PRESSURIZED FLUIDIZED-BED HYDRORETORTING OF EASTERN OIL SHALES

Progress Report for the Period December 1991-February 1992

By
F. S. Lau
M. C. Mensinger
M. J. Roberts
D. M. Rue

March 1992

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Work Performed Under Contract No.: DE-AC21-87MC11089

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia 26505

By
Institute of Gas Technology
Chicago, Illinois 60616

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EXECUTIVE SUMMARY

This report presents the work performed during the program quarter from December 1, 1991 through February 29, 1992, under U.S. Department of Energy (DOE) Contract No. DE-AC21-87MC11089 for the project "Pressurized Fluidized-Bed Hydroretorting (PFH) of Eastern Oil Shales." The Institute of Gas Technology (IGT) is the prime contractor for the overall program extension to expand the PFH data base to beneficiated shales. Four universities are working with IGT as subcontractors; their responsibilities and achievements in the program are discussed below in the appropriate tasks.

Some of the tasks in the original program were not continued in the current program extension. The task achievements discussed below represent the active tasks of the program.

In Subtask 3.6 (Cracking-Combustion Tests), IGT conducted isothermal and non-isothermal tests in the thermobalance to determine the combustion characteristics of hydroretorted beneficiated shale. The thermobalance tests were conducted at temperatures up to 982°C (1800°F) and pressures ranging from 0.2 to 7.0 MPa (15 to 1000 psig). The results show that for complete combustion of the shale, a temperature of at least 845°C (1550°F) will be required.

In Subtask 3.7 (Innovative Reactor Concept Testing), IGT conducted two methane cracking tests in the batch cracking-combustion unit. The first test was conducted at 1.4 MPa with no solids in the reactor; the second test was conducted at 0.45 MPa with combusted shale in the reactor. Gas samples were taken during each test as the unit temperature was increased in stages to 1205°C (2200°F). The results showed that the cracking of methane to carbon and hydrogen proceeded to the expected equilibrium values within 15-minutes at each temperature stage.

In Subtask 3.8 (Niche Market Studies), IGT conducted seven asphalt screening tests in the laboratory-scale batch PFH reactor to determine the conditions needed to produce the highest quantity of oil that could be utilized as an asphalt additive. The results showed that the highest oil yields were obtained at 482°C and 7.0 MPa (900°F and 1000 psig) and produced oil suitable for use as an asphalt additive. The planned series of screening tests has been completed. Next quarter, tests to characterize asphalt cement and asphalt pavement made with the shale asphalt additive will be conducted.

The University of Alabama Mineral Resources Institute (MRI) is responsible for the work being conducted in Task 4 (Beneficiation Research).

In Subtask 4.1.4 (Grinding-Flotation Circuit Design), MRI evaluated two grinding and sizing circuits that have the potential to reduce the cost to produce beneficiated shale. MRI also conducted flotation tests with water that had been recycled from the flotation tailings pond. The results showed that after five cycles of use, the pH of the water was fairly constant at about 2.8. However, the conductivity of the water increased from 550 to 2250 μmhos indicating a buildup of ions.

In Subtask 4.4 (Integrated Grinding and Flotation), the University of Kentucky Center for Applied Energy Research (UK-CAER) conducted tests to determine the effects of feed rate, air flow rate, frother type, pH, and retention time on the flotation characteristics of shale. The results showed that increasing the retention time increased the carbon recovery. Also, increasing the air flow rate improved carbon recovery, but reduced the concentrate grade. Using a foam jet bubble generator, UK-CAER achieved a 36% carbon product at a 68% recovery.

In Subtask 4.5. (Evaluation of Different Grinding Media), MRI conducted tests to evaluate the grinding efficiency of sand on raw shale. The results showed that sand is a feasible material for grinding shale.

In Subtask 4.6.1. (Oil Agglomeration and Pelletizing), MRI conducted abrasion tests with shale extrusions produced with and without addition of an anionic asphalt emulsion. The results showed that the extrusions produced with the emulsion were much more resistant to abrasion than those without. Further, oven drying the extrusions (with additive) also increased the resistance to abrasion compared to air drying.

In Subtask 4.6.2 (Bioflocculation of Kerogen), the University of Nevada, Reno (UN) conducted tests to determine the dewatering characteristics of shale agglomerates that had been bioflocculated with Mycobacterium phlei. Using a vacuum filtration apparatus, UN achieved a moisture content in the dewatered product of about 41 to 42 percent. UN also determined that using water recycled from bioflocculation for flotation, improved the grade from 24 to 31 percent carbon and the recovery from 85 to 91 percent, compared to tap water.

In Task 5 (Operation of PFH on Beneficiated Shale), IGT conducted both batch and continuous tests in the laboratory-scale units with beneficiated Alabama shale. The objective of these tests was to establish operating conditions for conducting a test using beneficiated shale in the bench-scale unit (BSU). Also, IGT completed equipment modifications to the BSU in preparation for the bench-scale test.

In Subtask 6.2.2 (Wastewater Treatability), Tennessee Technological University (TTU) completed treatability tests with methyl ethyl ketone (MEK) and initiated treatability tests with aniline. The results showed that MEK (250 mg/L initial concentration) was biodegraded by the acclimated culture within about 46 hours. Biodegradation experiments with aniline will be repeated next quarter to confirm the results. TTU continued acclimating microorganisms to 4-methyl pyridine.

In Subtask 6.4.1. (PFH Process Analyses), IGT continued work on modeling the PFH process by modifying the computer program that simulates a fluidized-bed reactor.

In Subtask 6.4.3. (Plant Energy Optimization), TTU continued the detailed exergy and thermoeconomic analyses of the PFH plant combined with a steam generating plant. The exergy destruction in the steam generator represents about 50 percent of the total exergy destruction in the combined plant.

The total exergy destruction in the five feed water preheaters could be reduced by improving the integration between the PFH plant and power plant.

Overall, TTU determined that the PFH plant exergetic efficiency was 85.4 percent. This is considerably higher than that of the steam power plant (35.9 percent).

Task 7 (Sample Procurement, Preparation, and Characterization) was completed by MRI during the previous program quarter.

In Task 8 (Project Management and Reporting), IGT personnel visited MRI during the quarter. IGT continued to monitor the progress and activities of the subcontractors working in the program via telephone and written reports.

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INTRODUCTION

The Devonian oil shales of the Eastern United States are a significant domestic energy resource. The overall objective of the multi-year program, initiated in October 1987 by the U. S. Department of Energy (Contract No. DE-AC21-87MC11089), is to perform the research necessary to develop the pressurized fluidized-bed hydroretorting (PFH) process for producing oil from Eastern oil shales. The program also incorporates research on technologies in areas such as raw shale preparation, beneficiation, product separation, and waste disposal that have the potential of improving the economics and/or environmental acceptability of recovering oil from oil shales using the PFH process. The program is divided into the following active* tasks:

- Task 3. Testing of Process Improvement Concepts
- Task 4. Beneficiation Research
- Task 5. Operation of PFH on Beneficiated Shale
- Task 6. Environmental Data and Mitigation Analyses
- Task 7. Sample Procurement, Preparation, and Characterization
- Task 8. Project Management and Reporting.

In order to accomplish all the program objectives, the Institute of Gas Technology (IGT), the prime contractor, is working with four other institutions; the University of Alabama/Mineral Resources Institute (MRI), University of Kentucky Center for Applied Energy Research (UK-CAER) the University of Nevada (UN), and Tennessee Technological University (TTU).

This report presents the work performed during the program quarter from December 1, 1991 through February 29, 1992.

* Some of the tasks in the original program were not continued in the current program extension. The task achievements discussed below represent the active tasks of the program.

ACHIEVEMENTS

Task 3. Testing of Process Improvement Concepts

The objective of this task is to obtain data on novel process concepts that have the potential for improving the overall economics of PFH processing with Eastern oil shales. This task is divided into three subtasks corresponding to the concepts being tested: 3.6. Combustion of Hydroretorted Beneficiated Shales, 3.7. Innovative Reactor Concept Testing, and 3.8. Niche Market Studies.

Subtask 3.6. Combustion of Hydroretorted Beneficiated Shales

The overall objective of this subtask is to evaluate the combustion of hydroretorted shale for energy recovery prior to disposal. This subtask is comprised of two subtasks: 3.6.1. Combustion Characterization and 3.6.2. Combustion Tests.

Subtask 3.6.1. Combustion Characterization

The objective of this subtask is to determine the combustion characteristics of hydroretorted beneficiated shale.

Discussion

During the quarter, IGT determined the combustion characteristics of hydroretorted beneficiated shale in a series of twelve thermogravimetric analysis (TGA) tests in an existing high-temperature, high-pressure thermobalance unit. The unit, shown schematically in Figure 3-1, senses and records the instantaneous weight of a sample undergoing reaction at temperatures and pressures up to 1038°C and 7.0 MPa (1900°F and 1000 psig).

In a typical thermobalance test, a weighed, representative sample of hydroretorted shale is held in a stainless steel screen basket suspended from a force transducer by a stainless steel wire. The basket is pretreated at test conditions to neutralize the basket surfaces so that no weight changes are due to the basket when a sample is being processed.

The twelve thermobalance tests included three non-isothermal tests and nine isothermal tests. In non-isothermal tests, the sample is positioned in the reactor and the unit is pressurized with air. Once the desired air flow rate is established, the reactor heaters are energized. The sample weight is continuously recorded as the reactor is heated from ambient temperature to 982°C (1800°F) at an average heating rate of 8.3°C/min (15°F/min). Samples are raised out of the heated zone of the reactor as soon as the temperature reaches 982°C.

In the isothermal tests, the sample is held under a nitrogen purge in a cooler, upper part of the reactor until test conditions are established. When the test conditions are established, the sample is then lowered into the hot zone of the reactor. Sample weight is continuously recorded during the 20

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Figure 3-1. SCHEMATIC DIAGRAM OF THE THERMOBALANCE REACTOR

minutes at isothermal conditions. The basket is raised out of the heated zone to stop the reaction.

The hydroretorted beneficiated shale for the thermobalance tests was produced in a laboratory-scale continuous test at 482°C (900°F) and 4.2 MPa (600 psig) in Subtask 5.1. The shale was screened to -20+40 mesh and riffled. Samples of about 1 gram were used for the thermobalance tests. Analyses of the raw and hydroretorted shale from Test 52-C-1A are presented in Table 3-1. The gross heating value of the hydroretorted shale sample has not yet been determined. The analyses do not total 100 percent, because metals in the shale mineral matter are oxidized during the analytical procedure.

Table 3-1. ANALYSES OF RAW AND HYDRORETORTED
BENEFICIATED ALABAMA SHALES

Sample	Raw	Hydroretorted
Moisture, wt %	1.53	0.00
Ultimate, wt % (dry)		
Ash	53.74	79.06
Carbon	31.90	15.37
Hydrogen	3.16	0.82
Sulfur	9.15	7.50
Nitrogen	0.77	0.51
Oxygen (by difference)	1.28	--
Gross Heating Value, MJ/kg	14.77	--*
Btu/lb	6354	--

* Not available.

