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**STUDY OF CATALYTIC EFFECTS OF MINERAL MATTER LEVEL ON COAL
REACTIVITY**

By

Nestor J. Mazzocco
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Donald Krastman

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**Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania**

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ON COAL REACTIVITY

By

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Table of Contents

Introduction	1
Process Flow Description	3
Equipment Design	4
I. High Pressure Components	4
II. Low Pressure Components	8
Description of Plant Feeds	9
1. Coal Feedstock	9
2. Pyrite Concentrate Disposable Catalyst	11
Experimental Procedure	15
1. Operating Conditions	15
2. PDU Control	16
3. Centrifuge Operation	17
4. Data Acquisition	18
Analysis	18
1. Gases	18
2. Solids and Liquids	19
3. Data Reduction	21
Results and Discussion	23
1. Pressure Series	25
2. Coal Mineral Effects	26
3. Catalyst Addition Series	28
Conclusions	32
Future Work	32
References	34

Tables

1.	Analysis of run-of-mine, "washed", and "rejects" fractions of Kentucky #11 hvAb coal.	37
2.	Elemental and mineral analysis of run-of-mine, "washed", and "rejects" fractions of Kentucky #11 coal	38
3.	Analysis of the feed pyrite concentrate	40
4.	Process conditions for Western Kentucky coal (SEAM #11) liquefaction in 400-lb/day unit	41
5.	Feed slurry composition for Western Kentucky #11 coal liquefaction in 400-lb/day unit	42
6.	Elemental forcing used to obtain forcing of the material balance	43
7.	Product yields for Western Kentucky coal (seam #11) liquefaction in 400-lb/day unit--elementally balanced yields based on MAF coal	44
8.	Product yields for Western Kentucky coal (seam #11) liquefaction in 400-lb/day unit--elementally balanced yields based on MAF coal	45
9.	Gas yields for Western Kentucky #11 coal liquefaction in 400-lb/day unit--elementally balanced yields based on MAF coal	46
10.	Gas yields for Western Kentucky #11 coal liquefaction in 400-lb/day unit--elementally balanced yields based on MAF coal	47
11.	PETC batch autoclave tests, product analysis	48
12.	Maceral composition of Western Kentucky #11 run-of-mine and "washed" coals	49
13.	Atomic percentage Fe in raw product oil determined by Mossbauer Spectroscopy and X-ray diffraction	50
14.	Production rate of product streams for Western Kentucky #11 coal liquefaction in 400-lb/day unit based on wt% of MF coal	51

Tables cont.

15.	Centrifuge liquid product component composition for Western Kentucky #11 coal liquefaction in 400-lb/day unit	52
16.	Centrifuge liquid product elemental composition for Western Kentucky #11 coal liquefaction in 400-lb/day unit	53
17.	Process conditions for washed Blacksville #1 coal liquefaction with added pyrite (75 μ)	54
18.	Feed slurry composition for Blacksville #1 coal liquefaction with catalyst addition	55
19.	Product yields for washed Blacksville #1 coal liquefaction with added pyrite (75 μ)	56
20.	Gas yields for washed Blacksville #1 coal liquefaction with added pyrite (75 μ)	57
21.	Analysis of feed coal Blacksville #1 (washed)	58

Figures

1.	Simplified schematic of 400-lb coal/day liquefaction unit	59
2.	Reactor tube assembly end fixtures for 400-lb/day hydrogenation of coal to liquid unit	60
3.	Thermocouple control plan for 400-lb/day liquefaction unit	61
4.	Viscosity as a function of run time (all six conditions)	62
5.	Effect of viscosity from hydrogenation of West Kentucky #11 coal with solvent recycle (Batch autoclave)	63
6.	Viscosity of centrifuged product oil as a function of total iron concentration in the slurry feed	64
7.	Total distillate and SRC yields as a function of total iron concentration in the slurry feed	65
8.	Total hydrocarbon gas and organic pyridine insolubles yield as a function of total iron concentration in the feed slurry	66

ABSTRACT

Coal liquefaction experiments using a 400-lb/day bubble-column reactor tested the catalytic effects of added mineral matter level on coal conversion, desulfurization, and distillate yields in continuous operation under recycle conditions, with specific emphasis on the use of a disposable pyrite catalyst indigenous to the feed coal. Western Kentucky #11 run-of-mine (ROM) and "washed" coals were used as feedstocks to determine the effects of levels of mineral matter, specifically iron compounds. Liquefaction reactivity as characterized by total distillate yield was lower for "washed" coal, which contained less mineral matter. Liquefaction reactivity was regained when pyrite concentrate was added as a disposable catalyst to the "washed" coal feed in sufficient quantity to match the feed iron concentration of the run-of-mine coal liquefaction test run.

Introduction

One project at the Pittsburgh Energy Technology Center (PETC) is devoted to the evaluation and development of inexpensive disposable catalysts (mineral matter in coal or other naturally occurring ores) for coal liquefaction. Such catalysts can result in improved product yields and quality, reduced severity of operation, or broadening of the feedstock base. The primary application of these process improvements will be in the SRC-II process.

It has been reported that the inherent mineral matter in coal has a definite catalytic effect on its behavior during liquefaction.¹⁻⁵ Iron, occurring principally as iron pyrite (FeS_2), is thought to be the primary catalytic agent in the mineral matter in many U. S. coals. The catalytically active form of iron in coal lique-

faction has not been identified conclusively, but it is thought to be a pyrrhotite. Iron pyrite, introduced with coal, is reduced under coal liquefaction conditions to pyrrhotites of varying stoichiometry. Some factors affecting its composition include temperature, pressure, and gas composition in the reactor.⁶ The stoichiometry of the formed pyrrhotites has not been definitely related to variations in observed catalytic activity.

Except for the work at the Merriam Laboratory of the Pittsburgh & Midway Coal Mining Company,⁷ most previous liquefaction studies with pyrite were performed in batch autoclaves. The objective of experimental series FB-65 at PETC was to establish the catalytic effect of mineral matter level on coal conversion, desulfurization, and distillate yield in continuous operation under recycle conditions, with specific emphasis on the use of a disposable pyrite catalyst indigenous to the feed coal. Western Kentucky #11 run-of-mine (ROM) and "washed" coals from the same source were used as feedstock to determine the effects of the level of the mineral matter, specifically iron compounds.

This report presents the results from a study consisting of three continuous runs made with run-of-mine feed coal, high in mineral matter content, at three different pressure levels: 3,000, 2,500, and 2,000 psig (20.6, 17.2, and 13.8 MPa); and of three continuous runs made at 2,000 psig (13.8 MPa), feeding "washed" feed coal, low in mineral matter content, with catalyst addition to give three different iron levels: 1.3%, 2.3%, and 4.7% on a moisture-free (MF) basis.

In summary, the "washed" feed coal demonstrated a lower reactivity at similar operating conditions than that observed for the ROM feed coal. Operations in a disposable catalyst mode with addition of formerly indigenous iron pyrite

to the "washed" feed coal duplicated the reactivity obtained with the ROM feed coal when sufficient catalyst was added to the "washed" coal to match the iron level in the ROM coal.

Process Flow Description

Though described previously,⁸ a simplified flow diagram of the unit as used in this work is given in Figure 1. Powdered coal, process derived recycle oil, and catalyst are mixed in the feed system; and the resulting feed slurry, together with hydrogen, is passed concurrently through the preheater and reactor assembly. The preheater and reactor assembly consists of five 27.9-mm ID x 4.42-m long empty tubes connected in series. Products exiting the reactor enter a gas disengager, where the primary vapor/liquid separation step is accomplished at system pressure.

The liquid phase (gross liquid product) is depressurized to atmospheric pressure, and then centrifuged to remove solids consisting of mineral matter, catalyst, and unconverted coal substance. Part of the centrifuged liquid product is recycled as slurry feed vehicle, while the remainder is withdrawn as net product oil.

Gases exiting the disengager are contacted in a pressurized scrubber with a caustic solution to remove H_2S , H_2O , and condensable hydrocarbon vapors. The purified gas, consisting of unconsumed H_2 and a small amount of C_1 - C_4 hydrocarbons, is recycled to the preheater, where it is reinjected along with additional hydrogen. A purge stream out of the recycle loop maintains hydrogen purity.

