F.

The reactor effluent is expanded to reduce the pressure and is partially quenched with a water spray. The primary quench is intended to reduce the effluent temperature to about 600° F, which should quench the reactions but allow the light oils to remain in the vapor phase. The vapor and condensed phases are separated. The light oil and water in the vapor-phase stream are condensed by cooling, separated from the gas stream, and further separated by decantation. The condensed-phase material will be accumulated in the heavy-oil decanter until the test is completed. The heavy oil and water-rich fractions in the condensed phase will be separated by decantation and filtered to remove the solid material. If the materials cannot be separated by filtration in a reasonable manner because of their tarry nature, then representative samples will be removed and analyzed.

PROGRESS DURING OCTOBER-DECEMBER 1975

Summary

During this quarter, construction of the cold-flow test unit for the transport and mixing tests was completed and plugging problems encountered in initial tests were resolved. Transport tests conducted in the cold-flow unit showed that pulverized coal can flow uniformly and consistently from the pressurized feeder without difficulty. Further analysis of void fraction and transport gas requirement data obtained previously indicated that the transport gas requirement is low. Injection elements and the two-phase flow probe for the mixing tests were fabricated. Preliminary design efforts were directed toward definition of the required hardware for the 1-ton-per-hour reactor system.

Laboratory Research

Construction of the cold-flow unit for the transport and mixing tests was completed during this quarter. Transport gas may be introduced to the unit through a ring manifold at the top of the exit cone in the main feeder. The coal injection process and pressure instrumentation ports

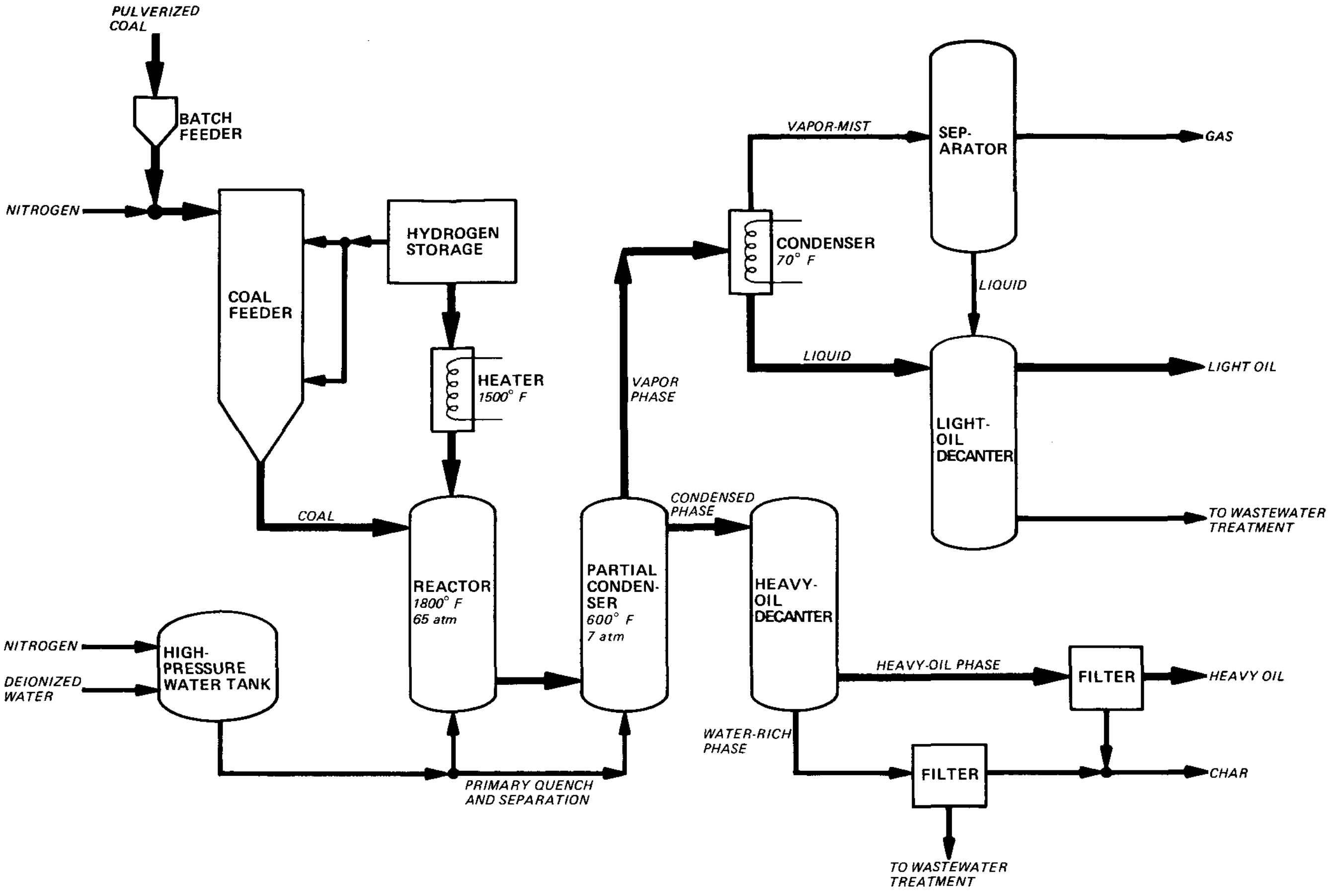


Figure VII-2. SCHEMATIC OF LIQUEFACTION OF COAL BY DIRECT HYDROGENATION

can be seen through a cylindrical acrylic window in the cold-flow chamber.

Some problems were encountered during initial tests in the unit. In one test, partial plugging of the transport line by a large piece of coal in the pulverized material led to erratic results. To correct the problem, a screen attachment is currently being fabricated for the loading system to remove any large coal particles, and the transport line is being checked frequently during test operations. Initial test results also indicated that coal which settled after the feed was shut off in the transport line led to plugging of the line when a subsequent test was attempted. (The transport line rises about 3 feet between the feeder and the cold-flow chamber.) The system was modified so that the transport line can be cleared of coal by a flow of nitrogen.