The carbon, sulfur, and nitrogen conversions achieved during the PFH test used to generate the hydroretorted shale were 67, 44, and 55 percent, respectively. The hydrogen-to-carbon weight ratio was reduced from 0.099 to 0.053. The hydroretorted shale sample is comprised of 24.2 percent carbon, hydrogen, sulfur, and nitrogen, which can be converted during combustion. A summary of the operating conditions and the overall weight losses and elemental conversions for the twelve combustion characterization tests conducted in the thermobalance is presented in Table 3-2.

Non-isothermal TGA tests with hydroretorted shale were conducted in air at pressures of 0.2, 1.5, and 7.0 MPa (15, 200, and 1000 psig). The corresponding oxygen partial pressures were 0.02, 0.31, and 1.47 MPa. Slow heating of shale produced a large, rapid weight loss peak between 250° and 350°C (480° and 660°F) and a period of slow weight loss at temperatures of 565° to 845°C (1050° to 1550°F). From 65 to 75 percent of the weight loss occurred during the low temperature, rapid weight loss period. As the oxygen partial pressure is increased, the temperature at which weight loss stops decreases. The temperature range over which the rapid weight loss occurs also decreases. The

Table 3-2. COMBUSTION CHARACTERIZATION TEST CONDITIONS AND RESULTS

Test No.	<u>31-T-1</u>	<u>31-T-2</u>	<u>31-T-3</u>	<u>31-T-4</u>	<u>31-T-5</u>	<u>31-T-6</u>
Operating Conditions						
Temperature, °C	-----	982	-----	-----	927	-----
Pressure, MPa	0.1	1.5	7.0	0.1	1.5	7.0
Heating	----	non-isothermal	----	-----	isothermal	-----

Results

Residue Analysis, wt % (dry)						
Ash	98.87	98.77	98.58	99.75	99.17	96.48
Carbon	0.04	0.08	0.02	0.05	0.06	0.06
Hydrogen	0.08	0.06	0.05	0.03	0.03	0.03
Sulfur	0.22	0.15	0.37	0.14	0.49	1.59
Nitrogen	0.11	0.00	0.01	0.03	0.01	0.02
Weight Loss, %						
Carbon	99.80	99.59	99.90	99.74	99.69	99.69
Hydrogen	92.32	94.26	95.18	97.11	97.11	97.05
Sulfur	97.69	98.43	96.10	98.52	94.83	82.91
Nitrogen	83.02	100.00	98.45	95.35	98.45	96.84

Test No.	<u>31-T-7</u>	<u>31-T-8</u>	<u>31-T-9</u>	<u>31-T-10</u>	<u>31-T-11</u>	<u>31-T-12</u>
Operating Conditions						
Temperature, °C	816	982	927	816	982	927
Pressure, MPa	1.5	1.5	4.2	1.5	7.0	1.5
Heating	-----	-----	isothermal	-----	-----	-----

Results

Residue Analysis, wt % (dry)						
Ash	98.43	99.48	97.48	98.62	97.30	101.77
Carbon	0.00	0.00	0.00	0.00	0.03	0.17
Hydrogen	0.02	0.02	0.02	0.02	0.03	0.02
Sulfur	0.67	0.39	1.27	0.53	1.90	0.31
Nitrogen	0.00	0.00	0.00	0.01	0.02	0.00
Weight Loss, %						
Carbon	100.00	100.00	100.00	100.00	99.84	--
Hydrogen	98.08	98.03	98.07	97.99	97.04	--
Sulfur	92.97	95.80	86.63	94.18	79.47	--
Nitrogen	100.00	100.00	100.00	98.39	96.82	--

results of these non-isothermal tests (presented in Table 3-3) suggest that shale combustion can be conducted at temperatures as low as 300°C (575°F), but that complete combustion of the shale organic matter will require a temperature of at least 845°C (1550°F).

The nine isothermal thermobalance tests were conducted at temperatures of 815° to 982°C (1500° to 1800°F) and pressures of 0.2 to 7.0 MPa (15 to 1000 psia). Weight loss was high for all tests in this range of combustion conditions. The carbon conversion was greater than 99 percent in all tests and did not appear to be affected by changes in temperature and pressure. The sulfur conversion increased with increasing temperature but decreased with increasing pressure. At 925°C (1700°F), sulfur conversion decreased from greater than 98 percent at 0.2 MPa to about 80 percent at 7.0 MPa total pressure.

Table 3-3. SHALE COMBUSTION WEIGHT LOSS PERIODS
FROM NON-ISOTHERMAL TESTS

Test No.	O ₂ Partial Press., MPa	Rapid	Slow	Wt. Loss
		Wt. Loss	Wt. Loss	End Point
		°C		
31-T-1	0.02	293-370	565-845	925
31-T-2	0.31	248-302	565-845	900
31-T-3	1.47	260-277	565-845	875

Sintering was observed in the isothermal tests conducted at severe conditions. At 925°C, part of the samples conducted at 4.2 and 7.0 MPa were sintered. For higher temperatures of 980 and 1040°C and a pressure of 1.5 MPa, more of the sample was incorporated into the sinter. The residue from Test 31-T-12 (1040°C and 1.5 MPa) was entirely sintered and could not be separated from the basket after the test.

The initial deformation temperature (oxidizing atmosphere) of a sample of combusted shale was found to be 1288°C (2350°F). This temperature is well above the combustion temperatures used in the thermobalance tests, but the combustion conditions used will clearly lead to sintering in a packed bed. Combustion of hydroretorted beneficiated shale should be conducted in a more active reactor (such as a fluidized bed) to prevent sintering.

Subtask 3.6.2. Fluidized-Bed Combustion Tests

The objective of this subtask is to demonstrate the combustion of hydro-retorted beneficiated shale in a fluidized-bed reactor. Laboratory-scale tests will be conducted at various temperatures, pressures, and shale residence times to evaluate combustion characteristics, attrition, and reactivity. Emissions from the tests will be monitored for environmental purposes as well as for performing overall and elemental material balances.

Discussion

Laboratory-scale fluidized-bed combustion tests will be conducted in an existing 5.1-cm (2-inch) diameter reactor. Feed shale for the combustion tests will be produced in Subtask 5.2. (Bench-Scale Continuous Tests) with beneficiated Alabama shale. Combustion tests will be conducted at pressures of 0.1 to 1.5 MPa (15 to 215 psia). Based on the results of combustion characterization tests in Subtask 3.6.1, the fluidized bed combustion tests will be performed at temperatures of 816° to 982°C (1500° to 1800°F) and residence times of 5 to 20 minutes.

Tests will be initiated after a sample of hydrotreated beneficiated shale is available from a bench-scale PFH test conducted in Subtask 5.2. Preparations for the combustion tests were made this quarter. Feed air and nitrogen cylinders were ordered and received, and the fluidized-bed reactor system was checked for operability.

Subtask 3.7. Innovative Reactor Concept Testing

The objective of this subtask is to demonstrate the technical feasibility of generating hydrogen by cracking the by-product hydrocarbon gases on spent shale and combusting the carbon produced by the cracking reactions. Work is divided into two subtasks: 3.7.1. Cracking Tests and 3.7.2. Cracking-Combustion Tests. A laboratory-scale reactor will be designed and built for the tests to be conducted in this subtask.

Subtask 3.7.1. Cracking Tests

The objective of this subtask is to demonstrate the generation of hydrogen by cracking by-product hydrocarbon gases.

Discussion

During the quarter, instrument calibrations were completed and the first two cracking tests were conducted. The batch cracking-combustion reactor has an internal diameter of 3.5 cm (1.4 inch) and a length of 61 cm (24 inch). The unit is capable of operating at 1200°C and 7 MPa (2200°F and 1000 psig). Ancillary equipment includes pressure and temperature controllers and indicators, gas feed and sampling systems, and a data logging recorder. All system components, except the reactor, are constructed from type 316 stainless steel. The reactor is fabricated from type 309 stainless steel which has superior high temperature properties.

Both cracking tests were conducted using a methane feed gas and the same operating procedure. Air was purged from the reactor with nitrogen, and the nitrogen was then replaced with methane by pressurizing and then depressurizing three times with methane. The reactor was sealed, pressurized with methane, and then heated to the first gas sampling temperature. The reactor was held at the gas sampling temperature for 15 minutes before the sample was taken. The same procedure was followed as the temperature was increased until all gas samples were taken.

A summary of the operating conditions and product gas concentrations for Tests 33-CR-1 and 33-CR-2 is presented in Table 3-4. The first test was conducted with methane at 1.4 MPa (15 atm) with no solids in the reactor. Test 33-CR-2 was performed at 0.45 MPa (4.5 atm) with combusted shale charged to the reactor.

The product gas compositions for samples taken in Test 33-CR-1 are plotted against the equilibrium methane concentrations in Figure 3-2. The equilibrium methane concentration is the lowest possible methane concentration at a given temperature and pressure. The results show that even with no shale present to catalyze the reaction, the methane cracking reaction proceeds to the equilibrium limit in 15 minutes (or less). The methane concentration decreased from 21.2 percent at 896°C (1643°F) to 2.7 percent at 1205°C (2200°F) (22.8 and 3.1 percent, respectively, on a nitrogen-free basis).

Table 3-4. SUMMARY OF CRACKING TEST CONDITIONS AND RESULTS

Test No.	<u>33-CR-1</u>	<u>33-CR-2</u>				
Pressure, MPa	1.4	0.45				
CH ₄ in Feed Gas, mol %	100	100				
Shale in Reactor	No	Yes				
Product Gas Composition, mol % at Temperature, °C (°F)						
	<u>H₂</u>	<u>CH₄</u>	<u>Other*</u>	<u>H₂</u>	<u>CH₄</u>	<u>Other*</u>
895° (1643°)	71.7	21.2	7.1	13.9	6.8	79.3
1020° (1868°)	82.0	10.0	8.0	29.8	11.3	58.8
1140° (2084°)	87.6	3.7	8.7	50.1	3.1	46.8
1205° (2200°)	85.4	2.7	11.9	62.7	2.3	35.0

* Nitrogen.

+ N₂, CO₂, SO₂.

Other than methane and hydrogen, nitrogen was the only gas detected in the samples from this test. Pressurizing three times with methane was apparently not sufficient to purge all of the nitrogen from the system.

The shale used in Test 33-CR-2 was hydroretorted in lab-scale continuous Test 51-C-1A and then combusted at 705°C (1300°F) for one hour in a muffle furnace. After combustion at this temperature, the shale contained 97.0 percent ash, 0.79 percent sulfur, and 0.04 percent carbon. The product gases contained methane and hydrogen as well as significant amounts of carbon dioxide, sulfur dioxide, and nitrogen. The CO₂ and SO₂ likely were formed by decomposition of mineral carbonates and sulfates present in the shale sample. The amount of methane cracked at 895° and 1020°C (1643° and 1868°F) was lower than dictated by equilibrium. At higher temperatures, the methane concentration was much closer to equilibrium values. This sample of combusted shale sintered during the cracking test.