Equipment Design

I. High-Pressure Components

1. Preheater and Reactor Assembly

The preheater and reactor assembly consists of five 1.1-in. ID by 14.5-ft long (27.9 mm ID x 4.42 m) empty tubes connected in series. High-pressure 304 SS (Stainless Steel) tubing, 5/16-in. ID by 5/8-in. OD (7.94mm ID x 15.9mm OD), connects the five tubes to provide upflow of the process fluid through each tube. The preheater and reactor tubes are fabricated from seamless stainless steel schedule double X, conforming to ASTM specification A-312, type 316 SS with 0.400-in. (10.16mm) wall thickness. Each tube is sealed on both ends with a high-pressure machine-threaded SS plug that thrusts on an expendable gasket that seals on the tube head seat, as indicated in Figure 2. The free volume of each tube is 0.096 ft^3 ($2.72 \times 10^{-3} \text{ m}^3$). The preheater and reactor assembly is designed for a pressure of 5,000 psig (34.5 MPa) at 525°C . All assemblies are hydrostatically pressure-tested at room temperature to 12,000 psig (82.7 MPa) before use. All of the end seals extend at least 18 inches (457mm) outside the heating furnaces and are not subjected to full operating temperatures.

2. High-Pressure Liquid Product Oil Receiver

This vessel, fabricated from a forged tube of austenitic stainless steel, American Iron and Steel Institute (AISI) Type 347, is designed for a pressure of 5,000 psig (34.5 MPa) and a temperature of 525°C . The inside length is 10 ft (3.05m), the bore 3 in. (76.2mm), with a wall thickness of 1.50 in. (38.1mm).

The free volume is 0.49 ft^3 (0.014 m^3). Collars, 4-in. (101.6mm) long by 1-in. (25.4mm) thick, were shrunk to the ends to reinforce the closures.

The monel sealing ring is compressed between the vessel wall and a threaded nut. After an initial seal is made by tightening the flat nut on the head, a final seal is obtained by the force of the internal pressure on the surface of the head, which is transmitted to the sealing ring. Galling of sealing surfaces and threads is reduced by using hardened (300-325 Brinell) materials where possible.

The top head is fitted with an internal cooling coil fabricated of high-pressure tubing through which cooling water is passed to condense low-boiling material in the product oil. In addition to the internal coil, the outside of the vessel is wrapped with a cooling water coil to provide cooling for the upper 6 ft (1.829m). The product oil and gases enter the vessel through an 8-ft long, 0.5-in. ID (2.43m x 12.7mm ID) dip leg in the top head. Gases exit through an overhead port provided with a reverse-flow check valve. The product oil is discharged into low-pressure receivers by a timer-activated liquid letdown valve.

3. High-Pressure Caustic Scrub Receiver

This vessel is identical in construction to the high-pressure liquid product oil receiver except that there are no internal or external cooling coils. A series of concentric baffles attached to the internal dip leg outside wall are used to impinge entrained mists from the exiting gases. The cleaned gases also pass through a demister element at the top before exiting to the recycle compressor and gas loop bleed-off. A timer-activated letdown valve is used to discharge the caustic scrub solution and condensed light oil into low-pressure receivers.

4. Recycle Gas Preheater

This assembly consists of an empty helical coil 7-in. (177.8mm) in diameter, of 5/16-in. ID by 5/8-in. (7.94mm ID x 15.9mm OD) high-pressure 304 SS tubing. The 60-ft (18.3m) long coil is immersed in an internally heat-controlled steel tank containing approximately 1,000 lb (453.6 kg) of molten lead. The free volume of this coil assembly is 0.03 ft^3 ($9.0 \times 10^{-4} \text{ m}^3$). A typical operating temperature for the lead bath is 450°C .

5. Heating and Temperature Control Systems of High-Pressure Vessels and Lines

A schematic drawing of the plant heating and control systems is presented in Figure 3. Both preheaters, the reactor, and the high-pressure product oil receiver are heated by sectional electrical furnaces. Heat is supplied to these components by sixteen separately controlled 440-volt, 3-phase electrical furnaces. Chromel alumel thermocouples firmly secured to the vessel outer walls are used as sensors for potentiometric controllers to independently control furnace sections.

The first three tubes of the preheater/reactor assembly form a bundle that is contained as a unit within six separately controlled, stacked furnace sections. Each 30-in. (762mm) long section is individually controlled by skin thermocouples attached to the third tube. Temperatures inside the three-tube preheater are measured by six internal thermocouples with two thermocouples inserted 0.5-in. (12.7mm) into the side of each tube.

The last two tubes of the preheater/reactor assembly are also heated as a unit within six separately controlled furnace sections. Each 30-in. (762mm)

long section is individually controlled by skin thermocouples attached to the first tube of the reactor. Temperatures inside the two-tube reactor assembly are measured with six internal thermocouples, with three thermocouples inserted 0.5 in. (12.7mm) inside each tube.

The temperatures inside the high-pressure product oil receiver are monitored through four internal, equally spaced thermocouples enclosed in the thermocouple well fixed to the vessel top head.

The temperatures of the recycle gas preheater are measured by two equally spaced thermocouples enclosed in a thermocouple well located in the molten lead bath, and by an internal thermocouple located at the gas outlet.

The transfer lines are individually heated with 220-volt, single-phase line tracers. Transfer line heater temperatures are measured and controlled with individual skin thermocouples

6. High-Pressure Compressors and Pumps

The make-up hydrogen compressors are reciprocating horizontal five-stage units rated at 15,000 psig (103 MPa) with a maximum capacity of 750 std. cfh ($21.24\text{m}^3/\text{hr}$), 60°F, 14.69 psia (15.6°C, 0.101 MPa). Each machine is of the two-shaft or tandem type, with the first, second, and fourth stages on one shaft and the third and fifth on the other. The output is controlled by manual adjustment of a variable-speed drive.

The recycle gas compressor is a reciprocating piston-type gas circulation pump. The machine is of horizontal design and operates at constant speed with

a variable output gas recycle loop controller. The unit is rated at 5,000 psig (34.5 MPa) with maximum capacity at 5,500 scfh (155.7m³/hr).

Duplex positive displacement piston pumps rated at 7,500 psig (51.7 MPa), having variable capacities of up to 100 lbs/hr (45.4 kg/hr) for coal oil slurry and up to 15 lbs/hr (6.8 kg/hr) for caustic scrub solution, are used to inject the liquids and slurries into the plant. A detailed description of the high-pressure plant slurry feed system has already been published.⁹

II. Low-Pressure Vessels and Components

1. Low-Pressure Vessels

The paste feed tanks and product oil receivers are mounted both on load weigh cells with digital readouts and on mechanical weigh scales. Tanks are connected to the fixed piping of the plant by short lengths of flexible tubing. These steam-jacketed tanks are equipped with stirrers. Contents of the tanks are also circulated by rotating, cavity-type Moyno* pumps to insure homogenization and suspension of solids. The product oil, vehicle oil surge, and paste feed tanks all have a capacity of 30 gallons (113.5 x 10⁻³ m³). All tanks are closed and operate with a low purge of inert gas. All of the piping and valves are steam-traced and insulated to maintain a 100°C temperature.

A trap is provided on the product tanks to collect oil and water condensed from gases exiting the product tanks.

* Disclaimer: Use of brand names facilitates understanding and does not necessarily imply endorsement by the U. S. Department of Energy.

The caustic scrub liquid receivers, 20-gallon ($75.7 \times 10^{-3} \text{ m}^3$) tanks with sight gages, are mounted on weigh scales and are normally not heated.

2. Centrifuge

A batch-type centrifuge is used to remove solids, such as catalyst, mineral matter, and unconverted organic material, from the gross liquid product. The centrifuge system consists of a holding tank, a circulation pump, and a rotating centrifuge bowl. Product oil is continuously circulated from the holding tank to the bottom of the rotating centrifuge bowl. Filtrate is discharged from the top of the bowl back to the holding tank. Solids are deposited as a cake against the wall of the bowl. The dimensions of the bowl are 4.5-in. ID by 30-in. long (114.3mm ID x 762mm). It rotates at 15,000 rpm, which is equivalent to exerting a force of 13,000 times gravity on the solids.

3. Gas Meters

All of the gas to and from the plant is measured at approximately atmospheric pressure and ambient temperature by bellow-type integrating dry-test meters. The recycle gas flow is measured at high pressure by an armored rotameter.

Description of Plant Feeds

1. Coal Feedstock

Western Kentucky #11 coal from the Homestead Mine, Ohio County, Kentucky, was specially prepared using magnetite heavy media techniques to yield three.

fractions -- run-of-mine (ROM); "washed", and "rejects". Analyses of the fractions are shown in Tables 1 and 2. Although a more detailed description of the equipment and procedures utilized to obtain these fractions is available,¹⁰ a summary is given here.

The coal was homogenized and separated into two piles. One pile was used as the ROM coal, while the remaining coal was used as feedstock for the coal washing operation. After having been crushed to pass through 0.75-in. (14.1mm) screen, the feedstock was water washed through a 28 mesh (0.589mm) sieve to generate two coal streams, a plus 28 mesh (0.589mm) fraction and a minus 28 mesh fraction.