Transport tests using the cold-flow unit showed that pulverized coal can flow uniformly and consistently from the pressurized feeder without difficulty. Pressure gradient results from transport tests using the cold-flow unit were compared with results obtained from the smaller transparent feeder system; the behavior is generally similar, although the gradients differ by a factor of about 2. This difference, and varying results from the transparent feeder system, indicate that the pressure gradient has a relatively high sensitivity to small changes in the flow system or the coal. Feeder-outlet pressure-drop test results for the larger feeder agreed with the results obtained thus far from tests made in the smaller feeder, even though the data from the larger feeder were obtained when the transport line was partially plugged. An approximate 5-fold increase in pressure drop was attributed to the large coal particle at the entrance to the transport line.

Prior to completion of the cold-flow unit, additional tests conducted in the transparent feeder confirmed the previously observed tendency toward increased pressure drop when coal was recycled through the equipment. This effect on pressure drop probably is caused by a loss of fine particles with repeated loadings. Other tests made with pulverized coal obtained from Pittsburg & Midway Coal Mining Company showed essentially the same flow characteristics as the earlier tests made with coarser coal.

Void fraction and transport gas requirement data obtained previously were analyzed further. Plots of the ratio of volumetric flow rates of solid-to-gas as a function of solids mass flux showed that flow occurs even under the very dense conditions that exist if coal exits from the feeder at its bulk density (about 53 pounds per cubic foot) without additional gas. This observation was reinforced by an analysis of the dispersed solids density data to infer the void fraction at the exit from the column. The results indicated that the transport gas requirement is low. Moreover, with this feeder approach, the flow has been found to be substantially more dense than any previously reported in the literature or known to Rocketdyne.

Fabrication of the two-phase flow probe and of different types of injector elements for the mixing tests was completed. The injection element of the probe assembly may be either a concentric tube element that involves coaxial flow of the coal and gas streams or a 4-on-1 element that has 4 streams of gas impinging on a central stream of coal.

The required size and general configuration of the quench system for the 1-ton-per-hour reactor were analyzed and determined. An available computerized analytical model, ordinarily used to predict the propellant spray in rocket engines, was used to predict the water-spray vaporization and temperature distribution in the quench system. A quench chamber 10-feet long with a 7-inch diameter was selected for the 1-ton-per-hour reactor system. The water flow used will be sufficient to reduce the outlet gas temperature to about 600° F. Based on computer analysis of the heat transfer and condensation in the condenser, a condenser surface area of about 1,000 square feet seems to be desirable for the 1-ton-per-hour reactor system. The analysis considered simultaneous condensation of two immiscible liquids in the presence of noncondensable gas.

VIII. FILTRATION PROCESS AND EQUIPMENT STUDIES

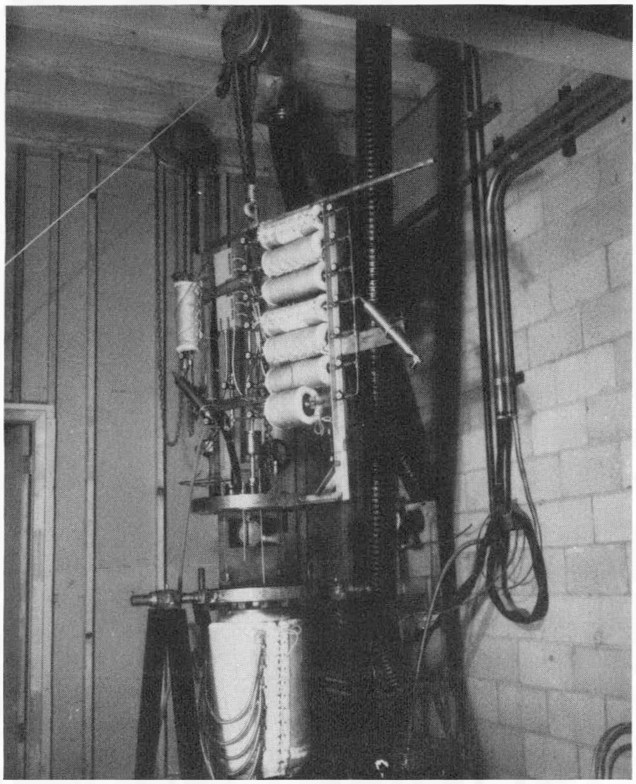
JOHNS-MANVILLE SALES CORPORATION
DENVER, COLORADO

Contract No. E(49-18)-2007
Total Funding: $190,000

INTRODUCTION

Under contract to ERDA, Johns-Manville Sales Corporation is conducting research to improve solid-liquid separation, a critical step in any coal liquefaction process. Specifically, Johns-Manville is studying filtration, the most viable method of separating solids from liquids yet developed, using a rotary-drum pressurized precoated filter. The objective of the research program is to achieve major improvements in the filtration process and in the filtration equipment used in the coal liquefaction process. The goals are to double the filtration rate reproducibly, reduce filter aid usage, and demonstrate the results on a pilot-plant scale.

The filtration research program is planned in two phases; only the first phase has been contracted. The objectives of Phase I, laboratory research, are to (1) develop basic knowledge of the coal oil filtration process and its dependence upon liquefaction process parameters and (2) apply the knowledge gained to improve the performance of filtration operations in existing liquefaction plants. If the initial filtration studies are successful, Phase II (not part of this contract) will be conducted. As currently planned, Phase II comprises the design and construction of a rotary-drum pressurized precoated filter to operate at pilot-plant scale. A viable system will be capable of filtering in excess of 20 gallons per square foot per hour of solid-liquid mixture. Data obtained from operation of the pilot-scale facility will be used to design filters for commercial-scale plants.