Figure 3-2. EFFECTS OF TEMPERATURE AND PRESSURE ON EQUILIBRIUM METHANE CONCENTRATION

The reactions of the shale, formation of CO₂, SO₂, and high-temperature water, and mineral oxide decompositions, influenced the methane cracking reaction. Additional tests will be performed with shale combusted at higher temperatures [871° to 982°C (1600° to 1800°F)] to determine the effect on methane cracking reactions.

Subtask 3.7.2. Cracking-Combustion Tests

The objective of this subtask is to demonstrate the combustion of carbon produced by the cracking of hydrocarbon gases.

Discussion

The same test unit constructed for the cracking tests in Subtask 3.7.1 will be used for the cracking-combustion tests. Each combustion test will be preceded by a cracking test. Carbon will be deposited on spent, combusted shale, and a combustion cycle will be performed to determine the conditions for combustion of the deposited carbon. One of the tests will consist of multiple cracking-combustion cycles to determine the effects of multiple cracking-combustion cycles on the shale and product gases.

No cracking-combustion tests were conducted this quarter. These tests will be performed next quarter.

Subtask 3.8. Niche Market Studies

The objective of this subtask is to determine the potential for producing hydroretorted shale oil co-products, such as asphalt additives. Tests will be performed to characterize hydroretorted shale oil asphalts and pavements containing these asphalts.

Discussion

During the quarter, IGT conducted seven asphalt screening tests in the batch laboratory-scale PFH reactor. The objective of these tests was to determine the conditions for producing the maximum amount of shale oil that could be used as an asphalt additive. The operating conditions, carbon conversions, and oil yields for these tests are presented in Table 3-5.

Table 3-5. ASPHALT SCREENING TEST OPERATING CONDITIONS AND RESULTS

Test No.	Temp.,	Press.,	Residence	Carbon Conversion, %			Oil Yield, GPT
	°C	MPa	Time, min	Oil	Gas	Res.	
35-B-1	485	1.5	20	49.5	10.4	40.1	45.5
35-B-2	650	1.5	20	30.7	27.7	41.6	27.5
35-B-3	485	4.2	20	61.4	11.1	27.5	55.6
35-B-4	565	4.2	20	56.1	16.5	27.5	49.9
35-B-5	650	4.2	20	43.1	30.3	26.6	36.9
35-B-6	485	7.0	20	71.2	13.2	15.6	65.7
35-B-7	650	7.0	20	39.3	37.6	23.0	32.0

The results showed that the highest oil yields were obtained at 485°C and 7.0 MPa. A simulation boiling point separation was performed on each of the asphalt screening test product oils by gas chromatography (GC). The shale oil fraction that will be combined with petroleum asphalt to serve as an asphalt additive will be separated by boiling point. The GC simulated boiling point data will allow determination of the PFH conditions needed to maximize the high-end fraction needed for blending with petroleum asphalt. The GC simulated boiling point data for the seven asphalt screening test shale oils are summarized in Table 3-6.

Table 3-6. ASPHALT SCREENING TEST GC SIMULATED BOILING POINT FRACTIONS

Test No.	Boiling Point, Cumulative wt %		
	196°C	254°C	516°C
35-B-1	9.8	18.3	29.0
35-B-2	12.1	23.5	36.6
35-B-3	9.8	18.0	28.6
35-B-4	10.0	16.3	28.8
35-B-5	10.6	21.1	34.0
35-B-6	10.7	20.1	32.1
35-B-7	6.3	16.8	29.8

The simulated boiling point data shows a large fraction of the product shale oil (70 to 80 percent) can be blended with petroleum asphalt as an additive. Boiling point fractions change with the operating conditions used to produce the oil, but the changes are smaller than the changes in oil yield experienced at various PFH conditions. Therefore, combining the oil yield and simulated boiling point results suggests that the highest yield of asphalt additive shale oil will be obtained at the same PFH oil yield conditions of 485°C and 7.0 MPa ((900°F and 1000 psig).

The asphalt screening tests have been completed. Additional analyses of the product oils will be conducted to determine the effects of PFH conditions on the properties of the asphalt additive fraction of the oil. The tests will include specific gravity analyses and elemental compositions, especially nitrogen, as a function of boiling point. The nitrogen content of various shale oil fractions is significant, because nitrogen-containing additives are commonly used to enhance asphalt properties.

The remaining analyses and tests in this subtask, Asphalt Cement Characterization and Asphalt Pavement Characterization, will be conducted next quarter after completion of the bench-scale PFH test in Subtask 5.2. Oil from the bench-scale test will be split, and the high end shale oil fraction will be used for the remaining work in this subtask.

Task 4. Beneficiation Research

The objective of this task is to test several novel and advanced grinding and beneficiation concepts, which have shown promising results with

coal, for processing Eastern shales. This task is divided into four subtasks: 4.1. Grinding Studies (Subtask 4.1.4. Grinding Circuit Design), 4.4. Integrated Grinding and Flotation, 4.5. Evaluation of Different Grinding Media, and 4.6. Evaluation of Concentrate Preparation Techniques (Subtasks 4.6.1. Oil Agglomeration and Pelletizing and 4.6.2. Bioflocculation of Kerogen).

Discussion

The overall responsibility for this task is assumed by the Mineral Resources Institute (MRI) of the University of Alabama. One of the subtasks (4.4) is being conducted by the University of Kentucky Center for Applied Energy Research (UK-CAER), as a subcontractor to MRI. Subtask 4.6.2 is being conducted by the University of Nevada, Reno (UN), also as a subcontractor to MRI. The achievements made during the quarter are described below.

Subtask 4.1. Grinding Studies

Subtask 4.1.4. Grinding-Flotation Circuit Design

During the quarter, MRI continued work on determining methods for reducing stirred ball mill (SBM) grinding costs. Two potential methods were evaluated in laboratory testing. The first method (Figure 4-1) represents a primary grinding circuit that produces -100-mesh discharge followed by hydrocycloning and screening circuits. The results of the test conducted with this circuit are shown in Table 4-1.

The results of mechanical cell flotation tests conducted on the cyclone overflow product are presented in Table 4-2. The results of the analyses conducted on the Derrick screen undersize product are presented in Table 4-3. The objective was to determine effect of flotation on kerogen grade and recovery. The data in Table 4-2 show that there should be no problems in flotation of a product having the size consist of the hydrocyclone overflow. Table 4-3 shows that while about 45 weight percent of the Derrick screen undersize can be rejected by flotation with only minor losses of the oil-bearing fraction, the concentrate produced would require subsequent SBM grinding and re-flotation to produce a high kerogen-content concentrate.

SBM grinding studies of the Derrick screen oversize product (shown in Figure 4-1) were conducted using sand as the grinding media. The results of those tests showed that sand is an effective substitute for steel grinding media and thus should reduce the costs of SBM grinding.

To test the concept of a rougher-cleaner column cell flotation circuit operating on feed material substantially coarser than 10 micrometers (μm), the sand-ground Derrick screen oversize product ($d_{90} = 17.5 \mu\text{m}$; $d_{50} = 6.5 \mu\text{m}$) was used. The results (Table 4-4) show the potential for utilizing a rougher-cleaner column cell circuit for treating a relatively coarse feed. However, at this size consist, the sulfur rejection in the concentrate is less than desired. The data also show that further adjustment in the operation of the cleaner column will be required to upgrade the concentrate produced. This will increase the amount of middling product that requires SBM grinding but may reduce the sulfur content of the concentrate. Size analyses of the three

Figure 4-1. CONTINUOUS GRINDING AND SIZING CIRCUIT NO. 1

Table 4-1. RESULTS OF TEST CONDUCTED WITH
ALABAMA SHALE IN GRINDING CIRCUIT No. 1

Product	Cumulative Weight, %	FA, GPT	Chemical Analysis				Distribution					Size	
			C	H	N	S	Oil wt %	C	H	N	S	d ₉₀ μm	d ₅₀
Cyclone Overflow	18.0	11.4	17.14	2.08	0.71	5.20	18.1	20.2	21.0	19.7	12.4	14.5	5.1
Derrick Screen Undersize	25.7	9.1	12.66	1.53	0.58	8.12	20.7	21.4	22.1	23.0	27.7	38.9	14.4
Oversize	56.3	12.3	15.78	1.80	0.66	8.02	61.2	58.4	56.9	57.3	59.9	111.9	41.5
Composite Cyclone Underflow	82.0	11.3	14.80	1.71	0.64	8.05	81.9	79.8	79.0	80.3	87.6	--	--
Composite -100 Mesh	100.0	11.3	15.23	1.78	0.65	7.54	100.0	100.0	100.0	100.0	100.0	--	--

* Results of FA analysis in triplicate.

Table 4-2. RESULTS OF MECHANICAL CELL FLOTATION TEST CONDUCTED
ON CYCLONE OVERFLOW PRODUCT (d₉₀ = 14.5 μm, d₅₀ = 5.1 μm)

Flotation Product	Cumulative Weight, %	Oil Yield,		Chemical Analysis				Distribution					
		FA	C	C	H	N	S	Oil(FA)	Oil(C)	C	H	N	S
		-- GPT --						wt %					
C3 Concentrate	42.9	26.8	27.9	32.32	3.42	1.04	7.17	100.0	88.1	81.7	72.1	68.2	56.6
M-3	7.6	--	5.2	7.98	1.26	0.49	4.83	--	2.9	3.6	4.7	5.7	6.8
Comp C2 Conc.	50.5	--	24.5	28.66	3.10	0.96	6.82	--	91.0	85.3	76.8	73.9	63.4
M-2	12.1	--	4.9	6.70	1.12	0.38	4.50	--	3.6	4.8	6.7	7.0	10.0
Comp C1 Conc.	62.6	--	20.5	24.41	2.71	0.85	6.37	--	94.6	90.1	83.5	80.9	73.4
M-1	15.3	--	2.3	4.84	0.94	0.34	4.10	--	2.8	3.6	7.5	8.4	12.3
Comp Ro Conc.	78.9	--	19.0	20.37	2.35	0.74	5.90	--	97.4	94.7	91.0	89.3	85.7
Ro Tails	21.1	--	1.7	4.27	0.87	0.33	3.68	--	2.6	5.3	9.0	10.7	14.3
Flotation Feed	100.0	11.4	13.6	16.97	2.04	0.65	5.43	100.0	100.0	100.0	100.0	100.0	100.0
Ro Tails + M-1	37.4	--	2.0	4.51	0.90	0.33	3.86	--	5.4	8.9	16.5	19.1	26.6
Ro Tails + M1+2	49.5	--	2.5	5.05	0.96	0.35	4.02	--	9.0	13.7	23.2	26.1	36.6
Ro Tails + M1-3	57.1	--	2.8	5.44	1.00	0.36	4.13	--	11.9	17.3	17.9	31.8	43.4

Table 4-3. RESULTS OF MECHANICAL CELL FLOTATION TEST CONDUCTED ON
DERRICK SCREEN UNDERSIZE PRODUCT ($d_{90} = 39 \mu\text{m}$, $d_{50} = 14.4 \mu\text{m}$)