The plus 28 mesh (0.589mm) crushed coal fraction was fed to a heavy media (magnetite medium with specific gravity 1.38) cyclone to obtain a "reject" and a "washed" fraction. Magnetite was separated from the "reject" and "washed" fractions by water washing over 28 mesh (0.589mm) sieve bends and rinse screens. Magnetite removal from the "washed" stream was maximized by contacting the stream with additional spray water over baffles.

The minus 28 mesh (0.589mm) crushed coal fraction entered a thickening cyclone before being fed to a froth flotation circuit. A 4:1 kerosene:methyl-isobutyl carbinol mixture was used as a conditioning flotation reagent. Flotation circuit "rejects" were settled and dried. Product from the flotation circuit was filtered, dewatered, and dried.

Products from both the plus 28 mesh (0.589mm) coal cleaning and the minus 28 mesh (0.589mm) coal cleaning were combined and homogenized as the "washed"

feed coal. "Reject" streams from both coal cleaning operations were combined and homogenized as the "reject" coal fraction. Overall yield of the "washed" coal from the purchased coal was 55%. Both the run-of-mine and the "washed" coal fractions were ground to Plant Consist (P.C.) size (70%-200 mesh, 0.074mm) and stored in polyethylene lined steel drums, with approximately 250 to 300 lbs (113.4 kg to 136.1 kg) of coal in each drum. The "reject" fraction was also stored in polyethylene lined steel drums.

2. Pyrite Concentrate Disposable Catalyst

An indigenous pyrite concentrate was prepared by Bituminous Coal Research, Inc. from the "reject" coal fraction and then ground to P.C. size so that it could be mixed with the feed coal for slurry preparation. To prepare the pyrite concentrate, the "reject" coal fraction was first dried and sized. Representative samples of each fraction were obtained and analyzed, and the analyses appear in Table A. The majority of the material was 3/8-in. by 6 mesh (9.52mm x 3.3mm).

TABLE A. - Analysis of Plus 6 Mesh and Minus 6 Mesh Products

	Moisture, <u>wt %</u>	Ash, <u>wt %</u>	Total Sulfur, <u>wt %</u>	Calculated Pyrite <u>wt %</u>
Plus 6 Mesh (3.3mm)	6.42	28.4	12.90	24.1
Minus 6 Mesh (3.3mm)	7.48	28.8	7.93	14.8

Both fractions were then combined and run on the Deister table, where a pyrite-rich fraction was obtained; its analysis appears in Table B.

TABLE B. - Analysis of the Pyrite-Rich Fraction

Moisture, <u>wt %</u>	Ash <u>wt %</u>	Total Sulfur, <u>wt %</u>	Calculated Pyrite <u>wt %</u>
0.90	65.6	40.9	76.5

Pulverization of the pyrite fraction was then started. The initial pulverizing unit tried was a Model B Pulva-Sizer, a swing hammer mill with a capacity of 3,600 pounds (1.63×10^3 kg) of coal per hour. Approximately one third of the pyrite-rich product was processed through this unit, utilizing a herringbone screen with an 0.022-in. (0.588mm) wide slot. The processing was exceedingly slow, and the unit continually ran hot because of the hardness of the material being processed. Pyrite has an MOHS' scale of hardness number of 6.5. The pulverized product size consist is shown in Table C.

TABLE C - Size Distribution of Pulverized Product Using Model B Pulva-Sizer

<u>Size</u>	<u>Weight, %</u>	<u>Cumulative weight, %</u>
Plus 50 Mesh (0.29mm)	8.2	8.2
50 x 100 Mesh (0.29mm x 0.147mm)	23.4	31.6
100 x 200 Mesh (0.147mm x 0.074mm)	22.0	53.6
Minus 200 Mesh (0.074mm)	46.4	100.0

The next unit tried was a smaller swing hammer mill utilizing a herringbone screen with an 0.014-in. (0.356mm) wide slot. This unit was a Mikro-Pulverizer, Type 1SH, Serial No. 62J689. Throughput increased drastically with no overheating of the unit. After an initial sample obtained early in the test proved to be satisfactory, the processing was continued, with a second sample being obtained near the end of the run. Table D shows the screen analysis of both samples.

TABLE D. - Size Distribution of the Pulverized Pyrite Concentrate using
Mikro-Pulverizer, Type 1SH

<u>Size</u>	<u>Cumulative</u> <u>Weight, %</u>	<u>Cumulative</u> <u>Weight, %</u>	<u>Cumulative</u> <u>Weight, %</u>	<u>Cumulative</u> <u>Weight, %</u>
Plus 50 Mesh (0.29mm)	0.5	0.5	1.0	1.0
50 x 100 Mesh (0.29mm x 0.147mm)	10.5	11.0	10.4	11.4
100 x 200 Mesh (0.147mm x 0.074mm)	18.2	29.2	17.4	28.8
Minus 200 Mesh (0.074mm)	70.8	100.0	71.2	100.0

Desliming of the concentrate using a hydroclassifier did not significantly change the analysis of the concentrate (Table E) from the analysis obtained of the 3/8-in. by zero (0) size (9.52mm x 0) from the Deister table (Table B).

TABLE E. - B.C.R. Analysis of Shipped Deslimed Pyrite Concentrate

<u>Moisture,</u> <u>wt %</u>	<u>Ash</u> <u>wt %</u>	<u>Total Sulfur,</u> <u>wt %</u>	<u>Calculated Pyrite</u> <u>wt %</u>
0.78	65.9	40.0	74.8

Analyses of the feed pyrite concentrate used as catalyst are shown in Table 3.

3. Caustic Scrub Solution

A 4 wt % aqueous solution of C.P. grade sodium hydroxide is mixed with distilled water to prepare the caustic scrub solution. It is charged to a large

supply surge tank as needed. Distilled water is used to minimize introduction of chlorine to the plant.

4. Gases

Commercial electrolytic hydrogen, delivered by tube trailer and vented into a low-pressure large gas holder, is the source of supply for the make-up hydrogen. Commercial nitrogen, delivered by tanker trucks, is vaporized as needed into a low-pressure gas receiver and is used for the inert supply.

Experimental Procedures

1. Operating Conditions

Test series FB-65 consisted of two separate operating periods. Conditions for the two series are listed in Tables 4 and 5. The first series, designated FB-65B-3000, FB-65B-2500, and FB-65B-2000, used ROM coal and varied the pressure. The second series, designated FB-65A, FB-65DC, and FB-65DCL, used "washed" coal and varied the catalyst addition level. The plant was disassembled, flushed, cleaned, and inspected between the two operating periods. This "turn around" process insured that all of the plant components were cleaned of any residual mineral matter or carbonaceous material that could have influenced the second operating period.

Since it was known from previous batch autoclave tests that the "washed" coal is less reactive than the ROM coal, three levels of pressure -- 3,000, 2,500, and 2,000 psig (20.6, 17.2, and 13.8 MPa) -- were run with the run-of-mine coal

to serve as potential base cases. If the 2,000 psig (13.8 MPa) test with the "washed" coal had proved to be inoperable, the pressure would have been increased until satisfactory operation was achieved. It turned out, however, that no difficulties were encountered at 2,000 psig (13.8 MPa) for FB-65A in feeding the low mineral matter "washed" coal. Therefore, direct comparison of coal reactivity at the different mineral levels can be made at 2,000 psig (13.8 MPa). The sequence of pressure level runs was from highest to lowest pressure. In order to maintain a constant superficial gas velocity of 0.71 ft/s (0.22m/s) through the reactor, the recycle rate was reduced when the pressure was decreased.

In the catalyst addition runs, the catalyst was first mixed with the feed coal, and the resulting mixture was slurried in recycle oil. The sequence of runs for the "washed" coal feed with catalyst addition was a) no catalyst addition, FB-65A; b) 10.0 wt % catalyst based on MF coal feed, FB-65DC; and c) 2.8 wt % catalyst, FB-65DCL. The 10.0 wt % catalyst addition matched the iron level in the run-of-mine coal. The series was voluntarily terminated at the conclusion of the third condition.

2. PDU Control

Among the product oil properties routinely determined, kinematic viscosity has been found to be a very sensitive indicator of product quality and process stability. Viscosity has been chosen as the primary parameter to be monitored daily to determine when steady state, or "line-out," is achieved for a specific set of plant conditions. Results from this daily analysis of the product oil for viscosity are plotted as a function of time for each set of plant conditions in Figure 4. Approximately 150 hours of continuous operation at each condition

were required to obtain a steady-state product. This steady-state condition was inferred when product oil kinematic viscosity approached a lined-out value. Analysis of material balance period products confirmed the fact that the unit had achieved a steady state.

