**Perform Research in Process Development for
Hydroretorting of Eastern Oil Shales
Volume II. Expansion of the Moving-Bed Hydroretorting
Data Base for Eastern Oil Shales**

Final Report

Work Performed Under Contract No.: DE-FC21-85LC11069

**For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
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November 1989

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EXECUTIVE SUMMARY

This report presents the work performed by the Institute of Gas Technology (IGT), during October 22, 1985, through September 30, 1988, under subcontract with HYCRUDE Corporation for their DOE Cooperative Agreement No. DE-FC20-85LC11069 for the project, "Expansion of Moving-Bed Hydroretorting Data Base for Eastern Oil Shales."

An extensive data base was developed for six Eastern oil shales: Alabama Chattanooga, Indiana New Albany, Kentucky Sunbury, Michigan Antrim, Ohio Cleveland, and Tennessee Chattanooga shales. The data base included the hydroretorting characteristics of the six shales, as well as the retorting characteristics in the presence of synthesis gas and ionized gas. Shale gasification was also successfully demonstrated. Shale fines (20%) can produce enough hydrogen for the hydroretorting of the remaining 80% of the shale. The amount of fines tolerable in a moving bed was also determined.

In Task 1 (Hydroretorting Characteristics), 62 successful tests were conducted in the laboratory-scale batch Hydroretorting Assay Unit (HAU) during this program. Tests were conducted to determine the effects of temperature (900° to 1200°F) and pressure (400 to 1000 psig) on yields for six Eastern shales. Oil yields as high as 27, 31, 19, 28, 24, and 23 gal/ton were obtained from the shales from Alabama, Indiana, Kentucky, Michigan, Ohio, and Tennessee, respectively. Tests were conducted with Indiana New Albany shale to determine if the use of a freeze-out train in the off-gas line would capture any liquids escaping as a mist and any heavy hydrocarbons that might be below the detectable limits of the gas chromatograph used for their analysis. The results show that essentially no liquids are escaping detection by the normal cooling and condensing system. Several tests were conducted to determine the effects of gas residence time on oil yield and hydrogen consumption. The results show that gas residence time has no effect on oil yield in the range of 14 to 54 seconds, however, there is a reduction in hydrogen consumption with decreased gas residence time. Several HAU tests were also conducted at mini-bench unit (MBU) design point conditions to permit a comparison of the results from HAU tests and MBU tests without extrapolation of the data. Minor differences in oil and gas yields were noted.

Nine MBU tests were conducted in Task 1. Six tests were conducted with shales from Indiana, Alabama, Tennessee, Kentucky, Michigan, and Ohio at

design point conditions chosen by HYCRUDE. The other three tests included replicate tests with Indiana and Kentucky shales and a test with Indiana shale at short gas residence time conditions. Oil yields ranged from 13.3 gal/ton for Kentucky shale to 25.9 gal/ton for Indiana shale. Organic carbon conversion to gas varied from 12% to 16% and the organic carbon selectivity to oil varied from 76% for Kentucky shale to 84% for Indiana shale. Tennessee shale, hydroretorted at 1210°F, produced more hydrocarbon gas and had a lower organic carbon selectivity to oil than the other shales. Normalized MBU oil yields for five of the shales tested were similar to yields predicted by HAU tests. Kentucky shale MBU oil yields were 15% below the HAU predicted yields. Overall organic carbon conversions and organic carbon conversions to gas were 2% to 5% and 5% to 10% higher for the MBU tests than for comparable HAU tests.

Sulfur conversions of 40% to 57% from MBU tests with five of the shales indicate pyrite is the main feed shale sulfur species. Kentucky shale had an MBU sulfur conversion of only 26% which suggests that its feed shale sulfur is not predominantly pyritic. Hydroretorting converts shale sulfur to hydrogen sulfide and trace amounts of other sulfur-bearing gases. Replicate test results with Indiana and Kentucky shales were similar. Oil yields were 25.9 and 25.3 gal/ton for the Indiana shale, and 12.9 and 13.6 gal/ton for the Kentucky shale. The test with Indiana shale at short gas residence time conditions was not completely successful. The high gas feed rate led to a high retorting zone temperature and a subsequently high hydrocarbon gas yield, and a hydrogen consumption 8% higher than in the long gas residence time tests. Feed and residue shale particle size analyses indicate an increase in -40 mesh shale of 5% to 15% after MBU hydroretorting. The decrease in particle size was primarily the result of shale abrasion by the discharge screw.

Trace element analyses were conducted on MBU feed and residue shales as well as product oils and sour waters. On a weight basis, the largest potential trace element pollutants are sodium, calcium, and chlorine, but no pollutant was detected in quantities exceeding 2 micrograms per gram of feed shale. The elements with highest mobility to product liquids and gas were found to be nitrogen, sulfur, and mercury. Sour waters were examined for potential pollutants. Hydrogen sulfide and ammonia together accounted for more than 90% of the pollutants with other pollutants in decreasing quantity

including thiocyanate, methyl mercaptan, acetonitrile, acetone, acetic acid, and pyrrole. An Environmental Sampling Train (EST) with acid (HCl) and base (NaOH) scrubs was used on the product gas stream for four MBU tests. The base scrub removed over 98% of the hydrogen sulfide from the product gas in all four tests.

A design point test and a replicate test were conducted in the BSU using Indiana New Albany shale. Nominal operating conditions for the BSU tests were a shale feed rate of 75 lb/h, hydrogen feed gas rate of 15 SCF/lb shale feed, reactor temperature of 1050°F, and reactor pressure of 600 psig. Results from the two tests show average reconciled oil yields, organic carbon conversions, and hydrogen consumptions of 20 gal/ton, 74.5%, and 2060 SCF/ton, respectively. The oil yields and organic carbon conversions for these tests are low and the conversions of feed carbon to gas are high compared to the results predicted by HAU and MBU data. A failed off-gas line which allowed gas bypassing and subsequent refluxing to occur is postulated as the reason for the low oil yields of about 145% of Fischer Assay, compared with 200% of Fischer Assay achieved in HAU tests.

In Task 2 (Environmental Mitigation Analysis), thermodynamic data and related information were transmitted to HYCRUDE Corporation to facilitate development of the computer program for the HYTORT process plant.

In Task 3 (Process Efficiency Improvement Tests), synthesis gas tests were conducted in the HAU with six Eastern shales. These tests were conducted at 1025°F, 1000 psig total pressure, a hydrogen partial pressure of 270 psig, and 25 mole percent steam in the feed gas. Oil yields from these tests are commensurate with those obtained by retorting in hydrogen at similar feed gas hydrogen partial pressures. Tests were conducted with Indiana New Albany shale at 1000 psig and 950° to 1200°F with synthesis gas-steam and CO-steam mixtures. Results from the CO-steam mixture tests showed a yield of 13 gal/ton, approximately the Fischer Assay yield for this shale. The tests conducted with synthesis gas mixtures gave yields of 14 to 20 gal/ton.

Seven synthesis gas retorting tests were conducted in the MBU. Two tests were conducted with Indiana shale, and tests were conducted with each of the Alabama, Tennessee, Kentucky, Michigan, and Ohio shales. When using synthesis gas instead of hydrogen for retorting, all six shales showed a decrease in oil yield, higher conversion of organic carbon to gas, and lower organic carbon

selectivity to oil. The oil yields were between 6% (Indiana) and 27% (Tennessee) below the hydroretorting oil yields. For each shale studied, the oil yields from HAU hydrogen and syngas and MBU hydrogen retorting tests were normalized and found to be linearly proportional to hydrogen partial pressure over the pressure range studied (400 to 1000 psi). Oil yields from MBU syngas retorting tests were lower than predicted by HAU tests and MBU hydroretorting tests. Oils produced in MBU synthesis gas retorting tests were lighter, less viscous, and had a lower nitrogen content than oils produced in MBU hydroretorting tests.

Four MBU tests were conducted with Indiana New Albany shale and ionized carbon dioxide to determine the effect of an ionized gas on oil recovery. In a batch system, ionized gas has been shown to form a mist. Forming an oil mist could reduce refluxing and enhance oil recovery. An apparatus using high-pressure ignition electrodes to ionize carbon dioxide was developed and tested. The apparatus was installed on the MBU feed gas system, and tests were conducted with steady-state periods having non-ionized and ionized carbon dioxide present. Preheat and retorting zone temperatures were lowered to increase refluxing. Oil yields were similar between periods with ionized and non-ionized carbon dioxide. Oil refluxing was not enhanced, and the presence of ionized carbon dioxide in the retort did not alter the oil yield by more than 6%.

In Task 4 (Fines Utilization Tests), 52 thermobalance tests were conducted with Indiana (22), Alabama (9), Tennessee (9), Kentucky (4), Michigan (4), and Ohio (4) shales. Indiana New Albany, the base shale, was gasified at temperatures of 1600° to 1900°F, pressures of 15 to 500 psig, and residence times between 5 and 30 minutes. Tests were conducted with 1:1 steam:hydrogen, a synthesis gas, and steam. Gasification tests with other shales were conducted under similar conditions. Alabama and Tennessee shale tests were only made at 30-minute residence times and were not made in steam. Kentucky, Michigan, and Ohio shale tests were only made at 30-minute residence times at 15 psig and were not made in steam. Indiana shale organic carbon conversion was found to be a function of gasification temperature and to increase with steam partial pressure. Organic carbon conversion was lower in synthesis gas indicating that hydrogen and carbon monoxide retard carbon gasification. Organic carbon conversions above 95% were achieved after 30 minutes in steam

at 1600°F and 135 psig and in steam:hydrogen at 1800°F and 15 psig. Sulfur conversion was also found to increase with temperature and steam pressure but was unaffected by the presence of other gases. The gasification of the other five shales was affected by temperature and gas partial pressures in the same way as the gasification of Indiana shale. Organic carbon reactivity decreases from Indiana and Ohio shales to the Chattanooga shales (Alabama and Tennessee) to the Kentucky and Michigan shales. Sulfur conversions were similar for all six shales.

Thirteen fluidization tests were conducted with nitrogen in a Plexiglas® column at ambient conditions. Six tests with raw and spent Indiana New Albany shale of 1/8, 1/16, and 1/32 inch showed that the complete fluidization velocity is between 2 and 3 times the minimum fluidization velocity and that the fluidization characteristics of raw and spent shale are similar. Fluidization tests with -20+40 mesh samples of the six raw shales showed complete fluidization velocity is between 1.8 and 2.2 times the minimum fluidization velocity. In general, increasing bulk density reflects a decrease in organic carbon content and results in an increase in fluidization velocities.

The final fluidization test was conducted with the same -20+40 mesh Indiana shale used in the Task 4.1.3 gasification tests. The velocity in the Plexiglas® column duplicated the value of a fluidized-bed gasification test. Results indicated slugging would occur at the gasification conditions. However, subsequent Task 4.1.3 gasification tests with lower superficial velocity did not show significantly improved shale conversions.

Fifteen ash agglomeration tests were conducted with the six Eastern shales at 1900° and 2000°F, and oxygen concentrations of 8% to 12%. Under all conditions studied, the majority of spent shale was recovered as clinkers. Good agglomerates were not formed in these tests.

Sixteen fluidized-bed gasification tests were conducted in the MBU. Ten synthesis gas tests were made with Indiana (8), Alabama (1), and Tennessee (1) shales. One steam:nitrogen test was made with each of the six shales at approximately 1750°F, 150 psig, and a 50-minute residence time. Indiana shale gasification in syngas showed organic carbon conversion increases with increasing temperature and residence time, but decreases with increasing pressure. Thermobalance tests showed the same effects of syngas test conditions on organic carbon conversion. Organic carbon conversions from

Indiana shale gasification in syngas were 43% to 60% in the MBU and were 10% to 15% higher in the thermobalance. Lower conversions in the MBU were found to be not due to slugging in the bed. Steam gasification in the MBU, as in the thermobalance, produced higher conversions under similar gasification conditions. Indiana shale gasified at 1750°F in the MBU had an organic carbon conversion of 54% when gasified in syngas for 55 minutes and 78% when gasified in steam for 43 minutes. Steam gasification resulted in high conversion of all shale species for all six shales. Organic carbon conversion was 78% for Indiana shale, 81% for Alabama shale, and between 92% and 98% for the other four shales.

The gasification of Eastern shales has been described by a model with kinetic correlations based on thermobalance data. Correlations apply over a temperature range of 1600° to 1900°F, a residence time of 3 to 30 minutes, steam and hydrogen pressures up to 250 psi, and carbon oxides pressures up to 23 psi. The model does not apply in the absence of steam or at high carbon oxides pressures and short residence times. Shale weight loss is described in terms of independent, simultaneous reactions of the various shale species. Species reactions are described as either fast or slow. Fast reactions, complete in less than one minute at the gasification conditions studied, include the conversion of moisture, mineral carbonates, organic hydrogen, nitrogen, and high-temperature water. The conversions of 10% of the organic carbon to hydrocarbon gases and 50% of the sulfur to hydrogen sulfide are also fast reactions.

The two slow reactions identified are the gasification of 90% of the organic carbon and 50% of the sulfur. Organic carbon gasification is described by the steam-carbon reaction. The rate constant for the steam-carbon gasification kinetic correlation is increased by increased steam pressure, but decreased by increased hydrogen and carbon monoxide pressures. Different constants were fit to describe the reactivities of the six shales. The rate constant in the slow sulfur gasification kinetic correlation is increased by increased steam pressure and unaffected by the presence of other gases. The same kinetic correlation was used to describe the slow sulfur gasification of all six shales.

Two tests were conducted with Indiana New Albany shale in an 8-inch-diameter fluidized-bed gasification process development unit (PDU). The tests

were conducted at 1800°F and 30 psig with a shale feed rate of 440 lb/h and a shale residence time of 30 minutes. A carbon conversion of 87% was achieved. The inorganic components of the extract from a residue solids leaching test were below EP method 1310 threshold limits. A preliminary conceptual gasifier design using a carbon conversion of 95% was developed.

Approximately 20% by weight of Eastern oil shale is converted to fines during mining and crushing. These fines have not been considered for processing in moving bed retorts. Attempts to operate moving-bed retorts with fines have led to operational problems because of uneven temperature distributions. However, this amount of shale is a significant resource. Therefore, tests were conducted to determine the effect of fines concentration in moving-packed beds on —

1. radial gas and solids distribution,
2. entrainment of fines in the off-gas stream,
3. fines migration laterally in the bed, and
4. oil yield.

The existing solids feeder configuration at the top of the bed produced an average particle-size distribution profile which had a "W" shape — with larger material at the walls and the center of the bed, and smaller material directly under the solids distribution cone. The measured gas-velocity profile also had a "W" shape, with higher gas flows measured at the walls and at the center of the bed (where the particle size distribution was large) and lower gas flows measured directly under the solids distribution cone (where the particle-size distribution was small). The spread between the minimum and maximum gas velocities in the "W" was greater for the higher fines concentrations tested.

Calculated oil yields, obtained from a kinetic model and utilizing measured particle-size and calculated gas-velocity profiles, showed that oil yield decreased with increasing fines concentration. The decrease in oil yield with fines concentration was a result of the nonuniformity of the fines distribution in the bed. The total amount of oil produced per ton of mined oil shale also decreased with increasing fines concentration.

The entrainment rate of shale fines in the off-gas from the unit was found to increase significantly with both fines concentration and gas velocity. The maximum measured entrainment rate of oil shale amounted to approximately 4.8% of the material flowing through the Cold-Flow Model (CFM).

Measurements also indicated that lateral fines movement in the moving-packed beds with gas flowing countercurrently to the shale flow, was minimal.

In Task 5 (Sample Procurement), sufficient quantities of oil shales from Alabama, Indiana, Kentucky, Michigan, Ohio, and Tennessee were selected, procured, and prepared for testing for the research program.

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PROGRAM OBJECTIVE

The overall objective of this program is to expand the process and environmental data base for moving-bed hydroretorting of Eastern oil shales. The process data will be used to define the operating conditions for efficient utilization of Eastern oil shales by moving-bed hydroretorting technology. Additionally, some concepts that have the potential for increasing process efficiency and resource utilization will be investigated. The environmental data will be used to assess the potential environmental impact of a commercial-scale moving-bed hydroretorting facility and to identify the suitable environmental control technologies for a moving-bed hydroretorting facility.

INTRODUCTION

Moving-bed retorting of oil shales in a hydrogen-rich atmosphere at elevated pressures has been shown to significantly enhance the oil yield potential of the Eastern oil shale resources in the U.S. The HYTORT Process, incorporating moving-bed hydrotretorting, has the capability of obtaining oil yields up to 250% of the Fischer Assay oil yields for these shales.

Research performed to date on the technology of moving-bed hydrotretorting for Eastern oil shale has resulted in the resolution of many technical issues and improvements in process economics. This research examined several Eastern oil shales; however, only one shale (Indiana New Albany) was examined in detail.

The objectives of the current 3-year program, initiated on October 22, 1985, are to —

- Optimize operating conditions for six Eastern shales
- Identify emissions from the retorting of these shales and determine the environmental implications of these emissions
- Improve process efficiency
- Increase resource utilization.

Under a subcontract to HYCRUDE Corporation, IGT conducted the experimental work in the above areas. This is the final report on this project, presenting the progress of the following tasks:

TASK 1. HYDROTRETORTING CHARACTERISTICS

- Subtask 1.1. Laboratory-Scale Batch Tests
- Subtask 1.2. Mini-Bench-Scale Tests
- Subtask 1.3. Bench-Scale-Unit (BSU) Tests

TASK 2. ENVIRONMENTAL MITIGATION ANALYSIS

- Subtask 2.2. Application of Environmental Control Technologies

TASK 3. PROCESS EFFICIENCY IMPROVEMENT TESTS

- Subtask 3.1. Retorting Gas Composition Effect
 - Subtask 3.1.1. Laboratory-Scale Batch Tests
 - Subtask 3.1.2. Mini-Bench-Scale Tests
- Subtask 3.2. Mist Generation Tests

TASK 4. FINES UTILIZATION TESTS

Subtask 4.1. Fines Gasification Tests

- Subtask 4.1.1. Thermobalance Tests
- Subtask 4.1.2. Fluidization and Agglomeration Tests
- Subtask 4.1.3. Mini-Bench-Scale Tests
- Subtask 4.1.4. Gasification Kinetic Correlation
- Subtask 4.1.5. Process Development-Scale Tests

Subtask 4.2. Cold-Flow-Model (CFM) Studies

TASK 5. SAMPLE PROCUREMENT

TECHNICAL PROGRESS REPORT

Task 1. Hydroretorting Characteristics

This task focuses on the expansion of the existing hydroretorting data base for an Indiana New Albany shale and the generation of a similar data base for five additional Eastern U.S. shales. The work in this task is divided into three subtasks: Subtask 1.1. Laboratory-Scale Batch Tests; Subtask 1.2. Mini-Bench-Scale Tests; and Subtask 1.3. Bench-Scale Unit (BSU) Tests.

Subtask 1.1. Laboratory-Scale Batch Tests

Laboratory-scale batch hydroretorting tests offer a cost-effective option for obtaining the data base to select optimum conditions for retorting specific shales. The data from batch tests will be used to develop an empirical correlation between the batch tests and the continuous tests in the mini-bench and bench-scale equipment.

Objective: The objective of this subtask is to perform hydroretorting tests in an existing batch retort to determine the effects of shale feedstock, temperature, and pressure on hydroretorting yields. Each of the six shales selected will be tested at temperatures ranging from 900° to 1200°F and at reactor pressures from 400 to 800 psig.

Experimental Equipment and Test Procedures: The tests for this subtask were conducted in the Hydroretorting Assay Unit (HAU). A schematic flow diagram of the HAU is shown in Figure 1. The HAU test system comprises a reactor, furnace, condenser, liquid collection vessel, feed and product gas metering systems, and a microprocessor for data acquisition and control. The HAU reactor consists of a 7/8-inch-diameter, 16-inch-long tube mounted concentrically within a pressure-retaining shell, 1-1/2 inches in diameter and 31 inches in length. This unit is enclosed in a three-zone electrically heated furnace. The heaters are computer-controlled to achieve the desired heat-up rate, to maintain the reactor at the operating temperature for a pre-determined period of time, and to maintain isothermal conditions vertically in the shale sample. The metered feed gas enters the bottom of the pressure shell, is preheated as it flows upward in the annular space surrounding the reactor tube and then enters the reactor. Product vapors from the reactor are cooled by an electrically powered chiller. The condensibles are collected in

Figure 1. HYDRORETORTING ASSAY UNIT SIMPLIFIED PROCESS FLOW DIAGRAM

a graduated glass container, and the gaseous product is collected and analyzed after the run. Test data, including temperatures, feed and product gas flow rates, and pressures, are continuously recorded.

Before the HAU tests are conducted, representative shale samples are crushed to -8 mesh particle size and riffled into approximately 100-gram samples. The test sample weight is then recorded, and the sample is charged into the reactor. The system is sealed, pressure-tested, and purged with feed gas. The operating conditions are programmed into the microprocessor, and a test is started by keying in the run command. The system is brought to the desired operating pressure, and the gas flow rate is set. The furnace heaters are activated and adjusted to achieve the desired heat-up rate. The reactor is maintained at the desired operating temperature for a predetermined period of time. At the end of a test, the furnace is shut down, and the reactor is allowed to cool to about 200°F. The residual shale is removed and weighed, the liquid products collected in the graduated glass container are centrifuged, the water and oil volumes are measured, and the entire liquid sample is weighed and analyzed. The entire volume of product gas is collected and analyzed.

Discussion: A total of 71 tests were conducted in the HAU for this program task of which 62 tests were successful. Tests were conducted to determine the effects of shale feedstock, temperature, and pressure on hydro-retorting yields. Six shales were studied, an Alabama Chattanooga, an Indiana New Albany, a Kentucky Sunbury, a Michigan Antrim, an Ohio Cleveland, and a Tennessee Chattanooga. These shales were selected because each shale type is available in sufficient quantity to support a commercial retorting facility, the selected shales represent a broad spectrum of the Eastern shale resource, and some data was already available on some of the shales from prior test programs. Tests were conducted at temperatures and pressures ranging from 900° to 1200°F and 400 to 1000 psig, respectively. Based on prior experience, these temperature and pressure ranges were expected to span the optimum (most economical) operating conditions for each of the selected shales.

Analyses of the six shales tested are shown in Table 1. The shales tested in this program had moisture contents ranging from 0.86 to 5.89 weight percent, organic carbon contents from 9.65 to 15.18 weight percent, and Fischer Assays from 8.4 to 14.0 gal/ton. The analysis shown for the Kentucky

Table 1. ANALYSES OF FEED SHALES

Shale Source	<u>Alabama</u>	<u>Indiana</u>	<u>Kentucky†</u>	<u>Michigan</u>	<u>Ohio</u>	<u>Tennessee</u>
Moisture, wt %	1.23	0.86	5.89	2.90	4.61	1.33
Ultimate Analysis, wt % (dry basis)						
Ash	74.52	77.75	82.34	78.53	81.13	81.07
Organic Carbon	15.18	12.67	9.65	11.86	10.93	11.67
Mineral Carbon	0.06	0.66	0.01	0.29	0.04	0.03
Hydrogen	1.61	1.50	1.14	1.52	1.38	1.31
Sulfur	7.86	4.58	1.20	3.76	2.93	5.13
Nitrogen	0.44	0.41	0.51	0.37	0.39	0.38
Gross Calorific Value, Btu/lb	3187	2608	1672	2438	2188	2405
Fischer Assay, GPT	13.1	13.8	8.4	14.0	11.9	9.7

*Oxygen is present as mineral oxides and high-temperature water included as ash; because the high-temperature (925°C) ashing procedure alters the composition of mineral matter existing in the original raw shale, e.g., the conversion of CaCO_3 plus pyrites to CaSO_4 and Fe_2O_3 , the sum of the elements may exceed 100%.

†This analysis differs from the analysis reported in the Annual Status Report for Program Year 2, December 1987. The analysis shown here is believed to be more representative of the shale used in this task.

Sunbury differs from that reported in the Annual Status Report for Program Year 2, December 1987. The analysis shown in Table 1 for the Kentucky shale is believed to be more representative of the shale used in this task. Previously reported HAU data on oil yields and elemental conversions for the Kentucky Sunbury shale were revised and the revised yields and conversions are included in Appendix A of this report. Detailed oil yields and elemental conversions for the Alabama Chattanooga, Indiana New Albany, Michigan Antrim, Ohio Cleveland, and Tennessee Chattanooga can be found in the previously published annual reports.^{1,2}

Summary of Test Results with Six Eastern Shales

Of the 62 successful tests conducted in the HAU, 10 tests were conducted with the Alabama shale, 16 with Indiana, 8 with Kentucky, 7 with Michigan, 9 with Ohio, and 12 with Tennessee. A summary of the ranges of results for these tests is presented in Table 2. For each of these shales, tests were conducted at three nominal temperature levels (900°, 1050°, and 1200°F) and two nominal pressure levels (400 and 800 psig). Except for a few anomalies, the trends observed are the same for all six shales tested. The oil yield and conversions of organic carbon, hydrogen, and nitrogen increase with increasing temperature and pressure. The water yield increases with increasing temperature but is relatively insensitive to changes in pressure. The gross calorific value of the spent shale decreases with increasing temperature and pressure, as expected, because it is strongly dependent on carbon content. Sulfur conversion is relatively insensitive to changes in temperature and pressure, probably because the sulfur exists in the raw shale primarily as pyrite and is reduced to iron sulfide and hydrogen sulfide at a relatively low temperature (less than 900°F).

A comparison of oil yields from Fischer and hydroretorting assay tests is shown in Figure 2. The hydroretorting tests were performed at 800 psig hydrogen pressure and 1200°F. The oil yields are shown on a weight percent organic carbon basis to permit an equitable comparison of shales with different kero-gen contents. The hydroretorting oil yields for all six shales were at least 200% of their respective Fischer Assay yields. Oil yields from conventional thermal retorting of Eastern shales are about 1 gal/ton per percent organic carbon^{3,4} (comparable to the Fischer Assay yield), whereas hydroretorting of the same Eastern shales can produce 2 gal/ton per percent organic carbon.