Flotation Product	Cumulative Weight, %	Oil Yield,		Chemical Analysis				Density g/mL	Distribution						
		FA	C	C	H	N	S		Oil(FA)	Oil(C)	C	H	N	S	
		GPT		wt %							wt %				
C1 Concentrate	55.1	15.7	16.2	19.75	2.12	0.68	9.14	2.18	91.1	92.8	85.0	78.6	76.7	68.0	
M-1	16.4	3.1	3.1	5.77	0.86	0.29	5.94	2.63	5.3	5.3	7.4	9.5	9.8	13.1	
Comp Ro Conc.	71.5	12.8	13.2	16.54	1.83	0.59	8.41	2.28	96.4	98.2	92.4	88.1	86.5	81.1	
Ro Tails	28.5	1.2	0.9	3.43	0.62	0.23	4.92	2.72	3.6	1.8	7.6	11.9	13.5	18.9	
Flotation Feed	100.0	11.4	13.6	16.97	2.04	0.65	5.43	2.41	100.0	100.0	100.0	100.0	100.0	100.0	
Waste	44.9	1.9	1.7	4.29	0.71	2.5	5.29	2.69	8.9	8.1	15.0	21.4	23.3	32.0	

Table 4-4. RESULTS OF ROUGHER-CLEANER COLUMN CELL TEST
WITH ALABAMA SHALE ($d_{90} = 17.5 \mu\text{m}$)

Product	Cumulative Weight, %	Chemical Analysis				Distribution				Size	
		C	H	N	S	C	H	N	S	d_{90}	d_{50}
		Wt %								μm	μm
Cleaner Conc.	34.2	35.98	3.73	1.10	9.16	78.3	70.4	65.8	39.1	21.1	8.1
Cleaner Tails	12.8	12.86	1.61	0.58	8.45	10.5	11.4	12.9	13.5	12.3	4.5
Comp. Ro. Conc.	47.0	29.68	3.15	0.96	8.97	88.8	81.8	78.7	52.6	18.7	7.1
Rougher Tails	53.0	3.34	0.62	0.23	7.17	11.2	18.2	21.3	47.4	16.5	5.9
Feed	100.0	15.72	1.81	0.57	8.02	100.0	100.0	100.0	100.0	17.5	6.5

flotation products also are shown in Table 4-4. The size analyses indicated that the inorganic constituents of shale are more readily ground than the kerogen.

A second method for reducing SBM capital and operating costs is shown in Figure 4-2. The results of bench-scale grinding studies to develop the time required to produce a nominal 325 mesh grind are shown in Table 4-5. The data indicate that a 20-minute grind is sufficient.

Table 4-5. EFFECT OF GRINDING TIME ON -10 MESH
ALABAMA SHALE PARTICLE SIZE DISTRIBUTION

Time, min	Size Distribution, mesh			-325 Mesh Size, μm			Size	
	+200	-200+325	-325	+24	-24+12	-12	d_{90}	d_{50}
	Wt %						μm	μm
10	15.7	24.2	60.1	30.9	27.1	41.3	39.7	14.9
20	0.4	8.9	90.7	26.7	28.4	44.3	39.5	13.8
30	--	2.2	97.8	20.9	28.9	49.4	34.1	12.1

Figure 4-2. CONTINUOUS GRINDING AND SIZING CIRCUIT NO. 2

The results of a preliminary mechanical cell flotation test conducted with the nominal 325 mesh grind are presented in Table 4-6. In this case, the rougher concentrate was cleaned four times and the rougher tails were combined as waste. The cleaner concentrate and the waste products were sized by sedimentation at 20, 15 and 10 μ m using the specific gravity of quartz (2.65) as the basis for the calculated settling times. The carbon losses in the -10 μ m waste fraction were unexpectedly high in this test. However, the results indicate the potential for utilizing the concept depicted in Figure 4-2.

Table 4-6. RESULTS OF KEROGEN FLOTATION TESTS
WITH -325 MESH GRIND PRODUCT

Flotation Product	Size, μ m	Weight %	Carbon	
			Content	Distribution
			----- wt % -----	
Concentrate	+20	12.6	19.08	15.9
Concentrate	-20+15	8.9	21.58	12.7
Concentrate	-15+10	5.8	24.57	9.7
Concentrate	-10	<u>8.2</u>	32.81	<u>17.7</u>
Composite Conc.		35.5	23.77	55.7
Waste	+20	19.3	16.36	20.8
Waste	-20+15	11.4	9.33	7.0
Waste	-15+10	6.5	6.26	1.7
Waste	-10	<u>27.3</u>	7.64	<u>13.8</u>
Composite Waste		<u>64.5</u>	10.41	<u>44.3</u>
Total		100.0	15.15	100.0

If subsequent column cell tests on shale ground to a nominal 325 mesh size indicate effective recovery of carbon, sufficient column cell concentrate and waste products will be generated for hydrocycloning and SBM studies to investigate this concept.

A series of flotation tests using recycled water was initiated during the quarter. The objectives of the test series are to monitor the quality of water that would accumulate in a tailings pond and determine the effect of water quality changes on flotation.

About 55 gallons (208.2 L) of water were accumulated during pilot plant operations in which a bulk sample of oil shale was ground to 100 mesh. The water was used to grind about 5 kg of shale for a series of column flotation tests. The same water was used in the flotation tests for dilution and wash water. At the end of the test, the dilute tailings were returned to the reservoir along with filtrate water from the concentrates. MRI has repeated this procedure on a bi-weekly basis, each time using water from the reservoir and returning it to the reservoir at the conclusion of the test. Samples of the water are taken at the beginning of each flotation test.

The pH and conductivity of the water are measured on each sample and the balance of each sample reserved for chemical analyses. Table 4-7 presents the

pH and conductivity at each cycle. These data show that the pH has remained essentially stable but the concentration of dissolved ions is increasing as indicated by the increasing conductivity.

Table 4-7. EFFECT OF WATER REUSE ON pH AND CONDUCTIVITY

	Cycle				
	1	2	3	4	5
pH	2.6	2.7	2.8	2.7	2.9
Conductivity, μmhos	550	1230	1550	1450	2250

The flotation response was consistent during the first three cycles, but yielded anomalous results during the fourth cycle. MRI will conduct additional cycles to determine whether the use of recycled water is affecting the quality of separation.

Subtask 4.4. Integrated Grinding and Flotation

The objective of this subtask is to evaluate the application of the advanced Ken-Flote column flotation technique in conjunction with a BDR Mill column (SYMUSEP Separator) to obtain a high grade [125.2 L/metric ton (>30 GPT)] oil shale at more than 90 percent recovery of kerogen. The SYMUSEP Separator utilizes a single stage grinding/cleaning column system that minimizes over grinding. The goals of the project are to remove up to 90 percent of the inorganic material from shale using minimum grinding energy.

During the quarter, UK-CAER continued column flotation tests to improve carbon recovery without sacrificing concentrate grade. The shale for the column flotation tests was ground using a Drais-Werke Mill. In this mill, samples can be ground to 90 percent passing 12 μm size in about 5 minutes, while about 60 minutes are required in the batch attritor mill.

Ken-Flote column tests were conducted using the pilot size 2-inch ID by 20- and 3-foot (5.1-cm by 6.1 and 0.9 meter) columns. For both columns porous rubber or ceramic tubes were used for generating bubbles. During the tests, samples of the froth and tailings were collected simultaneously and analyzed for organic carbon content.

The SYMUSEP Separator (Figure 4-3) was standardized for air, wash water and grinding media. A torque meter will be attached to the separator to monitor grinding energy consumed. Details of tests conducted with the SYMUSEP Separator will be presented next quarter.

Column flotation studies were conducted using a foam jet bubble generating device, which requires the addition of push water to generate fine size bubbles. In these tests, the push water and feed rate were varied, whereas the other column parameters [4-ft. (1.2-m) froth depth, 3 L/min air flow rate, 0.2 L/min wash water and 1.5 lb/ton (0.75 kg/metric ton) M252 frother] were constant. Figure 4-4 shows recovery and grade of the concentrate (percent carbon) for various feed rates using two different push water rates. It shows

Figure 4-3. LINE DIAGRAM OF THE "SYMUSEP" SEPARATOR

Figure 4-4. EFFECT OF FEED RATE AND PUSH WATER RATE ON RECOVERY OF CONCENTRATE AND ITS GRADE

that using 0.5 L/min push water and 0.5 L/min feed rate (retention time 10.5 min), carbon recovery was 68 percent. Increasing feed rate to 1.0 L/min (6-minute retention time) decreased carbon recovery to 55 percent. When 0.25 L/min push water was used, carbon recovery decreased from 52 to 45 percent as the feed rate was increased from 0.5 to 1.0 L/min. Grade of the concentrate remained essentially constant for each push water rate; 36 percent carbon for 0.5 L/min push water and 41 percent carbon for 0.25 L/min push water. These results show higher push water rates are desirable for higher carbon recovery, however concentrate grade decreases. Also evident is that longer retention times are desirable for higher carbon recovery.

A composite froth product was obtained with a grade of 40.0 percent carbon and a recovery of 48.5 percent using 0.25 L/min push water. Recleaning this concentrate under the same conditions provided a concentrate with 50.1 percent carbon at a recovery of 76.5 percent. The recovery of the overall two-stage process was 37.1 percent. Increasing the push water to 0.5 L/min provided a composite froth with 37.1 percent carbon (63 percent recovery) and recleaning improved the grade to 40.1 percent carbon at a recovery of 95.8 percent. The overall recovery with 0.5 L/min push water in a two-stage cleaning process was 60.3 percent. In summary, these tests show that a two-stage cleaning process can significantly increase the concentrate grade. Carbon losses were minimal in the cleaner flotation stage, however the overall recovery was only as high as 60.3 percent due primarily to carbon losses in the rougher flotation stage.

Various types of glycol frothers were evaluated to improve carbon recovery in rougher flotation; the results are shown in Figure 4-5. The best results were obtained with M420 frother, which improved the yield from 22 to 94 percent as the airflow was increased from 2 to 3.5 L/min. For the same conditions, carbon recovery improved from 42 to 90 percent while concentrate grade decreased from 30 to 18.5 percent carbon. Similar results were obtained with M252 frother, however the airflow requirements were higher (3.5 to 5 L/min). When M150 was used as frother, the yield and recovery remained essentially constant at 35 and 55 percent, respectively. These results show that both M252 and M420 are more suitable frothers for effective flotation of the oil shale.

UK-CAER has previously evaluated sodium metaphosphate (SMP) as a dispersant. The results showed that increasing dosages of SMP added during flotation had a depressing effect on carbon recovery. This quarter, UK-CAER added SMP during the grinding stage rather than the flotation stage to disperse clays from the surfaces of carbon-containing particles as new particle surfaces were generated. The results (Figure 4-6) show that SMP has a similar effect when added during the grinding or flotation stage. Carbon recovery was as high 68 percent at a SMP dosage of 2.5 lb/ton (1.25 kg/metric ton) regardless of when the dispersant was added.