Oil inventory level in the feed tank, plant, product oil tanks, and vehicle oil tank was maintained at a minimum to reduce the line-out time. The level varied between 270 and 310 pounds (117.7-135.1 kg). Oil in excess of the minimum inventory was drummed as centrifuged product oil. Using an average inventory from above and a typical oil production rate, a replacement time of about 65 hours was calculated. Assuming a perfectly stirred tank model, the 150 hours of line-out represent 2.3 inventory changes or 90% oil displacement.

Previous experience had indicated that product oil viscosity could be held at operable values by a temperature gradient along the high-pressure liquid product oil receiver. The internal temperature of the upper 6 ft (1.83m) of the vessel was maintained at 100°C, while the lower 4 ft (1.22m) was controlled at 125°C.

3. Centrifuge Operation

Product oil from each consecutive "batch" period was centrifuged at ambient pressure. A steady purge of inert gas through the centrifuge tanks minimized product degradation due to air contact. The centrifuge was operated at 100°C in order to reduce the product oil viscosity and thus increase the efficiency of the separation. A clean bowl was used for each of two consecutive one-half hour cycles through the centrifuge. After sampling the cake for analysis, the excess was either stored in plastic-lined steel drums for future test runs or discarded.

The major portion of the filtrate was used as the vehicle oil to slurry the feed coal, while the rest was drummed out as net product oil.

4. Data Acquisition

In general, crucial operating parameters were monitored continuously. In addition, the following time frame was used for recording data: a) every half hour -- slurry feed rates, product oil rates, and scrub liquid (caustic) rates; b) every hour -- gas rates; c) every two hours -- temperatures and pressures; and d) every eight hours -- current flows to electrically traced lines and sectional heaters.

Consecutive "batch" periods of 100 lb (45.4 kg) of feed slurry each were taken as unit "balance" periods. All sampling of solids, liquids, and gases entering and exiting the plant was coordinated with these "batch" periods. Sampling was routinely carried out, though only the samples taken during the "line-out" period, as determined by the daily control analysis, were submitted for analysis. Samples from at least twelve separate consecutive "balance" periods after line-out constituted the source of the information obtained for each run condition.

Analysis

1. Gases

Feed hydrogen is sampled at the low-pressure gas holder. The gas is metered before being fed to the make-up compressor.

The recycle gas stream is sampled at a high-pressure sample connection prior to contact with scrub solution. This gas sample is bled to a glass sample bottle through a double-block throttle valve system.

The bleed gas stream is metered after depressurization and sampled through a sample connection into a glass sample bottle.

Gases dissolved in the liquid products are metered before going to flare but not sampled.

All sampled gases are submitted for GC analysis for determination of H_2 , C_1 to C_4 hydrocarbon gases, carbon oxides, H_2S , and nitrogen.

2. Solids and Liquids

Ultimate analyses (carbon, hydrogen, nitrogen, and total sulfur), sulfur forms, ash, iron, and moisture are routinely obtained for the feed coal and the pyrite concentrate disposable catalyst. Oxygen is determined by difference. Major elements in feed coals and catalysts are measured by atomic absorption spectrophotometry.

The condensate samples are physically separated into organic and aqueous phases, weighed, and then submitted separately for analysis. The light oil phase determinations consist of ultimate analyses and distillation analyses, while for the water (caustic) phase, total carbon, inorganic carbon, and sulfur are measured. Condensed vapors from the product tank are also separated into an oil and water phase. The oil phase is analyzed in the same manner as light oil obtained from the spent caustic stream. The water phase is submitted for an ultimate analysis.

Feed slurry samples are submitted for several determinations: solvent analyses, ash, ultimate analyses, forms of sulfur, total iron, and iron forms such as HCl soluble Fe and HNO₃ soluble Fe, as well as specific gravity.

The uncentrifuged and centrifuged product oil analyses are the same as that for feed slurry, except that viscosity, Btu content, and distillation analyses are also required.

After the centrifuged filter cake is carefully sampled from the bowl, solvent, ash, and ultimate analyses are performed. The sulfur and iron forms are also determined.

The procedures used in the solvent analysis have been described previously in other publications.¹¹ The procedure used to obtain weight percent pyridine insolubles is referenced by Pittsburg & Midway Laboratory number, P&M-F129-76.¹²

The analytical procedures used in the distillations to characterize the coal liquefaction products are the D-1160-77 ASTM method¹³ and the D-86 ASTM method.¹⁴ The D-1160-77 covers the determination at reduced pressures of the boiling temperature ranges of products which can be partially or completely vaporized at a maximum liquid temperature of 750°F (399°C) at pressures down to 1-mm Hg (133 Pa) absolute. The D-86 ASTM distillation is used for the light oil and organic condensates.

The sulfur forms analysis covers the determination of the three commonly recognized forms of sulfur:¹⁵ sulfate sulfur, pyritic sulfur, and organic sulfur.

3. Data Reduction

A computer program is utilized to calculate a yield structure (product distribution) based on the elemental compositions, flow rates, and component compositions of the flow streams. Components are defined as any conveniently identifiable compounds, distillate fractions, or solvent fractions in the feed and product streams. Most components are handled in a straightforward manner. Several exceptions follow:

The computer program separates the mineral matter in the feed coal and catalyst into three fractions: an "inert" portion (silica, clay, etc.), iron, and sulfur associated with the iron (as in pyrite). The iron is accounted for separately in each stream because of its importance as catalyst. All of the sulfur, pyritic as well as organic, is treated as a portion of the organic feed, i.e., MAF coal (moisture and ash-free). This approach introduces little error, except when large amounts of catalyst are used. It does simplify the sulfur balance and also does not require a precise knowledge of the sulfur forms in the process streams or the source of the hydrogen sulfide product. The latter is assigned automatically to the MAF coal products.

Organic pyridine insoluble is defined as the pyridine insoluble portion of a stream minus the iron and "inert" mineral matter. The ashing procedure is assumed to convert all iron pyrite to Fe_2O_3 , and allowance is made for the uptake of oxygen during the ashing step when calculating mineral matter content. Organic oxygen is then determined by difference. Organic carbon in the product water (flush water plus make water) is assumed to be due to dissolved phenol ($\text{C}_6\text{H}_5\text{OH}$). This phenol is considered to be in the naphtha boiling range.

The yield of each component is calculated in the following manner: the gross sum of the rate of each component entering the unit is subtracted from the gross sum of the rate of each component leaving the unit, and the resulting value is divided by the MAF coal feed rate. Any organic pyridine insoluble part of the catalyst is also considered part of the MAF coal feed rate (as well as all sulfur as discussed above). The chemical hydrogen consumption is calculated as the net uptake of hydrogen by the coal, based upon the ultimate analysis of the products. This value includes hydrogen consumed by the catalyst in generating H_2S .

The program calculates a yield structure resulting from forcing elemental mass balance closure. The major effects of forcing the elemental closures are illustrated in Table 6.

Since several of the elemental closures are coupled, they cannot be forced independently. Three equations are solved simultaneously to decouple the closures on carbon, mineral matter (iron-free), and iron. This procedure adjusts the flow rate of centrifuged liquid product, the flow rate of residue, and the weight percent of iron in the residue.

An elemental balance on sulfur is achieved in one of two ways. If the sulfur in the product streams is greater than the sulfur in the feed streams, the weight percent sulfur in the residue is assumed to be in error and is decreased. If the sulfur in the feed streams is greater than the sulfur in the products streams, the typical situation, the weight percent of H_2S dissolved in the product water is increased. The elemental closure on nitrogen is forced by adjusting the weight percent of ammonia in the product water such that the sum of the elemental

nitrogen in minus the N_2 gas in the feed streams equals the elemental nitrogen out minus the N_2 out in the product streams. Three equations are solved simultaneously to decouple the closures on hydrogen, nitrogen, and oxygen. This procedure adjusts the flow rate of purge gas and feed gas, and the feed rate of caustic solution.

Results and Discussion

The results of both series of coal liquefaction runs are presented in Tables 4-10. Tables 4 and 5 list the operating conditions and compositions of the feed slurry, while Tables 7, 8, 9, and 10 give the complete product yield structure for each condition. The entries are essentially self-explanatory. It should be noted, though, that the nominal residence time and coal throughput were calculated using that portion of the preheater plus reactor volume above 400°C in temperature. This "active" volume was typically 0.013 m^3 (0.44 ft^3), whereas the actual volume of the preheater/reactor combination is 0.014 m^3 (0.48 ft^3). An estimate was also made of the gas holdup for this system, using the J. Hills correlations for bubble-column gas measurements.¹⁶ These correlations gave a total actual liquid residence time of 0.94 hours, calculated at run conditions for the portion of the preheater and reactor above 400°C .