Table 2. RANGES OF HAU HYDRORETORTING TEST RESULTS

Shale Source Member	Alabama Chattanooga	Indiana New Albany	Kentucky Sunbury	Michigan Antrim	Ohio Cleveland	Tennessee Chattanooga
Oil Yield, GPT*	22-27	23-31	13-19	23-28	18-24	15-23
Water Yield, GPT	5.1-11.1	4.5-12.9	25.3-34.3	8.2-12.3	15.2-19.0	4.6-6.8
Spent Shale, HHV, Btu/lb	1069-1492	444-811	416-783	376-702	403-722	632-1149
Elemental Conversions, wt % of feed						
Organic Carbon	62.4-78.5	72.3-89.6	56.8-77.0	69.9-88.5	67.5-82.9	56.6-83.2
Sulfur	48.6-51.3	45.5-50.8	21.0-23.4	41.1-51.7	40.8-48.6	48.6-53.3
Nitrogen	47.9-74.6	53.8-88.3	57.9-90.0	54.6-86.9	41.9-80.6	31.8-84.4
Hydrogen	70.4-86.6	70.1-90.4	56.8-85.8	73.8-89.2	67.0-87.8	63.8-87.1

*On a dry shale basis; oil yields are based on reconciled data as noted in the text.

Figure 2. A COMPARISON OF OIL YIELDS FROM FISCHER AND HYDRORETORTING ASSAY TESTS

A comparison of the results from hydroretorting at a temperature of about 1050°F and a shale heat-up rate of 23°F per minute for all six shales is shown in Figure 3. Shale residence time at temperature was 30 minutes for all cases. Oil yields are shown, normalized for organic carbon content, as a function of hydrogen partial pressure. The data points representing oil yields for each of the shales fit a linear interpretation of the data in the ranges tested: 400 to 1000 psig, and 900° to 1200°F. The lines represent a least square fit of the data for each respective shale. The oil yields for each of the shales tested actually begins to level off at the higher pressures so that extrapolation of the linear fit of these data to higher pressures is not recommended. Conversely, extrapolation of these data to lower hydrogen partial pressures is not recommended, because at the lower limit of 0 hydrogen partial pressure, the data do not extrapolate linearly to each shale's respective Fischer Assay. One may conclude from these data that the hydroretorting yields of each of the shales varies nonlinearly from Fischer Assay yields to a hydrogen partial pressure less than or equal to 400 psig, linearly in the range of 400 to 1000 psig, and nonlinearly above 1000 psig.

The normalized oil yields from the Alabama, Kentucky, and Tennessee shales are somewhat lower than the yields from the Indiana, Michigan, and Ohio shales at comparable operating conditions. The Fischer Assay (FA) oil yields for the Alabama, Kentucky, and Tennessee shales are 0.86, 0.87, and 0.83 gal/ton per percent feed organic carbon, whereas the FA oil yields for the Indiana, Michigan, and Ohio shales are 1.09, 1.18, and 1.09 gal/ton per percent organic carbon. The shales which had the higher FA normalized oil yield gave higher hydroretorting oil yields, normalized to the feed organic carbon.

The carbon balances for the hydroretorting tests, based on actual feeds and products collected, are in the range of 80% to 108%. About 63% of the tests show carbon balances in the range of 90% to 100%. Most of the missing carbon is expected to be in the uncollected oil.

To use the data for process design and to observe the trends of oil yields with temperature and pressure, it was necessary to reconcile the oil and gas yields so that the carbon balances were 100%. When the carbon balances were lower than 100%, the reconciled oil and gas yields were calculated by assigning 15% of the measured carbon in the gas phase to the gas

Figure 3. A COMPARISON OF HYDRORTORTING OIL YIELDS FOR SIX EASTERN OIL SHALES

yield, and the remainder of the missing carbon to oil. The gas phase adjustment was made to compensate for hydrocarbons not measured during depressurization, as noted in the discussion of the results of the tests using a freeze-out train in the off-gas line. For conditions at which replicate tests were conducted, the missing carbon was estimated by using the maximum observed oil and gas yields. For the tests where the balance was greater than 100%, the oil yield was assumed correct and the carbon conversion to gas was adjusted to obtain a 100% material balance. A helium tracer was added to the feed gas to improve gas flow measurements for the tests conducted in the last quarter of the second program year.

Reproducibility of Results

Hydroretorting tests were performed using the six shales in a batch retort to determine the effects of temperature and pressure on hydroretorting yields. A 2 x 3 matrix design was used. Each corner point was replicated only for tests with the Indiana shale. The replicate tests provided estimates of repeatability of the data. Replication of the Indiana New Albany tests at the corner point conditions showed that the measured oil yields had a standard deviation of 1.1 gal/ton. The replicate tests also demonstrated that the standard deviations of the carbon, hydrogen, sulfur, and nitrogen feed shale conversions were 1.4%, 1.8%, 0.5%, and 1.8%, respectively, on an absolute basis.

Standardized HAU Tests

Tests were conducted, one each with the shales from Indiana, Kentucky, Ohio, and Tennessee at temperatures and pressures of 1000°F and 1000 psig, respectively, to ascertain the oil yields achievable at the standardized hydroretorting assay conditions for which a large shale data base is available. Data on hydroretorting at the standardized HAU conditions was available for both the Alabama and Michigan shales from another test program. Table 3 shows a comparison of yields from shales hydroretorted at standardized HAU conditions. No reconciled oil yield data was available for the Alabama and Michigan shales tested. Oil yields and total carbon conversions for the shales ranged from 18 to 28 gal/ton and 73.3% to 84.6%, respectively. Water yields from the standardized tests ranged from 5.8 to 32.4 gal/ton. The Kentucky Sunbury shale had the highest water yield: 32.4 gal/ton, including 15 gal/ton due to moisture in the shale. The Kentucky Sunbury shale was the

Table 3. COMPARISON OF YIELDS FROM STANDARDIZED HAU TESTS

Run Identification	51286	20487	12887	70286*	11287	122286
	<u>Alabama*</u>	<u>Indiana</u>	<u>Kentucky</u>	<u>Michigan</u>	<u>Ohio</u>	<u>Tennessee</u>
Shale Source	Chattanooga	New Albany	Sunbury	Antrim	Cleveland	Chattanooga
Member						
Maximum Bed Temperature, °F	1002	1006	1002	999	1004	1007
Total Pressure, psia	1015	1017	1014	1017	1013	1018
Component Conversions, % of Feed Shale						
Total Carbon	79.8	84.6	73.3	87.0	81.8	76.7
Hydrogen	79.4	82.2	68.7	70.7	75.8	77.7
Sulfur	48.9	46.8	21.0	46.9	48.6	50.7
Nitrogen	65.6	79.6	88.1	77.2	75.9	63.8
Oil Yield, GPT Recovered	28	26	15	29	22	18
	Reconciled	27	18	—	24	23
Oil Properties: API, @60°F	20.3	17.4	13.6	13.5	20.0	15.6
C/H Ratio	8.00	8.22	8.87	8.75	8.29	8.62
S, wt%	—	0.88	1.14	—	0.80	1.17
N, wt%	—	1.84	1.72	—	1.62	1.50
Organic Carbon to Gas, %	18.6	15.3	6.0	2.5	7.2	9.6
Oil, %	61.2	69.3	67.3	84.5	74.6	67.1
Residue, %	20.2	15.4	26.7	13.0	18.2	23.3
Water Production, GPT	5.8	6.7	32.4	5.2	16.1	6.0

*Data was obtained from another test program, Beneficiation-Hydroretorting of U.S. Oil Shales.

least reactive of the shales tested, based on total carbon conversion. The Kentucky shale also had the lowest organic carbon content, 9.65%, the lowest Fischer Assay, 8.4 gal/ton, and the highest feed shale moisture content, 5.89%.

Effect of Freeze-Out Train

Two tests with Indiana New Albany shale were made to determine if the use of a freeze-out train in the off-gas line would capture any liquids escaping as a mist and any hydrocarbons which might be below the detectable limits of the gas chromatograph used for their analysis. A comparison of the results of hydrotreating Indiana New Albany shale with and without a freeze-out train in the off-gas line is shown in Table 4. A repeat test utilizing the freeze-out train in the off-gas line was conducted to verify the results from the previous test. A comparison of the results from the two tests show that the reconciled oil yields, as well as elemental conversions between the tests are, within the experimental precision for this equipment, in good agreement. No additional oil was collected in the tests which utilized the freeze-out train compared with the test which did not. Analysis of the depressurization gases of the runs indicated that about 15% carbon, relative basis, was present in the depressurization gas. These relative carbon values all represent only about 1% to 2% of the feed carbon in the shale. The information on gas depressurization was used to reconcile carbon balances for the HAU tests.

Effect of Feed Gas Residence Time

Tests were conducted with Indiana New Albany shale to determine the effects of gas residence time on oil yield and hydrogen consumption. Three tests were conducted at pressures and temperatures of 600 psig and 1050°F, respectively, with feed hydrogen flow rates of 2, 4, and 8 SCF/h which corresponded to gas residence times of 53.7, 27.2, and 13.7 seconds and gave oil yields of 27, 27, and 24 gal/ton, respectively. The test conducted at the highest gas flow rate (shortest gas residence time) showed a low reconciled oil yield due to an anomalously high amount of carbon oxides (from the shale mineral carbon) measured in the product gas for this test. A replicate test was conducted at the highest gas flow rate, however, and results were similar to the previous test in that there was an unusually high concentration of carbon oxides detected in the product gas. Detailed operating conditions and

Table 4. COMPARISON OF INDIANA NEW ALBANY SHALE HYDRORETORTING RESULTS
USING A FREEZE-OUT TRAIN IN THE OFF-GAS LINE

Run Identification	121785	90586	20487
Temperature, °F	1006	1000	1006
Pressure, psig	1002	1004	1002
Off-Gas Line	Condenser	-- Freeze-Out Train --	
Oil Yield, GPT Recovered*	28.1	28.2	26.0
Reconciled	NA	28.2	27.0
Feed Carbon to Gas, %	NA	15.2	15.3
Oil, %	68.6	70.8	69.2
Residue, %	15.8	14.0	15.5
Total	--	100.0	100.0
Feed Shale Elemental Conversions, wt %			
Total Carbon	84.1	86.0	84.5
Hydrogen	81.0	81.2	82.2
Sulfur	46.8	47.4	46.8
Nitrogen	83.7	73.7	79.6
Product Water Yield, GPT*	8.7	7.9	6.7
Spent Shale Calorific Value,** Btu/lb	434	452	444

* On a dry feed shale basis.

** Feed shale calorific value is 2608 Btu/lb.

NA = Not Available.

results of the HAU tests conducted to determine the effects of gas residence time are presented in Tables 5, 6, and 7.

Hydrogen consumption calculations by the appearance of combined hydrogen in the products for the tests with feed gas flow rates of 2, 4, and 8 SCF/h show hydrogen consumption values of 2930, 2650, and 2390 SCF/ton dry shale feed, respectively. Although the data show the general trend of reduced hydrogen consumption with reduced feed gas residence time, there is at least a ± 200 SCF/ton uncertainty in the reported values.

Design Point Tests

HAU tests were conducted at MBU design point conditions to permit a comparison of the results from HAU and MBU tests without extrapolation of the data for the Alabama, Indiana, Kentucky, Michigan, Ohio, and Tennessee shales.

Table 5. HAU RESULTS AND CONDITIONS OF TESTS TO DETERMINE EFFECTS OF GAS RESIDENCE TIME

Shale Type Run Identification	Indiana New Albany			
	41787	42787	40887	61287
Maximum Temperature, °F	1051	1051	1056	1058
Pressure, psig	600	601	599	600
Gas Residence Time, s	53.7	27.2	13.7	13.7
Heat-Up Rate, °F/min	24.2	24.0	24.8	24.0
Shale Feed, gm	99.16	100.30	100.33	100.48
Shale Residue, gm	81.56	82.07	81.05	81.61
Hydrogen Feed, SCF/h	2.0	3.94	7.81	7.81
Component Conversions, ^a % of Feed Shale				
Total Carbon	79.4	79.4	82.8	82.2
Hydrogen	78.5	81.4	82.3	81.7
Sulfur	41.0	45.5	40.1	47.8
Nitrogen	73.7	76.0	79.8	73.7
Spent Shale Gross Calorific Value, ^b Btu/lb	631	625	558	583
Recovered Oil Yield, lb/lb ^c	0.100	0.101	0.084	0.099
Recovered Oil Yield, GPT ^c	24	25	21	25
Reconciled Oil Yield, lb/lb ^d	0.111	0.109	0.098	0.099
Reconciled Oil Yield, GPT ^d	27	27	24	25
Water Yield, GPT ^e	11.7	7.5	9.2	5.1

^a Elemental conversions based on solids ash balance.

^b Feed shale gross calorific value is 2608 Btu/lb.

^c Recovered yields based on laboratory data (dry feed shale basis).

^d Dry shale basis. Carbon balance adjusted to 100% by adding 15% (relative) carbon to gas phase and then the rest to oil. This method gives a conservative oil yield.

^e Water not analyzed for NH₃, H₂S, CO₂ or hydrocarbons. Moisture accounts for 2.1 GPT of total.

Table 6. ANALYSES OF SHALE FEED AND PRODUCTS FROM TESTS TO DETERMINE EFFECTS OF GAS RESIDENCE TIME

Shale Type Run Identification	Indiana New Albany				
	Feed	41787	42787	40887	61287
Maximum Temperature, °F	--	1051	1051	1056	1058
Pressure, psig	--	600	601	599	600
Gas Residence Time, s	--	53.7	27.2	13.7	13.7
Proximate Analysis Moisture, wt %	0.86	0.10	0.00	0.10	0.02
Ultimate Analysis, wt % (dry basis)					
Ash*	77.75	93.87	94.99	93.83	93.61
Organic Carbon	12.67	3.32**	3.35**	2.77**	2.85**
Mineral Carbon	0.66	--	--	--	--
Hydrogen	1.50	0.39	0.34	0.32	0.33
Sulfur	4.58	3.26	3.05	3.31	2.88
Nitrogen	0.41	0.13	0.12	0.10	0.13
Gross Calorific Value, Btu/lb	2608	631	625	558	583
Shale Oil Ultimate Analysis, wt %					
Carbon	--	86.28	85.75	85.05	83.28
Hydrogen	--	9.90	10.09	10.24	10.12
Sulfur	--	1.67	1.84	1.72	0.78
Nitrogen	--	1.96	1.83	1.77	1.63
Ash	--	--	--	--	--
Oxygen (by difference)	--	0.19	0.49	1.22	4.19
Total	--	100.00	100.00	100.00	100.00
C/H Ratio	--	8.72	8.50	8.31	8.23
Specific Gravity (60/60°F), gm/mL	--	0.976	0.961	0.965	0.955
Gravity, °API	--	13.5	15.7	15.1	16.7

* Oxygen is present as mineral oxides and high-temperature water included as ash; because the high-temperature (925°C) ashing procedure alters the composition of mineral matter existing in the original raw shale, e.g., the conversion of CaCO_3 plus pyrites to CaSO_4 and Fe_2O_3 , the sum of the elements may exceed 100%.

** Value represents total carbon analysis, the sum of organic plus mineral carbon.

Table 7. HAU PRODUCT GAS COMPOSITIONS FROM HYDRORETORTING
INDIANA NEW ALBANY SHALE

Run Identification	<u>41787</u>	<u>42787</u>	<u>40887</u>	<u>61287</u>
Maximum Temperature, °F	1051	1051	1056	1058
Pressure, psig	600	601	599	600
Gas Residence Time, s	53.7	27.2	13.7	13.7
Composition,* mol. %				
Carbon Dioxide	20.9	15.5	37.3	40.3
Carbon Monoxide	20.3	6.7	36.7	35.9
Methane	37.2	46.0	18.9	19.1
Ethane	11.0	15.6	3.1	1.9
Ethene	1.0	1.7	0.5	0.4
Propane/Propene	5.6	8.9	2.1	1.4
Butane/Butenes	2.7	3.9	0.7	0.5
C ₅ ⁺	<u>1.3</u>	<u>1.7</u>	<u>0.7</u>	<u>0.5</u>
Total	100.0	100.0	100.0	100.0

* Hydrogen-, nitrogen-, and helium-free basis. Detection limit approximately 0.5%.

Minor differences in oil and gas yields, as well as product oil quality were noted. A detailed comparison of results from the HAU and MBU tests is presented in Task 1.2.

Subtask 1.2. Mini-Bench Unit (MBU) Tests

The MBU is a small-scale countercurrent moving-bed retort that provides steady-state data for a reliable process material balance from a continuous retorting system. The nominal shale feed rate for the MBU is about 1 lb/h.

Objective: The objective of this subtask is to perform moving-bed hydroretorting tests in the existing MBU system at the selected temperature and pressure determined from the results of Subtask 1.1, and to obtain steady-state data for characterizing the product gas, liquid, and solid effluent streams. Characterization of the effluents will be performed to meet the needs of Task 2 (Environmental Mitigation Analysis).

Experimental Equipment and Test Procedure: A flow diagram of the MBU is shown in Figure 4. The unit consists of a hydrotreating reactor with equipment for feeding and measuring the flow rates of shale and feed gas, and for collecting and/or measuring the flow rates of residue shale, and product liquids and gas. Simple controls are used to maintain reactor temperatures at the desired values, to maintain constant reactor pressure, and to collect representative samples of the feed and product gas.

Shale is fed by a screw feeder from a pressurized feed hopper filled with a sufficient amount of shale for the entire run (about 10 pounds). The cold shale enters the top of the reactor, and the residue shale is discharged from the bottom of the reactor into a pressurized residue receiver by a discharge screw.

The preheated feed gas enters the bottom of the reactor and the product gas and vapor exit the reactor through a 1/4-inch-diameter dip tube just above the shale bed. A small purge flow of the feed gas is continuously passed into the feed hopper during the test to displace the volume of shale being fed into the reactor, and to prevent gas containing liquid products from entering the feed hopper.

The reactor is a 39-1/8-inch-long piece of 2-inch, 316 stainless-steel pipe, Schedule 80 (ID of 1.92 inches). The reactor is heated by a six-zone electric heater. Each zone is 3 inches long and the heater extends from about 10 to 28 inches from the bottom of the reactor tube. An additional electric heater is used to heat a section of the reactor above the main heater. The temperature of each zone is controlled by a separate temperature controller. Six thermocouples are used to measure the inside temperatures along the reactor. These temperatures are recorded continuously, along with the temperatures of other major pieces of equipment.

The shale feed rate is set by adjusting the feed screw speed of rotation at the desired value. The rate of shale discharge is then set manually to give a constant shale-bed level. The shale-bed level is indicated by a nuclear-type level indicator and is continuously recorded. The weight of the shale feed is determined by subtracting the weight of shale present at the end of the test from the amount originally charged. The residue shale in the receiver is weighed after the run. Feed and residue shale rates are calculated by dividing these weights by the measured shale feeding time.

Figure 4. SCHEMATIC OF THE MINI-BENCH UNIT

The exit gas volume is measured by a dry test meter. Spot gas samples are taken throughout the steady-state test period. The exit gas is cooled in a single-stage condenser. The condensed liquids are then collected in a knockout pot. The pot is drained and the liquid weighed at approximately 15-minute intervals during the steady-state portion of the run to obtain product rates. Steady state is defined as a condition wherein the temperature profile in the shale bed is uniform; feed gas, purge gas, and exit gas flow rates are constant; reactor pressure is stable; and the shale feed rate and bed height are essentially constant.

The reactor is filled with fine silica sand prior to each run to establish a bed and a stable temperature profile. This prevents rapid heating of the initial shale feed, subjects all feed shale to a similar time-temperature history, and eliminates tar formation that occurs with a varying bed height at the start of a run.

Construction and installation of an Environmental Sampling Train (EST) for the MBU product gas was completed prior to conducting this series of MBU tests. The MBU product gas can be directed to flow through one of four lines containing sample bombs designated Acid (with 3N HCl), Base (with 6N NaOH), Organic (with methylene chloride), and knockout pot. Major environmental species were captured in the sample bombs and analyzed for specific compounds, as described in the work plan. Product gas was analyzed from each of the four EST lines. The raw product-gas analysis indicated that about 1% hydrogen sulfide was in the product gas. On a hydrogen- and nitrogen-free basis, about 20% hydrogen sulfide would be present in the product stream. The MBU gas sampling technique using glass sample bombs ensured a non-reacting environment for an accurate characterization of the sulfur in the product-gas streams.

Discussion

Summary of Test Results: Nine MBU tests were conducted in this program. One test with each of six Eastern shales was made at conditions chosen by HYCRUDE based on results from HAU tests conducted in Task 1.1. Replicate tests were made with Indiana New Albany and Kentucky Sunbury shales. Test 87MBU-2 was conducted with Indiana New Albany shale to study the effect of a short gas residence time on oil yield, conversions, and hydrogen consumption. A summary of the MBU test operating conditions and results is presented in Table 8.

Table 8. MINI-BENCH UNIT RUN SUMMARIES

Run Identification Shale Source	86MBU-5 Indiana	86MBU-8 Indiana	86MBU-9 Tennessee	86MBU-10 Alabama	87MBU-2 Indiana	87MBU-10 Ohio	87MBU-11 Michigan	87MBU-12 Kentucky	87MBU-17 Kentucky
Maximum Bed Temperature, °F	1100	1050	1210	1070	1220	1010	960	990	950
Total Pressure, psia	614	616	617	610	602	603	608	609	612
Hydrogen Partial Pressure, psia	568	577	580	572	568	571	571	569	570
Total Shale Residence Time, min	61	76	77	77	70	57	58	57	62
Shale Residence Time at Temperature, min	33	33	23	34	31	29	30	29	32
Oil Yield (gal/ton) Recovered	24.1	24.4	17.0	23.7	20.4	19.3	21.0	13.2	13.9
Reconciled	25.9	25.3	18.2	24.3	24.9	19.4	22.7	12.9	13.6
Oil Properties Pour Point, °F	-5	0	-10	-25	--	--	--	--	--
API, @ 60°F	15.3	15.1	15.3	15.3	13.3	15.4	15.6	9.3	9.9
C/H Ratio	8.37	8.26	8.60	8.63	8.52	8.51	8.31	8.78	9.03
S, wt%	1.44	1.81	1.57	2.00	1.23	0.66	0.95	1.17	1.21
N, wt%	2.03	2.09	1.62	1.46	2.07	1.82	1.53	1.96	2.14
Viscosity, SSU	76.4	82.0	61.6	58.6	--	--	--	--	--
Distillate Fractions									
Temperature, °F 10%	333	341	318	320	--	--	--	--	--
50%	677	670	664	652	--	--	--	--	--
E.P.	760	760	740	760	--	--	--	--	--
Hydrogen Consumption, SCF/ton*	2800	2800	3000	3500	2970	2200	2450	2450	3400
Organic Carbon Conversion, % (adjusted by ash balance)	83.8	83.9	76.3	72.8	88.9	76.2	84.8	68.6	67.3
Selectivity to Oil, % - Adjusted	85.4	82.6	72.0	77.7	78.0	82.1	80.8	75.6	77.5
Hydrocarbon Gas Yield, MM-Btu/ton Methane Equivalent - Adjusted	0.97	1.17	1.57	1.54	1.58	0.93	1.20	1.01	0.97
Organic Carbon to Gas, %	12.4	14.7	21.4	16.2	19.5	13.6	16.3	16.8	15.1
Oil, %	71.4	69.2	54.9	56.6	69.4	62.5	68.5	51.9	52.1
Residue, %	16.2	16.1	23.7	27.2	11.1	23.8	15.2	31.4	32.7
Sulfur Conversion to Gas, %**	48.5	44.5	55.1	49.0	51.2	41.8	38.0	27.0	13.8
Oil, %	3.2	4.1	2.2	2.6	2.6	1.9	2.5	5.3	5.9
Residue, %	48.3	51.4	42.7	48.4	48.2	56.3	59.6	67.7	80.3
Water Production, gal/ton	10.9	9.8	9.9	10.1	9.5	16.8	14.5	36.5	37.3
Water Production, gal/ton (less shale moisture)	9.3	7.4	7.2	7.4	7.0	10.2	7.4	14.9	15.3

* Hydrogen consumption is average of combined hydrogen and forced oxygen methods.

**Sulfur in gas includes dissolved gases in water.

All tests were made at 600 psig with hydrogen containing 2% by volume helium tracer. The feed hydrogen-to-shale ratio was 15 SCF/lb for the Indiana, Tennessee, and Alabama tests and 30 SCF/lb for the Ohio, Michigan, and Kentucky tests. Shale residence time was approximately 30 minutes in the retorting zone and 60 minutes in the preheat plus retorting zones for all tests. The maximum retorting temperature was different for each shale and varied from a low of 950°F for Kentucky shale to 1210°F for Tennessee shale. The nominal shale feed rate for all tests was 2 lb/h.

The various shales tested had different organic carbon conversions to oil but similar conversions to gas. The organic carbon conversion to oil varied from 52% for Kentucky Sunbury shale to 69% for the Indiana and Michigan shales. Product gas from all shales except Tennessee Chattanooga contained 12% to 16% of the feed shale organic carbon. Product gas from hydroretorting the Tennessee shale contained 21% of the feed shale organic carbon. The high carbon conversion to gas was caused by the high retorting temperature (1210°F). Moving-bed retorting temperatures above 1050°F are known to increase hydrocarbon gas yields and not significantly affect oil yields. Because gas yields are similar, organic carbon selectivity to oil increases with increasing organic carbon conversion to oil for all shales except Tennessee Chattanooga. The high hydrocarbon gas yield with Tennessee shale led to a low selectivity to oil of 72%. The selectivity to oil for the other shales ranged between 76% for the Kentucky Sunbury and 84% for Indiana New Albany shale. Hydroretorting of Eastern shale with high concentrations of pyrite produces hydrogen sulfide, as well as trace amounts of other sulfur-bearing gases. Pyrite reduction to iron sulfide as the sole source of hydrogen sulfide would result in an overall sulfur conversion of 50%. Pyrite appears to be the main sulfur-bearing species in the Indiana, Tennessee, Alabama, Ohio, and Michigan shales, which had hydroretorting sulfur conversions of 40% to 57%. A large fraction of the raw shale sulfur in the Kentucky shale is bound in species not as easily reduced as pyrite. Sulfur conversion for the Kentucky Sunbury shale was only 26%.