Retention time has a significant effect on carbon recovery as shown in Figure 4-7. Increasing the retention time from 8 to 14 minutes improved the carbon recovery from 56 to 86 percent. These results were obtained with minimum wash water addition (0.2 L/min) and concentrate grades, as expected, were low (20 to 24 percent carbon).

Figure 4-5. EFFECT OF VARIOUS FROTHERS ON YIELD, RECOVERY AND GRADE OF THE CONCENTRATE AT VARIOUS AIR FLOW RATES

Figure 4-6. EFFECT OF ADDITION OF SODIUM META PHOSPHATE ON RECOVERY AND GRADE OF THE CONCENTRATE AT VARIOUS AIR FLOW RATES

Figure 4-7. EFFECT OF RETENTION TIME ON RECOVERY AND GRADE OF THE CONCENTRATE

The effect of pH on flotation performance was investigated using a 2 inch diameter by 5 foot high column. As shown in Figure 4-8, pH had no significant effect on carbon recovery or concentrate grade. The effect of air flow rate at a pH of 7 (Figure 4-9) indicates that carbon recovery increases from 55 to 70 percent as airflow rate is increased, however, there is no significant change in grade of the concentrate which averaged about 35 percent.

Based on the results, UK-CAER concludes that

- With 0.5 L/min of push water in a foam jet bubble generator, a 0.5 L/min feed rate, a retention time of 10.5 min, yielded 36 percent carbon product at 68 percent recovery. Decreasing the push water to 0.25 L/min decreased carbon recovery to 52 percent, however, concentrate grade improved to 41 percent.
- Two-stage column flotation provided up to 10 percent improvement in grade of the concentrate (from 40 to 50.1 percent carbon), however, total recovery of carbon was about 40.0 percent.
- Both Betz M420 and M252 frothers provided similar grade and recovery of organic carbon.
- pH had no significant effect on grade or recovery of organic carbon.

Next quarter, UK-CAER will conduct tests using the SYMUSEP Separator, using the optimum column parameters identified in the Ken-Flote column.

Subtask 4.5. Evaluation of Different Grinding Media

During the quarter, MRI conducted tests to evaluate grinding efficiency of sand on raw Alabama shale. The raw shale used was +460 mesh Derrick Screen oversize fraction ($d_{90} = 112 \mu\text{m}$ and $d_{50} = 39.5 \mu\text{m}$) at 51 weight percent solids. The sand media used was -20+65 mesh. The energy size reduction data obtained is shown in Table 4-8. The data clearly indicate that sand is a feasible grinding media.

Table 4-8. RESULTS OF GRINDING TESTS CONDUCTED WITH SAND IN THE LME-4 NETZSCH MILL (John Option, 51% solids, 85% Loading)

rpm	Throughput, t/h	Specific Energy, kWh/t	Particle Size, μm	
			d_{90}	d_{50}
--	Feed	--	112.0	39.5
1800	0.0343	69.2	20.4	8.1
2000	0.0343	103.3	19.7	6.7
2000	0.0257	145.7	16.9	6.3
2000	0.0428	84.6	19.9	7.1
2000	0.0556	64.7	22.8	7.9
2350	0.0556	116.8	17.4	6.6

Figure 4-8. EFFECT OF pH ON RECOVERY AND GRADE OF THE CONCENTRATE

Figure 4-9. EFFECT OF AIR FLOW RATE AT NEUTRAL pH
ON RECOVERY AND GRADE OF THE CONCENTRATE

Based on the experiments conducted using sand media on rougher concentrate and raw shale, an attempt was made to compare their breakage behavior. Since the grinding carried out for these two materials was at different conditions (feed size, pulp density, and sand media size), the experimental data were fit to Charles energy-size reduction relationship. These relationships could then be used in comparing the energy requirements. The relationship obtained were -

$$E = 3.77 \times 10^4 d_{50,p}^{-3.0565} \quad \text{John Option - raw shale}$$

$$E = 1.07 \times 10^5 d_{50,p}^{-4.2853} \quad \text{John Option - rougher concentrate}$$

These energy-size reduction relationships fitted to the data are shown in Figure 4-10. The breakage behavior of the concentrate and raw shale is described by these models, then the raw shale will require higher specific energy input compared to the concentrate in achieving the same product size. Predictions of specific energy requirements based upon these relationships are listed in Table 4-9. It is interesting to note that the 6-fold energy advantage of coarse grinding of concentrate gradually decreases to 2- to 3-fold when the fine grinding ($d_{50} = 5$ to $6 \mu\text{m}$) is targeted in one step. It is clear that the material characteristics become secondary when fine grinding is targeted.

Table 4-9. PREDICTION OF GRINDING ENERGY REQUIRED BASED ON MODIFIED CHARLES RELATIONSHIPS FOR SAND AND ALABAMA SHALE

Product Median Size, $d_{50,p}$, μm	Raw Shale	Rougher Concentrate	Energy Advantage
	E_r	E_c	(E_r/E_c)
	----- kWh/t -----		
5	275.4	108.2	2.54
6	157.7	49.5	3.18
7	98.5	25.6	3.85
8	65.5	14.4	4.54
9	45.7	8.7	5.24
10	33.1	5.5	5.98

Therefore, in order to take energy advantage of the rougher concentrate grinding, primary stirred ball milling of the raw shale should be avoided. One should carry out the ball milling of raw shale to a reasonable fineness, perform column flotation and then carry out re-grinding of rougher concentrate in the stirred ball mill.

MRI plans to directly confirm this finding by conducting grinding tests on raw shale and concentrate having the same feed median size.

Figure 4-10. ENERGY SIZE REDUCTION RELATIONSHIPS USING JOHN OPTION AND SAND MEDIA FOR RAW ALABAMA SHALE AND CONCENTRATE

Subtask 4.6 Evaluation of Concentrate Preparation Techniques

Subtask 4.6.1 Oil Agglomeration and Pelletizing

The objective of this task is to investigate other techniques that have the potential to reduce the cost of preparing concentrate for the PFH process, such as oil agglomeration. The potential advantages of oil agglomeration are that filtration is not required and, because the agglomerating oil tends to fill the interstices between kerogen grains, only surface moisture must be removed by thermal drying.

Previously reported attempts at oil agglomeration and pelletizing of kerogen concentrates were unsuccessful. Oil agglomeration was attempted using pentane, asphalt emulsion, and a combination thereof. While in all cases some degree of flocculation was observed no growth of agglomerates was achieved. Pelletizing tests were unsuccessful due to the fine size distribution of the concentrates.

During the quarter, another agglomeration technique - extrusion - was tried. Two batches of 3/16-inch (4.76-mm) diameter extrusions were prepared from Alabama oil shale concentrates. One batch was made with no additive. The second batch was prepared with an addition of 5 weight percent anionic asphalt emulsion. The batch containing asphalt emulsion was divided into two lots, one of which was air dried while the other was oven dried at 50°C.

The three lots of extruded material were tested by tumbling in an 18-inch (45.7-cm) diameter drum. The drum contained three lifter bars and rotated at 20 rpm. The samples were screened on 10 mesh after tumbling periods of one and six minutes. The amount of -10 mesh material was recorded as the abrasion loss. The results of the tumbling test are presented in Table 4-10.

Table 4-10. RESULTS OF ABRASION TESTS
ON EXTRUDED OIL SHALE CONCENTRATES

<u>Sample</u>	<u>Abrasion Loss, %</u>	
<u>Tumbling Time, min</u>	<u>1</u>	<u>6</u>
No Addition	1.04	3.7
5% Asphalt (air dried)	0.08	1.2
5% Asphalt (oven dried)	0.03	0.08

As expected, the extruded materials containing asphalt emulsion were more abrasion resistant than the materials containing no asphalt. Oven drying proved to have a modest beneficial effect.

Further testing of the extrusion system is planned for next quarter. Tests will be conducted at lower moisture levels and lower concentrations of asphalt emulsion. Other factors to be investigated include extrusion pressure and asphalt type.

Asphalt has been selected as a binder because it is inexpensive, readily available, and may be produced from the PFH product slate.

Subtask 4.6.2. Bioflocculation of Kerogen

The objective of this subtask is to use hydrophobic microorganisms to selectively flocculate kerogen from enriched flotation concentrate to produce an ultrahigh grade product and simultaneously enhance subsequent dewatering of the concentrate. Another objective of the subtask is to use hydrophobic microorganisms as precursors for oil-assisted spherical agglomeration to produce oil enriched-water repellent kerogen agglomerates. This subtask is being conducted by the University of Nevada, Reno (UN).

During the quarter, UN conducted dewatering tests with flotation concentrates. Batch dewatering tests were conducted in both pressure and vacuum filtration units. The test objectives were to determine the effect of additives on concentrate dewatering characteristics, to determine the filter cake resistance for scale-up, and to determine the effect of using recycled water on subsequent flotation process.

UN conducted pressure filtration tests with concentrates without bioflocculant. The results showed residual moisture contents in the filter cake in the range of 50 to 55 weight percent. The results of vacuum filtration tests showed moisture contents in the range of 41 to 42 weight percent.

UN also conducted dewatering tests with bioflocculated concentrates using a vacuum filtration technique. The effects of three nonionic surfactants (GAF Igepal co-430, Igepal co-530, and Igepal co-630) on the dewatering characteristics of the bioflocculated concentrate were determined. The molecular weights of these surfactants range from 484 to 616. For each surfactant, there is a critical concentration at which the lowest equilibrium moisture content in the filter cake can be achieved. The critical concentrations for the Igepal 430, 530, and 630 were determined to be 25, 40, and 80 ppm, respectively. The equilibrium moisture contents were reduced slightly by the addition of the surfactants. The equilibrium moisture content of the sample without surfactant was 41.1 weight percent.

A few experiments were conducted to determine the effects of using recycled process water on the flotation process. It is well known that recycled process water generated by conventional thickening using polymeric flocculants, has an adverse effect on flotation. As shown in Figure 4-11, the kerogen concentrate produced with the recycled water (recycled from the bio-thickener) improved the grade and recovery compared to that produced with clean tap water. Flotation results using tap water show on 85 percent recovery of carbon at a grade of 24 percent carbon. Flotation results using recycled water show a 91 percent carbon recovery at a grade of 31 percent. These results suggest that the presence of some surfactant derived from

Figure 4-11. EFFECT OF USING RECYCLED WATER WITH *M. phlei* ON THE RECOVERY AND GRADE OF THE CONCENTRATE

Mycobacterium phlei is improving both grade and recovery. The data in Figure 4-11 are from a single-stage Denver flotation machine.

Next quarter, UN will continue filtration tests with nonionic surfactants. The effect of surface tension on dewatering will also be established.

Task 5. Operation of PFH on Beneficiated Shale

The objectives of this task are to expand the PFH data base by conducting laboratory- and bench-scale tests with beneficiated Alabama shale, and to characterize the effluent streams from these tests. This task is divided into two subtasks: 5.2.1. (Laboratory-Scale Tests) and 5.2.2. (Bench-Scale Continuous Tests), which will be performed by IGT.

Subtask 5.2.1. Laboratory-Scale Tests

The objective of this subtask is to conduct laboratory-scale batch and continuous tests with beneficiated shale to determine the operating conditions for bench-scale testing.