PROGRAM DESCRIPTION

The first phase of this program, initiated in late May 1975, is being implemented through laboratory bench-scale research. The initial step involves the design and construction of a laboratory test facility that will simulate the operation of a rotary-drum pressurized precoated filter and that is capable of operating at 750° F and 27 atm. A series of tests will then be conducted to study pressure precoat filtration variables at the temperatures and pressures expected in normal pilot plant operations. In these tests, four liquefaction process liquids will be used: H-Coal boiler fuel supplied by Hydrocarbon Research, Inc.; solvent-refined coal supplied by The Pittsburg & Midway Coal Mining Company (P&M); COED raw oil supplied by the FMC Corporation; and Synthoil boiler fuel supplied by the Pittsburgh Energy Research Center.

Upon completion of these tests, the apparatus will be moved to a P&M facility at DuPont, Washington and will be used to establish the relationships between test results obtained on fresh filter feed and results obtained on oil products that have been cooled and shipped. In cooperation with P&M, Johns-Manville will apply its filtration knowledge to improve the filtration rate and reduce the filter aid usage on the existing Goslin-Birmingham filters. Similar filter process optimization studies will then be conducted at other ERDA-sponsored coal liquefaction plants. Johns-Manville is also responsible for assisting in the selection of a suitable precoated filter for the Cresap Test Facility in Cresap, West Virginia, including (1) an investigation of the feasibility of modifying the existing filtration equipment to accommodate the experimental work or of using a belt filter, and (2) assistance in the start-up and establishment of operating conditions for the filter system selected.

PROGRESS DURING OCTOBER-DECEMBER 1975

Summary

The laboratory test facility was completed during this quarter to a point that test filtration runs were initiated to develop procedures to be used in the major experimental program. The first set of tests used water and organic media to establish precoating and cake cutting procedures. Difficulties in forming the filter cakes resulted in the use of a finer mesh wire on the filter leaf and a filter aid. Tests using coal oil pointed up the need for an effective equipment cleaning agent. In subsequent tests with coal oil, difficulties were encountered with the filter cakes decomposing.

Laboratory Research

Construction and assembly work on the laboratory-scale precoat filter-leaf system advanced to the point that pressure testing and a checkout of the heating system could be conducted. Efforts to eliminate leaks in joints of the system were made and the system was successfully tested at approximately 37 atm. In a check out of the heating system, two controllers for circuits of the main pressure vessel heating mantle were found to be defective and were replaced. All other components appeared to be operating properly. The computer system was inspected and approval was given to proceed with testing.

The purpose of the preliminary filtration tests was to develop techniques and procedures to be used in the major experimental program. To establish precoating and cake cutting procedures, test runs used water and organic media to form filter cakes of diatomite. A problem associated with the formation of the filter cakes was solved by using a filter leaf with a finer mesh wire cloth. A subsequent problem involved severe cracking of the filter cakes after formation. This problem was attributed to the manner in which the flocculation took place. A tentative solution was obtained using surface active agents, but the final solution hinges on the use of the Tacoma filter aid process solvent.

The use of coal oil in the filtration tests emphasized the need for adequately cleaning equipment. Experimentation with many solvents and solvent combinations resulted in the selection of a commercial paint brush cleaner with 10 percent pyridine added for use in cleaning the equipment.

The initial coal oil run, at temperatures in the 660° F to 750° F range and using the Tacoma solvent, was made without purging the system with nitrogen. Hydrogen, methane, and carbon monoxide gases were given off because of the decomposition of the filter feed slurry. (Residual pressures of 11 atm were experienced.) The decomposition was thought to have occurred because oxygen acted as a reactant. However, a second run, after purging the system with nitrogen, produced the same results. Further work is being done to determine the temperature restrictions necessary to avoid decomposition.

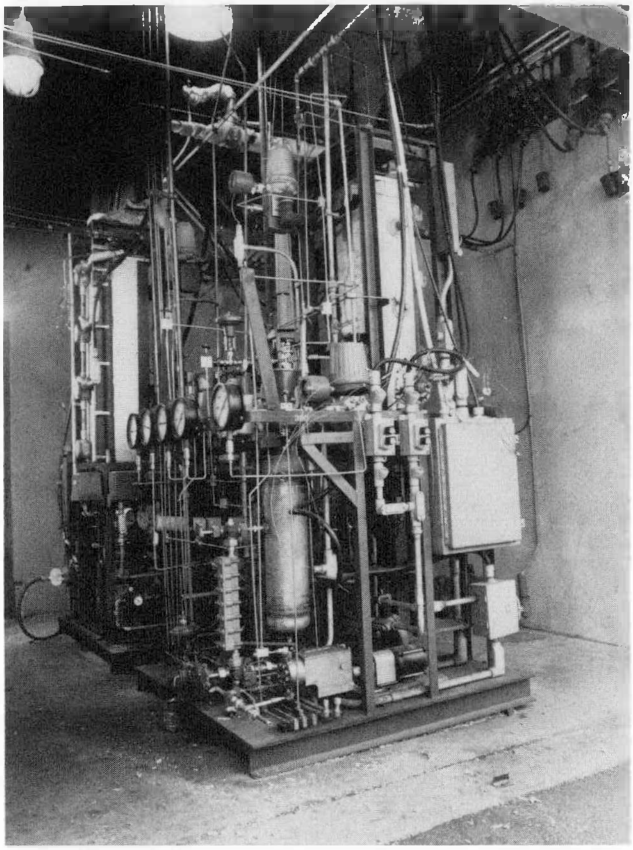
IX. CHEMICALS FROM COAL

THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN

Contract No. E(49-18)-1534
Total Funding: $342,896

INTRODUCTION

Historically, coal was used as a chemical feedstock, but petroleum and natural gas were substituted as cheaper feedstocks when they became available. However, because of the recent rising costs and lessened availability of petroleum and natural gas, The Dow Chemical Company, under the sponsorship of ERDA, is studying the possibility of using coal-derived liquids as chemical feedstocks. Specifically, Dow is testing liquids produced from four coal liquefaction processes (COED, Synthoil, H-Coal, and SRC) in standard petrochemical processing experiments and is evaluating these results to select one process for further study, based on process design, quality of chemicals produced, and overall plant economics. For the process selected, further development will include material balances and utility requirements for each major process step, a preliminary process flow sheet, and estimates of capital and operating costs for a commercial plant.