Like oil hydrotreating and hydrocracking, oil shale hydroretorting requires a large excess of hydrogen-rich gas to be passed through the reactor. In commercial designs, this gas is recycled as a heat carrier. Previous research at IGT has shown that for hydroretorting of Eastern shales, only

about 8% to 10% of the feed hydrogen reacts on one pass through the reactor. Therefore, determining hydrogen consumption in hydrotreating by subtracting the measured hydrogen gas flow rate leaving the reactor from that entering (due to small inaccuracies in flow measurement) can be subject to considerable uncertainty. This is because the resulting figure is a small difference between two large numbers. To provide measurements of chemical hydrogen consumption at an acceptable ($\pm 10\%$) level of confidence, it was necessary to obtain mutually-supporting measurements using several different techniques. Three methods were used to calculate H_2 consumption: the appearance of combined hydrogen in the product, forcing an oxygen balance, and taking direct measurements (difference between H_2 fed and H_2 in the product). The basis of each method is described below.

In the "Appearance of Combined Hydrogen" method, the total chemically-combined hydrogen in all reactants is subtracted from the total chemically-combined hydrogen in all products to obtain the hydrogen consumption. This method is sensitive to the measurements of shale moisture contents and water production rates. For the "Forced Oxygen Balance" method, the oxygen analyses of feed and spent shale, oil, and gas are assumed to be correct. The hydrogen consumption is then calculated from the water yield which has been calculated by a forced oxygen balance. In the "Direct Measurement" procedure, the hydrogen flow rate in the product gas is subtracted from the hydrogen feed gas flow rate to determine hydrogen consumption.

The hydrogen consumption values reported in Table 9 are the average of the combined hydrogen and forced oxygen methods. Hydrogen consumption varied between 2240 SCF/ton raw shale for Ohio shale and 3500 SCF/ton raw shale for Alabama shale. Hydrogen consumption, per barrel of oil produced, decreases with increasing organic carbon conversion to oil. Kentucky Sunbury shale, with 52% organic carbon conversion to oil, had the highest hydrogen consumption: 10,500 SCF/barrel of oil. Indiana New Albany shale, with a 70% organic carbon conversion to oil, had the lowest hydrogen consumption: 4600 SCF/barrel of oil.

Reproducibility of Results: Two pairs of replicate tests were conducted to study the reproducibility of MBU test results. Indiana New Albany shale was used for Tests 86MBU-5 and 86MBU-8, and Kentucky Sunbury shale was used for Tests 87MBU-12 and 87MBU-17. Operating conditions were

Table 9. HYDROGEN CONSUMPTION IN MBU TESTS

Test	Shale	Hydrogen Consumption	
		SCF/Ton	SCF/Barrel Oil
86MBU-5	Indiana	2800	4540
86MBU-8	Indiana	2800	4660
86MBU-9	Tennessee	3000	6930
86MBU-10	Alabama	3500	6050
87MBU-10	Ohio	2200	4830
87MBU-11	Michigan	2450	4540
87MBU-12	Kentucky	2450	7980
87MBU-17	Kentucky	3400	10,500

kept as constant as possible. Maximum retorting temperatures were within 50°F, retorting residence times were within 3 minutes, and hydrogen partial pressures were within 10 psi. Shale feed rates and feed gas to shale ratios were identical.

The results of the replicate tests with both shales were similar. Oil yields were 25.9 and 25.3 gal/ton for the Indiana and 12.9 and 13.6 gal/ton for Kentucky shale. Water yields were 9.2 and 7.4 gal/ton for Indiana and 14.9 and 15.3 gal/ton for Kentucky shale. Organic carbon conversions, organic carbon selectivities to oil, and oil properties were also similar for the replicate tests. The hydrogen consumption was 2800 SCF/ton for both Indiana shale tests, but the hydrogen consumptions with Kentucky shale were 2470 and 3420 SCF/ton in 87MBU-12 and 87MBU-17, respectively. Shale for the two Kentucky Sunbury MBU tests was riffled from the same large lot, but analyses of the two feed shales were different. Dry feed shale analyses for Tests 87MBU-12 and 87MBU-17 had 1.9 weight percent and 3.9% oxygen not bound in carbonate or hydroxyl groups. The higher hydrogen consumption observed in 87MBU-17 with Kentucky shale is a result of the greater amount of feed shale oxygen forming product water by reaction with free, gas-phase hydrogen.

Short Residence Time Test: Test 87MBU-2 was conducted with Indiana New Albany shale using the same nominal operating conditions as Tests 86MBU-5 and 86MBU-8, but with the feed gas rate doubled. The higher feed gas rate reduced the reactor gas residence time from 21 seconds used for Tests 86MBU-5 and 86MBU-8, to 11 seconds for Test 87MBU-2. The reduced reactor gas

residence time was expected to decrease hydrocarbon gas production and thus lower hydrogen consumption in the retort.

Operation of the MBU at the desired temperature was not completely successful during Test 87MBU-2. Because of the increased gas feed rates, the temperature at the bottom of the bed increased to 1220°F even though the feed gas was heated to only 1050°F and the furnace in the lower zone was turned off. A hydroretorting temperature above 1050°F is known to increase hydrocarbon gas production without significantly affecting oil production. The high bed temperature in 87MBU-2 produced the expected results along with the consequently higher hydrogen consumption. The oil yield from 87MBU-2 was 97% of the average of the other tests (86MBU-5 and 86MBU-8) while the hydrocarbon gas production was 44% higher. The hydrogen consumption in 87MBU-2 was 2970 SCF/ton, 220 SCF/ton (or 8%) higher than in the earlier tests because of the temperature increase in Zone 2.

The production of hydrocarbon gases has a very significant impact on hydrogen consumption because the hydrogen-to-carbon molar ratio is higher for the hydrocarbon gases than for the oil. The MBU tests made after 87MBU-2 using Ohio, Michigan, and Kentucky feed shales utilized the short gas residence time employed in Test 87MBU-2. For these tests, Zone 1 was used as a gas preheater to prevent the high retorting zone temperature experienced in 87MBU-2.

Shale Particle Integrity: Fines generation is a concern in retorting because fines may pack and form plugs or cause channeling of gas. Feed screw calibration tests for the six shales indicated Ohio Cleveland was the most friable of the six shales tested. All shales were abraded to some degree by the feed and discharge screws. Observed hydroretorting particle-size reductions for all shales were found to be due to screw abrasion and not hydroretorting. Abrasion was determined by comparing the weight percent residue shale below 40 mesh to the weight percent of the nominal -6+40 mesh feed shale below 40 mesh. The increase in -40 mesh solids during an MBU test was 15% for Ohio shale, 12% for Tennessee shale, and 5% to 10% for the other four shales.

Comparison of HAU and MBU Results: HAU tests were conducted at the same operating conditions — temperature, shale residence time, and hydrogen partial pressure — as MBU tests with each of the six Eastern shales. A

comparison of the results of the MBU and HAU tests at comparable conditions is presented in Table 10. Test conditions in the two units were not identical. Hydrogen partial pressures in the HAU were 33 to 43 psi higher than in the MBU, and the feed shale analyses had minor differences. To compare oil yields from the two units on the same basis, oil yields were normalized by determining gallons per ton per weight percent organic carbon. Figures 5 to 10 compare the normalized MBU oil yields with the oil yields from the HAU tests at comparable conditions, as well as HAU tests covering a range of hydrogen partial pressures. Several HAU normalized oil yields are shown for each shale at different hydrogen partial pressures to allow a comparison between comparable tests in the two units.

Normalized MBU oil yields for the Indiana, Tennessee, Alabama, Ohio, and Michigan shales were similar to the yields predicted by HAU tests. The MBU oil yields with Kentucky Sunbury shale were 15% below the HAU predicted oil yields. Overall organic carbon conversions and organic carbon conversions to gas were higher for the MBU tests than for the comparable HAU tests. For all shales except Michigan Antrim, overall organic carbon conversions were 2% to 5% higher and organic carbon conversions to gas were 5% to 10% higher for the MBU tests than for the comparable HAU tests. The Michigan Antrim MBU test overall organic carbon conversion and conversion to gas were 14% and 12% higher than for the comparable HAU test. Shale oils produced from MBU tests had 7% to 45% higher nitrogen contents and similar C/H ratios compared to HAU oils. The sulfur contents of MBU test shale oils were equal to, or greater than, the HAU test shale oil sulfur contents for five of the six shales. The Ohio shale oil sulfur content was 50% greater for the MBU compared to the HAU test.

Trace Elements and Pollutants Analyses: Environmental pollutant analyses were conducted on streams from the first four MBU tests: Tests 86MBU-5 and 86MBU-8 with Indiana, 86MBU-9 with Tennessee, and 86MBU-10 with Alabama shale. An environmental sampling train (EST) was used in these four tests to scrub the product gases with concentrated acid (sulfuric acid) and base (sodium hydroxide) solutions. Analyses included trace element analyses of feed and residue shales, sour waters, and product oils; pollutant analyses of sour waters, product-gas acid scrubs, and product-gas base scrubs; and trace sulfur analyses of product gases.

Table 10. COMPARISON OF MBU AND HAU TEST RESULTS

Run Identification	86MBU-8	42787	86MBU-9	122486	86MBU-10	42887
Shale Source	--- Indiana ---		-- Tennessee --		---- Alabama ----	
Test Unit	MBU	HAU	MBU	HAU	MBU	HAU
Maximum Bed Temperature, °F	1050	1051	1210	1205	1070	1050
Total Pressure, psia	616	616	617	613	616	617
Hydrogen Partial Pressure, psia	577	616	580	613	572	617
Total Shale Residence Time, min	76	65	77	70	77	66
Shale Residence Time at Temperature, min	33	30	23	30	34	30
Oil Yield, GPT Recovered	24.4	25.1	17.0	20	23.7	23.7
Reconciled	25.3	27.1	18.2	20	24.3	26.9
Oil Properties: API, @60°F	15.1	15.7	15.3	11.6	15.3	14.8
C/H Ratio	8.26	8.50	8.60	9.12	8.63	8.72
S, wt %	1.81	1.84	1.57	1.23	2.00	0.13
N, wt %	2.09	1.83	1.62	1.51	1.46	1.21
Organic Carbon to Gas, %	14.7	9.4	21.4	11.2	16.2	9.5
Oil, %	69.2	70.0	54.9	59.8	56.6	61.4
Residue, %	16.1	20.6	23.7	29.0	27.2	29.1
Water Production, GPT	9.8	7.5	9.9	4.7	10.1	8.2

Table 10, Cont. COMPARISON OF MBU AND HAU TEST RESULTS

Run Identification	87MBU-10	120887	87MBU-11	120787	87MBU-12	87MBU-17	120487
Shale Source	Ohio/Cleveland		Michigan/Antrim		Kentucky/Sunbury		
Test Unit	MBU	HAU	MBU	HAU	MBU	MBU	HAU
Maximum Bed Temperature, °F	1010	954	960	952	990	950	957
Total Pressure, psia	603	614	608	608	609	612	606
Hydrogen Partial Pressure, psia	571	614	571	608	569	570	606
Total Shale Residence Time, min	57	61	58	63	57	62	64
Shale Residence Time at Temperature, min	29	30	30	30	29	32	30
Oil Yield, GPT Recovered	19.3	19.5	21.0	21.0	13.2	13.9	12.9
	Reconciled	20.0	22.7	23.0	12.9	13.6	15.8
Oil Properties: API, @60°F	15.4	15.1	15.6	18.1	9.3	9.9	8.6
C/H Ratio	8.51	8.60	8.31	8.18	8.78	9.03	8.52
S/ wt %	0.66	0.93	0.95	0.97	1.17	1.21	1.06
N, wt %	1.82	1.25	1.53	1.42	1.96	2.14	1.80
Organic Carbon to Gas, %	13.6	8.4	16.3	4.6	16.8	15.1	9.5
Oil, %	62.5	65.2	68.5	66.0	51.9	52.1	54.7
Residue, %	23.8	26.4	15.2	29.4	31.4	32.7	35.8
Water Production, GPT	16.8	15.6	14.5	8.2	36.5	37.3	26.1

Figure 5. NORMALIZED OIL YIELD FROM HYDRORETORTING ALABAMA CHATTANOOGA SHALE IN THE HAU AND MBU

Figure 6. NORMALIZED OIL YIELD FROM HYDRORETORTING INDIANA NEW ALBANY SHALE IN THE HAU AND MBU

Figure 7. NORMALIZED OIL YIELD FROM HYDRORETORTING KENTUCKY SUNBURY SHALE IN THE HAU AND MBU

Figure 8. NORMALIZED OIL YIELD FROM HYDRORETORTING MICHIGAN ANTRIM SHALE IN THE HAU AND MBU

Figure 9. NORMALIED OIL YIELD FROM HYDRORETORTING CLEVELAND MEMBER OF OHIO SHALE IN THE HAU AND MBU

Figure 10. NORMALIZED OIL YIELD FROM HYDRORETORTING TENNESSEE CHATTANOOGA SHALE IN THE HAU AND MBU

Detailed results of analyses of feed and residue shales for 30 elements, and sour waters and product oils for 22 elements were presented in the annual reports^{1,2} previously published. Table 11 shows the quantities of potential trace element pollutants lost from the shales during hydroretorting. On a total weight basis, the largest potential trace element pollutants are sodium, calcium, and chlorine. No trace element pollutant was detected in quantities above 2 micrograms per gram of raw shale.

One parameter used in assessing the environmental impact of processing oil shales is mobility. Mobility is defined as the percent of an element present in the raw shale found in sour water, product oil and product gas after retorting. The mobility data of selected elements for these MBU tests are presented in Table 12. For the shales tested, the elements with high mobility are nitrogen, sulfur, and mercury.

The material balances of selected elements for the four MBU tests are presented in Table 13. The recovery for the majority of elements is between 90% and 110%. The poor recoveries of chlorine, fluorine, and lithium are probably due to their volatility (no analysis of product gas for trace elements was performed). Trace elements are assumed to be absent from the product gas, even though this assumption is not valid for some elements. Recoveries of boron, chromium, sodium, and vanadium in excess of 100% are caused by difficulties in obtaining quantitative values of these trace element concentrations.

Potential pollutant compounds in the sour waters from the four MBU tests are shown in Table 14. Quantities of pollutants have been determined in milligrams per gram of dry feed shale. Analyses were conducted for sulfur and nitrogen compounds, organic acids, alcohols, ketones, and aromatic hydrocarbons. For the three shales studies, hydrogen sulfide and ammonia together accounted for more than 90 weight percent of the pollutants examined. Other pollutants, in decreasing quantity produced, include thiocyanate, methyl mercaptan, acetonitrile, acetone, acetic acid, and pyrrole.

The carbon in sour water is 65% to 86% organic carbon. The remainder is mineral carbon assumed to be carbon dioxide. Of the total organic carbon in sour water, only about one-third has been accounted for by the GC/FID analyses for species. Low hydrocarbon solubilities in water make the presence of the remaining carbon as hydrocarbons unlikely. Nitrogen in the sour waters is

Table 11. POTENTIAL POLLUTANTS EMANATING FROM THE RETORT
PROCESSING EASTERN OIL SHALES

State Member	Indiana		Tennessee	Alabama
MBU Run No.	New Albany 86MBU-5	86MBU-8	Chattanooga 86MBU-9	Chattanooga 86MBU-10
	----- mg/gram of dry raw shale -----			
Sulfur Compounds Gas				
Carbonyl Sulfide	0.00000	0.00000	0.00000	0.0049
Hydrogen Sulfide	23.97	21.43	30.76	38.86
Dimethyl Sulfide	0.00061	0.00021	0.00035	0.00060
Carbon Disulfide	0.00075	0.0019	0.00021	0.00000
Methyl Mercaptan	0.16	0.13	0.13	0.22
Ethyl Mercaptan	0.082	0.060	0.099	0.16
i-Propyl Mercaptan	0.0088	0.0069	0.018	0.019
n-Propyl Mercaptan	0.013	0.0077	0.016	0.015
t-Butyl Mercaptan	0.0018	0.00019	0.0013	0.00062
Thiophene	0.0025	0.00089	0.0033	0.0019
Cl-Thiophene	0.0019	0.00021	0.00083	0.00038
Thiocyanate	0.90	0.49	0.53	2.06
Sulfate	0.53	0.19	1.17	0.68
	25.67	22.32	32.73	42.02
Oxygenated Compounds				
Methanol	0.0010	BDL	BDL	NA
Ethanol	0.0015	0.0011	BDL	NA
Acetone	0.010	0.014	0.0093	NA
MEK	0.0045	0.0045	0.0023	NA
Pentanone	0.00075	0.00045	0.00070	NA
Acetic Acid	0.010	0.0068	BDL	NA
Propionic Acid	0.0040	0.0032	BDL	NA
Butanoic Acid	0.0010	0.0023	BDL	NA
Pentanoic Acid	0.0010	0.00091	BDL	NA
Hexanoic Acid	BDL	0.00023	BDL	NA
Phenol	0.0027	0.0064	0.0027	NA
Methyl Phenol	0.0025	0.0018	0.0014	NA
	0.039	0.041	0.016	
Nitrogen Compounds				
Ammonia	1.65	1.71	1.99	1.44
Acetonitrile	0.022	0.018	0.017	NA
Propanenitrile	0.00300	0.0027	0.0019	NA
Aniline	0.0085	0.0064	0.023	NA
Methyl Aniline	0.0038	0.0030	0.0084	NA
Pyrrole	0.010	0.0086	0.0061	NA
Methyl Pyrrole	0.0095	0.0054	0.0033	NA
C2-Pyrrole	0.0030	0.0023	0.00070	NA
C3-Pyrrole	0.00075	0.00045	BDL	NA
Pyridine	BDL	BDL	BDL	NA
Methyl-Pyridines	0.00075	0.00068	0.0014	NA
C2-Pyridines	0.00050	0.00023	0.00023	NA
C3-Pyridines	0.0015	0.00091	BDL	NA
Cyanide	0.013	0.0069	0.022	NA
Nitrite	<0.000025	<0.000027	<0.000023	<0.000026
Nitrate	0.015	0.014	0.0086	0.01030
	1.74	1.78	2.08	1.44
Hydrocarbon				
Dihydroxybenzene	0.0033	0.0023	BDL	NA
Methyl Dihydroxybenzenes	0.00300	0.0023	BDL	NA
C2-Dihydroxybenzenes	0.0010	0.00068	BDL	NA
	0.0073	0.0053		
Miscellaneous Compounds				
Fluorine	0.00035	0.00018	0.00089	0.00028

NOTES: NA = Not available.
BDL = Below detection limit.

Table 11, Cont. POTENTIAL POLLUTANTS EMANATING FROM THE RETORT PROCESSING
OF EASTERN OIL SHALES

State Member MBU Run No.	Indiana		Tennessee	Alabama
	New Albany		Chattanooga	Chattanooga
	86MBU-5	86MBU-8	86MBU-9	86MBU-10
Trace Metals				
Ag	0.030	<0.023	0.028	0.041
Al	<0.25	<0.23	0.28	<0.23
As	<0.025	<0.023	0.051	0.10
Ba	<0.10	<0.091	<0.093	<0.092
Ca	0.050	0.091	0.33	0.092
Cd	0.015	0.014	0.014	0.014
Cl	<0.50	<0.45	<0.47	<0.46
Cr	0.025	0.023	0.033	0.023
Cu	0.27	0.10	0.17	0.083
Fe	0.35	0.91	0.14	0.77
Hg	0.075	0.068	0.14	0.12
K	0.15	0.91	0.19	0.28
Li	<0.050	<0.045	<0.047	<0.046
Mg	0.085	0.059	0.070	0.078
Mn	0.015	0.014	0.023	0.032
Na	1.25	0.91	0.61	0.078
Ni	0.10	0.091	0.093	0.14
Pb	<0.10	<0.091	<0.093	<0.092
Sb	<0.015	<0.014	<0.014	<0.014
Se	<0.20	<0.18	<0.19	<0.28
V	<0.10	<0.091	<0.093	<0.092
Zn	<u>0.37</u>	<u>0.30</u>	<u>0.44</u>	<u>0.34</u>
	4.13	3.91	3.61	3.50

Table 12. MOBILITY OF MAJOR AND TRACE ELEMENTS OF EASTERN OIL SHALES

State Member MBU Run No.	Indiana		Tennessee	Alabama
	New Albany		Chattanooga	Chattanooga
	86MBU-5	86MBU-8	86MBU-9	86MBU-10
	Mobility* in %			
Elements **				
N	77	93	73	61
S	52	49	57	52
Hg	--	--	<68	--
Al	<0.0014	<0.0009	<0.002	<0.0044
As	<0.51	--	0.17	0.34
Ba	<0.10	<0.11	<0.08	<0.08
Ca	0.0015	0.0014	0.006	0.056
Cr	--	<0.12	0.12	0.36
Cu	0.41	0.22	0.22	0.34
Fe	0.0009	0.0008	<0.002	0.0058
K	0.0016	0.0008	<0.002	0.0039
Mg	0.002	0.0012	0.002	0.007
Mn	<0.008	<0.007	0.02	<0.027
Ni	0.31	0.23	0.11	0.11
Pb	--	<0.71	<0.46	<0.43
V	<0.22	--	--	--
Zn	0.26	0.30	0.19	0.16

* Percent originally present in raw shale found in oil, gas and water.

** Trace elements are assumed to be absent in product gas. The recoveries for the trace elements listed in this table, which are based on the weight originally present in raw shale, vary approximately between 85 and 115 weight percent.

Table 13. RECOVERY* OF MAJOR AND TRACE ELEMENTS FOR EASTERN OIL SHALES

State Member MBU Run No.	Indiana		Tennessee	Alabama
	New Albany		Chattanooga	Chattanooga
	86MBU-5	86MBU-8	86MBU-9	86MBU-10
			Percent	
Elements				
N	90	104	98	102
S	83	97	88	105
Al	101	98	99	100
As	109	81	83	91
B	233	124	123	263
Ba	100	96	112	92
Ca	103	99	95	98
Cl	51	63	78	60
Cr	129	116	102	83
Cu	105	110	93	87
F	83	35	47	57
Fe	100	98	97	98
Hg	80	<141	<98	--
K	101	98	100	99
Li	36	<39	37	26
Mg	101	97	101	110
Mn	105	99	99	96
Na	183	192	219	167
Ni	95	107	100	94
Pb	124	92	90	90
Se	--	--	<48	--
V	109	147	149	81
Zn	92	101	88	84

* Trace elements are assumed to be absent in product gas. Recovery is based on weight percent originally present in the feed shale.

Table 14. MINI-BENCH UNIT COMPONENTIAL YIELDS FROM THE EST

Run Identification	<u>86MBU-5</u>	<u>86MBU-8</u>	<u>86MBU-9</u>	<u>86MBU-10</u>
<u>Sour Water</u>				
Component	-----	mg/g dry feed shale	-----	
Phenol	0.00765	0.000153	0.00287	0.00294
CN*	0.00156	0.000939	0.00187	0.00329
SCN	0.220	0.170	0.304	0.397
Sulfate	0.304	0.177	0.295	0.578
Sulfide	1.61	1.40	2.74	1.41
Total Sulfur	1.83	1.55	2.51	1.82
<u>Acid Scrub</u>				
Component	-----	mg/g dry feed shale	-----	
Phenol	0.000214	0.00415	0.000786	0.000157
NO ₂	0.000025	0.000027	0.000023	0.000026
NO ₃	0.0151	0.0141	0.00863	0.0103
<u>Base Scrub</u>				
Component	-----	mg/g dry feed shale	-----	
CN*	0.0116	0.00588	0.0203	0.0129
SCN	0.658	0.305	0.190	1.63
Sulfate	0.197	0.00199	0.169	0.0666
Sulfide	7.20	3.49	15.91	14.05

* Distinct from SCN.

essentially all ammonia. From 1% to 2% of feed nitrogen is in thiocyanate, 0.01% to 0.04% in cyanide, and 27% to 42% in ammonia. The total quantity of pollutants was higher from Alabama shale than from the other shales due to the high sulfur content (7.5%) of the Alabama shale. The trace pollutant compounds reported as MBU sour water components would be combined with the product gas in a commercial plant design because the sour water stream would be gaseous under the operating conditions of a commercial plant.

A summary of the hazardous compound analyses of sour waters and product-gas acid and base scrubs from the four MBU tests is presented in Table 14, shown previously. Analyses from the four tests were similar. Sour water analyses show the presence of more than 100 times as much thiocyanate as cyanide in all four tests. Sulfur compounds recovered in the sour water are mostly sulfides (70% to 90%) along with sulfates, thiocyanates, and other sulfur compounds. The product-gas acid scrubs contain low concentrations of both NO_2 and NO_3 , but with clearly higher levels of NO_3 . Product-gas analyses show the base scrub successfully removed more than 98% of the gas-phase sulfur in all four tests. The base scrubs held, on average, one-third of the trapped sulfur as sulfides. The remaining sulfur scrubbed from the product gas was not detected.

The results of product-gas trace sulfur compound analyses are given in Table 15. More than 99% of the product-gas sulfur in all four tests was in hydrogen sulfide. The remaining sulfur was mostly in mercaptans, decreasing in quantity from methyl to ethyl to propyl mercaptan. Trace amounts of thiophene and dimethyl sulfide were detected in the product gases.

Subtask 1.3. Bench-Scale-Unit (BSU) Tests

The bench-scale unit (BSU) can process about 100 lb/h of shale — about 100 times more than the nominal flow rates in the MBU. Indiana New Albany shale was selected for the BSU tests to provide a tie between the large data base existing on this shale collected during a prior feasibility study program and the data developed in Task 1.

Objective: The objective of this subtask is to perform tests with Indiana New Albany shale using IGT's 4-inch-diameter BSU to provide process information for conducting environmental analyses.

Table 15. SUMMARY OF PRODUCT GAS PHASE SULFUR COMPOUNDS

Run Identification	86MBU-5	86MBU-8	86MBU-9	86MBU-10	86MBU-5	86MBU-8	86MBU-9	86MBU-10
	concentration, ppm [†]				Yield, mg/g dry feed shale			
Compound								
COS, Carbonyl Sulfide	0	0	0	2.27	0	0	0	0.0052
H ₂ S, Hydrogen Sulfide	13000	13700	14700	28300	21.9	19.7	28.1	37.0
CH ₃ SH, Methyl Mercaptan	64.3	67.7	49.7	117.7	0.153	0.137	0.134	0.217
CS ₂ , Carbon Disulfide	0.2	0.5	0.08	0	0.0007	0.0016	0.0003	0
SO ₂ , Sulfur Dioxide	0	0	0	0.13	0	0	0	0.0003
C ₂ H ₅ SH, Ethyl Mercaptan	24.3	23.3	28.3	66.7	0.0746	0.0611	0.0986	0.159
(CH ₃) ₂ S, Dimethyl Sulfide	0.27	0.08	0.13	0.23	0.0008	0.0002	0.0005	0.0005
CH ₃ C ₂ H ₅ S, Methyl Ethyl Sulfide	0	0	0	0	0	0	0	0
C ₃ H ₇ SH, Propyl Mercaptans	5.1	4.6	7.8	10.7	0.0192	0.0148	0.0333	0.0313
C ₄ H ₄ S, Thiophene	0.57	0.2	0.63	0.53	0.0024	0.0007	0.0030	0.0017
C ₄ H ₉ SH, C ₄ -Mercaptans	0.3	0.05	0.27	0.13	0.0013	0.0002	0.0014	0.0005
(CH ₃) ₂ S ₂ , Dimethyl Disulfide	0	0	0	0	0	0	0	0
C ₅ H ₆ S, C ₁ -Thiophene	0.4	0.05	0.17	0.07	0.0019	0.0002	0.0009	0.0003
C ₅ H ₁₁ SH, C ₅ Mercaptans	0	0	0	0	0	0	0	0
C ₆ H ₁₃ SH, C ₆ [†] Mercaptans	0	0	0	0	0	0	0	0

* Calculations based on reconciled balances. H₂S yield corrected to close S balance.