During the quarter, IGT conducted thirteen batch tests and nine continuous tests (including four successful continuous tests) in the 5.1-cm (2-inch) diameter batch and continuous PFH reactors. The tests were performed to determine the effects of temperature, hydrogen pressure, and residence time on carbon conversions and oil yields. The batch test results will be used to select conditions for the bench-scale PFH test in Subtask 5.2.2. The continuous test results will confirm the batch test results and also provide preliminary information on the feeding and discharging of shale from a continuous fluidized-bed reactor.

The batch PFH tests were conducted with beneficiated Alabama shale with a nominal feed size of -16+70 mesh. An analysis of the feed shale is presented in Table 5-1. The operating conditions of the batch PFH tests include temperatures in the range of 455° to 565°C (850° to 1050°F), pressures of 2.9 to 7.0 MPa (400 to 1000 psig), and residence times of 5 to 30 minutes. The operating conditions, carbon conversions, and oil yields for the batch tests are summarized in Table 5-2.

Feed shale was sized to -16+70 mesh for all tests except Tests 51-B-6 and 51-B-8 with a -50+80 mesh consist and Test 51-T-9 with a -20+30 mesh consist. The results show that the oil yield increased with increasing pressure and was highest at 510°C. The oil yields from all the tests were in excess of 205 percent of Fischer Assay. The maximum oil yield at 510°C and 7.0 MPa was 264 percent of the Fischer Assay oil yield.

Carbon conversion to gas increased with increasing temperature but was unaffected by changes in pressure. Particle size variations over the range studied (-20+30 to -50+80 mesh) had no effect on the carbon conversion to oil or gas.

Table 5-1. ANALYSES OF BENEFICIATED ALABAMA SHALE

Moisture, wt %	1.87
Ultimate, wt % (dry)	
Ash	54.30
Carbon	32.15
Hydrogen	3.11
Sulfur	9.15
Nitrogen	0.85
Oxygen (HTW)	4.72
F. A. Oil Yield, L/metric ton	94.0
GPT	22.5
Bulk Density, g/mL	0.741
Sieve Analysis, mesh, wt %	
+16	1.0
-16+20	22.8
-20+30	29.4
-30+50	21.4
-50+60	16.8
-60+70	2.9
-70+80	1.4
-80+100	1.5
-100+Pan	2.8
Total	100.0

Table 5-2. OPERATING CONDITIONS AND RESULTS OF TESTS CONDUCTED
IN THE BATCH PFH REACTOR WITH BENEFICIATED ALABAMA SHALE

Test No.	Temp, °C	Press, MPa	Residence Time, min	Carbon Conv., %			Oil Yield, GPT
				Oil	Gas	Res.	
51-B-1	510	7.0	30	66.5	14.5	19.0	59.3
51-B-2	510	7.0	10	64.6	11.8	23.6	57.3
51-B-3	510	7.0	5	58.4	10.7	30.8	51.9
51-B-4	465	7.0	20	51.9	8.5	39.6	46.7
51-B-5	565	7.0	10	64.0	15.9	20.0	57.0
51-B-6	510	7.0	10	66.0	11.8	22.2	58.8
51-B-7	510	4.2	10	59.0	14.4	26.6	52.7
51-B-8	510	4.2	10	56.4	12.6	31.0	51.4
51-B-9	510	4.2	10	60.6	10.3	29.1	54.9
51-B-10	465	2.9	20	55.8	9.2	35.0	50.5
51-B-11	510	2.9	10	56.7	11.3	31.9	51.4
51-B-12	565	2.9	10	57.7	12.2	30.1	51.9
51-B-13	510	7.0	10	64.3	13.1	22.5	56.7

IGT conducted a total of nine tests in the laboratory-scale continuous PFH unit at nominal conditions of 482°C and 7.0 or 4.2 MPa (900°F and 1000 or 600 psig). The particle size distribution of the beneficiated Alabama shale was -20+50 mesh for the first six tests and -40+80 mesh for the next three tests. The objective of these tests was to confirm the results of the batch PFH tests.

The nominal conditions for the first test (Test 1) were a temperature of 482°C and pressure of 7.0 MPa. This test was not successful because the beneficiated shale accumulated in the reactor and could not be discharged through the overflow tube to the residue receiver. The reactor with a vertical baffle through the center was used for the next five tests. The fluidization velocity was increased in the first three baffle reactor tests (Tests 2, 3 and 4) to insure that the bed was sufficiently active to promote movement of shale out of the reactor and into the overflow tube. However, these tests were terminated when solids fed to the reactor could not be discharged into the residue receiver.

In the next test (Test 5), the pressure was reduced to 4.2 MPa (600 psig) to permit higher gas velocities to be achieved. This test was partly successful. However, for the next four tests, the non-baffled reactor was used and successively higher fluidization velocities and shorter residence times were used in an effort to achieve good fluidization. Test 6 was not successful; no solids could be discharged. In the next test (Test 7), the particle size consist was reduced to -40+80 mesh to reduce the minimum fluidization velocity of the particles. Tests 7, 8, and 9 were successful and solids, liquids, and gas samples were collected for analyses.

A test was conducted in the cold-flow model with the feed shale, which demonstrated that fluidization could be established. At elevated temperatures and pressures, however, the shale appears to form large aggregates, which are difficult to fluidize.

Subtask 5.2.2. Bench-Scale Continuous Tests

During the quarter, IGT also continued preparing the BSU for a test to be conducted with beneficiated shale. The BSU was assembled and successfully pressure tested. In addition, a flow test was conducted with shale being fed and discharged from the BSU. A hot-flow test was conducted in which sand was fed to establish a bed in the BSU. The sand was removed from the BSU by the discharge screw. During the hot-flow test, the gas-fired heater was activated and the liquids condenser and collection systems were tested as well as the instrumentation used for controlling the flows and recording data.

The BSU test will be conducted next quarter. The nominal operating conditions for this test are a temperature of 496°C (925°F), pressure of 7.0 MPa (1000 psig), and a shale residence time in the fluidized bed of 20 minutes. The Environmental Sampling Train will be used during this test.

Task 6. Environmental Data and Mitigation Analyses

The overall objectives of Task 6 are to obtain environmental data relating to PFH and shale beneficiation, and also to analyze the potential environmental impact of the integrated PFH process. This task is divided into four subtasks: 6.1. Characterization of Processed Shales, 6.2.2 Wastewater Treatability, 6.4.1. PFH Process Analyses, and 6.4.3. Plant Energy Optimization.

Subtask 6.1. Characterization of Processed Shales

The objective of this subtask is to determine the effects of PFH processing on the physical and chemical characteristics of raw and spent beneficiated shale.

Discussion

This subtask will be completed next quarter when appropriate samples of hydrotreated shale are available from the laboratory- and bench-scale units.

Subtask 6.2. Water Availability and Treatment Studies

Subtask 6.2.2. Wastewater Treatability

The objective of this subtask is to determine suitable techniques for treating wastewater generated during shale processing. Tennessee Technological University (TTU) is conducting the work on this subtask.

Discussion

During the quarter, TTU established the standard curve for the determination of aniline in solution by gas chromatography (GC). The data generated for the standard curve is shown in Figure 6-1. Linear regression of the data provided the following equation for determining aniline concentration in solution, based on GC peak area -

$$[\text{aniline}] = 1.796 \times 10^{-4} \times (\text{peak area}) + 0.428$$

TTU also completed the treatability studies with methyl ethyl ketone (MEK). A second treatability test was conducted with MEK to confirm the results of another test conducted during the previous quarter. The initial MEK concentrations were 50, 100, and 250 mg/L. The change in the chemical oxygen demand (COD) with time is presented in Figure 6-2. COD stabilization was completed after about 33 hours. Upon analyzing the samples for MEK, it was determined that the MEK concentrations were lower than expected. Thus, the experiment was repeated (without inoculation with biological seed) to assess the impact, if any, of air stripping.

Experiment 3 was conducted using reactors similar to those used in experiments 1 and 2, but void of biological activity. Each reactor was sterilized and contained three liters of about 300 mg/L MEK prepared with sterilized distilled water. The air used was also filtered through cotton

Figure 6-1. STANDARD CURVE FOR THE DETERMINATION OF ANILINE
BY GAS CHROMATOGRAPHY

Figure 6-2. COD vs. TIME FOR MEK BATCH EXPERIMENT 2

prior to entering the reactors. The reactors operated at air flow rates of about 133, 257, and 474 mL/min/L. Figure 6-3 shows the change in COD with time for these three flow rates. The results show that the removal due to stripping can be significant at higher flow rates.

A fourth MEK experiment was performed to establish the amount of MEK removed as a result of biodegradation versus air stripping. The experiment was structured so that the total amount removed and the amount removed by air stripping were determined concurrently. From these data the net amount removed by biodegradation can be determined. The data from these tests is presented in Figures 6-4, 6-5, and 6-6. It should be noted that even though stripping occurred in these batch treatability studies with MEK, stripping may not occur in a continuous flow reactor. In a continuous flow reactor the concentration of biomass will be much greater and will, therefore, increase the uptake rate of the MEK, or any other biodegradable carbon source present. The air stripping occurred in these batch reactors at very low concentrations of biomass. In the absence of stripping, the stabilization of the MEK was completed within 35 to 40 hours. When these data are compared to the 33 hours required for stabilization by biological degradation and air stripping (experiment 2), the effect of air stripping is minimal.

Treatability studies with aniline were initiated. Prior to proceeding with these studies, a test was performed to determine if aniline could be removed by air stripping under the conditions to be used in the treatability studies. The reactors were prepared the same as those for the air stripping tests with MEK. The initial concentrations of aniline in the reactors were 150, 300, and 600 mg/L. The results (Figure 6-7) show that over a period of 48 hours, the COD of aniline present in solution was not reduced by air stripping at an aeration rate of about 180 mL/min/L. The COD concentrations were relatively constant at 350, 725, and 1450 mg/L, respectively.

Aniline treatability studies were performed using 1.5-L reactors and initial concentrations of 150, 300, and 600 mg/L. The changes in COD and aniline with time for experiment 1 are shown in Figures 6-8, 6-9, and 6-10. With initial aniline concentrations of about 150 and 300 mg/L, the aniline was biodegraded to a concentration less than 1 mg/L in about 62 hours. For the reactor with an initial aniline concentration of 600 mg/L, an aniline concentration of less than 1 mg/L was reached in 33 hours. The difference between 33 and 62 hours required for degradation may be due to the age of the microorganisms used as seed. This experiment will be repeated for confirmation.

Next quarter, treatability studies with aniline will continue. As time permits, treatability studies with phenol, MEK, and aniline will be conducted in combinations of two and three compounds. Experiments to acclimate organisms to 4-methyl pyridine (4-picoline) by using this compound as the sole source of nitrogen will be initiated. A draft final report will be prepared.