Problems were encountered with the determination of pyridine insolubles in some of the products, especially at low concentrations. The preasphaltene yield was therefore estimated from spot sampling and results from the 1,000-lb/day continuous coal liquefaction unit with Homestead coal at similar conditions.

Reaction temperatures listed in Table 4 are averages of eight internal thermocouple readings.

Some discussion of hydrodynamics as it is believed to apply to the 400-lb/day bubble column reactor is in order before presenting specific details of the liquefaction results. Although the fluid dynamics in a coal liquefaction reactor is in reality a three-phase flow problem, as a first approximation it is assumed that the slurry behaves as a homogeneous phase. Several flow pattern maps have been reported in the literature for two-phase vertical upflow in empty tubes at various gas and liquid flow conditions and column dimensions.^{17,18,19}

A particularly relevant investigation by Oshinowo and Charles¹⁷ characterized flow patterns in a 25.4 mm ID by 7.62 m long empty tube for air-water and air-glycerol solutions. Their correlation of flow patterns was found to be applicable to other published studies involving organic liquids such as heptane and heavy oils. From the flow conditions in our study, it appears that operation falls into the slug flow regime, described as gas flow in large, well-defined, bullet-shaped bubbles.

In this regime, knowledge of the extent of liquid dispersion, or backmixing, is helpful in evaluating the performance of the reactor. A liquid dispersion coefficient of $3.8 \times 10^6 \text{ m}^2/\text{s}$ was calculated according to the procedure of Baird and Rice (1975).²⁰ This dispersion coefficient, together with typical run conditions, was used to estimate a Peclet number of 25. If dispersion is small and a simplified dispersion model is applicable, as in the present case, then the relationship presented by Levenspiel (1962)²¹ gives 13 for an equivalent number of stirred tanks. This calculation indicates that the reactor operation approached the plug flow limit.

1. Pressure Series

The first series of tests with run-of-mine Western Kentucky coal (FB-65B-2000, FB-65B-2500, and FB-65B-3000) investigated the impact of operating pressure from 2,000 to 3,000 psig (13.8 to 20.6 MPa) on the product distribution. Excellent liquefaction activity was observed at all three pressures with this "active" coal, containing 17.2% ash. Total distillation yields ($C_5 \times 850^\circ\text{F}$ (454°C)) of up to 45 wt % MAF coal were obtained with only 10% C_1 and C_4 hydrocarbon gas make. Hydrogen consumption remained at an acceptable 4.4 wt % or below. Inspection of the distillate distribution reveals an unusually low naphtha yield compared to SRC II. Some naphtha may have been lost by evaporation during the liquid product centrifugation step, which was carried out at 100°C . Since the computer program closes the carbon balance by adjusting the yield of the entire liquid product, any such unaccounted for loss would contribute toward an artificially low value for total distillate yield.

The best results were obtained at the intermediate pressure of 2,500 psi (17.2 MPa), apparently the condition most favored by reactor hydrodynamics. The superficial gas velocity through the reactor was held constant by decreasing the hydrogen to slurry feed ratio at lower pressures in an attempt to maintain hydrodynamic similarity. It now appears likely that the reactor void volume did not remain constant despite these efforts. More experimental and theoretical work is obviously needed to resolve this question.

The yield structure obtained in the 400-lb coal/day unit compares favorably with that reported for Ft. Lewis SRC-II run, SR-7,²² that produced 42 wt% (MAF coal) total distillate and 18 wt% hydrocarbon gas with 4.8 wt% hydrogen consumption.

Since the Ft. Lewis run used a different Western Kentucky coal (Colonial) at the higher reactor temperature of 461°C, a strict quantitative evaluation is not being made.

2. Coal Mineral Effects

a. Results of "Washed" Coal versus ROM Coal

The base case for the second series of tests, FB-65A, was operated with "washed" (deeply cleaned) coal containing 6.0 wt% ash at nominally the same conditions as FB65B-2000, which used the 17.2 wt% ash ROM coal as feed-stock. A significant loss in liquefaction reactivity was observed with the "washed" coal, which yielded about 3 wt% (MAF coal) less distillate and 3 wt% additional SRC. Viscosity measurements of the product oil, Figure 4, also support this difference, a higher viscosity being an indicator of lower quality product oil. FB-65A oil measured 156 SSF ($337 \times 10^{-6} \text{ m}^2/\text{s}$) at 180°F (82.2°C) vs. 22 ($45 \times 10^{-6} \text{ m}^2/\text{s}$) for FB65B-2000 oil. It may be concluded that a coal "washing" process that removes pyrite is likely to have a serious detrimental effect upon the "washed" coal's liquefaction reactivity.

b. Batch Autoclave Support

The difference in reactivity between ROM and "washed" coal has also been demonstrated in batch tests at PETC.²³ Their product analyses are given in Table 11. Figure 5 from that work clearly shows improved product quality from ROM coal liquefaction. In these autoclave experiments, product oil from the previous cycle was used as vehicle oil for the next liquefaction test in the

sequence. By this procedure, the percentage of the vehicle oil derived from coal at the conditions being tested increases as the cycle number increases.

c. Coal Feedstock Comparison

Petrographic analyses were performed by Penn State University on both the ROM and the "washed" feed coal. Results,²⁴ presented in Table 12, show similar maceral compositions for the two coals. Apparently, the loss in activity was not due to less reactive macerals being concentrated in the "washed" fraction during the coal cleaning process. The ROM coal vitrinite was determined to have a maximum reflectance of 0.574, whereas the "washed" coal vitrinite reflectance was 0.576. This similarity in reflectances of the two vitrinites indicates again that the coal cleaning process had no effect upon their composition.

Both coals were subjected to mineral composition analyses; and their ashes, to elemental determinations, Table 2. Almost no preferential reduction or concentration of the major elements occurred in any fraction as a result of coal cleaning. The mineral composition simply reflects the factor of approximately three in the total mineral matter level between the ROM and "washed" coals. It should be pointed out here, though, that the "washed" coal did become somewhat contaminated with magnetite during the heavy media separation step.

The presence of magnetite was initially detected by X-ray diffraction in material that had been separated from the "washed" coal with a magnet.²⁵ Further verification and quantification was then obtained by Mossbauer spectroscopy, which identified $20\% \pm 5\%$ of the total iron in the "washed" coal as magnetite.²⁶ The fate of the magnetite at liquefaction conditions is not known for certain.

Presumably it is sulfided to a pyrrhotite and may therefore contribute some catalytic activity.

3. Catalyst Addition Series

a. Effect of Iron Pyrite Addition

In the second series of tests, iron pyrite concentrate was added at two levels to the "washed" coal to measure its catalytic effect on coal liquefaction. A clear picture of the results is obtained in Figure 6, which presents the viscosity of centrifuged products as a function of the total iron concentration in the slurry feed to the reactor. Viscosity has traditionally been used as a sensitive measure of liquefaction activity. Product viscosity decreased dramatically (liquefaction increased) with increased iron concentration.

The product yield structure, Table 7 and 8, indicates the same trend of increasing liquefaction with increasing iron concentration. Total distillate yields increased from 37 wt% (MAF coal) to 43 wt%. A corresponding decrease in "SRC" was noted from 34 wt% to 29 wt%. In addition, the solvent fractionation breakdown of the SRC indicates that the iron catalyst improved its quality, i.e., produced a higher percentage of pentane soluble material. SRC is here defined as pyridine soluble, non-distillable material ($> 850^{\circ}\text{F}$, 454°C). This improvement in SRC quality resulted mainly from a net conversion of the asphaltene fraction into distillate. It is not yet clear, however, to what extent parallel as opposed to consecutive reaction pathways, i.e., asphaltene $\rightarrow$ oil ($> 454^{\circ}\text{C}$) $\rightarrow$ distillate ($< 454^{\circ}\text{C}$), dominate in the system.

These yields are plotted in Figures 7 and 8 as functions of iron concentration in the slurry feed stream. Total iron concentration was chosen as the independent variable, since the active form of the catalyst has not been ascertained.

Also, this approach attempts to account for the magnetite in the "washed" coal.

The hydrocarbon gas yields remained nearly constant, Figure 8, indicating that it is an insensitive parameter that cannot readily be used to monitor changes in catalytic activity at typically severe liquefaction conditions. The organic pyridine insolubles (OPI) yields decreased slightly with addition of catalyst.

Since pyrrhotite, generated from the intrinsic iron pyrite in the coal and from the added pyrite, is thought to be the catalytic agent existing at typical coal liquefaction conditions, this iron species was recovered from the raw product oils produced in this series of tests and submitted for analysis. Mossbauer spectroscopy and X-ray diffraction were used to estimate the atomic percentage Fe in the pyrrhotite, Table 13.²⁷ Other than a small systematic difference between the two, both techniques show no significant variation in composition of the pyrrhotite with changes in pyrite feed level. The improvement in product yield structure with added pyrite cannot be related to pyrrhotite composition, only to the amount of pyrrhotite.