PROGRAM DESCRIPTION

The liquids produced by the four processes are subjected to standard petrochemical processing operations to ascertain the advantages and disadvantages of using coal-derived liquids for petrochemical feedstocks. The experimental work is being carried out in miniplants capable of operating unattended at pressures up to 204 atm, temperatures to 1,300° F, and feed rates from 25 milliliters per hour to 400 milliliters per hour.

The processing sequence used for all of the samples is: (1) distillation into nominally three cuts–straight-run naphtha (350° F or less), mid-distillate (350° F to 650° F), and heavy gas oil (650° F to 950° F); (2) hydrocracking of the mid-distillate and heavy gas oil to reduce molecular weight; (3) hydrotreating of the straight-run naphtha and hydrocrackate naphtha to remove heteroatoms; and (4) reforming of the hydrotreated naphthas to maximize aromatics. Steam coil cracking of some of the fractions is also performed to evaluate potential ethylene yields.

Characterization studies on all of the samples as well as the intermediates in the hydroprocessing experiments are performed using the following procedures:

- Componential analysis of the hydrocarbons
- Atmospheric, vacuum, and simulated American Society for Testing Materials (ASTM) distillations
- Elemental analysis (carbon, hydrogen, oxygen, nitrogen, sulfur)
- Trace metal analysis
- Liquid chromatography for class separations (aliphatics, monoaromatics, diaromatics).

PROGRESS DURING OCTOBER-DECEMBER 1975

Summary

During the quarter, the COED naphtha was hydrotreated in two stages to obtain a low-nitrogen and low-sulfur product. The entire Synthoil sample was distilled to obtain a mid-distillate; it was decided not to study the Synthoil light-oil fraction, since only a nominal amount is produced. The H-Coal naphtha was further reformed using Aeroform PHF-4 platinum reforming catalyst and hydrocracking of the H-Coal straight-run vacuum-gas oil was completed. The hydrocracked SRC product was received from the U.S. Bureau of Mines.

Petrochemical Processing Experiments

COED Syncrude

The COED naphtha was hydrotreated in two stages using Harshaw HT-100 E 1/8-inch nickel-molybdenum catalyst to obtain a product containing low levels of nitrogen and sulfur. Temperature and pressure for the first stage were 797° F and 64 atm, respectively; for the second stage, temperature was 752° F and pressure, 62 atm. For both stages, weight hourly space velocity was maintained at 3 grams per gram hour and the hydrogen ratio was 2,500 standard cubic feet per barrel of feed. Partial analyses showed that sulfur content was reduced from 40 parts per million to less than 2 parts per million after the second stage and that nitrogen content was reduced from 470 parts per million to 6 parts per million after the second stage.

Synthoil

The entire Synthoil sample was distilled to obtain a mid-distillate. About 34 percent of the sample was converted into distillate at 650° F. The bottoms product, the fuel-oil fraction, plasticized at 210° F; this fraction cannot be termed fluid below 240° F. Because so little light oil is produced in the Synthoil process, it was decided not to study the Synthoil light oil fraction as a possible petrochemical feedstock. Also, a study of Synthoil gas is not feasible. Distillation of the gas oil is difficult and the resulting residual fuel oil has too high a melting point to be useful as a feedstock.

H-Coal Oil

Reforming of the H-Coal naphtha that was hydrotreated through two stages last quarter was accomplished using Aeroform PHF-4 platinum reforming catalyst from American Cyanamid. The first experiment was conducted at 18 atm and 932° F, a liquid hourly space velocity of 1.59, and a hydrogen ratio of 2,500 standard cubic feet per barrel of feed. The experiment resulted in an 86.3 volume percent yield of C_5+ and a 67 weight percent yield of C_6-C_9 aromatics. (Before the naphtha was reformed, it contained 33 weight percent C_6-C_9 aromatics.)

It is possible to convert 92 to 95 percent of C_6-C_9 naphthenes to aromatics using the Aeroform PHF-4 catalyst. Because the percentage of aromatics in the C_6-C_9 stream is so high, it is probably uneconomical to remove the nonaromatics by steam coil cracking from the stream for use in olefin production. Therefore, no further experiments on the two-stage hydrotreated naphtha will be made.

The Aeroform PHF-4 platinum reforming catalyst deactivated rapidly during the experiment.

Because of the limited amount of feed available for the reforming study, efforts to determine the cause of catalyst degradation were curtailed.

Hydrocracking of the straight-run vacuum gas oil was completed using Harshaw HT-400 E 1/8-inch cobalt-molybdenum catalyst. (A limited number of experiments were run on the gas oil because of the small amount of gas oil available.) The gas oil contained fine particles that tended to plug the pumps in the reactor system. Preliminary data indicated that hydrocracking the gas oil above 960° F had little additional effect in increasing the conversion to a mid distillate-range product. Elemental and componential analyses of the hydrocrackates are being conducted.

SRC Product

The hydrocracked SRC product was received from the U.S. Bureau of Mines. Characterization studies included ASTM distillation, viscosity, and elemental analyses. Simulated distillation data indicated a low conversion level for the mid distillate-range oil. Therefore, studies on SRC product as a feedstock will be limited to the light oil produced in the process.