Subtask 6.4.1. PFH Process Analyses

The objective of this subtask is to analyze the data obtained in Subtask 5.2 and to refine correlations previously developed for raw shale to describe the performance of beneficiated Alabama shale in the PFH process. The refined

Figure 6-3. EFFECT OF AIR FLOW RATE ON MEK STRIPPING
(INITIAL MEK CONCENTRATION WAS 300 mg/L)

Figure 6-4. COD AND MEK vs. TIME FOR MEK EXPERIMENT WITH AND WITHOUT AIR STRIPPING (INITIAL MEK CONCENTRATION WAS 50 mg/L)

Figure 6-5. COD AND MEK vs. TIME FOR MEK EXPERIMENT WITH AND WITHOUT AIR STRIPPING (INITIAL MEK CONCENTRATION WAS 100 mg/L)

Figure 6-6. COD AND MEK vs. TIME FOR MEK EXPERIMENT WITH AND WITHOUT AIR STRIPPING (INITIAL MEK CONCENTRATION WAS 250 mg/L)

Figure 6-7. REMOVAL OF ANILINE BY AIR STRIPPING AT AN AERATION RATE OF ABOUT 180 mL/min/L

Figure 6-8. COD AND ANILINE vs. TIME (Initial Aniline Concentration Was 150 mg/L, Air Flow Rate Was 180 mL/min/L)

Figure 6-9. COD AND ANILINE vs. TIME (Initial Aniline Concentration Was 300 mg/L, Air Flow Rate Was 180 mL/min/L)

Figure 6-10. COD AND ANILINE vs. TIME (Initial Aniline Concentration Was 600 mg/L, Air Flow Rate Was 180 mL/min/L)

correlations will be incorporated into an existing computer program that simulates the PFH process. The program will be used to estimate the compositions and quantities of effluent streams for a commercial-scale PFH plant.

Subtask 6.4.1. PFH Process Analyses

The objective of this subtask is to analyze the data obtained in Subtask 5.2 and to refine correlations previously developed for raw shale to describe the performance of beneficiated Alabama shale in the PFH process. The refined correlations will be incorporated into an existing computer program that simulates the PFH process. The program will be used to estimate the compositions and quantities of effluent streams for a commercial-scale PFH plant.

During the quarter, IGT continued work on modeling the PFH process by modifying the computer program that simulates a fluidized-bed reactor. Minor errors were detected and corrected in Fortran statements in the computer program that simulates the PFH process. Data based on a bench-scale test conducted previously with beneficiated Indiana shale (Test OSAMRR-10) will be prepared and inputted to the PFH simulation program next quarter. IGT also is adopting a computer program developed at the University of Sheffield (England) for modeling fluidized-bed combustion processes to simulate the PFH retort. The program rigorously performs material and energy balances throughout the fluidized bed including thermodynamic and kinetic calculations. Preliminary output from the simulation is fairly consistent with experimental results achieved by IGT in bench-scale tests conducted with raw Alabama shale (Tests OSAMRR-4 and -5). Next quarter, specific assumptions made concerning operating parameters as well as the kinetics of the shale hydroretorting reactions will be adjusted as appropriate.

Subtask 6.4.3 Thermoeconomic Evaluation

The objective of this subtask is to provide an initial evaluation of the PFH plant design from thermodynamic and economic viewpoints. The goals of this study are to identify thermodynamic losses, to assist in developing cost-effective solutions to reduce those losses, to improve the understanding of the cost/benefit tradeoffs in the design, and to facilitate future optimization studies. This subtask is also being conducted by TTU.

During the quarter, the first results from the thermoeconomic evaluation of the PFH plant design were obtained. The detailed results, which will be presented in the final report, include the following:

- Monetary flow rate associated with each plant stream
- Cost per unit of total, chemical and physical exergy for each plant stream
- Cost of fuel, product and exergy destruction for each plant component
- Various component-related thermoeconomic variables, which assist in the evaluation of the component cost effectiveness.

IGT provided TTU with the investment costs for specific groups of components in the PFH plant flow diagram, such as shale retorting, gas scrubbing, desalting and hydrotreating, as shown in Figure 6-11. The numbers shown in Figure 6-11 are process stream numbers. Table 6-1 summarizes the most important variables for the thermoeconomic evaluation of selected component groups. The following variables are given in Table 6-1: 1) The flow rate of exergy destruction is a measure of the absolute value of "energy waste" in the group. 2) The exergetic efficiency is an objective measure of the thermodynamic efficiency of the processes in the component group. 3) The cost rate of exergy destruction represents the expenses caused by the exergy destruction in the group. 4) The thermoeconomic variable r is the relative cost difference between average cost per exergy unit of product and average cost per exergy unit of fuel. 5) The thermoeconomic factor f expresses the contribution of capital costs to the relative cost difference r .

Table 6-1 shows that shale retorting is a relatively efficient operation. However, the rates of exergy destruction and cost of exergy destruction in shale retorting are the highest in the plant. Any change in the shale retorting process that would reduce the exergy destruction in this group, would improve its cost effectiveness. Cost effective changes relate to design changes that would reduce the cost of oil generated by the PFH plant.

Table 6-1. EXERGY DESTRUCTION FLOW RATE, EXERGETIC EFFICIENCY, COST RATE OF EXERGY DESTRUCTION AND THERMOECONOMIC VARIABLES r AND f FOR SELECTED GROUPS OF PLANT COMPONENTS

Component Group	Exergy Destruction, MW	Exergetic Efficiency, %	Cost Rate of Exergy Destruction, \$/h	Cost Rate	
				r	f , %
Shale Retorting	244.8	97.6	3572	0.04	41.3
Gas Scrubbing	22.6	99.8	345	0.01	74.0
Acid-Gas Removal	11.4	99.8	174	0.01	76.0
Hydrogen Recov.	30.4	99.5	531	0.02	81.1
Compr. & Heat Ex.	44.1	96.8	1105	0.08	54.9
Reformer Furnace	153.6	90.1	2710	0.37	62.9
Shift Conv. & CO ₂ Removal	61.9	95.2	1739	0.11	50.1
Desalting & Hydrotreating	96.9	97.7	1771	0.07	66.3

The cost effectiveness of gas scrubbing, acid gas removal and hydrogen recovery can be increased mainly through savings in the investment costs as the relatively high values of the factor f indicate. Since the exergy destruction in these component groups is relatively small and to a large extent independent of the investment costs, the general objective for these groups should be to minimize the overall investment costs. The only exception to that is associated with the recycle gas compressors, the cost effectiveness of which would increase by increasing their efficiency, and, consequently, their investment costs.

The cost rate of exergy destruction in compression and heat exchange is relatively large. This group could become more cost efficient by increasing the efficiency of the hydrogen compression process and by adding the high-pressure steam (Stream 115) to the hydrogen plant after stream 101 has been preheated in the first heat exchanger.

The value of the thermoeconomic variable r in the reformer furnace is the highest among all plant components. The factor f indicates that this high r value is mainly caused by the high investment costs of this component. Since the cost rates associated with both the exergy destruction and the investment costs are high, particular attention should be paid to this component. A more detailed study is required to optimize this component from the thermoeconomic viewpoint. The same recommendation applies to shift conversion and CO_2 removal group, which shows the second highest r value in the plant.

The conceptual design of a conventional, subcritical steam power plant was developed. Characteristics of this plant include using the spent shale and the fuel gas generated in the PFH plant as fuel, providing the PFH plant with the net steam required from external sources, using preheated feed water and the excess steam from the PFH plant.

Figure 6-12 presents the steam power plant flow diagram. The connections between the PFH plant and the steam power plant are shown in Figure 6-13. Table 6-2 shows the thermodynamic data used for the steam power plant streams. The major products of the combined plant (PFH plant and steam plant) are oil and electric power.

The flow diagrams for the combined plant are shown in Figures 6-11 through 6-13. Table 6-2 shows the mass flow rates, temperatures, pressures and the flow rates of enthalpy, entropy and exergy of the material streams in the conventional steam power plant. The corresponding information for the PFH plant was presented in the previous quarterly report. For each plant component, Table 6-3 shows the heat loss, the power supplied (generated), the exergy destruction flow rate, the exergy destruction ratio (exergy destruction in the component being considered divided by the sum of exergy destruction in the total plant), the ratio between the component exergy destruction and the exergy of raw shale supplied to the total plant, and, finally, the component exergetic efficiency.

The exergy destruction in the steam generator is significant and represents about 50 percent of the total exergy destruction in the combined plant. The exergetic efficiency of the steam generator (48.8 percent) is the lowest among all combined plant components. The exergy destruction in the steam turbines is mainly due to friction. State-of-the-art steam turbines were assumed in the design of the power plant. The total exergy destruction in the five feed water preheaters could be reduced by improving the integration between the PFH plant and power plant.

Figure 6-12. FLOW DIAGRAM OF THE STEAM POWER PLANT

Figure 6-13. INTEGRATION OF THE PFH PLANT WITH A STEAM POWER PLANT

Table 6-2. THERMODYNAMIC PROPERTIES FOR THE STEAM CYCLE

STREAM NO.	m [lb/hr]	T [F]	P [psia]	H [MMBtu/hr]	S [MBtu/hrR]	E [MBtu/hr]
D	1080822.	650.0	1.0	-4119.66	480.95	3995.47
115	552602.	648.9	653.5	-3075.50	1320.92	284.05
141	1772437.	97.4	580.2	-12080.75	1711.47	7.14
142	1772437.	397.4	522.1	-11538.95	2488.06	145.37
301	4008777.	1000.4	2422.1	-21737.27	9512.95	2670.28
305	340841.	648.8	653.5	-1896.96	814.72	175.19
306	3115335.	648.8	653.5	-17338.52	7446.65	1601.28
310	3115335.	1000.4	588.7	-16713.47	7972.11	1953.28
314	133780.	831.9	313.7	-728.49	343.56	72.48
316	2981555.	589.3	110.5	-16575.44	7701.63	1252.37
317	199693.	488.8	614.7	-1134.13	456.25	90.86
318	166217.	589.3	110.5	-924.05	429.35	69.82
319	2815338.	589.3	110.5	-15651.38	7272.27	1182.55
321	2815338.	589.0	108.3	-15651.38	7278.33	1179.40
322	165091.	297.7	64.7	-941.64	409.26	54.43
325	89668.	161.7	4.9	-518.36	236.72	15.15
326	2725670.	112.3	1.4	-15939.07	7254.42	247.61
327	166217.	118.2	1.6	-966.45	449.19	17.12
328	2891887.	112.3	1.4	-16905.52	7706.51	263.22
329	2891887.	103.6	1.4	-19697.20	2825.60	8.00
330	165091.	243.6	590.3	-1101.09	197.90	4.82
331	210110.	411.1	2860.1	-1364.19	297.24	19.71
333	89668.	105.8	4.2	-610.55	87.96	0.26
334	3544574.	96.8	1.4	-24167.09	3419.91	8.06
335	3544574.	96.8	65.3	-24166.25	3420.21	8.75
337	1772437.	96.8	65.3	-12084.14	1710.25	4.38
338	1772137.	148.9	61.4	-11989.91	1868.35	14.25
340	1772137.	96.8	65.3	-12082.10	1709.96	4.37
343	674314.	252.6	162.4	-4491.79	817.51	20.51
344	2611542.	242.6	57.7	-17423.35	3128.97	71.60
345	2446451.	243.6	590.3	-16316.81	2932.62	71.42
346	474621.	347.8	273.0	-3115.04	636.50	29.23
347	2611542.	243.6	590.3	-17417.90	3130.52	76.24
348	2446451.	340.4	554.9	-16074.19	3256.11	145.93
349	340841.	427.1	568.7	-2207.94	491.02	32.43
350	4218888.	411.1	2860.1	-27392.16	5968.43	395.73
351	4218888.	404.3	521.6	-27434.54	5958.69	358.42
352	4008777.	411.1	2860.1	-26027.97	5671.19	376.03
353	4008777.	482.5	2688.6	-25717.00	6016.96	507.32
354	166217.	588.2	102.4	-924.05	430.73	69.10
355	4678288.	60.0	14.7	-18.96	7661.29	4.22
358	1080822.	650.0	14.7	-4119.66	480.95	3995.47
359	793283.	800.3	14.5	-4100.64	275.37	48.45
361	5061552.	557.4	15.0	-4746.60	9087.82	554.26
362	2446451.	409.3	521.6	-15895.58	3470.53	213.11
365	563019.	60.0	14.7	-3859.34	504.79	0.60
366	3454906.	96.5	1.4	-23556.54	3331.94	7.81