Inspection of Tables 14, 15, and 16 indicates that very little, if any, additional desulfurization was observed with added pyrite catalyst, all tests giving 0.3 to 0.4 wt% sulfur in the liquid product. Also, no significant improvement in denitrogenation was found.

b. Literature Support

An extensive body of literature already exists on batch autoclave experiments documenting the catalytic effect of coal minerals on coal liquefaction. Some work in this field in continuous bench units has also been reported by investigators at the Merriam Lab of P&M, Tables 17, 18, 19, 20 and 21.⁷ Merriam results have been corrected for H_2S formed from the added pyrite and put on an MAF basis.

In their work, washed Blacksville #1 coal was treated at $455^{\circ}C$, 15.5 MPa (2,250 psig) H_2 , and a coal throughput of 346 kg/hr-m^3 (21.3 lb/hr-ft^3). A 7 wt% increase in total distillate yield (from 40 wt% to 47 wt%) was observed when 7.5 wt% pyrite (MF coal basis) was added to the feed slurry in their SRC-II style of operation. By comparison, we found an increase of 6 wt% in distillate yield upon adding 7.2% pyrite (10% concentrate) to "washed" Western Kentucky coal.

The iron concentration in the feed slurry was estimated by us for the Merriam runs, since they were not reported. Even though similar amounts of pyrite were added at both laboratories, the SRC-II operating mode at Merriam concentrated the iron level substantially. Insufficient information is available so far to assess clearly the impact of this difference in operating procedure.

c. Indigenous versus Added Pyrite

The high catalyst addition level run in the series, FB-65DC, matched the iron concentration existing in the run of mine coal tests, FB-65B-2000. The

results of the latter run are also represented in Figures 6, 7, and 8, and Tables 7 and 8. It is clear that liquefaction activity was regained, if not enhanced further, by the addition of properly prepared pyrite. Inspection of the light distillate (knockout pot oil) yields of the two test series, Table 14, reveals that a systematically improved physical recovery was obtained in the catalyst addition series. It is felt that the probable loss of light oil resulted in a negative bias of close to 2% in the total distillate yield as reported for the ROM coal tests, and this explains the apparent discrepancy between FB-65DC and FB-65B-2000. This loss was not taken into account when the reported detrimental effect of coal washing was discussed in section 2, Coal Mineral Effects. That is, the true effect may be worse than that stated in section 2.

In the catalyst addition tests, catalyst replaced some of the vehicle in the slurry mixture, and therefore the MF coal feed rate remained constant in the series. Additional mineral matter being fed as catalyst increased the centrifuge residue stream rate as shown in Table 14. The centrifuged product stream rate remained constant. The composition of the latter stream, however, duly reflected increasing distillate concentration with increasing pyrite addition. It may be argued in retrospect that removing the inactive components of the mineral matter from coal prior to liquefaction can reduce considerably the size of the residue stream and thus affect economics in the downstream processing of that stream. This beneficial result may become substantial, since only small amounts of added pyrite were found to be very effective in re-establishing reactivity similar to that of ROM coal.

CONCLUSIONS

Excellent liquefaction was observed with the "active" ROM coal. The best results were obtained at the intermediate pressure of 2,500 psig (17.2 MPa). Coal cleaning before use can have a significantly detrimental effect upon the coal's liquefaction reactivity. Greater reactivity is defined as more total distillate and less SRC. Liquefaction reactivity is restored when indigenous iron pyrite concentrate is added to "washed" coal to match the pyrite level in the run-of-mine coal. Addition of an intermediate amount of pyrite shows a disproportionately positive effect. Removing inactive components of the mineral matter from coal prior to liquefaction will significantly reduce the size of the solid separation and residue handling section. No significant additional desulfurization or denitrogenation results from adding the pyrite catalyst. A swing hammer mill with an 0.014-in. (0.356mm) slot is effective in producing a pyrite concentrate with an acceptable size consist.

FUTURE WORK

Many questions still remain to be answered in continuous units. For instance, information is incomplete on the particle size required for effective utilization of the pyrite catalyst. This will have a strong impact on the economics of its preparation. Also, the active form of the iron catalyst at reactor conditions has not been determined, and it is not known whether iron compounds recycled in the SRC-II mode exhibit the same activity as freshly introduced forms. They may be subject to poisoning just as the more exotic catalytic metals are. Furthermore, coals of different reactivity may not show the same susceptibility to pyrite catalysis. Current work at PETC is designed to address some of these concerns.

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TABLE 1 - Analysis of run-of-mine, "washed", and "rejects"
fractions of Kentucky #11 hvAb coal

<u>As Received Coal</u>	<u>Run-of-Mine</u>	<u>"Washed"</u>	<u>"Rejects"</u>
H ₂ O, %	2.4	2.8	6.4
Ash, %	17.2	6.0	29.3
 <u>MAF Basis</u>			
C, %	76.5	79.4	72.1
H, %	5.3	5.5	5.0
O, %	9.2	9.9	8.6
N, %	1.6	1.6	1.7
S, %	7.4	3.6	12.6
H/C ratio	0.83	0.83	0.83
 <u>Sulfur Forms</u>			
Pyritic, %	4.68	1.13	8.72
Organic, %	2.32	2.35	2.49
Sulfate, %	0.38	0.08	1.37

TABLE 2 - Elemental and mineral analysis of run-of-mine,
"washed" and "rejects" fractions of Kentucky #11 coal

	<u>Run-of-Mine</u>	<u>"Washed"</u>	<u>"Rejects"</u>
<u>Major Elements in Ash</u>			
Fe, %	24.9	25.2	27.7
Si, %	18.9	18.0	17.0
Al, %	9.9	9.7	10.0
Ca, %	0.6	0.8	0.5
Na, %	0.1	0.2	0.1
K, %	1.3	1.5	1.0
Mg, %	0.3	0.4	0.3
Ti, %	1.0	1.1	0.5
<u>Trace Elements in Coal</u>			
Cu, ppm	13	9	36
Cr, ppm	23	14	28
Ni, ppm	28	12	30
Mn, ppm	46	19	70
Zn, ppm	42	16	38
Pb, ppm	5	3	8
Cd, ppm	0.8	0.1	0.5

TABLE 2 - Elemental and mineral analysis of run-of-mine,
"washed" and "rejects" fractions of Kentucky #11 coal
continued

	<u>Run-of-Mine</u>	<u>"Washed"</u>	<u>"Rejects"</u>
<u>Mineral Composition (%)</u>			
Pyrite + Marcasite	9.5	3.3	17.4
Kaolinite	5.5	1.7	10.3
Illite	4.3	1.7	5.5
Quartz	2.2	0.6	2.9
Calcite	0.3	0.1	0.2
Total MM	21.8	7.4	36.3
LTA MM	22.9	8.2	38.5

TABLE 3 - Analyses of the feed pyrite concentrate

Ultimate analysis, wt % moisture-free sample

Carbon	6.4
Hydrogen	0.3
Oxygen	0.1
Nitrogen	0.2
Sulfur	38.5
Fe	34.2

Sulfur forms

Sulfate	0.51
Pyritic	37.99
Organic	0.00

Major elements in concentrate, wt % moisture-free sample

Si	3.8
Al	2.2
Fe	34.2
Ca	0.2
Na	0.1
K	0.3
Mg	0.1
Ti	0.1

TABLE 4. - Process conditions for Western Kentucky coal (SEAM #11) liquefaction in 400-lb/day unit

Coal Used	FB65B 3000 run-of-mine	FB65B 2500 run-of-mine	FB65B 2000 run-of-mine	FB65A "washed"	FB65 DCL "washed"	FB65DC "washed"
Catalyst, %MF coal	none	none	none	none	2.8	10.0
Operating Conditions						
Feed slurry rate, kg/hr	11.2	11.2	11.3	11.2	11.2	11.0
Coal feed rate, kg/hr	3.85	3.83	3.86	3.80	3.79	3.74
Coal feed rate, lb/hr-ft ³ (kg/hr-m ³)	19.1 305.5	19.0 303.7	19.1 306.2	19.0 304.0	18.9 303.2	18.6 297.2
Wt % Fe in feed	1.55	1.54	1.57	0.54	0.84	1.67
Nominal reactor residence time, hrs	1.29	1.30	1.28	1.28	1.29	1.29
Hydrogen feed gas, purity, M %	95.2	95.3	96.7	96.4	96.5	96.2
Hydrogen to slurry ratio, lb H ₂ /100 lb slurry	27.5	23.2	19.3	19.1	19.8	19.6
MSCF/TON of mf coal	302.0	254.8	211.9	212.2	220.0	222.0
Average reactor temp, °C	448.	451.	451.	453.	455.	455.
Reactor pressure, psig (MPa)	3000. 20.6	2500. 17.2	2000. 13.8	2000. 13.8	2000. 13.8	2000. 13.8
Reactor superficial gas velocity, ft/sec (m/sec)	0.70 0.21	0.70 0.21	0.72 0.22	0.72 0.22	0.74 0.23	0.74 0.23
CLP* viscosity, SSF @180°F (m ² /sec)@82.2°C	23.9 46.0x10 ⁻⁶	16.1 24.0x10 ⁻⁶	22.4 45.0x10 ⁻⁶	156.3 337.0x10 ⁻⁶	68.2 146.0x10 ⁻⁶	31.6 65.0x10 ⁻⁶