[†] ppm in product gas.

Experimental Equipment and Test Procedure: The BSU equipment (Figure 11 and Table 16) consists primarily of a reactor with associated equipment for feeding and measuring the flow rates of the feed shale and feed gas and equipment for collecting and measuring the flow rates of residue shale, liquid product, and product gas. Analog controllers are used to maintain reactor temperatures at the desired values, to maintain feed rates at constant values, and to maintain the reactor at constant pressure. Representative samples of the spent shale and feed and product gases are taken every 15 minutes during steady-state operation. The capacity of the unit is 200 lb/h of shale. Shale-gas contacting occurs in a truly continuous, countercurrent manner.

Shale is fed to the top of the reactor by a screw feeder from a pressurized hopper that, before testing, is filled with sufficient shale for the entire run. The residue shale is discharged from the bottom of the reactor into a pressurized residue receiver by a second screw feeder. The feed gas enters the bottom of the reactor above the discharge screw and the exit gas leaves through a dip tube extending down into the top of the reactor.

The reactor consists of a 24-inch-ID, 23-foot-long cold pressure shell containing an internal reactor tube (Incoloy 800, 4 inches IPS, Schedule 40), which is heated by a seven-zoned Kanthal electric heater. Each heater is 31 inches long and has an ID of about 7 inches. The temperature of each zone is controlled individually. The space between the reactor outer wall and the electric heater is packed with refractory-fiber-type insulation. The pressure outside the tube is controlled by a pressure-balancing system to keep the pressures inside and outside the heated reactor tube nearly equal (to keep it from rupturing when hot). The reactor pressure and bed pressure drops are recorded continuously, as are all the reactor-tube temperatures. Thermocouples are attached to the outside wall of the reactor, and six are installed internally.

The flow rates of the hydrogen feed gas and the purge gas are metered by both orifice meters and mass flowmeters. These meters are calibrated against the exit-gas meter before each test. Both screw feeders are also calibrated. The shale is fed at the desired rate by setting the shale feed-screw rotation speed at the desired value. The rate of shale discharge is then controlled to give a constant shale-bed level. The shale-bed level is indicated by a nuclear-type level indicator and is continuously recorded. The bed level can

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Figure 11. BENCH-SCALE UNIT (BSU)

Table 16. LEGEND FOR FIGURE 11

1	Main hydrogen supply to retort system
2	Helium tracer supply to retort system (optional)
3	Pre-mixed hydrogen/helium flow to bottom of retort
4	Pre-mixed hydrogen/helium purge to top of retort
5	Product gas
6	Purge gas mixture
7	Pressurization gas mixture (H_2/He)
8	Purge nitrogen stream from shell to reactor
A	Shale feed
B	Shale discharge
C	Solids in condensed liquids
D	Spent shale sample from steady-state sampler
E	Spent shale sample from residue receiver
1	Product oil
2	Sour water
S-1	Feed gas sample point
S-2	Product gas sample point
ST	Sampling train
FG	Flash gas system
CF	Cold finger for freeze-out sample
GC	Gas chromatograph
IR	Infrared gas analyzers
Vent	Product gas vent to atmosphere
MFM	Mass flow meter

be controlled to within an inch. The weight of the shale fed is measured accurately for the entire run by weighing the shale initially charged to the feed hopper and that present at the end of the run. The residue shale is also weighed after the run. Feed and residue shale rates are calculated by dividing these weights by the measured shale feeding time. Residue shale rates are also calculated by "ash-balance," from the feed and spent-shale ash analyses.

The exit-gas volume is measured by two conventional iron-case-type direct-reading meters in series. An "aliquot" sample of the exit gas is taken by feeding a portion of it at a constant rate into a 10-ft³ water-sealed holder during the steady-state test portion of each run. "Spot" samples are also taken throughout each steady-state period. The exit-gas specific gravity is monitored continuously by a recording gravitometer.

The exit gas is cooled in a multiple-stage condenser, and the condensed liquids are collected in a knockout pot. The pot is drained, and the liquid is weighed at frequent intervals during the steady-state portion of each run to obtain liquid product rates.

A sampling probe is placed into the BSU exit-gas line downstream of the condenser and liquid knockout pot to collect samples for accurate characterization of the product gas for possible pollutants. This environmental sampling system (EST) provides filtration and bulk solids removal at the operating pressure of the reactor prior to any pressure reduction for sampling. This on-line sampling train provides immediate capture and stabilization of reactive and volatile species. The EST exit-gas flow rate is measured to provide a means to calculate the actual species loadings in the gas stream.

Discussion: A design point test and a replicate test were conducted in the BSU using Indiana New Albany shale. Operating conditions were chosen by HYCRUDE based on results from HAU and MBU tests conducted in Tasks 1.1 and 1.2, respectively. Four BSU tests were conducted, two of which were successful. Nominal operating conditions for all the BSU tests were a shale feed rate of 75 lb/h, hydrogen feed gas rate of 15 SCF/lb shale feed, reactor temperature of 1050°F, and reactor pressure of 600 psig.

Summary of Test Results with Indiana New Albany Shale: A summary of the results from the two successful BSU tests conducted with Indiana New

Albany shale is presented in Table 17. Results from Tests 87BSU-3 and 87BSU-4 show reconciled oil yields of 19.9 and 20.2 gal/ton, organic carbon conversions of 75.1% and 74.0%, and hydrogen consumptions of 2150 and 1970 SCF/ton. The overall material balances and elemental carbon, hydrogen, nitrogen, oxygen, and sulfur balances for Tests 87BSU-3 and 87BSU-4 are 100.5% and 98.8%, 101.5% and 98.4%, 97.1% and 98.5%, 89.9% and 84.8%, 139.3% and 92.0%, and 95.9% and 97.7%, respectively. The nitrogen balances, 89.9% and 84.8%, for the two tests are somewhat low because there is only a small quantity of bound nitrogen present in the feed shales and even less in the spent shales. The nitrogen conversion is therefore calculated by the difference of two numbers which are nearly equal. The oxygen balance for Test 87BSU-3, 139.3% is high. Detailed operating conditions and results for Test 87BSU-3 are in Appendix B. Detailed results for Test 87BSU-4 were presented in a prior report².

The oil yields and organic carbon conversions for these tests are low and the conversions of feed carbon to gas are high compared to the results predicted by HAU and MBU data at similar operating conditions. Post-run inspection of the BSU equipment had revealed that an internal off-gas line in the reactor head failed during or prior to the BSU tests; this failed line may have allowed product gas to flow through the preheat zone of the reactor and cause refluxing which lowered the oil yield and increased the gas yield. The organic carbon conversions to gas for the BSU tests are higher than the conversions predicted by HAU and MBU data.

Trace Element Distributions: Trace elemental analyses and distributions for the BSU tests are shown in Tables 18 and 19. The distributions of trace elements in the feed shales from the BSU tests show that at least 80% of the elements remain with the spent shale with the exception of chlorine, fluorine, mercury, and selenium. The distribution of mercury to products show that only 12% to 24% remains in the spent shale and about 50% is found in the sour water. There was no attempt to quantify the amount of mercury in the product gas. Material balances for most of the trace elements ranged from 80% to 125%. For Test 87BSU-4, the amount of copper and chlorine measured in the products greatly exceeded the quantity originally present in the feed. A review of the trace elemental distributions of copper and chlorine for Test 87BSU-4 did not show any obvious errors in the analytical data; it may be

Table 17. BENCH-SCALE UNIT RUN SUMMARIES

Run Identification	87BSU-3	87BSU-4
Shale Source	Indiana	Indiana
Maximum Bed Temperature, °F	1079	1094
Total Pressure, psia	609	587
Hydrogen Partial Pressure, psia	540	522
Total Shale Residence Time, min	46.4	45.1
Shale Residence Time at Temperature, min	29.3	28.5
Oil Yield (gal/ton) Recovered	20.6	19.8
Reconciled	19.9	20.2
Oil Properties Pour Point, °F	-40	-40
API, @ 60°F	12.1	13.0
C/H Ratio	8.54	8.69
S, wt %	1.37	1.37
N, wt %	1.92	1.71
Viscosity, SSU	123.5	106.3
Distillate Fraction		
Temperature, °F 10%	344	341
50%	658	657
E.P.	742	753
Hydrogen Consumption, SCF/ton*	2150	1970
Organic Carbon Conversion, % (adjusted by ash balance)	75.1	74.0
Selectivity of Oil, % — Adjusted	79.4	77.0
Hydrogen Gas Yield, MM-Btu/ton		
Methane Equivalent — Adjusted	1.23	1.34
Organic Carbon to Gas, %	15.6	16.9
Oil, %	59.5	57.1
Residue, %	24.9	26.0
Sulfur Conversion to Gas, %**	48.0	56.6
Oil, T	2.8	3.0
Residue, %	49.2	40.4
Water Production, lb/h	4.25	3.56
Water Production, lb/h (less shale moisture)	2.43	1.87

* Hydrogen consumption is determined by combined hydrogen method.

** Sulfur in gas includes dissolved gases in water.

Table 18. TRACE ELEMENTAL ANALYSIS AND DISTRIBUTION FOR 87BSU-3

Symbol	Name	Trace Element Analysis, ppm/w, except as noted				Trace Element Distribution, % of Feed Shale			
		Feed Shale	Residue Shale	Product Oil	Product Water	Residue Shale	Product Oil	Product Water	Total
Ag	Silver	<2	<2	<2	<0.04	86	8.49	0.11	95
Al	Aluminum	5.48%	6.27%	2	0.3	99	0.0003	0.00003	99
As	Arsenic	90	85	1.8	1.5	82	0.17	0.09	82
B	Boron	28	26	--	--	80	--	--	80
Ba	Barium	250	300	<5	<0.5	104	0.17	0.01	104
Be	Beryllium	3.4	3.2	--	--	81	--	--	81
Ca	Calcium	1.01%	1.48%	<1.2	3.8	127	0.0010	0.0020	127
Cd	Cadmium	3.6	3.6	<2	0.2	86	4.72	0.30	91
Cl	Chlorine	100	80	50	1000	69	4.25	53.40	127
Cr	Chromium	60	72	<1	0.1	104	0.14	0.01	104
Cu	Copper	86	90	<1	<0.1	90	0.10	0.01	91
F	Fluorine	330	200	11	250	52	0.28	4.05	57
Fe	Iron	4.84%	5.12%	29	0.3	91	0.01	0.00003	91
Hg	Mercury	0.13	0.02	<0.15	1	12	9.80	41.08	63
K	Potassium	1.86%	2.08%	<1.2	0.40	97	0.0005	0.0001	97
Li	Lithium	24	24	<1.2	<0.1	86	0.42	0.02	87
Mg	Magnesium	0.45%	0.42%	0.3	0.5	81	0.0006	0.0006	81
Mn	Manganese	180	240	<1.6	0.3	115	0.08	0.01	115
Mo	Molybdenum	210	220	--	--	91	--	--	91
Na	Sodium	0.41%	0.44%	2.5	3.5	93	0.005	0.0046	93
Ni	Nickel	110	130	7.2	1	102	0.56	0.05	103
Pb	Lead	38	41	<10	<1	93	2.23	0.14	96
Sb	Antimony	1.1	<1	<1	<0.02	79	7.72	0.10	86
Se	Selenium	5.3	3.2	<30	<1	52	--	1.01	53
Si	Silicon	25.8%	30.9%	--	--	104	--	--	104
Sr	Strontium	26	27	--	--	90	--	--	90
Ti	Titanium	0.34%	0.37%	--	--	94	--	--	94
V	Vanadium	290	310	<12	<1.2	92	0.35	0.02	93
Zn	Zinc	240	280	<4	1	101	0.14	0.02	101

Table 19. TRACE ELEMENTAL ANALYSIS AND DISTRIBUTION FOR 87BSU-4

Symbol	Name	Trace Element Analysis, ppm/w, except as noted				Trace Element Distribution, % of Feed Shale			
		Feed Shale	Residue Shale	Product Oil	Product Water	Residue Shale	Product Oil	Product Water	Total
Ag	Silver	<2	<2	<2	<0.04	85	8.09	0.10	93
Al	Aluminum	5.44%	6.05%	5.7	<0.5	94	0.0008	0.00005	94
As	Arsenic	56	77	1.9	2.2	117	0.27	0.20	117
B	Boron	33	32	--	--	82	--	--	82
Ba	Barium	280	340	<5	<0.5	103	0.14	0.01	103
Be	Beryllium	3.1	3.2	--	--	88	--	--	88
Ca	Calcium	0.91%	1.12%	3.1	4.5	105	0.0028	0.0025	105
Cd	Cadmium	3.40	3.8	<2	<0.2	95	4.76	0.30	100
Cl	Chlorine	50	176*	<50	840	295*	8.09	86.49	394*
Cr	Chromium	62	70	<1	0.1	96	0.13	0.01	96
Cu	Copper	84	1000*	<1	<0.1	1011*	0.10	0.01	1011*
F	Fluorine	390	200	7.2	220	44	0.15	2.90	47
Fe	Iron	4.47%	5.09%	25	0.3	97	0.0045	0.00003	97
Hg	Mercury	0.13	0.04	<0.15	1.5	24	9.33	59.4	92
K	Potassium	1.67%	2.10%	<1.2	0.6	107	0.0006	0.0002	107
Li	Lithium	21	25	<1.2	<0.1	101	0.46	0.02	102
Mg	Magnesium	0.30%	0.53%	0.5	0.8	150	0.0013	0.0014	150
Mn	Manganese	160	220	<1.6	0.3	117	0.08	0.01	117
Mo	Molybdenum	200	220	--	--	93	--	--	93
Na	Sodium	0.23%	0.34%	5.4	2.8	126	0.02	0.01	126
Ni	Nickel	110	130	4.6	0.9	100	0.34	0.04	101
Pb	Lead	35	41	<10	<1	100	2.31	0.15	102
Sb	Antimony	1	1	<1	<0.02	85	8.09	0.10	93
Se	Selenium	7	1.8	<10	1	22	11.56	0.74	34
Si	Silicon	26.6%	31.1%	--	--	99	--	--	99
Sr	Strontium	16	27	--	--	143	--	--	143
Ti	Titanium	0.33%	0.33%	--	--	85	--	--	85
V	Vanadium	290	300	<12	<1.2	88	0.33	0.02	88
Zn	Zinc	320	250	46	9.9	66	1.16	0.16	68

*Samples may have been contaminated.

that the sample was contaminated. The analytical data obtained in Test 87BSU-3 for copper and chlorine distributions do not indicate contamination and may be used since the two BSU tests were replicates.

The trace distributions for sulfur and nitrogen compounds for the BSU tests are presented in Tables 20 and 21. As expected, most of the converted feed shale sulfur is detected as hydrogen sulfide in the gas phase. A summary of oxygenated trace compounds in the product water from BSU runs is presented in Table 22. Acetic acid is the trace component with the highest concentration detected in the sour water with concentrations of 610 and 350 mg/l for Tests 87BSU-3 and 87BSU-4, respectively.

The results of an EP toxicity test on processed shale from 87BSU-4 is shown in Table 23. The concentrations of leachates detected from the test are all below the allowable limits identified in Volume 40 of the Federal Register (40CFR261).

Task 2. Environmental Mitigation Analysis

The overall objective of this task is to evaluate the capability of existing environmental control technologies to comply with federal, state, and local environmental regulations as applied to a moving-bed hydroretorting plant utilizing various Eastern U.S. oil shale feedstocks. The specific objectives of this task are to identify the range of concentrations for potential pollutants, the appropriate environmental regulations and suitable control technologies, and define the effluent streams for a moving-bed hydroretorting plant.

This task is divided into two subtasks: Subtask 2.1., Environmental Control Technology Assessment; and Subtask 2.2., Application of Environmental Control Technologies. IGT conducted work on only Subtask 2.2.

Subtask 2.2. Application of Environmental Control Technologies

IGT provided its expertise regarding environmental control technologies to HYCRUDE as requested. HYCRUDE expressed a need to do calculations to determine the disposition of raw product gas constituents in various quench systems, before proceeding with identification of environmental control technologies that might be employed in a commercial plant. IGT made available to the HYCRUDE staff the Gas Processors Association (GPA) package of vapor-liquid equilibrium programs. This package includes the Soave-Redlich-Kwong, the

Table 20. DETAILED ANALYSIS OF SULFUR COMPOUNDS IN THE PRODUCT GAS FROM BSU RUNS

Run Identification	<u>87BSU-3</u>	<u>87BSU-4</u>	<u>87BSU-3</u>	<u>87 BSU-4</u>
	----- ppm -----	-----	----- mg/g dry feed shale -----	-----
Compound				
COS, Carbonyl Sulfide	0	4	0	0.01
H ₂ S, Hydrogen Sulfide	8,300*	11,200*	11.8	16.3
CH ₃ SH, Methyl Mercaptan	35	62	0.07	0.13
CS ₂ , Carbon Disulfide	0.2	1.3	0.0006	0.004
C ₂ H ₅ SH, Ethyl Mercaptan	15	29	0.04	0.08
(CH ₃) ₂ S, Dimethyl Sulfide	0.2	0.2	0.0005	0.0005
C ₃ H ₇ SH, Propyl Mercaptans	5.8	12.5	0.02	0.04
C ₄ H ₄ S, Thiophene	1.6	1.5	0.006	0.005
C ₄ H ₉ SH, C ₄ -Mercaptans	0	1.5	0	0.006
C ₅ H ₆ S, C ₁ -Thiophene	3.0	3.5	0.01	0.01
C ₆ H ₁₃ SH, C ₆ [†] Mercaptans	0	2.2	0	0.01

* Calculations based on reconciled balances. H₂S yield corrected to close S balance.

Table 21. COMPONENT ANALYSIS OF THE PRODUCT WATER FROM ESU RUNS

Test No.	<u>87BSU-3</u> ----- mg/l -----	<u>87BSU-4</u> -----	<u>87BSU-3</u> ----- mg/g dry feed shale -----	<u>87BSU-4</u> -----
Nitrogen Compounds				
Pyridine	28	20	0.0015	0.0010
Tetrahydropyridine	7	12	0.0004	0.0006
Pyrrole	235	175	0.013	0.009
Acetonitrile	430	350	0.023	0.018
Propanenitrile	23	23	0.0012	0.0012
Aniline	97	71	0.005	0.004
Indole	12	9	0.0006	0.0005
Quinoline	4	3	0.0002	0.0002
Benzeneamine	112	85	0.0060	0.0043
Sulfur Compounds				
Hydrogen Sulfide	1200	350	0.064	0.018
Sulfur Dioxide	820	360	0.0044	0.019
Methyl Mercaptan	2	1	0.0001	0.00005
Hydrocarbons				
Benzene	20	BDL	0.001	--
Heptane	17	BDL	0.0009	--
Unidentified Compounds	660	580	0.035	0.030

BDL = Below detection limit.

Table 22. OXYGEN-CONTAINING COMPONENTS IN PRODUCT WATER FROM BSU RUNS

Test No.	<u>87BSU-3</u>	<u>87BSU-4</u>	<u>87BSU-3</u>	<u>87BSU-4</u>
	-----	-----	-----	-----
Component	mg/l	mg/l	mg/g dry feed shale	mg/g dry feed shale
Methanol	40	34	0.0021	0.0018
Ethanol	18	16	0.0010	0.0008
Propanol	7.5	5	0.0004	0.0003
Hydroxybenzyl	10	6	0.0005	0.0003
Benzenediol	85	77.4	0.0045	0.0040
Butanone	94	70	0.0050	0.0036
Hexanone	8.6	BDL	0.0005	--
Cyclopentanone	16	12.1	0.0009	0.0006
Cyclohexanone	6	BDL	0.0003	--
Acetic Acid	610	340	0.033	0.018
Propionic Acid	284	151	0.015	0.0078
Butanoic Acid	138	59	0.007	0.003
Pentanoic Acid	110	58	0.006	0.003
Hexanoic Acid	64	BDL	0.003	--
Phenol	204	190	0.011	0.0098
Methoxyphenol	19	15	0.0010	0.0008
Aminophenol	7	5	0.0004	0.0003

BDL = Below detection limit.

Table 23. RESULTS OF EP TOXICITY 1310 TEST ON PROCESSED SHALE FROM 87BSU-4

<u>Element</u>	<u>Symbol</u>	<u>Test Results</u> ----- concentration, mg/l -----	<u>Allowable* Limits</u> -----
Silver	Ag	<0.03	5.0
Arsenic	As	0.17	5.0
Barium	Ba	<0.7	100.0
Cadmium	Cd	<0.03	1.0
Chromium	Cr	<0.08	5.0
Mercury	Hg	<0.001	0.2
Lead	Pb	<0.3	5.0
Selenium	Se	<0.04	1.0

* Concentration limits of leachates identified in Volume 40 of the Federal Register (40CFR261). "Test Methods for Evaluating Solid Waste — Physical/Chemical Methods", 5W-846, 2nd ed., US/EPA, 1984.

Peng-Robinson, the Chao-Seader-Redlich-Kwong, and the Grayson-Streed-Redlich-Kwong correlations for predicting vapor-liquid equilibrium for gas- and oil-containing systems. It was also indicated to HYCRUDE that the Soave-Redlich-Kwong and the Peng-Robinson correlations would probably do the best job in their process simulations.

A few years ago under Contract No. DE-AC21-80MC14705, these four correlations were evaluated by IGT for their ability to predict the vapor-liquid equilibrium characteristics of mixtures of H₂, CO, CO₂, CH₄, C₂H₆, C₂H₄, H₂S, C₃H₈, COS, and C₆H₆ and other similar mixtures. It was determined that for these systems at temperatures between 100° and 350°F and pressures between 100 and 3000 psia, the Peng-Robinson and the Soave-Redlich-Kwong correlations were the best. However, even these two correlations do not predict the K values accurately for all the components.

Task 3. Process Efficiency Improvement Tests

The overall objective of this task is to obtain data on some processing concepts that have the potential of improving the overall process efficiency for moving-bed hydrotreating of Eastern shales. The specific objectives of this task are 1) to determine the effects of synthesis gas composition and its synergism with operating temperatures, pressures, and heat-up rates, and 2) to

determine the effects of mist generation in the retort to improve selectivity for oil make. Consistent with the specific objectives, the task is divided into two subtasks: Subtask 3.1, Retorting Gas Composition Effects and Subtask 3.2, Mist Generation Tests. Discussion of each subtask follows:

Subtask 3.1. Retorting Gas Composition Effects

The objective of this subtask is to determine the effects of synthesis gas composition and its synergism with operating temperature, pressure, and heat-up rate on the retorting characteristics of various Eastern shales.

Work in this subtask is further divided into two subtasks for conducting tests in both a laboratory-scale batch unit and a continuous mini-bench-scale unit. Descriptions of each of these subtasks follow:

Subtask 3.1.1. Laboratory-Scale Batch Tests

Objective: The objective of this subtask is to perform retorting tests in the HAU using various synthesis gas compositions, heat-up rates, temperatures, and pressures to determine their effects on the retorting characteristics of Eastern shales. The results of Subtask 3.1.1 will be used to select operating conditions for the mini-bench-unit tests.

Experimental Equipment and Test Procedures: The tests for this subtask were conducted in the HAU, modified to feed steam. A schematic flow diagram of the unit is shown in Figure 12. The test system is composed of a reactor, furnace, condenser, high-pressure humidifier, liquid collection vessel, feed- and product-gas metering systems, and a microprocessor. The reactor consists of a 7/8-inch outside diameter, 16-inch-long tube mounted concentrically within a pressure-retaining shell, 1-1/2 inches outside-diameter and 31 inches in length. The reactor is enclosed in a three-zone electrically heated furnace. The heaters are computer-controlled to achieve the desired heat-up rate, to maintain the reactor at the operating temperature for a predetermined period of time, and to maintain isothermal conditions vertically in the shale sample. The high-pressure humidification chamber is constructed of 1-1/2-inch, Schedule 120, stainless-steel pipe, 18 inches high. The metered feed gas enters the bottom of the reactor pressure shell, is preheated as it flows upward in the annular space surrounding the reactor tube, and then enters the reactor from the top. Product vapors from the reactor are cooled by a chiller. The condensibles are collected in a graduated glass container. The

Figure 12. LABORATORY-SCALE UNIT SIMPLIFIED PROCESS FLOW DIAGRAM

gaseous product is either continuously depressurized and metered by a dry test meter prior to venting, or collected and analyzed after the run, as is the case in this program. During each test, temperatures, feed-, and product-gas flow rates, and pressures, are continuously recorded.

For the batch laboratory-scale tests, representative shale samples are crushed to -8 mesh particle size and riffled into approximately 100-gram samples. The weight of the test sample is then recorded, and the sample is charged into the reactor. For each test, 100 grams of shale solids are retorted with synthesis gas in the laboratory-scale unit using 4-standard-cubic-feet per hour of synthesis gas at a nominal heat-up rate of 25°F per minute. The system is pressure tested and purged with feed gas. The operating conditions are programmed into the microprocessor, and a test is started by keying in the run command. The system is brought to operating pressure and the gas flow is adjusted to the specified rate. The furnace heaters are activated and adjusted to achieve the desired heat-up rate. Since the steam feed requirements for the batch test unit were quite small, a humidification chamber with temperature controls was designed, constructed, and used to feed steam to the reactor, rather than using a small water metering pump and furnace combination. The humidification chamber is filled to a predetermined level with a weighed amount of water prior to each test. The feed gas is bubbled through the chamber and the amount of humidification (steam feed) is regulated by adjusting the temperature in the chamber with a temperature controller whose output regulates a furnace surrounding the chamber. The amount of water left in the chamber is measured after each test and the actual steam rate to the laboratory-scale reactor is calculated. The reactor is maintained at the desired operating temperature for a predetermined period of time. At the end of the test, the furnace is shut down, and the reactor is allowed to cool to about 200°F. The residual shale is removed and weighed, the liquid products in the graduated glass container are centrifuged, the water and oil volumes are measured, and the entire liquid sample is weighed and the oil is analyzed. The entire volume of product gas is collected and analyzed.