Table 6-3. HEAT LOSS, POWER SUPPLIED, EXERGY DESTRUCTION FLOW RATE, EXERGY DESTRUCTION RATIO, EXERGY DESTRUCTION TO SHALE EXERGY RATIO, AND EXERGETIC EFFICIENCY FOR PLANT COMPONENTS

COMPONENT	HEAT LOSS [MW]	POWER [MW]	EXERGY DESTR. [MW]	EXD RATIO [%]	EXD/ Eshale [%]	EXERG. EFFIC. [%]
1 PREHEAT	104.00	0.00	34.63	2.26	0.55	21.83
2 RETORT	50.59	8.24	104.00	6.79	1.65	97.68
3 COOLING	4.86	0.00	6.79	0.44	0.11	58.43
4 MIXING 1A+2=3	0.00	0.00	3.77	0.25	0.06	99.93
5 HEAT EXCHANGER	0.00	0.00	3.37	0.22	0.05	87.46
6 GAS-OIL SEPARATOR	0.00	0.00	0.30	0.02	0.00	100.00
7 GAS COOLER I	0.00	0.00	4.42	0.29	0.07	90.16
8 KNOCK-OUT DRUM I	0.00	0.00	0.29	0.02	0.00	100.00
9 GAS COOLER II	0.00	0.00	0.97	0.06	0.02	39.28
11 3-PHASE SEPARATOR	0.00	0.00	0.08	0.01	0.00	100.00
12 LEAN OIL SCRUBBER	0.77	0.00	0.81	0.05	0.01	99.99
13 LEAN OIL STRIPPER	16.94	1.96	8.13	0.53	0.13	99.58
14 ACID GAS REMOVAL	34.37	0.75	11.41	0.74	0.18	99.81
15 GAS COMPRESSOR 31/34	1.22	1.93	0.92	0.06	0.01	52.11
16 KNOCK-OUT DRUM III	5.27	0.00	0.48	0.03	0.01	99.92
19 CLAUSS & SCOT UNITS	13.61	1.31	14.76	0.96	0.23	82.96

Table 6-3 (Continued). HEAT LOSS, POWER SUPPLIED, EXERGY DESTRUCTION
FLOW RATE, EXERGY DESTRUCTION RATIO, EXERGY DESTRUCTION TO SHALE
EXERGY RATIO, AND EXERGETIC EFFICIENCY FOR PLANT COMPONENTS

COMPONENT	HEAT LOSS [MW]	POWER [MW]	EXERGY DESTR. [MW]	EXD RATIO [%]	EXD/ Eshale [%]	EXERG. EFFIC. [%]
20 HEAVY OIL FLASH DRUM	18.51	0.00	5.34	0.35	0.08	99.72
21 HYDROGEN RECOVERY	0.05	0.00	14.68	0.96	0.23	99.37
22 RECYCLE GAS COMPR. 82/86	10.05	21.16	7.64	0.50	0.12	63.89
23 RECYCLE GAS COMPR. 84/85	0.00	5.87	1.65	0.11	0.03	71.87
24 RECYCLE GAS COMPR. 94/95	5.07	10.53	4.03	0.26	0.06	61.69
25 COMPR. TO H2 PLANT 92/93	7.63	12.02	4.42	0.29	0.07	63.26
26 MIXING WITH NATURAL GAS	0.00	0.00	0.05	0.00	0.00	100.00
27 STEAM ADDITION 115	0.00	0.00	13.02	0.85	0.21	98.91
28 HEAT EXCHANGER 102/103	0.00	0.00	0.00	0.00	0.00	0.00
29 FEED PROD HEAT EXCHANGER	0.00	0.00	5.22	0.34	0.08	78.81
30 REFORMER FURNACE	0.00	0.00	149.54	9.76	2.38	56.12
31 QUENCH WATER	0.00	0.00	20.34	1.33	0.32	98.52
32 HEAT EXCHANGER 108/109	0.00	0.00	3.01	0.20	0.05	71.76
33 SHIFT CONVERSION	0.64	0.00	0.25	0.02	0.00	99.98
34 HEAT EXCHANGER 110/111	0.00	0.00	18.02	1.18	0.29	61.06
35 KNOCK-OUT DRUM IV	0.00	0.00	0.00	0.00	0.00	100.00
36 HEAT EXCHANGER 111/112	0.00	0.00	28.65	1.87	0.46	26.15
37 KNOCK-OUT DRUM V	0.00	0.00	0.13	0.01	0.00	99.99
38 ABSORBER/REGENERATOR	22.78	1.01	1.22	0.08	0.02	99.90
39 COMPR. TO DES. & HYDR.	15.78	19.75	9.47	0.62	0.15	52.03

Table 6-3 (Continued). HEAT LOSS, POWER SUPPLIED, EXERGY DESTRUCTION
FLOW RATE, EXERGY DESTRUCTION RATIO, EXERGY DESTRUCTION TO SHALE
EXERGY RATIO, AND EXERGETIC EFFICIENCY FOR PLANT COMPONENTS

COMPONENT	HEAT LOSS [MW]	POWER [MW]	EXERGY DESTR. [MW]	EXD RATIO [%]	EXD/ Eshale [%]	EXERG. EFFIC. [%]
40 DESALTING & HYDROTREATING	148.70	5.09	83.48	5.45	1.33	98.03
41 SOUR WATER & NH3 RECOVERY	3.57	3.50	2.94	0.19	0.05	94.66
42 NATURAL GAS THROTTLING	0.00	0.00	5.08	0.33	0.08	99.17
43 FIRED HEATER	0.00	0.00	92.41	6.03	1.47	60.30
44 HEAT EXCHANGER AFTER HEATER	0.00	0.00	1.89	0.12	0.03	71.07
45 AIR FAN 78/79	0.00	3.83	0.75	0.05	0.01	80.49
46 STEAM GENERATOR	101.43	20.56	773.09	50.46	12.29	48.81
47 HP TURBINE	0.00	-164.79	13.92	0.91	0.22	92.21
48 IP TURBINE	0.00	-169.59	14.59	0.95	0.23	92.08
49 LP TURBINE	0.00	-231.51	37.14	2.42	0.59	86.18
50 PUMP 1	0.00	0.26	0.06	0.00	0.00	77.24
51 PUMP 4	0.00	1.05	0.24	0.02	0.00	77.24
52 PREHEATER 1	0.00	0.00	1.47	0.10	0.02	66.39
53 PREHEATER 2	0.00	0.00	5.16	0.34	0.08	80.27
54 PUMP 2	0.00	1.68	0.32	0.02	0.01	80.95
55 PREHEATER 3	0.00	0.00	7.35	0.48	0.12	74.82
56 PREHEATER 4	0.00	0.00	2.49	0.16	0.04	88.77
57 PUMP 3	0.00	12.42	1.48	0.10	0.02	88.06
58 TURBINE 5	0.00	-12.47	3.02	0.20	0.05	80.44
59 PREHEATER 5	0.00	0.00	3.36	0.22	0.05	91.97

Table 6-3 (Continued). HEAT LOSS, POWER SUPPLIED, EXERGY DESTRUCTION
FLOW RATE, EXERGY DESTRUCTION RATIO, EXERGY DESTRUCTION TO SHALE
EXERGY RATIO, AND EXERGETIC EFFICIENCY FOR PLANT COMPONENTS

COMPONENT	HEAT LOSS [MW]	POWER [MW]	EXERGY DESTR. [MW]	EXD RATIO [%]	EXD/ Eshale [%]	EXERG. EFFIC. [%]
60 CONDENSER	818.18	0.00	74.81	4.88	1.19	---
61 SUM	1383.64	-445.38	1532.03	100.00	24.35	---
62 EXERGY LOSSES	---	---	428.58	---	---	---
63 PFH PLANT	464.03	96.95	781.05	43.63	10.62	85.26
64 STEAM POWER PLANT	919.61	-522.40	1094.73	56.37	13.73	35.89
65 TOTAL PLANT	1383.64	-425.45	1960.61	---	---	68.85

Table 6-3 shows that the PFH plant with a total exergy destruction of 781 MW and an exergetic efficiency of 85.26 percent is considerably more energy efficient than the steam power plant (exergy destruction = 1095 MW; exergetic efficiency = 35.89 percent). These numbers show that the PFH plant design is energy efficient. It should be noted, however, that first, there is some potential for cost-effective improvement of the PFH plant design, and second, a power producing plant has, in general, a lower efficiency than a fuel-conversion plant.

Next quarter, the thermoeconomic evaluation of the combined plant will be completed. Design options to improve the overall efficiency and cost effectiveness of the combined plant will be developed. The effect of these design changes on the overall plant performance will be determined.

Task 7. Sample Procurement, Preparation, and Characterization

The objective of this task is to procure, prepare, and characterize raw and beneficiated Eastern oil shale samples for all of the experimental tasks of the program extension.

MRI completed all of the components of this task during the previous quarter.

Task 8. Project Management and Reporting

The objective of this task is to coordinate all aspects of the program among DOE, IGT, and the various subcontractors to insure that a cohesive program is maintained.

Discussion

During the quarter, IGT presented a project status report to DOE at the Mineral Resources Institute of the University of Alabama. MRI presented a status report describing their activities as well as those of UK-CAER and UN. IGT's presentation included the overall status of the program and summaries of activities conducted by IGT and TTU. DOE and IGT personnel were given a tour of the MRI and the University of Alabama facilities.

Also, IGT personnel prepared project status reports for December, January, and February as well as the quarterly technical progress report for the period September through November 1991. IGT continued to review the reports and oversee the research activities of the subcontractors participating in the project.

FUTURE PLANS

Work on the scheduled tasks will continue as planned.

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UN:	Professor M. Misra
TTU:	Professor W. P. Bonner

END

**DATE
FILMED**

8 / 19 / 92