*Centrifuged Liquid Product

TABLE 5. - Feed slurry composition for Western Kentucky #11 coal liquefaction in 400-lb/day unit

	FB65B 3000	FB65B 2500	FB65B 2000	FB65A	FB65 DCL	FB65DC
Coal Used	<u>run-of-mine</u>	<u>run-of-mine</u>	<u>run-of-mine</u>	<u>"washed"</u>	<u>"washed"</u>	<u>"washed"</u>
Catalyst added, %MF coal	none	none	none	none	2.8	10.0
Feed slurry comp. wt %						
Coal, dry	34.3	34.3	34.3	33.9	33.9	33.9
Catalyst	0.0	0.0	0.0	0.0	1.0	3.4
Solvent	36.6	42.7	37.7	32.1	35.7	37.1
SRC	27.4	21.6	25.9	27.6	25.5	23.0
Ash(recycle oil)	0.2	0.2	0.3	0.6	0.5	0.3
OPI(recycle oil)	<u>1.5</u>	<u>1.2</u>	<u>1.8</u>	<u>5.8</u>	<u>4.4</u>	<u>2.3</u>
Total	100.0	100.0	100.0	100.0	100.0	100.0

TABLE 6 - Elemental forcing used to obtain closure
of the material balance

<u>Component</u>	<u>Affected quantity</u>
Carbon	Centrifuge product oil yield
Nitrogen	Ammonia yield
Sulfur	Hydrogen sulfide yield
Oxygen	Water yield
Hydrogen	Hydrogen feed gas rate
Iron	Iron concentration in centri- fuge residue
Mineral matter (iron-free)	Centrifuge residue yield

TABLE 7. - Product yields for Western Kentucky coal (SEAM #11) liquefaction in 400-lb/day unit--elementally

balanced yields based on MAF Coal

[illegible]

TABLE 8. - Product yields for Western Kentucky coal (SEAM #11) liquefaction in 400-lb/day unit--elementally

balanced yields based on MAF coal

[illegible]

TABLE 9. - Gas yields for Western Kentucky #11 coal liquefaction in 400-lb/day unit--elementally

balanced yields based on MAF coal

RUN	FB65B 3000			FB65B 2500			FB65B 2000		
	<u>ROM</u>			<u>ROM</u>			<u>ROM</u>		
Catalyst, %MF Coal	none			none			none		
Balance Period	1	2	AVG	1	2	AVG	1	2	AVG
CO	1.3	0.1	0.7	0.0	0.0	0.0	0.0	-0.6	-0.3
CO ₂	0.8	0.5	0.7	0.4	0.3	0.4	0.4	0.3	0.3
H ₂ S	5.3	5.2	5.2	5.8	5.9	5.9	5.1	5.1	5.1
94 NH ₃	<u>0.6</u>	<u>0.6</u>	<u>0.6</u>	<u>0.6</u>	<u>0.7</u>	<u>0.6</u>	<u>0.5</u>	<u>0.6</u>	<u>0.5</u>
Non-Hydrocarbons	8.0	6.4	7.2	6.8	6.9	6.9	6.0	5.4	5.6
C ₁	3.6	3.6	3.6	3.5	3.6	3.5	3.2	3.0	3.1
C ₂	2.7	2.8	2.8	2.7	2.9	2.8	2.4	2.2	2.3
C ₃	2.4	2.4	2.4	2.4	2.6	2.5	2.2	2.0	2.1
C ₄	<u>1.1</u>	<u>1.0</u>	<u>1.0</u>	<u>1.2</u>	<u>1.1</u>	<u>1.2</u>	<u>1.3</u>	<u>1.0</u>	<u>1.1</u>
Hydrocarbon Gases	9.8	9.8	9.8	9.8	10.2	10.0	9.1	8.2	8.6

TABLE 10. - Gas yields for Western Kentucky #11 coal liquefaction in 400-lb/day unit--elementally
balanced yields based on MAF coal

RUN Coal used	FB65A "washed"			FB65DCL "washed"			FB65DC "washed"		
	1	2	AVG	1	2	AVG	1	2	AVG
Catalyst, %MF Coal		none			2.8			10.0	
Balance Period	1	2	AVG	1	2	AVG	1	2	AVG
CO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO ₂	0.0	-0.4	-0.2	0.0	0.2	0.1	0.0	0.0	0.0
H ₂ S	2.1	2.1	2.1	1.9	3.2	3.0	4.3	4.3	4.3
NH ₃	<u>0.4</u>	<u>0.4</u>	<u>0.4</u>	<u>0.4</u>	<u>0.3</u>	<u>0.3</u>	<u>0.5</u>	<u>0.4</u>	<u>0.5</u>
Non-Hydrocarbons	2.5	2.1	2.3	3.3	3.7	3.5	4.8	4.7	4.8
C ₁	4.2	4.2	4.2	3.9	3.6	3.8	3.8	3.6	3.7
C ₂	3.3	3.1	3.2	3.0	3.2	3.1	3.0	3.0	3.0
C ₃	2.6	2.4	2.5	2.6	2.7	2.7	2.8	2.7	2.8
C ₄	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>	<u>0.9</u>	<u>1.1</u>	<u>1.0</u>	<u>1.5</u>	<u>1.4</u>	<u>1.4</u>
Hydrocarbon Gases	11.1	10.7	10.9	10.4	10.6	10.5	11.1	10.7	10.9

TABLE 11 - PETC batch autoclave tests, product analysis

	<u>"Washed" Coal</u>	<u>Run-of-Mine</u>	<u>"Rejects"</u>
<u>Product Viscosity, cps at 60° C</u>			
-Cycle 1	63	30	< 20
-Cycle 2	140	30	< 20
-Cycle 3	246	37	< 20
-Cycle 4		40	< 20
-Cycle 5	320	40	< 20
<u>Product Solvent Analyses, %</u>			
-Benzene Insolubles	14.9	3.2	1.7
-Asphaltenes	23.7	21.3	23.0
-Oils	61.4	75.5	

TABLE 12 - Maceral composition of Western Kentucky #11
run-of-mine and "washed" coals

Maceral Type	<u>Run-of-Mine Coal</u>		<u>"Washed" Coal</u>	
	As	Mineral	As	Mineral
	<u>Received</u>	<u>Free*</u>	<u>Received</u>	<u>Free*</u>
Vitrinite	69.1	89.6	85.6	93.3
Pseudovitrinite	0.0	0.0	0.3	0.3
Fusinite	2.2	2.9	1.7	1.9
Semifusinite	2.8	3.6	1.6	1.7
Massive Micrinite	0.0	0.0	0.1	0.1
Granular Micrinite	1.4	1.8	1.2	1.3
Exinite	1.6	2.1	1.2	1.3
Resinite	0.0	0.0	0.1	0.1

*Differences >1.9% for vitrinite are statistically significant at 95% confidence level.

Differences >1.4% for fusinite and semifusinite are statistically significant at 95% confidence level.