Discussion: Several hydrogen production alternatives are available to produce hydrogen needed for moving-bed hydroretorting of Eastern oil shale, including reforming of hydrocarbon gases produced within the retort, partial

oxidation of a part of the oil produced in the retort, reforming of purchased natural gas, and gasification of oil shale fines and/or spent shale. All of the above hydrogen production alternatives produce synthesis gas, which is further processed in a catalytic reactor to convert the carbon monoxide to hydrogen. If synthesis gas can be effectively used in moving-bed hydroretorting, the CO-shift reaction step could be eliminated, and the overall process efficiency of moving-bed hydroretorting could be improved.

Fourteen tests were conducted in the modified HAU to determine the effects of using synthesis gas at various operating conditions on retorting characteristics. A series of 7 scoping tests were performed using various synthesis gas and CO-steam mixtures for retorting at several temperatures and hydrogen partial pressures using Indiana New Albany shale. The synthesis gas composition was chosen as being representative of the product gas from a fossil fuel conversion pilot plant. Based on the results of the scoping tests, subsequent retorting of the Eastern shales from Alabama, Kentucky, Michigan, Ohio, and Tennessee were performed at nominal reactor conditions of 1025°F, 1000 psig total pressure, a hydrogen partial pressure of 270 psig, and a steam feed of 25 percent by volume of the total feed gas. Detailed operating conditions and results, and analyses of products from retorting using synthesis gas in the laboratory-scale batch reactor are presented in Tables 24 and 25.

Effect of Temperature: The first three tests using synthesis gas feed were made at temperatures of 900°, 1050°, and 1200°F, and a total pressure of 1000 psig using Indiana New Albany shale feed. Reconciled oil yields from these first three tests were all about 150% of Fischer Assay with total carbon conversions ranging from 64.5% to 69.2%. Because synthesis gas retorting operation at 1200°F caused higher conversions of hydrogen and nitrogen with essentially no additional oil yield, the remaining test program focused on operation at 1050°F. The higher hydrogen conversion results in additional high-temperature water and hydrocarbon gas formation which is undesirable. The higher nitrogen conversion results in additional ammonia production or generation of larger quantities of poly-cyclic nitrogen compounds present in the oil, neither of which is desirable.

Because it was noted in Task 1.2 that the HAU and MBU hydroretorting results for operation at comparable conditions showed good agreement, it was

Table 24. HAU SYNGAS OPERATING CONDITIONS AND RESULTS USING INDIANA SHALE FEED

Run Identification Shale Source	1	2	3	4	5	6	7	8	9	10 Rpt	11	12 Rpt
	-----	-----	-----	Indiana	-----	-----	-----	Ohio	Kentucky	Michigan	Alabama	Tennessee
Maximum Temperature, °F	1201	1055	935	1063	1052	1061	1055	106	1013	1020	1024	1018
Total Pressure, psig	1006	998	998	1002	1002	1001	1002	1005	1002	1000	998	995
Feed Hydrogen Partial Pressure, psig	332	331	329	281	0	0	277	266	276	260	274	257
Heat-up Rate, °F/min	24.9	22.7	22.4	23.9	24.4	23.7	23.9	23.1	23.5	23.5	23.3	23.1
Shale Feed, gm	100.74	100.65	101.04	100.44	99.63	101.40	101.06	100.29	100.18	100.39	100.06	98.29
Steam Feed, gm/min	0.181	0.193	0.201	0.467	0.519	0.492	0.492	0.53	0.45	0.45	0.45	0.46
Shale Residue, gm	93.98	85.82	86.81	85.61	87.21	89.65	86.26	84.81	83.01	84.77	84.78	87.24
Feed Gas, ^a SCFH	3.81	4.08	4.08	4.02	4.02	4.00	4.00	3.57	4.01	4.00	3.91	4.00
Feed Gas Composition, mol %												
Helium	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.2	0.0	1.2
Hydrogen	34.0	34.1	33.9	29.1	--	--	28.7	27.5	28.6	27.1	28.5	26.9
Carbon Dioxide	22.9	22.9	22.8	19.6	--	--	19.3	19.3	20.2	19.9	20.1	19.8
Carbon Monoxide	24.8	24.8	24.6	21.2	73.6	74.5	20.9	20.7	21.6	22.1	21.5	22.0
Methane	6.6	6.6	6.6	5.7	--	--	5.6	5.5	5.8	5.9	5.7	5.9
Steam	11.7	11.6	12.1	24.4	26.4	25.5	25.5	27.0	23.8	23.8	24.2	24.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.00	100.0
Conversions, ^b % of Feed Shale												
Total Carbon	67.7	69.2	64.5	67.1	50.1	46.0	68.6	65.9	59.1	70.6	52.2	52.5
Hydrogen	80.1	75.9	71.0	75.3	65.7	65.5	73.0	63.5	63.7	73.8	69.8	61.4
Sulfur	46.1	48.3	47.2	47.7	49.0	49.3	50.2	49.3	21.7	36.5	47.1	44.4
Nitrogen	66.7	62.2	42.7	60.0	28.5	41.0	60.1	88.7	35.6	53.2	51.5	24.0
Feed Shale Gross Calorific Value, ^c Btu/lb												
	2608	2608	2608	2608	2608	2608	2608	2183	1921	2438	3188	2405
Spent Shale Gross Calorific Value, ^c Btu/lb												
	892	780	902	828	1217	1304	799	758	802	702	1750	1445
Fischer Assay, GPT	13.8	13.8	13.8	13.8	13.8	13.8	13.8	11.9	8.4	14.0	13.1	9.7
Recovered Oil Yield, GPT ^c	20.0	18.3	16.4	19.1	^e	11.3	14.3	18.6	14.2	23.0	18.7	12.7
Reconciled Oil Yield, GPT ^d	21.4	21.6	21.6	22.1	--	12.9	18.7	19.3	15.0	22.0	20.0	15.5

^a Does not include steam feed.^b Elemental conversions based on solids ash balance.^c Recovered yields based on laboratory data (dry feed shale basis).^d Dry feed shale basis. Carbon balance adjusted to 100% by distributing missing carbon equally into the gas phase and liquid phase; this method gives a generally conservative oil yield.^e Some liquid loss occurred in this test; oil yield not reliable.

Table 25. ANALYSES OF SHALE PRODUCTS FROM LABORATORY-SCALE BATCH SYNGAS TESTS

Run Identification	1	2	3	4	5	6	7	8	9	10 Rpt	11	12 Rpt
Shale Source	Indiana							Ohio	Kentucky	Michigan	Alabama	Tennessee
Maximum Temperature, °F	1201	1055	935	1063	1052	1061	1055	1016	1013	1020	1024	1018
Total Pressure, psig	1006	998	998	1002	1002	1001	1002	1005	1002	1000	998	995
Feed Hydrogen Partial Pressure, psig	332	331	329	281	0	0	277	266	276	260	274	257
Shale Proximate Analysis Moisture, wt %	0.12	0.10	0.11	0.12	0.13	0.09	0.04	0.24	0.23	0.07	0.04	0.00
Ultimate Analysis, wt % (dry basis)												
Ash	90.99	90.28	89.34	90.17	87.53	86.72	90.31	91.72	92.60	90.72	87.32	89.79
Total Carbon	5.04	4.76	5.44	5.12	7.49	8.03	4.86	4.23	4.80	4.12	8.53	6.15
Hydrogen	0.35	0.42	0.50	0.43	0.58	0.56	0.47	0.49	0.47	0.46	0.57	0.56
Sulfur	2.89	2.75	2.78	2.78	2.63	2.59	2.65	1.68	1.04	2.76	4.87	3.16
Nitrogen	0.16	0.18	0.27	0.19	0.33	0.27	0.19	0.05	0.23	0.20	0.25	0.32
Spent Shale Gross Calorific Value, Btu/lb	892	780	902	828	1217	1304	799	758	802	702	1750	1445
Shale Oil Ultimate Analysis, wt %												
Carbon	83.30	83.89	83.99	85.93	85.41	86.10	86.45	86.14	86.11	86.37	86.54	86.25
Hydrogen	9.86	10.16	10.02	10.09	9.91	9.88	9.57	10.23	9.24	10.31	10.23	10.32
Sulfur	1.79	1.52	1.50	1.70	†	1.76	1.27	1.68	1.63	1.87	2.31	0.73
Nitrogen	1.70	1.64	1.80	1.80	1.88	1.58	1.54	1.47	1.69	1.30	0.90	1.07
Ash	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Oxygen (by difference)	3.35	2.79	2.69	0.48	--	0.68	1.17	0.48	1.33	0.15	0.02	1.63
Total	100.00	100.00	100.00	100.00	97.30	100.00	100.00	100.00	100.00	100.00	100.00	100.00
C/H Ratio	8.45	8.26	8.39	8.51	8.62	8.71	9.03	8.42	9.32	8.38	8.46	8.36
Specific Gravity (60/60°F), gm/ml	0.947	0.945	0.960	0.969	0.969	0.970	0.984	0.957	1.000	0.983	0.958	0.955
Gravity, °API	17.9	18.2	15.9	14.5	14.5	14.4	12.3	16.4	10.0	12.4	16.2	16.7

* Moisture present in spent shale recovered from SYNGAS runs was probably due to water absorbed during run shutdown.

** Oxygen is present as mineral oxides and high-temperature water included as ash; because the high-temperature (925°C) assaying procedure alters the composition of mineral matter existing in the original raw shale, e.g., the conversion of CaCO_3 plus pyrites to CaSO_4 and Fe_2O_3 , the sum of the elements may exceed 100%.

† Insufficient sample for analysis.

decided to operate the HAU at 1050°F for the remainder of the synthesis gas test program to allow a comparison of results between the HAU and the MBU at similar operating conditions. Most of the hydrotreating design point tests for the MBU were conducted at 1050°F. Operation at 900°F would not permit interpolation of the data to lower temperatures as would operation at 1050°F. It was noted above that operation at 1200°F was not desirable.

Effect of CO-Steam Operation: For the fourth test using synthesis gas feed, the feed gas contained approximately 24% steam rather than the 12% steam used in the first three tests. The higher steam concentration was expected to shift the CO-steam equilibrium reaction such that additional hydrogen would be formed. This newly-formed hydrogen was believed to be more reactive than the hydrogen fed with the original synthesis gas mixture. This theory was further examined by making an additional test (No. 5) with only CO and steam. In Test No. 5, however, the large volume of condensed steam collected caused the centrifuge tube to overflow, resulting in liquid loss. This test was repeated (Test No. 6) and the operating procedure was modified so that the reactor was preheated above the dew point of the feed gas mixture prior to feeding steam to the reactor. The yield for Test No. 6 was 12.9 GPT, about the Fischer Assay yield for this shale. The oil yield results indicate that at the retorting conditions tested the CO-steam is less reactive than the hydrogen used alone or in the tests using synthesis gas feed.

The run procedure utilized for previous tests (Tests No. 1 to 5) may have caused condensation to occur in the reactor, reducing oil yields and elemental conversions; therefore, one of the previous tests (Test No. 4) that used a synthesis gas feed was repeated. Elemental conversions from the original test and the repeat test using the modified procedure were nearly the same (Table 24, Test No. 4 and Test No. 7). The oil yield from the repeat test (Test No. 7) was slightly lower than that from Test No. 4; however, the oil yield and elemental conversion results indicate that if condensation did occur in Tests No. 1 to 5 because of the run procedure used, it did not adversely affect oil yields or elemental conversions.

Because the elemental carbon balances for the tests conducted with shales from Michigan and Tennessee showed carbon balances of 72% and 84%, respectively, there was considerable uncertainty in reconciling the balances to 100%. The repeat tests for the shales from Michigan and Tennessee show

carbon balances of 102% and 91% and reconciled oil yields of 157% and 160% of Fischer Assay, respectively. Only these repeat tests are shown in the table. A helium tracer was added to the feed gas for the repeat tests to allow a more accurate determination of product gas flow measurements and yields. Carbon balances are reconciled by first adding an additional 15% of the measured carbon as gas to the gas phase, and then closing the balance by assuming that the remainder of the missing carbon is due to unrecovered oil. This method accounts for unmeasured dissolved gases in the liquid phase lost during depressurization of the unit and gives a generally conservative oil yield. A repeat test was also conducted with the Indiana New Albany shale to verify product gas composition. The repeat test verified the product gas composition of the original test.

Effect of Water-Gas Shift Reaction: The tabulated results show reconciled oil yields ranging from 15.0 to 22.0 gal/ton, which represent oil yields of 152% to 178% of Fischer Assay. There was net water consumption in all of the tests conducted using synthesis gas feed, that is, the numerical sum of the weights of water present as moisture in the feed shales, and the weights of steam feeds exceeded the measured product water weights. An explanation for the net water consumptions is the water-gas shift reaction, which consumes carbon monoxide and water while producing carbon dioxide and hydrogen. This is contrary to the experience in retorting in hydrogen, which always results in net water production.

An examination of the feed gas compositions for all the batch laboratory-scale tests shows that at maximum reactor temperatures the gas mixtures are not at equilibrium, and that up to 56 to 85 psig additional hydrogen partial pressure could be formed if the water-gas shift reaction would go to equilibrium at the indicated temperatures.

Effect of Feed Shale Hydrogen to Organic Carbon Weight Ratio: Plots of the effect of feed hydrogen to organic carbon weight ratio on the normalized oil yields in gallons/ton per percent organic carbon for the Fischer Assay and for retorting in synthesis gas are shown in Figure 13. The data show that the higher the H/C ratio in the feed shale, the greater the normalized oil yield both for Fischer Assay and retorting in synthesis gas. Six shales from five distinct rock formations were utilized for the tests; the data points representing the oil yields from retorting the shales as a Fischer

Figure 13. EFFECT OF HYDROGEN TO ORGANIC CARBON WEIGHT RATIO ON OIL YIELDS

Assay and in synthesis gas are represented by straight lines. The lines were determined by linear regression of the data. The Fischer Assays for the six Eastern shales tested range from a low of about 0.8 gal/ton per unit weight percent organic carbon, to about 1.1 gal/ton. Other researchers have published work indicating that oil yields from thermal retorting of Eastern shale are about 1 gal/ton per weight percent organic carbon.^{3,4}

The oil yields obtained by retorting using synthesis gas, for the same six shales for which the Fischer Assay data was obtained, range from about 1.3 to 1.9 gal/ton per weight percent organic carbon, or about a 65% to 70% improvement over Fischer Assay yields.

Effect of Hydrogen Partial Pressure: The data representing the oil yields for all six shales obtained by retorting using synthesis gas with approximately 270 psig hydrogen partial pressure appear to indicate that retorting using synthesis gas gives oil yields which depend primarily on the inlet hydrogen partial pressure of the feed gas. The data representing the oil yields obtained from retorting in hydrogen represent both the hydrogen partial pressure and the total pressure because the retorting feed gas was 100% hydrogen. All tests which used a synthesis gas feed were conducted at a total pressure of about 1000 psig.

A comparison of the data representing oil yields from retorting in synthesis gas and retorting in hydrogen at the same inlet feed hydrogen partial pressures is shown in Figure 14. The data confirm that oil yield is primarily a function of the inlet hydrogen partial pressure.

Subtask 3.1.2. Mini-Bench-Scale Tests

Objective: The objective of this subtask is to perform moving-bed retorting tests at selected conditions of temperature, pressure, synthesis-gas composition, and heat-up rate to broaden the data base on the hydroretorting characteristics of Eastern shales. The test conditions will be chosen based on results of the HAU tests performed in Subtask 3.1.1.

Experimental Equipment and Test Procedure: A flow diagram of the MBU is shown in Figure 15. The unit consists of a hydroretorting reactor with equipment for feeding and measuring the flow rates of shale and feed gas, and for collecting and/or measuring the flow rates of residue shale, and product liquids and gas. Simple controls are used to maintain reactor temperatures at

Figure 14. COMPARISON OF OIL YIELDS FROM HYDRORETORTING AND RETORTING IN SYNTHESIS GAS

Figure 15. SCHEMATIC DIAGRAM OF THE MINI-BENCH UNIT

the desired values, to maintain constant reactor pressure, and to collect representative samples of the feed and product gas.

Shale is fed by a screw feeder from a pressurized feed hopper filled with a sufficient amount of shale for the entire run (about 10 pounds). The cold shale enters the top of the reactor, and the residue shale is discharged from the bottom of the reactor into a pressurized residue receiver by a discharge screw.

Preheated hydrogen and steam are mixed with syngas. This feed gas stream is subjected to additional heating and enters the reactor several inches below the heated zones through an inlet gas jet. To insure upward gas flow in the entire reactor tube, a feed hydrogen stream enters the bottom of the reactor. The product gas and vapor exit the reactor through a 1/4-inch-diameter dip tube just above the shale bed. A small purge flow of the feed gas is continuously passed into the feed hopper during the test to displace the volume of shale being fed into the reactor, and to prevent gas containing liquid products from entering the feed hopper.

The reactor is a 39-1/8-inch-long piece of 2-inch, Schedule 80 (ID of 1.92 inches), 316 stainless-steel pipe. The reactor is heated by a six-zone electric heater. Each zone is 3 inches long, and the heater extends from about 10 to 28 inches from the bottom of the reactor tube. An additional electric heater is used to heat a section of the reactor above the main heater. The temperature of each zone is controlled by a separate temperature controller. Six thermocouples are used to measure the inside temperatures along the reactor. The temperatures are recorded continuously, along with the temperatures of other major pieces of equipment.

The shale feed rate is set by adjusting the feed-screw speed of rotation to the desired value. The rate of shale discharge is then set manually to give a constant shale-bed level. The shale-bed level is indicated by a nuclear-type level indicator and is continuously recorded. The weight of the shale feed is determined by subtracting the weight of shale present at the end of the test from the amount originally charged. The residue shale in the receiver is weighed after the run. Feed and residue shale rates are calculated by dividing these weights by the measured shale feeding time.

The exit gas volume is measured by a dry test meter. Spot feed and product-gas samples are taken throughout the steady-state test period. The exit gas is cooled in a single-stage condenser. The condensed liquids are then collected in a knockout pot. The pot is drained and the liquid weighed at approximately 15-minute intervals during the steady-state portion of the run to obtain product rates. Steady-state is defined as a condition wherein the temperature profile in the shale bed is uniform; feed gas, purge gas, and exit gas flow rates are constant; reactor pressure is stable; and the shale feed rate and bed height are essentially constant.

The reactor is filled with gravel prior to each run to establish a bed and a stable temperature profile. This prevents rapid heating of the initial shale feed, subjects all feed shale to a similar time-temperature history, and eliminates tar formation that occurs with a varying bed height at the start of a run.

Several MBU modifications were made for the synthesis gas tests. The liquid knockout pot was changed to allow high-pressure operation. The feed gas manifold was altered to allow synthesis gas feed and sampling. A high-pressure piston-type water pump capable of accurately delivering the desired water rate was installed. A high-pressure hydrogen manifold with the capability of providing two metered feed hydrogen streams was installed. The reactor inlet gas system was modified to allow the majority of the feed gas to enter through a jet which introduces gas just below the heated reactor zones. One of the feed hydrogen streams was connected to the bottom block gas inlet port.

Care was taken in the introduction and halting of gas streams during the synthesis gas tests. Improper operation can result in carbon deposition from the feed synthesis gas or wetting of the solids with condensed steam or product oil. The problems could cause blockage of the inlet gas line or the formation of a solids plug in the reactor and necessitate an involuntary shutdown. The following description is an outline of the procedure used for the synthesis gas tests.

Sufficient shale (10 to 12 pounds) for the test is charged to the feed hopper. Gravel (4 to 5 pounds) is charged to the reactor. The gravel charged is enough to give a positive reading on the level detector. Filters are installed on the exit gas line. The filters and the residue hopper are

positioned for unsteady-state operation and collection. The MBU system is then sealed and pressure-tested to 1000 psig H_2 pressure at room temperature. After successful completion of the pressure test, heating tapes and insulation are placed on the top and bottom blocks, and on the feed gas line between the preheat furnace and the reactor.

Hydrogen gas flows are established to the bottom block (1 to 2 SCF/h) and the inlet gas jet (8 SCF/h). Power is then supplied to all heating tapes and furnaces. The bottom reactor zone (Zone 1) is set 100°F below the retorting zone temperature to provide additional heating for the inlet gas. Zones 2 to 4 are set at the retorting temperature. Zones 5 to 7 are set at decreasing temperatures to provide a shale preheat zone.

All temperatures are at their nominal values before starting the feed and discharge screws. The internal top block temperature is always the slowest to reach the desired value. This temperature must be above 300°F before beginning shale feed to prevent oil condensation in the top block. When temperatures are stable, the feed and discharge screws are turned on simultaneously. The feed screw rate is maintained at the desired value, while the discharge screw rate is changed to maintain the desired bed height.

Hydrogen feed rates to the jet and bottom block are adjusted to the steady-state values of 8 SCF/h. A minimum of 30 minutes of operation is conducted with a constant bed level, a uniform shale feed rate, and the steady-state hydrogen feed rates. During this time, the reactor becomes hot enough to prevent steam condensation in the bed. The water pump is adjusted to deliver 2.3 g/min of water and is then put on-line. The feed synthesis gas is started 5 to 10 minutes after putting the water pump on-line. The delay provides time for steam to be present in the feed gas lines and prevent the possibility of carbon deposition from the synthesis gas.

The reactor is operated under steady-state flow, temperature, and pressure conditions, until all gravel and shale not experiencing the steady-state time-temperature profile is discharged to the unsteady-state side of the residue hopper. This unsteady-state period of operation requires 2 to 2.5 hours of solids discharge. When shale (which has been processed at steady-state conditions) is being discharged, the bed level is constant, and all solids and gas flow rates are constant, the reactor is deemed to be at steady-state conditions. At the start of the steady-state period, the exit

line filters and the residue hopper are switched to the steady-state sides. All flows, temperatures, and pressures are held constant.

Steady-state operation is maintained for two hours to provide sufficient time and material (liquids, residue solids, and gas) for a complete material and elemental balance. Liquids are collected in separate jars every 15 minutes throughout the entire test. Product gas samples are taken every 30 minutes during steady-state, and feed synthesis gas samples are collected at the beginning and end of the steady-state period.

At the end of steady-state operation, the feed and discharge screws are halted. The synthesis gas feed is stopped, but steam is fed to the reactor for an additional 30 minutes to prevent carbon deposition. The steam feed is then stopped. All heating tapes and furnaces are left on for another 30 minutes to allow all water to be driven from the reactor. All furnaces and heating tapes are then turned off, and the reactor is allowed to cool. When the reactor has cooled to below 600°F, and the possibility of further oil production has been eliminated, the hydrogen feeds are stopped. The reactor is slowly depressurized and allowed to cool to ambient conditions. Weights of feed not charged to the reactor, unsteady-state and steady-state residue solids, and exit-gas line filters are obtained. Feed and product gases, steady-state liquids, and feed and steady-state residue shale are submitted to the analytical laboratory for analysis.

Discussion: Seven synthesis gas-retorting tests were conducted with Eastern shales in the continuous mini-bench unit (MBU). Tests included two tests with Indiana shale and one test with each of the Kentucky, Ohio, Tennessee, Michigan, and Alabama shales. Operating conditions were chosen to be the same as the conditions for MBU hydroretorting tests with the six Eastern shales in Task 1.2. Temperatures and shale residence times for the synthesis gas tests were similar to the conditions used for MBU hydroretorting tests. For the first synthesis gas test with Indiana shale, the hydrogen partial pressure was approximately 400 psi and the feed gas was not in water-gas shift equilibrium at the reactor temperature. Hydrogen partial pressures for the other six synthesis gas tests were 20 to 50 psi lower than the 550 psi of hydrogen used for the comparable hydroretorting tests. Synthesis gas compositions were chosen to be in water-gas shift equilibrium at the maximum retort temperature to prevent hydrogen shifting from affecting the retort gas

composition. Total pressure for the synthesis gas tests was 950 psig compared to 600 psig for the hydroretorting tests. Compositions of feed gas used for the seven synthesis gas retorting tests are presented in Table 26.

Summaries of the operating conditions and results of the seven MBU synthesis gas retorting tests are presented in Table 27. Summaries of MBU hydroretorting tests at similar conditions with the same shales are included to aid in comparing the test results. Detailed test results for a typical MBU synthesis gas retorting test is presented in Appendix C.

Indiana Shale Synthesis Gas Tests: Two synthesis gas tests were conducted with Indiana New Albany shale with similar retorting temperatures (1050° and 1075°F) and shale residence times (33 and 26 minutes). Although the total pressures were the same, different feed gas compositions led to hydrogen partial pressures of 408 psi in Test 86MBU-16, and 542 psi in Test 88MBU-3. The hydrogen partial pressure increase led to increased oil yield and higher organic carbon conversion to gas, but decreased selectivity of organic carbon to oil. Reconciled oil yields in Tests 86MBU-16 and 88MBU-3 were 21.2 and 23.9 gal/ton, respectively. Organic carbon conversion to gas was 15.2% and 18.7% in Tests 86MBU-16 and 88MBU-3, respectively. Oil quality and sulfur conversion were not affected by the difference in hydrogen pressure between the two Indiana shale synthesis gas tests.

The hydrogen consumptions for the two Indiana synthesis gas tests were very different. The difference was a result of the different feed synthesis gases used for the tests. Test 86MBU-16 was made with a feed synthesis gas in water-gas equilibrium at 1615°F. The feed hydrogen consumption in this test was a very low 400 SCF/ton dry shale, while the consumption of hydrogen and carbon monoxide combined was 1800 SCF/ton. Test 88MBU-3 was made with a feed synthesis gas in water-gas equilibrium, at 1170°F, only 100°F above the retorting zone temperature. The hydrogen consumption was 2800 SCF/ton while the consumption of hydrogen and carbon monoxide combined was only slightly higher at 2900 SCF/ton. The higher consumption of hydrogen plus carbon monoxide in Test 88MBU-3 compared to Test 86MBU-16 is a result of the higher conversion of organic carbon to hydrocarbon gas and oil. The large difference seen in Test 86MBU-16 between the consumption of hydrogen and the consumption of hydrogen plus carbon monoxide indicates the water-gas shift reaction occurred and shifted steam to hydrogen, and carbon monoxide to carbon dioxide.