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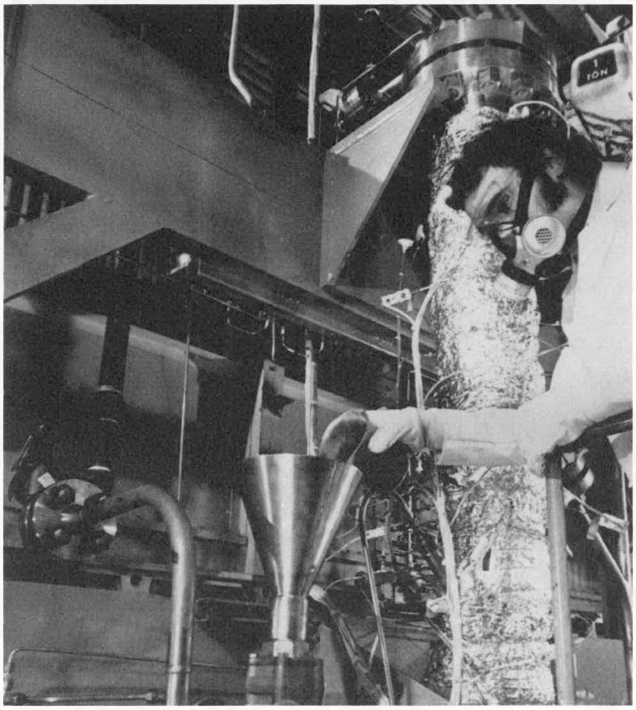
X. R&D ENGINEERING SERVICES— HYDROCARBONIZATION

OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE

Contract No. E(49-18)-1740
Funding: $400,000



INTRODUCTION

Under contract with ERDA, the Oak Ridge National Laboratory (ORNL) is conducting several research and development projects in support of the increased utilization of coal as a source of clean energy. Research and development projects supporting liquefaction involve hydrocarbonization. Specifically, ORNL is to estimate the optimum operating conditions of a fluidized-bed hydrocarbonization reactor; design, construct, and operate a fluidized-bed reactor capable of continuously processing 10 pounds of coal per hour at pressures of at least 20 atm and at temperatures up to 1,250° F.

PROGRAM DESCRIPTION

Hydrocarbonization is an important type of coal liquefaction process that combines high-temperature, high-pressure, and fluidized-bed operation using hydrogen-rich gas for fluidization. The hydrocarbonization process can produce desulfurized char, liquid fuels, and substitute natural gas. The relative yields of these products can be controlled. The char is suitable for use without stack gas treatment in boilers. The liquid fuels include naphtha, light gas oils, and heavy gas oils. Conditions for hydrocarbonization include temperatures of up to 1,500° F and pressures of up to 80 atm.

Work under this hydrocarbonization research and development project, initiated in November 1974, is divided into three tasks:

- Review and evaluation, which involves analysis of prior work to estimate operating conditions and guide reactor design.
- Experimental development, including batch autoclave and component tests to guide reactor design and support operation.
- Bench-scale studies, which require the design, construction, and operation of a hydrocarbonization system.

As part of the review and evaluation task, completed in the second quarter of 1975, ORNL summarized data (including process information, yields, and catalyst usage) on various coal hydrocarbonization and carbonization processes. To develop a basis for selecting a range of operating conditions, ORNL conducted a parametric surface study with liquid and gaseous hydrocarbon yields, char yields, and hydrogen consumption as the dependent variables and temperature, hydrogen partial pressure, residence times, and coal compositions as the independent variables. A computer program was prepared to guide the design of the reactor.

To aid in experimental development, ORNL constructed a two-dimensional mock-up of a recirculating fluidized-bed reactor. The mock-up consists of one central tube in which the solids are lifted in dilute-phase transport and two tubes in which the solids are recycled to the bottom of the column in a dense-phase transport. This type of reactor offers several advantages for hydrocarbonization, including rapid heating of the coal, short vapor-product residence times, and minimal solids agglomeration.

Work on the bench-scale hydrocarbonization system included the selection of operating conditions: coal feed rate of about 10 pounds per hour, pressure of at least 20 atm, temperature of 1,250° F, and gas superficial velocity in the reactor of less than 2 feet per second. The smallest size reactor, a 4-inch-diameter tube (nominal pipe size), that would give meaningful process data was also selected.

PROGRESS DURING OCTOBER-DECEMBER 1975

Summary

During this quarter, the results of two experimental runs conducted last quarter were reported, and three more experimental runs were conducted. The installation of the bench-scale system was completed and further shakedown tests were made using nitrogen as the feed gas; two tests were run at 5 atm and two at 20 atm. The bench-scale system was prepared for the first scheduled runs with hydrogen.

Experimental Development

The results of a product gas analysis; proximate and ultimate analyses of feed coal, tar, and char; and a carbon balance for Run AHC-5 (conducted last quarter) were reported. The carbon balance was closed to within 2 percent, but the relative yields of char, liquid, and gas indicated that at the operating temperature used (about 1,100° F), considerable cracking of liquid products may have occurred. The preliminary analyses of product gases from Run AHC-6, also conducted last quarter, showed lower methane yields than in Run AHC-5, indicating that the lower operating temperature of the run (1,050° F) lessened the severity of cracking of the liquid products. Preliminary proximate and ultimate analyses of feed coal, char, and tar have been calculated; the carbon balance showed a lack of closure resulting from tar and char losses in the line between the reactor and the cyclone.

Run AHC-7 was to duplicate the conditions of Run AHC-6, but the run was aborted because of a plug in the line between the reactor and the cyclone. The bulk of the plug evidently consisted of residue from the previous run, sealed by a carry-over of fines; the line was cleaned. Run AHC-8, with a maximum temperature of 1,060° F and Run AHC-9, maximum temperature of 1,000° F, were successfully completed. The installation of a recirculating fluidized-bed reactor and associated subsystems was begun at the end of the quarter.

Bench-Scale Studies

Installation of the bench-scale system was completed and further shakedown tests conducted. The system was pressurized at ambient temperature, heated to design conditions at atmospheric pressure, and operated successfully using nitrogen as the feed gas. The spray nozzle in the scrubber was installed, and the scrubber, pump, and heat exchangers were successfully tested. The system was prepared for full operation at system pressure of 5 atm; reactor temperature, 1,050° F; preheater temperature, 1,200° F; rate of feed gas (nitrogen), 5 standard cubic feet per minute; and coal feed rate, about 10 pounds per hour. A leak in the flanged top of the scrubber, which had not been properly resealed, caused a shutdown of the shakedown run shortly after start-up. The top was resealed and tested successfully.