TABLE 13 - Atomic percentage Fe in raw product oil
determined by Mossbauer Spectroscopy and X-ray diffraction

Run	FB65B 2000	FB65 A	FB65 DCL	FB65 DC
Coal used	<u>run-of-mine</u>	<u>"washed"</u>	<u>"washed"</u>	<u>"washed"</u>
Catalyst, %MF coal	none	none	2.8	10.0
Wt% Fe in feed slurry	1.57	0.54	0.84	1.67
Mossbauer spectroscopy	48.2	47.8	48.1	48.1
X-ray diffraction	47.8	47.6	47.8	47.8

Mossbauer by Pedro Montano - U. of West Virginia

X-ray diffraction - PETC

TABLE 14 - Production rate of product streams for Western Kentucky #11 coalliquefaction in 400-lb/day unit based on wt% of MF coal

RUN	FB65B 3000	FB65B 2500	FB65B 2000	FB65A	FB65 DCL	FB65DC
Coal used	<u>ROM</u>	<u>ROM</u>	<u>ROM</u>	<u>"washed"</u>	<u>"washed"</u>	<u>"washed"</u>
Catalyst, %MF coal	none	none	none	none	2.8	10.0
Production rate of product streams, wt% of MF coal						
Centrifuged liquid product rate	50.0	53.1	51.7	65.6	65.0	64.7
Light oil +Phenol in H ₂ O	0.8	0.8	0.8	2.4	2.5	2.5
Residue rate	30.8	27.9	32.1	13.5	16.8	22.6

TABLE 15. - Centrifuge liquid product component composition for Western Kentucky#11 coal liquefaction in 400-lb/day unit

RUN	FB65B 3000	FB65B 2500	FB65B 2000	FB65A	FB65 DCL	FB65DC
Coal Used	<u>ROM</u>	<u>ROM</u>	<u>ROM</u>	<u>"washed"</u>	<u>"washed"</u>	<u>"washed"</u>
Catalyst, %MF coal	none	none	none	none	2.8	10.0
Naphtha (C ₅ -193°C)	2.9	3.1	2.1	2.9	2.8	2.5
Middle Dist (193°C-288°C)	10.0	18.7	19.0	11.7	11.1	17.3
Heavy Dist (288°C-454°C)	<u>42.2</u>	<u>42.9</u>	<u>35.9</u>	<u>32.9</u>	<u>40.3</u>	<u>38.5</u>
Total Distillates	55.1	64.7	57.0	47.5	54.2	58.3
52 Pentane sol +454°C	19.0	12.0	16.2	14.0	10.7	15.0
Asphaltenes	23.3	21.2	23.7	28.7	28.7	22.4
Preasphaltenes	—	—	—	—	—	—
SRC	42.3	33.2	39.9	42.7	39.4	37.4
OPI	2.3	1.9	2.6	8.0	5.8	3.8
Mineral matter +Fe	<u>0.3</u>	<u>0.2</u>	<u>0.5</u>	<u>0.9</u>	<u>0.6</u>	<u>0.5</u>
Total	100.0	100.0	100.0	100.0	100.0	100.0

TABLE 16 - Centrifuge liquid product elemental composition for Western Kentucky#11 coal liquefaction in 400-lb/day unit

RUN	FB65B 3000	FB65B 2500	FB65B 2000	F65B A	FB65 DCL	FB65 DC
Coal used	<u>ROM</u>	<u>ROM</u>	<u>ROM</u>	<u>"washed"</u>	<u>"washed"</u>	<u>"washed"</u>
Catalyst, %MF coal	none	none	none	none	2.8	10.0
Carbon	87.7	88.3	88.2	88.1	87.7	87.9
Hydrogen	7.8	8.0	7.7	7.1	7.4	7.6
Nitrogen	1.4	1.4	1.4	1.6	1.7	1.6
Sulfur	0.4	0.3	0.3	0.4	0.4	0.3
Oxygen	2.4	1.8	1.9	1.9	2.2	2.1
Mineral matter	0.2	0.2	0.4	0.8	0.5	0.4
Iron	<u>0.1</u>	<u>0.04</u>	<u>0.1</u>	<u>0.1</u>	<u>0.1</u>	<u>0.1</u>
Total	100.0	100.0	100.0	100.0	100.0	100.0

TABLE 17 - Process conditions for washed Blacksville #1
coal liquefaction with added pyrite (75 μ)

Run	GU211R	GU210R	GU209R
Unit	Merriam	Merriam	Merriam
Catalyst, %MF coal	none	3.0	7.5
Operating Conditions			
Feed slurry rate, kg/hr	1.03	1.05	1.05
Coal feed rate, kg/hr	0.31	0.31	0.31
Coal feed rate, lb/hr-ft ³	21.3	21.5	21.2
(kg/hr-m ³)	341.2	344.4	339.6
Wt% Fe	1.4	3.1	5.6
Nominal reactor			
residence time, hrs	0.99	0.99	1.01
Hydrogen feed gas			
purity, M %	100.0	100.0	100.0
Hydrogen to slurry ratio,			
lb H ₂ /100 lb slurry	4.71	4.62	4.61
Average reactor temp, °C	455.	455.	455.
Reactor pressure, psig	2250.	2250.	2250.
(MPa)	15.5	15.5	15.5
Reactor superficial gas			
velocity, ft/sec	0.033	0.033	0.033
(m/sec)	0.010	0.010	0.010

TABLE 18 - Feed slurry composition for Blacksville #1
catalyst addition

Run	GU211R	GU210R	GU209R
Unit	Merriam	Merriam	Merriam
Catalyst, %MF coal	none	3.0	7.5
Feed slurry comp. wt%			
Coal, dry	30.0	29.7	29.3
Catalyst	0.0	0.9	2.2
Solvent	21.5	20.9	23.8
SRC	34.3	32.7	26.4
Ash (recycle oil)	7.4	9.6	12.4
OPI (recycle oil)	<u>6.8</u>	<u>6.2</u>	<u>5.9</u>
Total	100.0	100.0	100.0

TABLE 19 - Product yields for washed Blacksville #1 coal
liquefaction with added pyrite (75 μ)

Run	GU211R	GU210R	GU209R
Unit	Merriam	Merriam	Merriam
Catalyst, %MF coal	none	3.0	7.5
H ₂	-5.6	-6.1	-6.0
Non-Hydrocarbons	3.3	3.2	2.7
Water	6.2	6.4	7.2
Hydrocarbon gases (C ₁ -C ₄)	17.8	18.3	18.6
Naphtha (C ₅ -193 ⁰ C)	7.8	10.0	12.0
Middle dist (193-249 ⁰ C)	7.3	8.4	8.2
Heavy dist (>249 ⁰ C+loss)	<u>25.0</u>	<u>25.0</u>	<u>27.0</u>
Total distillates	40.1	43.4	47.2
Pentane sol+454 ⁰ C	.	.	.
Asphaltenes	.	.	.
Preasphaltenes	<u>.</u>	<u>.</u>	<u>.</u>
SRC	31.9	29.2	24.8
OPI	<u>6.3</u>	<u>5.6</u>	<u>5.5</u>
Total	100.0	100.0	100.0

TABLE 20. - Gas yields for washed Blacksville #1 coal
liquefaction with added pyrite (75 μ)

RUN	GU211R	GU210R	GU209R
Unit	Merriam	Merriam	Merriam
Catalyst, %MF Coal	none	3.0	7.5
CO	0.4	0.4	0.5
CO ₂	0.7	0.6	0.5
H ₂ S	1.6	1.5	1.0
NH ₃	<u>0.6</u>	<u>0.7</u>	<u>0.7</u>
Non-Hydrocarbons	3.3	3.2	2.7
C ₁	6.4	6.3	6.2
C ₂	4.4	4.5	4.6
C ₃	4.0	4.2	4.3
C ₄	<u>3.0</u>	<u>3.3</u>	<u>3.5</u>
Hydrocarbons Gases	17.8	18.3	18.6

TABLE 21 - Analysis of feed coal Blacksville #1 (washed)

<u>Proximate analysis wt% dry coal</u>	
Ash	6.4
Volatile Matter	37.1
Fixed Carbon	56.5
Btu/lb	14279.
<u>Sulfur Forms, wt% dry coal</u>	
Pyritic	1.0
Sulfate	0.0
Organic	<u>1.4</u>
Total	2.4
<u>Ultimate analysis wt% dry coal</u>	
Carbon	78.4
Hydrogen	5.1
Nitrogen	1.2
Chlorine	0.1
Sulfur	2.4
Ash	6.4
Oxygen	<u>6.4</u>
Total	100.0
Fe in coal, wt% dry coal	0.96

Figure 1 - Simplified schematic of 400 lb-coal/day liquefaction unit.

Figure 2 - Reactor tube assembly end fixtures for 400 lb/day hydrogenation of coal to liquid unit.

7-10-80 L-17748

Figure 3- Thermocouple control plan for 400 lb./day liquefaction unit.

Figure 4 - Viscosity as a function of run time (all six conditions).

7-10-80 L-17745

Figure 5 - Effect on viscosity from hydrogenation of West Kentucky No. II coal with solvent recycle. (Batch autoclave)

7-10-80 L-17744

Figure 6 - Viscosity of centrifuged product oil as a function of total iron concentration in the slurry feed .

Figure 7 - Total distillate and SRC yields as a function of total iron concentration in feed slurry .

12-12-80 L-18051

Figure 8- Total hydrocarbon gas and organic pyridine insolubles yield as a function of total iron concentration in feed slurry.

7-10-80 L-17747