Table 26. FEED SYNTHESIS GAS COMPOSITIONS FOR MBU TESTS

Test Shale Source	86MBU-16 Indiana	88MBU-3 Indiana	88MBU-6 Kentucky	88MBU-7 Ohio	88MBU-3 Tennessee	88MBU-9 Michigan	88MBU-12 Alabama
Feed Gas, vol %							
CO	15.0	6.1	6.6	6.9	7.0	6.7	7.2
CO ₂	13.9	5.8	6.5	6.7	6.6	6.4	6.9
H ₂	37.6	59.2	58.7	61.9	61.8	58.6	61.9
H ₂ O	28.7	27.0	26.1	22.3	22.3	26.2	21.7
CH ₄	4.0	1.6	1.8	1.8	1.9	1.8	1.9
He	<u>0.8</u>	<u>0.3</u>	<u>0.3</u>	<u>0.4</u>	<u>0.4</u>	<u>0.3</u>	<u>0.4</u>
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 27. SUMMARY OF HYDROGEN AND SYNTHESIS GAS MBU TESTS WITH EASTERN SHALE

Run Identification	86MBU-5	86MBU-8	86MBU-16	88MBU-3	87MBU-12	87MBU-17	88MBU-6	87MBU-10	88MBU-7	86MBU-9	88MBU-8	87MBU-11	88MBU-9	86MBU-10	88MBU-12
Shale	Indiana				Kentucky			Ohio		Tennessee		Michigan		Alabama	
Feed Gas	H ₂	H ₂	Syngas	Syngas	H ₂	H ₂	Syngas	H ₂	Syngas	H ₂	Syngas	H ₂	Syngas	H ₂	Syngas
Maximum Bed Temperature, °F	1100	1050	1050	1075	990	950	980	1010	985	1210	1165	960	1055	1070	1055
Feed Gas WGS Equilibrium Temperature, °F	NA	NA	1615	1170	NA	NA	1155	NA	1090	NA	1095	NA	1165	NA	1085
Total Pressure, psig	599	601	950	942	594	597	935	588	940	602	940	593	933	601	937
Hydrogen Partial Pressure, psig	551	561	408	542	554	555	505	556	540	564	539	564	520	554	536
Shale Residence Time, min	61	76	76	57	57	62	54	57	56	78	57	58	65	77	53
Shale Residence Time at Temperature, min	33	33	33	20	29	32	31	29	30	23	30	30	34	34	30
Oil Yield (gal/ton), Recovered	24.1	24.4	20.6	19.8	13.2	13.9	11.2	19.0	15.8	17.0	13.3	21.0	18.6	23.7	20.5
Reconciled	25.9	25.3	21.2	23.9	12.9	13.6	11.2	19.5	17.4	18.2	13.3	22.7	18.6	24.3	20.8
Water Yield ² (gal/ton)	9.3	7.4	-4.2	4.3	15.0	15.3	4.2	10.2	4.6	7.2	1.7	7.4	-0.6	7.4	5.2
Oil Properties, Pour Point, °F	-5	0	NA	-10	NA	NA	-5	NA	0	-10	-40	NA	-5	-25	-65
API, @ 60°F	15.3	15.1	NA	17.0	9.3	9.9	14.9	15.4	20.1	15.3	20.3	15.6	16.8	15.3	16.4
C/H Ratio	8.37	8.26	8.05	8.30	8.78	9.03	8.80	8.51	8.27	8.60	8.60	8.31	8.33	8.63	8.79
S, wt %	1.44	1.81	0.55	0.85	1.17	1.21	1.38	0.66	1.15	1.57	1.29	0.95	1.06	2.00	2.04
N, wt %	2.03	2.09	1.62	1.22	1.96	2.14	1.46	1.82	1.38	1.62	1.17	1.53	1.33	1.46	1.22
Viscosity, SSU	76.4	82.0	NA	52.7	NA	NA	51.0	NA	41.9	61.6	36.4	NA	69.3	58.6	265
Distillate Fractions															
Temperature, °F, 10%	333	341	302	288	NA	NA	290	NA	286	318	200	NA	316	320	270
50%	677	670	604	606	NA	NA	590	NA	577	664	540	NA	657	652	592
E.P.	760	760	760	745	NA	NA	1018	NA	760	740	970	NA	751	760	750
Hydrogen Consumption, ³ SCF/ton	2800	2800	400	2800	2500	3400	1600	2200	1700	3000	2200	2450	1800	3500	3000
Hydrogen + CO Consumption, SCF/ton	--	--	1800	2900	--	--	2050	--	1900	--	2100	--	1800	--	3100
Organic Carbon Conversion, % (adjusted by ash balance)	83.8	83.9	74.4	81.5	68.6	67.3	63.2	76.2	68.2	76.3	64.3	84.8	80.8	72.8	68.0
Selectivity to Oil, % (adjusted by ash balance)	85.3	82.5	79.0	77.1	75.6	77.5	72.1	82.3	78.4	71.9	59.4	80.8	67.9	77.8	69.6
Hydrocarbon Gas Yield, MM-Btu/ton (adjusted)	0.97	1.17	1.20	1.47	1.01	0.97	0.99	0.91	0.97	1.57	1.93	1.20	1.87	1.54	1.95
Organic Carbon to Gas, %	12.4	14.7	15.2	18.7	16.8	15.1	16.5	13.5	14.7	21.4	26.1	16.3	25.9	16.2	20.7
Oil, %	71.5	69.2	59.2	62.8	51.9	52.1	42.6	62.7	53.5	54.8	38.2	68.5	54.9	56.7	47.3
Residue, %	16.2	16.1	25.6	18.5	31.4	32.7	40.9	23.8	31.8	23.7	35.7	15.2	19.2	27.2	32.0
Sulfur Conversion to Gas, %	48.5	44.5	49.3	48.7	27.0	13.8	28.1	41.8	48.5	55.2	48.2	38.0	50.0	49.0	50.3
Oil, %	3.2	4.0	0.9	1.7	5.3	5.9	5.1	1.9	2.8	2.2	1.3	2.5	2.0	2.6	2.0
Residue, %	48.3	51.4	49.8	49.6	67.7	80.3	66.8	56.3	48.7	42.7	50.6	59.6	48.0	48.4	47.7

¹WGS = Water-Gas Shift.²Water production less shale moisture³Hydrogen consumption is average of combined hydrogen and forced oxygen methods.

Synthesis Gas Retorting and Hydroretorting MBU Tests: The six Eastern shales were retorted under similar conditions in both hydrogen and synthesis gas. The effects of a synthesis gas feed (instead of hydrogen) on oil yields and conversions can therefore be directly determined.

When using synthesis gas instead of hydrogen for retorting, all six Eastern shales showed a decrease in oil yield, higher conversion of organic carbon to gas, and a lower organic carbon selectivity to oil. The oil yields using synthesis gas were between 6% and 27% lower than the corresponding hydroretorting oil yields. Indiana shale oil yield decreased only 6%, from 25.2 to 23.9 gal/ton, while Tennessee oil yield decreased 27%, from 18.2 to 13.3 gal/ton. The other four shales had oil yield decreases from 11% to 18% (2 to 4 gal/ton). The organic carbon conversion to oil was between 7% lower (Indiana shale) and 17% lower (Tennessee shale) in synthesis gas.

Synthesis gas retorting of all six Eastern shales led to increases in organic carbon conversions to gas of 0.5% (Kentucky shale) to 10% (Michigan shale). Higher organic carbon conversions to gas in the synthesis gas tests do not appear to be a result of oil cracking to form gas because the shales with the largest gas yield increases are not the same as the shales with the largest oil yield decreases. The increases in organic carbon conversion to gas were less than the decreases in conversion to oil for all shales. Therefore, the organic carbon left in the residue shale after retorting increased between 2% (Indiana shale) and 12% (Tennessee shale) in synthesis gas compared to hydrogen retorting.

Distinct differences were found in the oils produced by synthesis gas and hydrogen retorting. Oil produced during synthesis gas retorting was lighter, less viscous, and had a lower nitrogen content. Sulfur content of the oils, produced when using synthesis gas and hydrogen were similar. Organic carbon conversions and oil analyses suggest that the heavier oil fractions produced during hydroretorting of Eastern shales are not produced with a synthesis gas feed.

Sulfur conversions were similar during Eastern shale retorting in hydrogen and synthesis gas. For five of the shales, sulfur conversions to gas ranged from 38% to 55%. Pyrite appears to be the main feed sulfur species in these shales, and the decomposition of pyrite to FeS is the main reaction contributing to sulfur conversion and hydrogen sulfide formation. For

Kentucky shale, sulfur conversion to gas ranged from 14% to 28%, indicating pyrite is not the principal feed sulfur species for this shale.

Hydrogen Partial Pressure Effect on Oil Yield: During this program, a number of different retorting tests were conducted with each of the six Eastern shales of interest. All six shales had Fischer Assays performed on them in which no feed hydrogen gas is supplied. The shales were hydrotretorted in the batch HAU at hydrogen partial pressures from 400 to 1000 psi. They were also hydrotretorted in the continuous MBU at 550 psi of hydrogen. Synthesis gas retorting of the six shales was conducted in the HAU at 300 psi of hydrogen, and in the MBU at 550 psi of hydrogen. To compare the oil yields of each shale in different units and gas environments, oil yields were plotted against average hydrogen partial pressures in the retorting processes. Oil yields were normalized to gal/ton weight percent organic carbon to compensate for differences in feed shale organic carbon contents. Plots of normalized oil yield by the various retorting processes versus hydrogen partial pressure are presented in Figures 16 through 21.

The figures show that normalized oil yields from HAU hydrotretorting, HAU synthesis gas retorting, and MBU hydrotretorting tests for five shales, increase linearly with increasing hydrogen partial pressure. The linear relationship for each shale is valid over the hydrogen partial pressure range studied (400 to 1000 psi), but the Fischer Assay oil yields show the relationship is non-linear at lower hydrogen partial pressures. The oil yields from the Kentucky shale MBU hydrotretorting tests were lower than the values predicted by the HAU tests with this shale. The change in hydrotretorting unit scale from the batch HAU to the continuous MBU had no significant effect on the oil yield for five of the six Eastern shales. The hydrotretorting oil yield was lower in the MBU only for Kentucky shale.

Oil yields from MBU synthesis gas retorting tests with all six Eastern shales were lower than predicted by HAU retorting tests and MBU hydrotretorting tests. MBU synthesis gas retorting oil yields were 15% to 25% (0.25 to 0.4 gal/ton weight percent organic carbon) lower than the oil yields predicted by the other retorting tests. The reason for lower-than-expected oil yields from MBU synthesis gas retorting tests is unclear. The lower oil yields and higher organic carbon conversions to gas during MBU synthesis gas retorting compared to hydrotretorting may indicate the retorting process has lower

Figure 16. NORMALIZED OIL YIELDS FROM RETORTING ALABAMA CHATTANOOGA SHALE

Figure 17. NORMALIZED OIL YIELDS FROM RETORTING INDIANA NEW ALBANY SHALE

Figure 18. NORMALIZED OIL YIELDS FROM RETORTING KENTUCKY SUNBURY SHALE

Figure 19. NORMALIZED OIL YIELDS FROM RETORTING MICHIGAN ANTRIM SHALE

Figure 20. NORMALIZED OIL YIELDS FROM RETORTING OHIO CLEVELAND SHALE

Figure 21. NORMALIZED OIL YIELDS FROM RETORTING TENNESSEE CHATTANOOGA SHALE

selectivity to oil in a synthesis gas environment. However, synthesis gas retorting in the HAU did not adversely affect the oil yield.

Subtask 3.2. Mist Generation Tests

Objective: The objective of this subtask is to determine the potential of reducing oil refluxing by generating a mist. Introducing a charged gas stream into a moving-bed hydrotretorting gas stream will increase product oil yield by decreasing oil refluxing. A mist generation system is to be constructed and tested and then installed on an existing reactor system (MBU). The reactor with the mist generation system is to be operated under actual hydrotretorting conditions.

Experimental Equipment and Test Procedures: Mist generation tests were conducted in the Mini-Bench Unit (MBU). Detailed descriptions of the MBU equipment and test procedures are presented in Subtasks 1.2 and 3.1.2. The only significant MBU modification made for the mist generation tests was the addition of a chamber containing high-pressure ignition electrodes to enable the introduction of a feed stream of ionized carbon dioxide to the MBU. Descriptions of the ignition electrode configurations and test procedures for the mist generation tests are provided in the Discussion section for this subtask.

Discussion: Because previous work on mist generation and ionization has been at atmospheric or low pressures, a small test apparatus was designed to test the effect of pressure and spark-plug gap on the voltage required to generate a spark. This test apparatus was then modified for use with the MBU to test the effect of ionized gas on enhancing oil recovery by reducing refluxing. Reduced oil refluxing improves the overall process efficiency.

A mist generation system was constructed by installing two high-pressure ignition electrodes in a sealed high-pressure sight gauge. The system contained a flow control valve, check valve, pressure gauge, and backpressure regulator. The ignition electrodes were fired using individual step-up transformers with a maximum output (secondary) voltage of 10,000 volts. The sight gauge permitted visual observation of sustained sparking. Bench-top testing using carbon dioxide as the charged gas, showed that the pressure at which sparking could be sustained increased as the ignition electrode gap was decreased and as applied voltage was increased. Sustained sparking in carbon

dioxide was found to vaporize (consume) the anode wire and effectively widen the ignition exciter gap. A 25-minute sustained spark was achieved at 600 psig of flowing carbon dioxide using an initial gap setting of 0.003 inch. After the successful bench-top testing was completed, the mist generation system was installed on the MBU for Test 87MBU-3.

Four successful MBU tests were conducted. The first three tests were conducted in the second program year. The final test, 88MBU-14, was performed in the third program year.¹ Detailed test calculations are presented in Appendix D.

A brief summary of the operating conditions and test results for the eight steady-state periods of the four mist generation MBU tests is presented in Table 28. All tests were made with -6+40 mesh Indiana New Albany shale and charged carbon dioxide injected between the retorting and preheat zones. In Test 87MBU-3, the mist generation device with two ignition electrodes was used. The temperatures of the retorting zone and top of the preheat zone were 1050°F and 575°F, respectively. The test was voluntarily terminated after 60 minutes of steady-state operation with uncharged carbon dioxide and 45 minutes of steady-state operation with charged carbon dioxide.

In Test 87MBU-5, three ignition electrodes were used in the mist generation device. The temperatures were lowered to study the effects of ionized carbon dioxide in a retort in which greater refluxing was occurring. The retorting zone and top of the preheat zone were 1010°F and 470°F, respectively. Steady-state operation with 60 minutes of non-ionized carbon dioxide, 15 minutes of transition, and 27 minutes of ionized carbon dioxide flow was achieved. In Test 87MBU-7, a cam was added to activate electrodes sequentially instead of a single electrode continuously. The modified device worked well; presumably the new configuration kept the electrodes cooler and reduced wear on the anode wires. The temperature profile was the same as used for 87MBU-5. The carbon dioxide flow rate was increased to study the effects of carbon dioxide flow rate on organic carbon selectivity to oil. Steady-state operation with 60 minutes of non-ionized carbon dioxide, 15 minutes of transition, and 60 minutes of ionized carbon dioxide flow was achieved before the run was voluntarily terminated.

Test 88MBU-14 was conducted to obtain accurate material balances on the steady-state periods with non-ionized and ionized carbon dioxide. The cam was

Table 28. MINI-BENCH UNIT RUN SUMMARIES

Run Identification	87MBU-3	87MBU-3	87MBU-5	87MBU-5	87MBU-7	87MBU-7	88MBU-14	88MBU-14
Shale Source					Indiana			
CO ₂ Ionization	No	Yes	No	Yes	No	Yes	No	Yes
Minimum Bed Temperature, °F	575	575	470	470	503	490	540	530
Maximum Bed Temperature, °F	1050	1050	1010	1010	1020	1020	940	950
Steady-State Period, min	60	45	60	27	60	60	90	90
Total Pressure, psig	570	570	571	571	573	573	630	630
Hydrogen Partial Pressure, psig	503	505	526	520	461	471	420	428
CO ₂ Rate, SCF/lb dry shale	2.2	2.1	0.69	0.63	4.5	3.9	4.2	4.7
Total Shale Residence Time, min	65.0	65.1	72.4	72.7	68.0	67.8	68.5	75.9
Shale Residence Time at Temperature, min	28.5	28.6	31.8	31.9	29.8	29.7	30.8	34.1
Oil Yield, gal/ton, Recovered	21.0	22.6	21.8	24.4	24.6	20.3	16.3	16.2
Reconciled	21.6	22.4	22.9	21.5	22.1	22.4	21.2	22.4
Oil Properties, API, @ 60°F	18.2	15.0	--	--	13.9	16.0	23.1	23.3
C/H Ratio	8.03	8.38	7.94	7.90	8.55	8.20	7.90	7.79
S, wt %	1.67	1.68	1.26	1.30	1.39	1.60	1.30	1.27
N, wt %	1.76	2.78	1.80	1.79	1.92	1.71	1.40	1.34
Viscosity, SSU	53.3	72.2	--	--	111.7	76.4	37.6	37.0
Hydrogen Consumption, SCF/ton*	3340	2920	2640	2980	2274	2485	2308	2277
Organic Carbon Conversion, % (Adjusted by ash balance)	79.4	79.4	79.2	79.2	75.5	75.5	67.6	67.6
Selectivity to Oil, % Adjusted	74.6	78.9	79.7	75.3	81.6	81.2	79.5	83.1
Hydrogen Gas Yield, MM-Btu/ton Methane Equivalent - Adjusted	1.52	1.34	1.28	1.56	1.11	1.14	1.14	0.94
Organic Carbon to Gas, %	20.1	16.7	16.1	19.6	13.9	14.2	13.9	11.4
Oil, %	59.3	62.7	63.1	59.6	61.6	61.3	53.7	56.1
Residue, %	20.6	20.6	20.8	20.8	24.5	24.5	32.4	32.4
Sulfur Conversion to Gas, %**	50.1	49.9	47.6	47.7	48.9	48.5	43.8	44.8
Oil, %	3.0	3.2	2.4	2.3	2.6	3.0	2.2	2.2
Residue, %	46.9	46.9	50.0	50.0	48.5	48.5	54.0	53.0
Water Production, gal/ton	11.7	11.0	7.7	8.8	7.9	8.5	9.5	10.6
Water Production, gal/ton (less shale moisture)	9.2	8.6	5.4	6.4	7.8	8.4	6.8	7.9

* Hydrogen consumption is average of combined hydrogen and forced oxygen methods.

** Sulfur in gas includes dissolved gases in water.

NA = Not available.

again used to fire three ignition electrodes sequentially and enabled the achievement of a 90-minute non-ionized CO₂ steady-state period, a 15-minute transition period, and a 90-minute ionized CO₂ steady-state period. To induce refluxing, the product gas exit line was raised to 5 inches above the bed, the carbon dioxide rate was increased, and the preheat zone was operated as cool as possible. The retorting zone and top of the preheat zone were 950° and 530°F, respectively.

The injection of carbon dioxide into the preheat zone in these tests reduced the hydrogen partial pressure and decreased the average oil yield. The range of carbon dioxide to shale ratios used did not alter the hydrogen partial pressure sufficiently to affect the oil yield. When non-ionized carbon dioxide was used, hydrogen partial pressures varied between 420 psig and 526 psig and reconciled oil yields increased 8%, from 21.2 to 22.9 gal/ton. Sulfur conversions were not affected by changes in hydrogen partial pressure. With ionized carbon dioxide, hydrogen partial pressures between 428 psig and 505 psig produced a reconciled oil yield of 22.4 gal/ton while 520 psig hydrogen produced an oil yield of 21.5 gal/ton.

Oil yields for the four tests did not vary significantly between steady-state periods with non-ionized and ionized carbon dioxide. Differences in oil yields between the steady-state periods for each test were within the accuracy of the reconciled yield calculations. For three tests, 87MBU-3, 87MBU-7, and 88MBU-14, reconciled oil yields were found to be between 0.3 and 1.2 gal/ton (1% to 6%) higher with ionized carbon dioxide than with non-ionized carbon dioxide. The reconciled oil yield for 87MBU-5 was 1.4 gal/ton (8%) lower with ionized carbon dioxide than with non-ionized carbon dioxide.

HAU tests (Task 1.1) with Indiana shale at similar hydrogen partial pressures predict oil yields of 26.5 gal/ton instead of the 21.2 to 22.9 gal/ton achieved in the eight steady-state periods of these four MBU tests. The 15% to 20% decrease in oil yields from the HAU predicted value appear to be caused by refluxing, the result of lower operating temperatures in the retorting zone and at the top of the preheat zone.

Ionizing the feed carbon dioxide did not improve oil yield by reducing oil refluxing. For the four MBU tests, organic carbon conversion to hydrocarbon gas was 13.9% to 20.1% with non-ionized carbon dioxide and 11.4% to 19.6% with ionized carbon dioxide.

Sulfur conversions were not affected by carbon dioxide ionization. The six steady-state periods for the first three tests had retorting zone temperatures between 1010° and 1050°F and sulfur conversions between 50% and 53%. The fourth test, 88MBU-14, had lower retorting zone temperatures (940° and 950°F) and sulfur conversions (46% and 47%) during the two steady-state periods. Water production was also not affected by ionization of the feed carbon dioxide. Water yields ranged from 5.4 to 9.2 gal/ton in the eight steady-state periods for the four tests.

Oils produced during the four mist enhancement tests were similar to, or lighter than, the oils produced from the same Indiana shale during the MBU hydroretorting tests conducted in Task 1.2. The API gravity was 15 for the oil produced in the hydroretorting tests and was 14 to 18 for oil produced in the first three mist enhancement tests. The final mist enhancement test, with a lower retorting zone temperature of 940°F, produced a light oil with an API gravity of 23. Oil sulfur contents were similar for all hydroretorting and mist enhancement tests and varied between 1.3 and 1.8 weight percent. The nitrogen content of oils from hydroretorting and the first three mist enhancement tests varied from 1.7 to 2.8 weight percent. The oil nitrogen content was lower (1.4 weight percent) from the final mist enhancement test with lower retorting temperature.

Task 4. Fines Utilization Tests

The overall objective of this task is to conduct tests for producing data to facilitate evaluation of increased fines utilization in a moving-bed hydroretorting process. Task 4 is divided into two Subtasks: Subtask 4.1, Fines Gasification Tests; and Subtask 4.2, Cold-Flow-Model Studies.

Subtask 4.1. Fines Gasification Tests

The overall objective of this subtask is to produce data for evaluating the potential of using shale fines for producing synthesis gas or hydrogen for hydroretorting. High carbon conversions have been achieved in coal gasification processes using fluidized beds. The thermal efficiencies for these processes are better than those for ash-slugging, entrained-flow gasifier systems because of the lower operating temperature required for an ash agglomeration gasifier. To gasify shale fines, therefore, a fluidized-bed gasification system is envisioned. Gasification of coals in fluidized beds

operating at conditions that achieve ash agglomeration has been successfully demonstrated. The ash agglomerates discharged from such gasifiers meet the Environmental Protection Agency standards for "nonleachable" material for disposal purposes. Therefore, an attempt will also be made in this task to produce spent shale agglomerates in a fluidized-bed gasifier.

This subtask is further divided into five subtasks:

- 4.1.1. Thermobalance Tests
- 4.1.2. Fluidization and Agglomeration Tests
- 4.1.3. Mini-Bench-Scale Tests
- 4.1.4. Gasification Kinetic Correlation
- 4.1.5. Process-Development-Scale Tests.

Subtask 4.1.1. Thermobalance Tests

Objective: The objective of this subtask is to obtain differential-rate kinetic data using a thermobalance to gasify Eastern shale fines at various temperatures, pressures, and synthesis gas compositions.

Experimental Equipment and Test Procedures: The thermobalance is particularly useful in obtaining fundamental gasification information because it measures gasification rates at constant well-defined environmental conditions. The thermobalance is capable of continuously weighing a shale sample that is undergoing reactions in a gaseous environment of a desired composition at a constant pressure. The temperature can be kept constant or can be varied. The shale sample is contained in a wire mesh basket as shown in Figure 22. Gas flow rates used with this system are sufficiently large relative to gasification rates so that changes in gas composition can be neglected. A schematic diagram of the entire thermobalance reactor system is shown in Figure 23.

In a typical test, the wire mesh basket is initially in the upper, cooled portion of the reactor in which a downward, inert gas flow is maintained. During this time the desired temperature and pressure conditions are established in the lower, heated portion of the reactor in the presence of flowing reactant gases. The test is initiated by lowering the basket into the heated reaction zone, a procedure that takes about 5 to 6 seconds. The sample is kept in the heated portion of the reactor for the specified time while its

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Figure 22. THERMOBALANCE REACTOR

Figure 23. SCHEMATIC DIAGRAM OF THE THERMOBALANCE REACTOR

weight is continuously recorded. The test is terminated by raising the basket back to the upper, cooled portion of the reactor.

During the test, the dry feed gas flow rates are measured by high pressure rotameters and the dry product gas flow rates are measured by a wet-test meter. Feed and product water vapor rates are measured gravimetrically. The solid residues are analyzed for the same species as the feed shale.

Because the gas flow rates in the reactor are sufficient to minimize changes in gas composition, the gasification of shale occurs under a constant, known environment. Under these conditions the weight loss-versus-time characteristics during individual gasification tests can be used to obtain the kinetic rate data.

Discussion: Thermobalance gasification tests were conducted with six Eastern shales. The 52 successful tests were made using Indiana New Albany (22 tests), Alabama Chattanooga (9), Tennessee Chattanooga (9), Kentucky Sunbury (4), Michigan Antrim (4), and Ohio Cleveland (4) oil shales. Test samples were taken from batches of the shales that were sized to -20+40 mesh and then riffled. Feed analyses of the six shales studied are presented in Table 29.

Indiana New Albany was chosen as the base shale and was studied more thoroughly than the other shales. Indiana shale gasification temperatures and pressures were varied from 1600° to 1900°F and 15 to 500 psig, respectively. Samples of Indiana shale were gasified for 30 minutes in 19 tests, 15 minutes in two tests, and 5 minutes in one test. Gasification environments used were steam:hydrogen (50:50), steam:nitrogen (75:25), and synthesis gas. The synthesis gas composition was chosen to be representative of a fossil fuel conversion process product gas and contained steam, hydrogen, carbon oxides, and methane. The synthesis gas analysis is shown in Table 30.