Before further runs were made, a Bendix gas chromatograph was installed in the process gas line. Two 3-way valves in series were installed to split the incoming gas between the preheater and pneumatic transport line and to provide a temperature trim by allowing a portion of cold gas to bypass the preheater. Other modifications and improvements included heating the line between the preheater and the reactor and the line between the reactor and the scrubber, installing a pressure equilization line on the char overflow leg between the reactor and the char receiver, welding a 2-inch ball valve to the top of the feed hopper, and installing a coal flow monitor on the pneumatic transport line.

Two shakedown runs were made during November, using a total of 25 pounds of coal with a nominal mesh size of –50+140. For the first run, the system was pressurized to 5 atm with nitrogen; the preheater was heated to 1,250° F and the reactor to 1,050° F; and the system was checked for leaks. A coal-feed rate of about 5 pounds per hour was started. The run was stopped after only about 5 pounds of coal had been fed to the reactor because the orifice flow meter malfunctioned and the feed gas could not be accurately measured or controlled. Other problems were also encountered during the run: the coal feed rate seemed to be unstable; a large amount of fines was apparently carried over to the scrubber; and minor difficulties with process instrumentation were detected. The orifice flow meter on the feed-gas line was repaired, a coal-flow meter was installed on the coal-feed line, and process instrumentation was corrected.

The second shakedown run was conducted under the same conditions as the first except that the coal-feed rate was about 10 pounds per hour instead of 5 pounds per hour. The feed-gas control was satisfactory, and the coal-flow meter performed well. The remaining 20 pounds of coal were transported to the reactor, and about 8 pounds of char overflowed to the char receiver.

There was some difficulty during the run with plugging of the pressure taps used to measure differential pressure through the fluidized bed of the reactor. Other parts of the system worked well. Although no attempt was made to recover products for a material balance calculation, some qualitative observations were made. The char from the char receiver was free-flowing, and the particle-size distribution was similar to that of the feed coal. The liquid from the scrubber appeared to contain three phases: a lighter-than-water phase, an aqueous phase, and a heavy tar phase. The liquid was easily flushed from the scrubber. The filter on the effluent gas line was slightly caked with tar. The two shakedown runs proved the overall performance of the bench-scale system to be satisfactory. No problems occurred with gas leaks, thermal expansion of vessels, or any of the major process components.

Several ancillary components of the system were installed before further shakedown runs. The coal trap was readied by installing cooling coils and the coolant circulation system. (Temperature between ambient and about –940° F can be obtained by varying the circulation rate of the dry-ice coolant through the coils.) The remaining thermocouples and pressure switches were connected. Work on instruments and controls included start-up and successful shakedown testing of the on-line process gas chromatograph, completion of balancing pressure control on the scrubber pump, and completion and testing of the fire-detection sensors in the equipment room. Construction of the hydrogen trailer station is nearing completion. The hydrogen supply station and two hydrogen tube trailers (owned by Union Carbide, Nuclear Division) will be ready in time for the first scheduled run with hydrogen during the following quarter.

Two shakedown runs using nitrogen as the feed gas were made during December at 20 atm pressure, and temperatures of 1,400° F for the preheater and 1,250° F for the reactor. Maintaining coal feed was the only problem encountered in both runs.

Coal feed problems resulted from bridging in the feed hopper and the formation of loose compacts of coal in the cavities of the feeder valve. Neither of the problems occurred during previous runs at 5 atm. The problems were probably aggravated by the large amount of fines in the feed coal. The coal feeder was modified to correct the problems. The feed hopper was aerated and pressurized with the gas used for pneumatic transport of the feed coal; the packing in the ball-valve coal feeder was replaced; and the pneumatic transport gas was redirected to impinge on the downstream side of the feeder valve to break up the loose compacts of coal in the feeder. Testing of the modified feeder at atmospheric pressure was completed successfully, and tests at 20 atm are being conducted.

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XI. R&D ENGINEERING SERVICES—CARBONIZATION OF RESIDUE

OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE

Contract No. E(49-18)-1740
Funding: $200,000

INTRODUCTION

Under contract with ERDA, the Oak Ridge National Laboratory (ORNL) is conducting several research and development projects in support of the increased utilization of coal as a source of clean energy. Research and development projects supporting liquefaction involve the carbonization of residue. Specifically, ORNL is to evaluate the design and operation of the low-temperature carbonizer at the Cresap Test Facility; modify an existing atmospheric batch reactor to operate continuously; and operate the reactor with residual material from the H-Coal, Solvent-Refined Coal (SRC), and Consol Synthetic Fuel (CSF) processes. (The CSF process is being developed at the Cresap Test Facility.) The ORNL project began in November 1975.

PROCESS DESCRIPTION

In this process, shown schematically as currently planned in Figure XI-1, residual material from coal liquefaction processes is to be converted to char by carbonizing the material. Residual material is to be transported to the reactor using inert gas. Additional inert gas will be preheated and fed to the reactor for fluidization. The design of the reactor will be a fluidized bed, capable of operating at temperatures up to 1,200° F. The char level will be maintained by connecting the char overflow pot to one of two overflow tubes and plugging the other side of the reactor. Inert gas passing up through a draft tube will transfer the char from the reactor to a cyclone where the gas and solid phases will be separated. The gas will be scrubbed and filtered before being discharged.