Alabama and Tennessee shale gasification was studied over the same ranges of temperature and pressure that were used with Indiana shale. Gasification environments employed were limited to steam:hydrogen (50:50) and synthesis gas. All tests were made with a 30-minute shale residence time. Kentucky, Michigan, and Ohio shales were not studied in great detail. Temperature was varied from 1700° to 1900°F, and pressure was constant at 15 psig for tests conducted with these shales. Tests were conducted in steam:hydrogen (50:50)

Table 29. FEED ANALYSES OF OIL SHALES USED IN THERMOBALANCE TESTS

Shale Source	Alabama	Indiana	Kentucky	Michigan	Ohio	Tennessee
Moisture, wt %	0.70	0.80	6.86	2.26	3.05	0.64
Ultimate Analysis, wt % dry						
Organic Carbon	14.80	12.82	8.63	10.68	10.59	11.30
Carbon Dioxide	0.09	2.42	0.03	0.97	0.04	0.06
Hydrogen	1.57	1.52	1.05	1.39	1.38	1.32
Sulfur	7.81	4.61	1.24	3.73	2.52	5.47
Nitrogen	0.40	0.45	0.15	0.17	0.19	0.37
Oxygen (by HTW)	3.25	2.48	3.46	3.86	4.37	2.86
Ash	74.86	76.69	83.34	79.41	80.77	80.65

Table 30. SYNTHESIS GAS COMPOSITION

<u>Component</u>	<u>mol %</u>
Hydrogen	24.8
Carbon Monoxide	20.5
Carbon Dioxide	19.3
Methane	5.4
Steam	<u>30.0</u>
Total	100.0

and synthesis gas environments. The same gas composition was used for synthesis gas tests with all six Eastern shales.

A summary of the thermobalance test conditions and overall conversions is presented in Table 31. Overall conversions are given on both a full-weight basis and a moisture-, ash-free (maf) basis. Moisture-, ash-free weight loss represents the combined conversion of all species except moisture that can be lost from the shale. For four shales — Indiana, Alabama, Tennessee, and Michigan — maf weight loss was determined using the gasification weight loss. Kentucky and Ohio shales had high, and variable moisture contents. For these shales, the effects of the variable moisture contents on the conversion calculations were avoided by determining maf weight losses using an ash balance. Ash balances for all 52 thermobalance tests were between 98% and 102%.

Shale Compositions: The six shales studied had varied compositions within the ranges expected for Eastern shales. Moisture contents were 1% for Indiana, Alabama, and Tennessee shales, 2% to 3% for Michigan and Ohio shales, and 6% for Kentucky shale. Organic carbon varied from a lean 8.6% in Kentucky shale to a comparatively rich 14.8% for Alabama shale. All shales had a low organic hydrogen-to-carbon ratio (0.071 to 0.094 on a weight basis) typical of the Eastern shales. Four of the shales, Alabama, Tennessee, Kentucky, and Ohio, had very little mineral carbon present. Mineral carbon conversions for these shales were below the detectable limits of the analytical procedures used. Mineral carbon was present in the other two shales studied and accounted for 2.4% of the Michigan shale total carbon, and 4.9% of the Indiana shale total carbon.

Table 31. SUMMARY OF THERMOBALANCE TEST CONDITIONS AND CONVERSIONS

Test 4.1.1-	Shale	Temperature, °F	Pressure, psig	Gasification Atmosphere	Shale Conversion, %	Shale Conversion maf, %	Organic C Conversion, %	Mineral C Conversion, %	H Conversion, %	S Conversion, %	N Conversion, %	HTW Conversion, %
1	Indiana	1600	500	Steam/H ₂	20.3	81.1	73.4	100.0	75.7	93.0	91.1	NA
2	Indiana	1700	500	Steam/H ₂	21.5	85.8	81.9	100.0	89.6	97.1	100.0	NA
3	Indiana	1600	135	Steam/H ₂	19.6	78.1	68.1	98.8	84.7	87.3	89.2	NA
4	Indiana	1700	135	Steam/H ₂	21.1	84.1	75.1	98.8	92.1	92.6	92.9	NA
5	Indiana	1600	15	Steam/H ₂	19.6	77.9	67.4	97.5	91.5	81.0	92.8	NA
6	Indiana	1700	15	Steam/H ₂	21.1	84.1	75.6	99.4	92.7	92.6	91.2	NA
7	Indiana	1800	15	Steam/H ₂	23.8	95.2	95.1	99.4	90.4	97.2	100.0	NA
8	Indiana	1900	15	Steam/H ₂	24.0	96.3	96.6	100.0	92.9	97.8	100.0	NA
9	Indiana	1800	135	Steam/H ₂	23.5	94.4	95.3	98.8	95.4	98.7	100.0	NA
10	Indiana	1600	15	Syn. Gas	18.5	73.3	63.8	98.8	94.0	67.5	79.7	NA
12	Indiana	1900	135	Steam/H ₂	24.0	96.3	98.0	100.0	95.2	99.9	100.0	NA
14	Indiana	1700	15	Syn. Gas	19.5	77.5	67.7	NA	100.0	81.0	NA	NA
15	Indiana	1790	250	Steam/H ₂	22.4	89.5	79.5	NA	87.6	95.2	96.5	NA
48	Indiana	1710	135	Syn. Gas	20.3	81.0	68.7	95.0	99.3	91.1	65.6	89.3
49	Indiana	1750	135	Syn. Gas	19.8	79.1	65.6	94.7	98.9	93.3	85.6	96.1
51	Indiana	1750	15	Steam/H ₂	21.2	84.6	77.9	96.7	97.9	95.7	85.9	97.4
52	Indiana	1710	135	Steam	24.2	97.7	99.9	100.0	99.5	96.5	91.5	83.4
55	Indiana	1710	135	Steam/H ₂	20.5	81.9	75.6	95.4	93.1	94.4	NA	76.4
56 [†]	Indiana	1710	135	Steam/H ₂	20.4	81.1	72.9	93.4	94.2	85.2	NA	66.0
57 ^{††}	Indiana	1700	135	Steam/H ₂	18.4	73.0	61.4	98.0	96.2	53.8	NA	82.4
58	Indiana	1600	135	Steam	24.2	97.2	96.1	95.3	94.5	94.9	NA	65.5
59 [†]	Indiana	1890	15	Steam/H ₂	23.8	95.4	91.5	93.3	97.0	93.2	NA	90.4

HTW - High-temperature water.

BDL - Below detectable limit.

NA - Not available.

maf = Moisture, ash-free basis.

Tests 4.1.1-11, -13, -19, -27, -50, -53, and -54 were not successful.

[†] 15-minute residence time.^{††} 5-minute residence time.

* By ash balance.

Table 31, Cont. SUMMARY OF THERMOBALANCE TEST CONDITIONS AND CONVERSIONS

Test 4.1.1-	Shale	Temperature, °F	Pressure, psig	Gasification Atmosphere	Shale Conversion, %	Shale Conversion maf, %	Organic C Conversion, %	Mineral C Conversion, %	H Conversion, %	S Conversion, %	N Conversion, %	HTW Conversion, %
16	Alabama	1620	15	Steam/H ₂	20.5	71.3	60.2	BDL	91.2	87.8	84.0	86.5
17	Alabama	1760	15	Steam/H ₂	24.6	86.1	82.8	BDL	95.2	99.6	100.0	87.6
18	Alabama	1900	15	Steam/H ₂	27.4	96.2	97.9	BDL	98.6	99.2	83.5	100.0
20	Alabama	1610	500	Steam/H ₂	18.6	64.4	56.5	BDL	86.4	68.8	73.3	69.7
21	Alabama	1815	500	Steam/H ₂	25.4	89.0	88.6	BDL	95.2	98.8	96.2	90.1
22	Alabama	1750	135	Syn. Gas	22.1	77.2	56.9	BDL	93.0	85.8	78.4	84.6
30	Alabama	1750	135	Steam/H ₂	23.1	80.8	73.4	BDL	95.1	94.4	100.0	90.0
32	Alabama	1750	15	Syn. Gas	20.1	70.0	59.7	BDL	94.9	73.6	100.0	95.5
34	Alabama	1690	15	Steam/H ₂	23.3	81.7	NA	BDL	NA	NA	NA	NA
23	Tennessee	1755	135	Syn Gas	14.8	66.8	56.3	BDL	91.6	86.4	93.1	84.7
24	Tennessee	1605	15	Steam/H ₂	15.1	68.2	57.0	BDL	90.3	84.4	93.1	91.9
25	Tennessee	1755	15	Steam/H ₂	16.6	74.9	67.6	BDL	90.5	91.6	86.4	93.2
26	Tennessee	1895	15	Steam/H ₂	19.9	90.9	94.1	BDL	95.1	98.2	97.8	89.3
28	Tennessee	1605	500	Steam/H ₂	15.7	70.9	63.3	BDL	89.4	81.7	88.5	80.4
29	Tennessee	1750	500	Steam/H ₂	18.6	84.3	79.7	BDL	92.6	98.4	100.0	83.1
31	Tennessee	1750	135	Steam/H ₂	17.6	80.8	75.3	BDL	93.7	97.3	100.0	86.4
33	Tennessee	1750	15	Syn. Gas	15.1	68.2	57.6	BDL	93.5	80.2	100.0	93.3
35	Tennessee	1825	15	Steam/H ₂	20.3	92.4	NA	BDL	NA	NA	NA	NA
36	Kentucky	1690	15	Steam/H ₂	21.8	75.7*	67.1	BDL	92.0	95.9	100.0	86.9
37	Kentucky	1810	15	Steam/H ₂	22.5	78.3*	73.0	BDL	91.3	97.3	100.0	83.6
38	Kentucky	1900	15	Steam/H ₂	22.6	94.0*	94.4	BDL	93.7	94.6	100.0	92.6
39	Kentucky	1750	15	Syn. Gas	19.0	71.0*	54.8	BDL	91.7	93.7	100.0	99.5
40	Michigan	1750	15	Syn. Gas	20.6	87.0	79.0	100.0	98.8	95.9	NA	96.0
41	Michigan	1710	15	Steam/H ₂	19.6	79.9	68.5	100.0	97.0	96.7	NA	87.9
42	Michigan	1800	15	Steam/H ₂	20.4	85.2	79.1	94.1	97.7	96.1	NA	88.2
43	Michigan	1900	15	Steam/H ₂	20.4	87.2	79.6	100.0	97.7	97.8	NA	93.9
44	Ohio	1700	15	Steam/H ₂	19.8	81.6*	73.8	BDL	96.4	98.7	NA	90.7
45	Ohio	1800	15	Steam/H ₂	21.6	93.9*	91.6	BDL	98.8	99.4	NA	96.5
46	Ohio	1900	15	Steam/H ₂	22.6	98.0*	98.9	BDL	99.4	100.0	NA	99.5
47	Ohio	1750	15	Syn. Gas	19.7	81.4*	73.3	BDL	97.6	98.0	NA	90.1

NA = Not available.

All six shales contained significant amounts of sulfur and high-temperature water, and small amounts of nitrogen. Sulfur contents ranged from 1.2 weight percent for Michigan Antrim shale to over 5.4 weight percent for the two Chattanooga shales. High-temperature water contents were in the range of 2.5 weight percent to 4.4 weight percent, with the Cleveland member of the Ohio shale having the highest value. Nitrogen contents were found to be between 0.15 weight percent and 0.45 weight percent for all six shales. The accuracy of nitrogen conversions are not as reliable as the carbon or sulfur conversions due to the low feed-shale nitrogen contents.

The shale analyses, when determined on a dry, ash-free basis, show the major species are organic carbon (51% to 59%), sulfur (9% to 28%), and high temperature water (11% to 27%). With the conversion of high-temperature water to free water during gasification, the major gasification reactions of interest are those of organic carbon and sulfur.

Indiana New Albany Gasification Conversions: Gasification test results show that organic carbon, sulfur, and overall conversions increase with increasing temperature and steam partial pressure. An organic carbon conversion of over 95% can be achieved with a 30-minute residence time in steam at 1600°F or steam:hydrogen at 1800°F. Shale reactivity decreases when the gasification environment is changed from steam to steam:hydrogen to synthesis gas.

Mineral carbon conversion, producing carbon dioxide, was greater than 93% under all gasification conditions and was not a function of the gasification temperature or pressure in the ranges tested. High-temperature water conversion varied from 65% to 97% and was also not a function of the gasification temperature or pressure over the ranges studied. Short residence time tests at 5 and 15-minutes showed mineral carbon and high-temperature water conversions are complete within 5 minutes at the gasification conditions studied and are, therefore, significantly faster than the organic carbon and sulfur gasification reactions. Nitrogen conversions are difficult to determine accurately because of the low feed shale nitrogen content. Nitrogen conversion was between 80% and 100%, and was not related to temperature or pressure over the operating ranges studied.

The effects of gasification temperature and pressure on the dry, ash-free weight loss, organic carbon conversion, and sulfur conversion of Indiana shale

are shown in Figures 24 to 26. Gasification temperature and pressure have similar effects on dry, ash-free weight loss and organic carbon conversion. The close similarity is expected because over half the feed dry, ash-free weight of Indiana shale is organic carbon.

Organic carbon conversion is sensitive to gasification temperature. In a steam:hydrogen environment, the organic carbon conversion is less than 70% at 1600°F but shows a significant increase, to above 90%, between 1700° and 1800°F. A change in steam:hydrogen pressure from 15 to 135 psig has no effect on organic carbon conversion. However, increasing the pressure from 135 to 500 psig for the temperature range of 1600° to 1700°F increases organic carbon conversion by about 16%. Tests at 1700°F and 135 psig, with different residence times, showed that a significant fraction of the organic carbon is lost rapidly at gasification conditions. Organic carbon conversion was 61% after 5 minutes and increased to only 76% after 30 minutes.

The conversion of Indiana shale sulfur, like organic carbon, increases with temperature and pressure. The large organic carbon conversion increase between 1700° and 1800°F was not seen in the sulfur conversion. Sulfur conversion, unlike organic carbon conversion, increases with an increase of steam:hydrogen pressure from 15 to 135 psig. Increasing the steam:hydrogen pressure from 135 to 500 psig also increases the sulfur conversion. At 1600°F in steam:hydrogen, the sulfur conversion was 81%, 87%, and 93% at 15, 135, and 500 psig, respectively. Tests at 1700°F and 135 psig with different residence times showed that a significant fraction of the sulfur is lost rapidly at gasification conditions. Sulfur conversion was 54% after 5 minutes, 85% after 15 minutes, and 94% after 30 minutes.

Indiana shale gasification tests were conducted in synthesis gas and steam environments to study the effects of gas pressure on conversions. Shale samples were gasified in synthesis gas at pressures of 15 and 135 psig and temperatures of 1600° to 1750°F. Conversions of organic carbon and sulfur were lower in synthesis gas than in steam:hydrogen under similar operating conditions and were affected in the same ways by increases in pressure. Organic carbon conversion in synthesis gas was not affected by a change in pressure from 15 to 135 psig. In a synthesis gas environment, organic carbon conversions of 64% to 69% were 3% to 9% lower than in steam:hydrogen at the

Figure 24. EFFECT OF GASIFICATION TEMPERATURE ON DRY, ASH-FREE WEIGHT LOSS OF INDIANA SHALE

Figure 25. EFFECT OF GASIFICATION TEMPERATURE ON ORGANIC CARBON CONVERSION OF INDIANA SHALE

Figure 26. EFFECT OF GASIFICATION TEMPERATURE ON
 SULFUR CONVERSION OF INDIANA SHALE

same conditions. Sulfur conversion in synthesis gas was significantly increased by a pressure increase from 15 to 135 psig. A comparison of sulfur conversions in synthesis gas and steam:hydrogen shows sulfur conversions were 12% lower at 15 psig and 3% lower at 135 psig in synthesis gas than in steam:hydrogen.

Organic carbon and sulfur conversions were compared for similar tests in steam:hydrogen and steam at 1600°F and 1700°F and 135 psig. Gasification tests in a steam environment (with a nitrogen carrier gas present) produced significantly higher organic carbon and sulfur conversions than in steam:hydrogen under similar conditions. Organic carbon conversion at 1600°F and 135 psig was 68% in steam:hydrogen and 96% in steam. At 1700°F and 135 psig, organic carbon conversion was 75% in steam:hydrogen and 100% in steam. Sulfur conversion at 1600°F and 135 psig was 87% in steam:hydrogen and 95% in steam. At 1700°F and 135 psig, sulfur conversion was 93% in steam:hydrogen and 96% in steam.

Thermobalance tests have provided insights into the gasification characteristics of Indiana New Albany shale. Weight loss traces and conversions suggest that conversion reactions range from rapid to slow. Reactions complete in under 5 minutes under the conditions studied include the conversions of mineral carbon, high-temperature water, nitrogen, and a fraction of the organic carbon and sulfur. Slower reactions, complete in more than 5 minutes under the conditions studied, include the gasification of much of the organic carbon and sulfur. Tests in different gas environments indicate organic carbon conversion is increased by higher steam pressures, but retarded in steam/gas mixtures in which hydrogen and carbon monoxide partial pressures are increased. Sulfur conversion is increased by higher steam pressure, but retarded by increases in hydrogen partial pressure in steam/gas mixtures. The relationships of temperature and gas partial pressures to gasification conversions have been described in a gasification model. A detailed description of the gasification model is presented in Subtask 4.1.4, Gasification Kinetic Correlations.

Gasification Conversions of the Other Five Eastern Shales:

Gasification tests were conducted with 5 other Eastern shales to determine the gasification characteristics of a variety of shales. The gasification conditions used for tests with Alabama, Tennessee, Kentucky, Michigan, and Ohio

shales were within the ranges used for the study of Indiana New Albany shale. Alabama and Tennessee shales were gasified in steam:hydrogen and synthesis gas at temperatures between 1600° and 1900°F and pressures between 15 and 500 psig. Kentucky, Michigan, and Ohio shales were gasified in steam:hydrogen and synthesis gas at temperatures between 1700° and 1900°F and a pressure of 15 psig. Test conditions were chosen to enable comparisons of the 6 shales. Summaries of the gasification conditions and conversions from thermobalance tests with all shales were previously presented in Table 31. Comparisons of the moisture-, ash-free weight losses, organic carbon conversions, and sulfur conversions of the six shales when gasified in steam:hydrogen at 15 psig, are presented in Figures 27 to 29.

The comparisons of the gasification behavior of the six shales show the effects of temperature and gas partial pressures on conversions are similar for the shales. Organic carbon conversions of Alabama and Tennessee shales were similar at 15 and 135 psig. Tennessee shale, like Indiana shale, shows an increase in organic carbon conversion when the pressure is increased from 135 to 500 psig. Alabama shale organic carbon conversions that are similar at 15, 135 and 500 psig. Gasification of Alabama and Tennessee shales in synthesis gas shows the same decrease in organic carbon conversion compared to gasification in steam:hydrogen that was seen for Indiana shale. Also, like Indiana shale, Alabama and Tennessee shales show no effect of changing the synthesis gas pressure from 15 to 135 psig on the organic carbon conversion.

Although the organic carbon conversion relationships to temperature and pressure were similar for the six shales, there were clear differences in organic carbon reactivity. Under similar gasification conditions, the highest organic carbon conversions were exhibited by the Indiana and Ohio shales. Alabama and Tennessee, and the two Chattanooga shales, showed intermediate organic carbon reactivities. And the Kentucky and Michigan shales showed the lowest organic carbon reactivities. The difference in organic carbon conversion between the least and most reactive shales was found to be as much as 20% after 30 minutes of shale gasification at 1800°F and 15 psig steam:hydrogen.

Sulfur conversions showed the same relationships to gasification temperature and pressure for all six shales. There were, however, no clear differences between the sulfur conversions of the various shales under similar

Figure 27. DRY, ASH-FREE CONVERSIONS FROM GASIFICATION OF EASTERN SHALES IN STEAM:HYDROGEN AT 15 PSIG

Figure 28. ORGANIC CARBON CONVERSIONS FROM GASIFICATION OF EASTERN SHALES IN STEAM:HYDROGEN AT 15 PSIG

Figure 29. SULFUR CONVERSIONS FROM GASIFICATION OF EASTERN SHALES
AT STEAM:HYDROGEN AT 15 PSIG

gasification conditions. Sulfur conversions for the six shales at similar conditions were found to differ by less than 7%, and there was no evidence that any shale possessed more or less reactive sulfur than any other shale. Conversions of high-temperature water and nitrogen, where measurable, were similar under all gasification conditions for all shales and showed no clear relationships to temperature or pressure.

Subtask 4.1.2. Fluidization and Agglomeration Tests

Objectives: The objectives of this subtask are to determine the agglomeration conditions and fluidization characteristics of the shale fines.

Experimental Equipment and Test Procedures — Fluidization Tests:

Incipient and complete fluidization experiments were conducted in a 2-inch-diameter Plexiglas® tube with raw and spent shales. A sintered stainless-steel porous plate is used as the gas distributor. Magnehelic gauges are used to indicate differential pressures across the shale bed. A rotameter calibrated with a positive displacement gas meter is used to meter the nitrogen fluidization gas.

A typical test consists of filling the fluidization column with a pre-sized, weighed amount of oil shale, fluidizing the bed for about 5 minutes, and then turning off the feed gas quickly to obtain a well-mixed bed. The static height of the bed is noted and recorded at this time. The gas feed to the column is then resumed, starting at low flow rates. Pressure drops and various observations about the bed condition are recorded. After 5 to 10 times the minimum fluidizing velocity is achieved, the gas flow is decreased in small steps. The bed-pressure drop, bed height, and conditions of the bed are recorded as the velocities are decreased until the gas flow is stopped.

Experimental Equipment and Test Procedures — Agglomeration Tests: A 2-inch fluidized-bed column capable of operating at temperatures and pressures of up to 2100°F and 300 psia, respectively, was utilized to determine preliminary operating conditions necessary for agglomerating Eastern oil shales.

A schematic diagram of the 2-inch-ID fluidized-bed reactor and the ancillary equipment is shown in Figure 30. The major pieces of equipment shown are the steam generator, reactor, cyclone, heat exchanger, and water collection pot. The fluidized-bed reactor is fabricated from a 2-inch, Schedule 40, 446

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Figure 30. SCHEMATIC DIAGRAM OF THE ASH-AGGLOMERATING REACTOR SYSTEM

stainless steel pipe. The bottom section is fitted with a gas distributor and a central jet to closely simulate the fluid dynamics and mixing characteristics of the pilot plant bed. Steam and feed gases are metered by calibrated rotameters and fed to the reactor. Product gas, vapor and entrained solids exit the top of the reactor and enter a cyclone where any fines elutriated from the bed are separated and collected. The hot product fluid is then cooled, condensing primarily water, and the cooled product gas is then metered by a wet test meter. The unit is adequately instrumented for temperature and pressure measurements and operates in a batch mode.

The shale is subjected to various operating conditions of temperature and velocities for a predetermined length of time before the shale is examined for ash agglomerate formation. Each sample is examined for the presence of agglomerates and/or sinter formation.

During the first year of the test program, the Indiana New Albany shale was tested in the 2-inch fluidized-bed reactor after fluidization tests were completed in the Plexiglas® column.

Discussion: Thirteen fluidization tests were conducted with six Eastern shales in this program. The first six tests were made with Indiana New Albany shale to compare the fluidization characteristics of raw and spent shale and to determine the effect of shale particle size on fluidization characteristics. Results of these tests are presented in Table 32. Raw and spent shale with 1/8, 1/16, and 1/32 inch particle sizes had complete fluidization velocities between 2 and 3 times the minimum fluidization velocities. Little difference was observed between the fluidization characteristics of raw and spent Indiana shales with the same particle size. Based on this result, only the raw shale fluidization characteristics were determined for the other five shales.

The minimum and complete fluidization velocities for samples of the six raw shales were determined. All samples were sized to -20+40 mesh to match the shale particle size used for MBU gasification tests in Subtask 4.1.3. The results of the fluidization tests, along with the shale bulk densities and organic carbon contents, are presented in Table 33. The bulk densities and fluidization velocities of the six shales were similar. Increasing bulk density, in general, reflects a decrease in organic carbon content. An expected correlation was found between bulk density and fluidization

Table 32. MINIMUM AND COMPLETE FLUIDIZATION VELOCITIES
FOR RAW AND SPENT SHALE SAMPLES

Indiana New Albany Shale	Size, Inch	Fluidization Velocity, ft/s	
		Minimum	Complete
Raw	-1/8	2.4	4.7
Raw	-1/16	1.1	4.1
Raw	-1/32	0.5	1.7
Spent	-1/8	2.1	3.9
Spent	-1/16	1.5	3.5
Spent	-1/32	0.9	1.7

Table 33. FLUIDIZATION CHARACTERISTICS OF -20+40 MESH RAW SHALES

Location	Bulk Density, g/cm ³	Organic C Content, wt % dry	u_{mf} , ft/s	u_{cf} , ft/s	u_{cf}/u_{mf}
Indiana	0.99	12.24	0.80	1.72	2.15
Alabama	0.99	14.67	0.82	1.82	2.22
Kentucky	1.02	10.19	0.87	1.78	2.05
Tennessee	1.05	11.58	0.92	1.82	1.98
Michigan	1.08	11.92	1.07	1.94	1.81
Ohio	1.14	11.02	0.94	1.95	2.07

velocities. For particles of similar size, minimum and complete fluidization velocities increase with increasing bulk density. The ratio of complete to minimum fluidization velocity is between 1.8 and 2.2 for all six shales and is not a function of the shale bulk density.

The final fluidization test was conducted with the same -20+40 mesh Indiana shale used in the Task 4.1.3 fluidized-bed gasification tests. The velocity in the Plexiglas column was carefully chosen to simulate the velocity in a fluidized-bed gasification test. The objective of the fluidization test was to determine if solids-slugging might be responsible for reduced average shale gasification conversions due to reduced average shale residence times. Slugging was observed in the fluidization test indicating the need to use lower fluidization velocities in the fluidized bed gasification tests.

However, subsequent tests with lower superficial velocity in the mini-bench unit did not significantly improve shale conversion.