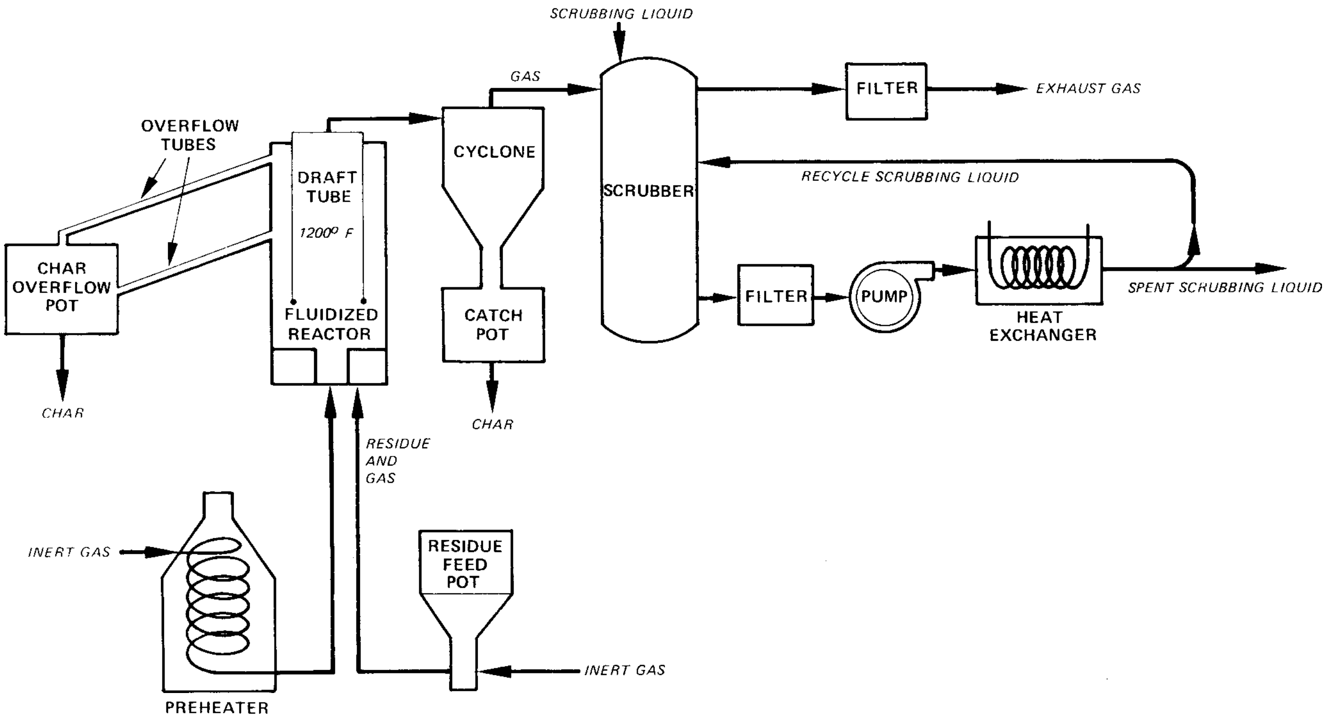

Figure XI-1. SCHEMATIC OF CARBONIZATION OF RESIDUE PROCESS

PROGRESS DURING NOVEMBER-DECEMBER 1975

During the quarter, literature concerning the design and operation of the Cresap test facility carbonizer was reviewed. Modifications were made to the bench-scale batch reactor converting it to a continuous-feed-flow fluidized reactor.

The only residue for which any data is currently available is that of the H-Coal vacuum tower bottoms. This material, finely ground, can be transported pneumatically to the reactor. A second feed system is being designed in case the one currently planned is not successful. The second system consists of slurrying the residue with 25 percent to 50 percent toluene and pumping it into the reactor as a spray. Fabrication of the feed system and overflow pot are continuing.

GLOSSARY

The intent of this glossary is to give a general definition of terminology as used in this report. A glossary is considered desirable because of the diverse origin of the technology and broad spectrum of potential readers. For more precise and detailed definitions, the reader is referred to *The Annual Book of ASTM Standards* published by the American Society for Testing Materials (ASTM), *Chemical Engineers' Handbook* by R. H. Perry and C. H. Chilton, and *A Dictionary of Mining, Mineral, and Related Terms* published in 1968 by the U.S. Department of the Interior.

Å – Angstrom unit, a unit of length equal to 10^{-10} meters or 10^{-4} microns, generally used as the unit for describing interatomic distances; as an example, the carbon atoms in diamond are 1.5 Å apart.

absorption – the dissolution of a gas in a liquid.

adiabatic – any process where heat is neither given off nor absorbed.

adsorption – the physical and chemical adherence of a gas to the surface of a solid.

anthracite coal – any coal containing 86 to 98 percent fixed carbon, on a dry, mineral-matter-free basis.

aromatic hydrocarbon – an unsaturated cyclic hydrocarbon containing one or more six-carbon rings.

ash – theoretically, the inorganic salts contained in coal; practically, the residue from the combustion of dried coal that has been burned at 1,380° F.

bituminous coal – a broad class of coals containing 46 to 86 percent fixed carbon and 20 to 40 percent volatile matter.

blow down – the removal of liquids from a process vessel by the application of pressure.

bottoming cycle – the lower temperature thermodynamic power cycle of a combined-cycle system.

Btu – British thermal unit, the quantity of energy required to raise the temperature of one pound of water one degree Fahrenheit.

caking – the softening and agglomeration of coal as a result of the application of heat.

calcine – to heat a solid to a high temperature to cause the decomposition of hydrates and carbonates.

char – the solid residue from coal after the removal of moisture and volatile matter, i.e., essentially ash plus fixed carbon.

closed cycle – a thermodynamic power cycle in which the working fluid is recycled.

coal – a natural solid material consisting of amorphous elemental carbon with various amounts of organic and inorganic compounds.

coke – a solid consisting primarily of amorphous carbon having certain properties of strength, cell structure, and minimum impurities, and manufactured by the thermal decomposition of petroleum residues and certain types of coal.

coke breeze – coke particles smaller than 1/2 inch in size.

combined cycle – two sequential thermodynamic power conversion systems operating at different temperatures.

coupon – a polished metal strip used to measure the rate of corrosion of the metal in a specific gaseous or liquid environment.

cracking – the partial decomposition of high-molecular-weight organic compounds into lower-molecular-weight compounds, generally as a result of high temperatures.

cyclone separator – essentially a settling chamber to separate solid particles from a gas, in which gravitational acceleration is replaced by centrifugal acceleration.

dolomite – a mineral having the chemical formula $CaMg(CO_3)_2$, i.e., a carbonate of calcium and magnesium.

Dowtherm – trademark for a series of eutectic mixtures of diphenyl oxide and diphenyl used as high-temperature heat-transfer fluids.

economizer – a heat exchanger for recovering heat from flue gases and using it to heat feedwater or combustion air.

elutriation – the preferential removal of the small constituents of a mixture of solid particles by a stream of high-velocity gas.

endothermic – a process in which heat is absorbed.

enthalpy – a form of thermal energy defined as the sum of the internal energy of a system plus the product of the system's volume and pressure.

eutectic – that combination of two or more components which produces the lowest melting temperature.

exothermic – a process in which heat is liberated.

fixed bed – solid particles in intimate contact with fluid passing through them, but too slowly to cause fluidization.

fixed carbon – theoretically, the carbon content of coal which exists in the elemental state; practically, the difference between 100 percent and the sum of ash, moisture, and volatile matter percentages.

fluidization (dense phase) – the turbulent motion of solid particles in a fluid stream; the particles are close enough as to interact and give the appearance of a boiling liquid.

fluidization (entrained) – solid particles transported by a high-velocity fluid stream with little or no solid interaction.

freeboard – the space in a fluidized-bed reaction between the top of the bed and the top of the reactor.

free swelling index – a standard test that indicates the caking characteristics of coal when burned as a fuel.

gasification of coal – the conversion of solid coal into a gaseous form by any of a variety of chemical processes.

high-Btu gas – a gas, largely methane, having a heating value of 900 to 1,000 Btu per cubic foot, which approaches the value for natural gas.

high heating value (HHV) – the heat liberated during a combustion process in which the product water vapor is condensed to a liquid.

hydrocracking – the combination of cracking and hydrogenation of organic compounds.

hydrotreating – a process involving the reaction of hydrogen with hydrocarbon mixtures for the removal of such impurities as oxygen, nitrogen, and sulfur.

ideal gas – any gas whose equation of state is expressed by the ideal gas law, namely $PV=RT$ where P is the pressure, V is the volume of one mole, R is the gas constant, and T is the absolute temperature.

ignition temperature – the minimum temperature necessary to initiate self-sustained combustion of a substance.

lignite – a low rank of coal between peat and subbituminous.

limestone – a sedimentary rock composed mostly of calcium carbonate ($CaCO_3$) and possibly some magnesium carbonate ($MgCO_3$).

liquefied petroleum gas (LPG) – those hydrocarbons that have a vapor pressure (at 70° F) slightly above atmospheric (such as propane and butane); kept in liquid form under a pressure higher than 1 atm.

lock hopper – a mechanical device that permits the introduction of a solid into an environment of different pressure.

low-Btu gas – a gas having a heating value of 150 to 350 Btu per cubic foot; when made from coal, water, and air, it contains varying quantities of carbon monoxide, carbon dioxide, nitrogen, hydrogen, and methane.

methanation – the production of methane (CH_4) from a mixture of carbon monoxide and hydrogen.

micron – a unit of length equal to one millionth of a meter.

noncoking – a coal that does not form coke under normal coking conditions.

olefinic hydrocarbon – a class of unsaturated hydrocarbons containing one or more double bonds and having the general chemical formula C_nH_{2n}.

open cycle – a thermodynamic power cycle in which the working fluid passes through the system only once and is then exhausted to the atmosphere.

perfect gas – see ideal gas.

pilot plant – a chemical process plant containing all the processes of a commercial unit, but on a smaller scale, for the purpose of studying the process.

prilling tower – a tower that produces small solid agglomerates by spraying a liquid solution in the top and blowing air up from the bottom.

process development unit – a laboratory-sized system used to study the effects of process variables on performance.

proximate analysis – analysis of coal based on the percentages of moisture, volatile matter, fixed carbon, and ash.

pyrolysis – thermal decomposition of organic compounds in the absence of oxygen.

refractory – a material capable of withstanding extremely high temperatures and having relatively low thermal conductivities.

saturated hydrocarbon – a hydrocarbon in which all bonds are single covalent bonds and none are double or triple bonds.

sensible heat – that heat which results in only the elevation of the temperature of a substance with no phase changes.

sintering – the agglomeration of solids at temperatures below their melting point, usually as a consequence of heat and pressure.

slag – a molten mixture of various metallic oxides and salts.

slurry – a suspension of pulverized solid in a liquid.

space velocity – the volume of a fluid (usually measured at standard conditions) passing through a unit volume in a unit time; units are in reciprocal time.

standard cubic foot (SCF) – the volume of a gas at standard conditions of temperature and pressure. The

American Gas Association uses moisture-free gas at 60° F and 30 inches of mercury (1.0037 atm) as its standard conditions. The pressure standard is not universal in the gas industry; 14.7 psia (1.000 atm) and 14.4 psia (0.980 atm) are also used. The scientific community uses 32° F and 1 atm as standard conditions.

stoichiometry – the definite proportions in which molecules react chemically to form new molecules.

stripping – the removal of the more volatile components from a liquid mixture of compounds.

subbituminous coal – the rank of coal between bituminous and lignite, classified by ASTM as having a range of heating values between 8,300 and 11,000 Btu per pound on a moist mineral-matter-free basis.

superficial velocity – the linear velocity of a fluid flowing through a bed of solid particles calculated as though the particles were not present.

superheater – a heat exchanger which adds heat to the saturated steam leaving a boiler.

synthesis gas – a mixture of hydrogen and carbon monoxide which can be reacted to synthesize a hydrocarbon.

tar (coal) – a dark brown or black, viscous, combustible liquid formed by the destructive distillation of coal.

topping cycle – the higher temperature thermodynamic power cycle of a combined-cycle system.

turned down – the reduction of reactor flow rates to a fluidized-bed reaction vessel.

ultimate analysis – the analysis of coal based on the percentages of chemical elements.

volatile matter – those constituents of coal, exclusive of moisture, that are liberated from a sample when heated to 1,750° F (for 7 minutes) in the absence of oxygen.

water gas shift – the reaction between water vapor and carbon monoxide to produce hydrogen and carbon dioxide or the reverse: $CO + H_2O \rightleftarrows H_2 + CO_2$.