Ash agglomeration tests were conducted with the six raw shales. The 15 tests included 5 with Indiana shale and 2 with each of the other 5 shales. Feed shales were all -6+40 mesh and were tested for 30 minutes at temperatures of 1900° to 2000°F with oxygen concentrations of 8% to 12%, and gas superficial velocities of 1.2 to 2.0 ft/s. Test conditions are summarized in Table 34. The majority of the shale in all 15 tests was incorporated into large clinkers. Some agglomerates were formed in tests with all six shales. Increases in temperature (up to 2000°F) and superficial velocity did not affect the amount of clinkering in the reactor.

Ash fusion temperatures were determined for Indiana, Alabama, and Tennessee shales. Results are presented in Table 35 and show that ash fusion temperatures are all above 2000°F. Indiana shale has the lowest ash fusion temperatures of the six shales studied.

Subtask 4.1.3. Mini-Bench-Scale Tests

Objective: The objective of this subtask is to obtain integral-bed kinetic data using a modified MBU at temperatures and residence times in the ranges of 1600° to 1900°F and 30 to 60 minutes, respectively.

Experimental Equipment and Test Procedures: A flow diagram of the modified MBU is shown in Figure 31. Shale is fed by a screw feeder from a pressurized feed hopper that is filled with a sufficient amount of shale for the entire run (about 7 pounds). Raw shale is screw fed into the bottom of the reactor. The residue shale overflows from the fluidized bed into a standpipe connected to the residue receiver. A high-temperature furnace is used to achieve gasification temperatures in the reactor.

The gasification reactor is 48 inches long with a 2-inch, Schedule 80, 316 stainless-steel reaction zone and a 4-inch, Schedule 80 solids-disengaging zone. The 18-inch-long reaction zone is electrically heated by a three-zone furnace. The temperature of each zone in the furnace is individually controlled. Five thermocouples are used to measure the inside temperatures of the reactor — three in the fluidized-bed and two in the freeboard. These temperatures are recorded along with the temperatures of other process streams.

Table 34. ASH AGGLOMERATION TEST CONDITIONS

Test	Oil Shale	Feed Consist, mesh	Temperature, °F	Pressure, psig	Residence Time, min	Superficial Gas Velocity, ft/s	Oxygen Concentration mol %
86AA-1	Indiana	-6+40	1900	1	30	1.2	8
86AA-2	Indiana	-6+40	1900	1	30	1.2	10
86AA-3	Indiana	-6+40	2000	1	30	1.2	10
86AA-4	Indiana	-6+40	2000	1	30	2.0	10
86AA-5	Indiana	-6+40	1900	1	30	2.0	12
87AA-1	Alabama	-6+40	1900	1	30	1.2	10
87AA-2	Alabama	-6+40	2000	1	30	2.0	10
87AA-3	Tennessee	-6+40	1900	1	30	1.2	10
87AA-4	Tennessee	-6+40	2000	1	30	2.0	10
87AA-5	Kentucky	-6+40	1900	1	30	1.2	10
87AA-6	Kentucky	-6+40	2000	1	30	2.0	10
87AA-7	Michigan	-6+40	1900	1	30	1.2	10
87AA-8	Michigan	-6+40	2000	1	30	2.0	10
87AA-9	Ohio	-6+40	1900	1	30	1.2	10
87AA-10	Ohio	-6+40	2000	1	30	2.0	10

Table 35. ASH FUSION TEMPERATURES

Shale Atmosphere	Indiana New Albany		Alabama		Tennessee	
	<u>Reducing</u>	<u>Oxidizing</u>	<u>Reducing</u>	<u>Oxidizing</u>	<u>Reducing</u>	<u>Oxidizing</u>
Initial Deformation, °F	2090	2265	2135	2360	2140	2310
Softening, °F	2165	2410	2295	2450	2265	2415
Hemispherical, °F	2340	2505	2445	2540	2405	2515
Fluid, °F	2575	2630	2625	2625	2550	2625

The feed gas enters the bottom of the reactor after passing through a preheater, and the product gas leaves the top of the reactor through a sintered metal filter. A small flow of nitrogen is continuously passed into the feed hopper during the test to make up for the volume of shale lost from the feed hopper as shale is fed into the reactor, and to keep gas-containing steam and liquid product from entering the feed hopper.

The exit gas is cooled to ambient temperature in a single-stage condenser. The condensed liquids are then collected in a knockout pot, which is drained at set intervals to obtain product rates. After the exit gas is depressurized, its volume is measured by a dry test meter. Samples of the exit gas are taken by flowing a portion of the gas into a glass sample bomb.

The screw feeder is calibrated and the shale is fed at the desired rate by adjusting the feed-screw speed. The weight of the shale fed is determined by weighing the shale initially charged to the feed hopper and the shale present at the end of the run. The residue shale is also weighed after the run. Feed and residue shale rates are calculated by dividing these weights by the recorded shale feeding time.

All balances and conversions are determined over the steady-state portion of the test. Steady state is defined as a condition wherein the temperature profile in the shale bed is uniform; feed gas, purge gas, and exit gas flow rates are constant; reactor pressure is stable; and the shale feed rate is essentially constant.

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Figure 31. SCHEMATIC DIAGRAM OF THE MODIFIED MINI-BENCH-SCALE GASIFICATION UNIT

Discussion: The MBU fluidized-bed reactor was used for 22 tests, including 16 successful tests, in this program. Ten gasification tests were conducted with Indiana, Tennessee, and Alabama shales in synthesis gas, and one test was conducted with each of the six Eastern shales in a steam/nitrogen atmosphere. All synthesis gas tests were made with gas having the same composition as the gas used in the thermobalance tests (Subtask 4.1.1.). Indiana New Albany shale was used for eight of the ten synthesis gas tests to study the effects of temperature (1600° to 1800°F), pressure (10 to 135 psig), and shale residence time (20 to 60 min) on fluidized-bed gasification conversions. These conditions were selected based on thermobalance test results. Tennessee and Alabama shales were gasified in synthesis gas to enable comparison of the gasification behavior of several shales in synthesis gas.

The steam gasification tests with all six Eastern shales were conducted at approximately 1750°F and 60 psig with a 50-minute shale residence time. Tests were conducted in steam to determine the severity of hydrogen and carbon monoxide inhibitions to the gasification reactions and to compare the gasification behavior of the six shales. A summary of the operating conditions and results of the 16 MBU gasification tests is presented in Table 36. Feed and residue shale analyses from the last ten MBU tests are presented in Table 37. Product-gas analyses from the last ten tests are presented in Table 38.

Shale size consists used for tests at pressures above 10 psig were reduced from -6+40 mesh to -20+40 mesh due to limits on the flow capacity of the equipment used. In all tests, the axial bed temperatures (measured by 3 thermocouples) were uniform and steady, indicating fluidization was achieved and maintained. Purge nitrogen in the feed screw housing helped keep the shale at ambient temperature until introduced to the fluidized bed.

The results of syngas gasification tests with Indiana New Albany shale showed that overall conversions, as well as the conversion of organic carbon and sulfur, increase with increasing temperature and shale residence time. Organic carbon conversion was found to decrease with increasing pressure. Thermobalance tests with Indiana shale under similar operating conditions in synthesis gas showed the same effects of temperature, residence time, and pressure on organic carbon and sulfur conversions. Indiana shale organic carbon conversions were between 43% and 60% in the MBU fluidized bed, but were some 10% to 15% higher in thermobalance tests at similar conditions.

Table 36, Part 1. SUMMARY OF SHALE FLUIDIZED BED TESTS

Test Identification	4.1.3-2	4.1.3-3	4.1.3-4	4.1.3-6	4.1.3-7	4.1.3-8
Shale Identification			Indiana	New Albany		
Shale Consist, mesh	-6+40	-6+40	-20+40	-20+40	-20+40	-6+40
Temperature, °F	1600	1700	1700	1700	1700	1800
Pressure, psig	10	10	135	60	60	10
Feed Gas	Syngas	Syngas	Syngas	Syngas	Syngas	Syngas
Gas Superficial Velocity, ft/s	3.57	3.75	0.84	0.92	0.92	4.24
Residence Time, min	49	23	24	23	23	22
Shale Feed Rate, lb/h	0.843	1.763	1.839	1.895	1.846	1.856
Conversions, ** dry basis, %						
Overall	13.6	16.0	14.0	15.0	15.0	16.9
Total Carbon	57.0	59.3	44.7	44.3	49.0	61.9
Organic Carbon	54.6	57.6	42.7	44.2	47.8	60.1
Hydrogen	89.9	90.5	88.9	89.1	92.7	95.1
Sulfur	48.0	53.2	49.3	49.4	48.3	62.2
Nitrogen	82.3	92.2	83.7	79.7	75.4	79.7
High-Temperature Water	79.4	82.8	98.1	74.0	84.7	87.3
Carbon Distribution, %						
Residue Solids	43.0	40.7	55.3	55.7	51.0	38.1
Oil Phase Compounds	3.2	1.3	2.8	1.2	0.9	3.9
Water Phase Compounds	--	--	1.3	0.8	0.8	0.4
CO						
CO ₂						
CH ₄	53.8	58.0	40.6	42.3	47.3	57.6
C ₂ H ₄						
C ₆						
Total	100.0	100.0	100.0	100.0	100.0	100.0
Sulfur Distribution, %						
Residue Solids	52.0	46.8	50.7	50.6	51.7	37.8
Liquids (by difference)	48.0	53.2	49.3	49.4	48.3	13.0
H ₂ S†	††	††	††	††	††	49.2
Total	100.0	100.0	100.0	100.0	100.0	100.0
Solids HHV Change, %	-53.2	-54.2	-42.7	-42.6	-45.6	-60.5
Solids Energy Reduction, %	60.8	61.9	51.3	51.8	59.2	67.5

*Full weight basis.

**Based on ash balance.

†Trace amounts of COS.

††Included in liquids.

Table 36, Part 2. SUMMARY OF SHALE FLUIDIZED BED TESTS

Test Identification	4.1.3-9	4.1.3-10	4.1.3-11	4.1.3-13	4.1.3-16
Shale Identification	Indiana New Albany	Indiana New Albany	Tennessee Chattanooga	Alabama Chattanooga	Indiana New Albany
Shale Consist, mesh*	-20+40	-20+40	-20+40	-20+40	-20+40
Temperature, °F	1724	1686	1780	1751	1748
Pressure, psig	75	77	74	67	70
Feed Gas	Syngas	Syngas	Syngas	Syngas	Steam
Gas Superficial Velocity, ft/s	0.86	0.70	0.89	0.93	1.09
Residence Time, ** min	55	58	88	52	43
Shale Feed Rate, * lb/n	0.742	0.700	0.481	0.797	0.914
Conversions, ** dry basis, %					
Overall	16.4	16.0	15.0	17.0	17.8
Total Carbon	54.5	48.9	55.3	46.9	78.6
Organic Carbon	53.6	NA	55.2	46.0	78.4
Hydrogen	91.0	85.6	90.6	92.9	95.6
Sulfur	84.4	75.2	88.8	56.2	86.1
Nitrogen	86.1	86.0	79.8	100.0	100.0
High-Temperature Water	90.2	83.8	89.2	90.6	93.7
Carbon Distribution, %					
Residue Solids	45.5	51.1	44.7	53.1	21.4
Oil Phase Compounds	0.1	0.5	0.2	0.2	0.5
Water Phase Compounds	0.5	0.4	0	0.1	0.8
CO					19.1
CO ₂	49.9	43.8	51.9	44.0	43.5
CH ₄					12.8
C ₂ H ₄	1.6	1.9	1.3	1.6	1.1
C ₆ +	2.4	2.3	1.9	1.0	0.8
Total	100.0	100.0	100.0	100.0	100.0
Sulfur Distribution, %					
Residue Solids	15.6	24.8	11.2	43.8	13.9
Liquids (by difference)	0.4	0.4	1.6	3.9	3.4
H ₂ S†	84.0	74.8	87.2	52.3	82.7
Total	100.0	100.0	100.0	100.0	100.0
Solids HHV Change, %	NA	NA	NA	NA	NA
Solids Energy Reduction, %	NA	NA	NA	NA	NA

* Full weight basis.

** Based on ash balance.

† Trace amounts of COS.

Table 36, Part 3. SUMMARY OF SHALE FLUIDIZED BED TESTS

Test Identification	4.1.3-18	4.1.3-19	4.1.3-20	4.1.3-21	4.1.3-22
Shale Identification	Alabama	Tennessee	Ohio	Michigan	Kentucky
Shale Consist, mesh*	Chattanooga -20+40	Chattanooga -20+40	Cleveland -20+40	Antrim -20+40	Sunbury -20+40
Temperature, °F	1733	1742	1751	1753	1753
Pressure, psig	75	70	73	76	77
Feed Gas	Steam	Steam	Steam	Steam	Steam
Gas Superficial Velocity, ft/s	1.07	1.10	1.10	1.05	1.00
Residence Time, ** min	46	49	57	48	64
Shale Feed Rate, * lb/h	0.934	0.923	0.758	0.878	0.662
Conversions, ** dry basis, %					
Overall	22.3	19.1	15.5	17.7	11.2
Total Carbon	81.0	92.4	95.2	95.0	98.0
Organic Carbon	81.2	92.5	95.3	95.0	98.0
Hydrogen	92.9	97.0	96.4	97.3	96.3
Sulfur	83.5	95.1	91.8	93.8	96.4
Nitrogen	12.1	78.8	93.1	81.7	72.6
High-Temperature Water	90.8	86.2	88.0	90.2	86.2
Carbon Distribution, %					
Residue Solids	19.0	7.6	4.8	5.0	2.0
Oil Phase Compounds	0.3	0.6	0.2	0.3	0.3
Water Phase Compounds	0.2	0.2	1.0	0.6	1.3
CO	49.5	54.2	56.4	53.9	57.9
CO ₂	19.5	25.4	25.8	26.0	27.0
CH ₄	10.7	10.6	10.1	12.2	9.5
C ₂ H ₄	0.2	0	0.9	0.5	1.0
C ₆ +	0.6	1.4	0.9	1.5	1.0
Total	100.0	100.0	100.0	100.0	100.0
Sulfur Distribution, %					
Residue Solids	16.5	4.9	8.2	6.2	3.6
Liquids (by difference)	0.1	0.1	4.9	4.1	4.9
H ₂ S†	83.4	95.0	86.9	89.7	91.5
Total	100.0	100.0	100.0	100.0	100.0
Solids HHV Change, %	NA	NA	NA	NA	NA
Solids Energy Reduction, %	NA	NA	NA	NA	NA

*Full weight basis.

**Based on ash balance.

†Trace amounts of COS.

Table 37. FLUIDIZED BED TEST SOLIDS ANALYSES

Test Shale Location	4.1.3-9 Indiana	4.1.3-10 Indiana	4.1.3-11 Tennessee	4.1.3-13 Alabama	4.1.3-16 Indiana
<u>Feed Solids</u>					
Moisture, wt %	2.12	2.12	1.08	0.99	1.94
Ultimate Analysis, wt % dry					
Ash	77.61	77.61	79.94	74.24	79.96
Carbon	12.11	12.11	11.63	14.71	12.52
Organic Carbon	11.85	11.85	11.58	14.67	12.24
Carbon Dioxide	0.95	0.95	0.18	0.17	1.02
Hydrogen	1.58	1.58	1.36	1.65	1.49
Sulfur	3.96	3.96	5.16	7.59	3.89
Nitrogen	0.36	0.36	0.42	0.23	0.29
Oxygen (HTW*)	4.09	4.09	2.98	3.87	3.94
<u>Residue Solids</u>					
Moisture, wt %	0	0	0	0	0
Ultimate Analysis, wt % dry					
Ash	92.80	92.39	94.04	89.41	97.32
Carbon	6.59	7.37	6.12	9.40	3.26
Organic Carbon	6.57	NA	6.11	9.39	3.22
Carbon Dioxide	0.05	NA	0.04	0.04	0.12
Hydrogen	0.17	0.27	0.15	0.14	0.08
Sulfur	0.74	1.17	0.68	4.00	0.66
Nitrogen	0.06	0.06	0.10	0	0
Oxygen (HTW*)	0.48	0.79	0.38	0.44	0.30

* High-Temperature water.

Table 37, Cont. FLUIDIZED BED TEST SOLIDS ANALYSES

Test Shale Location	4.1.3-18 Alabama	4.1.3-19 Tennessee	4.1.3-20 Ohio	4.1.3-21 Michigan	4.1.3-22 Kentucky
<u>Feed Solids</u>					
Moisture	0.99	1.08	3.13	2.36	5.90
Ultimate Analysis, wt % dry					
Ash	74.24	79.94	84.16	81.64	88.28
Carbon	14.71	11.63	11.04	12.12	10.21
Organic Carbon	14.67	11.58	11.07	11.92	10.19
Carbon Dioxide	0.17	0.18	0.07	0.75	0.10
Hydrogen	1.65	1.36	1.41	1.54	1.19
Sulfur	7.59	5.16	2.59	3.31	1.24
Nitrogen	0.23	0.42	0.49	0.54	0.55
Oxygen (HTW*)	3.87	2.98	4.43	3.69	3.80
<u>Residue Solids</u>					
Moisture, wt %	0	0	0	0	0
Ultimate Analysis, wt % dry					
Ash	95.50	98.85	99.46	99.26	99.46
Carbon	3.59	1.09	0.62	0.73	0.23
Organic Carbon	3.55	1.07	0.61	0.72	0.23
Carbon Dioxide	0.14	0.06	0.02	0.03	0
Hydrogen	0.15	0.05	0.06	0.05	0.05
Sulfur	1.61	0.31	0.25	0.25	0.05
Nitrogen	0.26	0.11	0.04	0.12	0.17
Oxygen (HTW*)	0.46	0.51	0.63	0.44	0.59

* High-Temperature water.

Table 38. FLUIDIZED BED TEST GAS ANALYSES

Test	4.1.3-9	4.1.3-10	4.1.3-11	4.1.3-13	4.1.3-16
Feed Gas, vol %					
CO	13.1	18.1	17.5	22.1	0
CO ₂	19.9	18.6	18.8	18.7	0
H ₂	29.8	24.3	26.1	24.1	0
H ₂ O	28.8	28.3	27.7	28.6	66.2
CH ₄	3.5	4.8	5.2	5.7	0
N ₂	4.2	4.9	3.7	0	33.8
He	<u>0.7</u>	<u>1.0</u>	<u>1.0</u>	<u>0.8</u>	<u>0</u>
Total	100.0	100.0	100.0	100.0	100.0
Product Gas, vol %					
CO	24.2	23.6	23.3	23.6	0.6
CO ₂	16.8	15.4	16.7	16.5	1.3
H ₂	22.6	24.5	24.8	23.7	3.5
H ₂ O	29.0	28.9	27.4	28.5	60.6
CH ₄	5.1	4.8	4.8	5.1	0.38
C ₂ H ₄	0.03	0.04	0.01	0.04	0.02
C ₆ +	0.01	0.01	0.01	0.01	0.01
H ₂ S	0.24	0.28	0.29	0.45	0.32
N ₂	1.2	1.2	1.7	1.1	33.3
He	<u>0.8</u>	<u>1.3</u>	<u>1.0</u>	<u>0.9</u>	<u>0</u>
Total	100.0	100.0	100.0	100.0	100.0

Table 38, Cont. FLUIDIZED BED TEST GAS ANALYSES

Test	4.1.3-18	4.1.3-19	4.1.3-20	4.1.3-21	4.1.3-22
Feed Gas, vol %					
CO	0	0	0	0	0
CO ₂	0	0	0	0	0
H ₂	0	0	0	0	0
H ₂ O	67.4	67.1	67.5	67.4	69.9
CH ₄	0	0	0	0	0
N ₂	32.6	32.9	32.5	32.6	30.1
He	0	0	0	0	0
Total	100.0	100.0	100.0	100.0	100.0
Product Gas, vol %					
CO	0.8	0.9	0.7	0.8	0.6
CO ₂	2.1	2.0	1.4	1.7	1.3
H ₂	6.1	6.0	4.3	4.9	3.5
H ₂ O	59.3	58.8	61.9	60.6	62.8
CH ₄	0.46	0.39	0.26	0.38	0.20
C ₂ H ₄	0.01	0	0.01	0.01	0.01
C ₆ +	0.01	0.01	0.01	0.01	0.01
H ₂ S	0.17	0.43	0.19	0.33	0.06
N ₂	31.0	31.5	31.2	31.3	31.6
He	0	0	0	0	0
Total	100.0	100.0	100.0	100.0	100.0

Two MBU tests, 4.1.3-9 and 4.1.3-10, were conducted with Indiana shale to determine if low MBU organic carbon conversions were due to slugging in the bed. Slugging in the bed could reduce the average residence time by causing a fraction of the feed shale to be discharged from the bed almost immediately after injection. Both tests were conducted at temperature and pressure similar to those in Test 4.1.3-7, 1700°F and 75 psia. The first test, 4.1.3-9, studied the effect of solids residence time on conversions by increasing the residence time from 23 to 55 minutes. The gas superficial velocity was reduced from 0.92 to 0.86 ft/s, and temperature was increased from 1700° to 1724°F. Results from this test show total carbon and dry shale conversions of 57% and 16.4%, respectively, compared to 49% and 15.0%, respectively, for Test 4.1.3-7.

Test 4.1.3-10 was conducted at a lower superficial gas velocity of 0.70 ft/s, just above the minimum fluidization velocity. The residence time was similar at 58 minutes, and the average bed temperature was 1686°F. Test 4.1.3-10, with a lower feed gas velocity and a 40°F lower bed temperature, had lower overall conversion (16.0% vs. 16.4%), lower carbon conversion (49% vs. 54%), lower sulfur conversion (75% vs. 84%) and lower high-temperature water conversion (84% vs. 90%). Thermobalance data show that a 40°F lower reactor temperature can result in about a 3% drop in carbon conversion. Therefore, slugging does not appear to be a significant factor in the MBU over the feed gas velocity range used. Lower MBU gasification conversions compared to thermobalance conversions appear to be due to the synthesis gas composition used.

Tests 4.1.3-11 and 4.1.3-13 were conducted with Tennessee and Alabama shales in syngas. Tennessee shale gasified at 1780°F for 88 minutes had a 55% organic carbon conversion and an 89% sulfur conversion. Alabama shale gasified at 1750°F for 52 minutes had a 47% organic carbon conversion and 56% sulfur conversion. Sulfur conversion differences may be due to variations in feed shale sulfur type.

Syngas gasification with three shales produced small amounts of oil (0.1% to 0.5% of the feed shale carbon) and only small amounts of hydrocarbons with greater molecular weights than methane (3% to 4% of the feed shale carbon). The remaining carbon lost from the shale formed carbon oxides and methane. The fraction of the feed shale carbon forming carbon monoxide, carbon dioxide,

and methane could not be accurately determined since all three compounds were present in both the feed and residue gas, the water-gas shift reaction altered the amounts of carbon oxides present, and the great majority (90% to 95%) of the carbon in the reactor was introduced with the feed gas.

Test 4.1.3-16 with Indiana shale in steam/nitrogen was conducted under conditions similar to those in Test 4.1.3-9 with syngas. Although the residence time was 12 minutes less in steam/nitrogen (43 compared to 55 minutes), the organic carbon conversion was much higher. The organic carbon conversion was 54% and 78% in syngas and steam, respectively. Conversions of other non-ash species — mineral carbon, hydrogen, sulfur, nitrogen, and high-temperature water — were similar in the two tests.

The final five tests were conducted with five different shales at approximately the same conditions as Test 4.1.3-16. The final five tests showed fluidized-bed conversions even higher than the Indiana shale. Alabama shale had an organic carbon conversion (81%) similar to Indiana shale. The other four shales had organic carbon conversions between 92% and 98%. As was seen for Indiana shale in both syngas and steam, conversions of other non-ash species, including sulfur, were higher than organic carbon conversion for the final five shales.

The percentage of feed shale carbon-forming methane was similar for all six shales in steam gasification — 10% to 12%. The percentage forming higher hydrocarbons, 2%, was much lower and also constant over the six shales. The percentage forming oil and water phase compounds, 0.5% to 1.5%, was low for the six shales. The great majority of feed shale carbon converted was recovered as carbon oxides. Higher conversions of organic carbon in steam versus syngas gasification suggest that the steam-carbon reaction producing carbon monoxide and hydrogen is the main reaction leading to carbon oxides production. In the steam tests, higher steam partial pressures and lower carbon monoxide and hydrogen partial pressures would promote the steam-carbon reaction. In the steam tests, carbon dioxide was approximately two-thirds of the total carbon oxides recovered. Carbon dioxide was produced from mineral carbonate decomposition and from the water-gas shift reaction.

The major sulfur-containing product was hydrogen sulfide. Between 0.1% and 5% of the feed shale sulfur was recovered in the condensed water, and

traces of carbonyl sulfide were detected in every test. For all tests, hydrogen sulfide accounted for more than 90% of the converted sulfur.

Gasification of Indiana, Alabama, and Tennessee shales in the MBU resulted in generally lower conversions than similar gasification tests in the thermobalance. Slugging in the fluidized-bed reactor does not appear to be the cause of this difference. The product gas from MBU synthesis gas tests with all three shales had similar steam and hydrogen contents but higher carbon monoxide content (24% versus 20%) compared to the synthesis gas used for thermobalance tests. The MBU synthesis gas, through inhibition of steam-carbon gasification by carbon monoxide, could cause lower organic carbon conversions in the MBU syngas tests. Steam gasification tests with Indiana shale also show lower conversions in the MBU than in the thermobalance. These results suggest lower conversions in the fluidized-bed reactor are a consequence of the behavior of the shale in the fluidized bed.

Subtask 4.1.4. Gasification Kinetic Correlations

Objective: The objective of this subtask is to correlate the differential-rate kinetic data obtained in the thermobalance and the integral-bed kinetic data obtained from the MBU.

Discussion: A model has been developed to describe the gasification behavior of Eastern shales. The kinetic expressions are based on the results of fifty-two thermobalance tests with six different shales conducted in Subtask 4.1.1. Gasification conditions for which the model is valid are presented in the discussion of the model, but specific ranges should be summarized. Conversions are defined for temperatures between 1600° and 1900°F, steam and hydrogen pressures up to 18 atm, and carbon oxide pressures up to 1.5 atm. Steam pressure must be non-zero because the model is not valid for gasification in the absence of steam. High carbon dioxide pressure may result in unreliable calculation of the organic carbon conversion because the carbon-carbon dioxide reaction is not included in the model. Shale residence time must be greater than 3 minutes to obtain reliable conversion data from the model. No conversion data was obtained for thermobalance tests at residence times of less than 5 minutes.

Gasification tests were conducted in a continuous, fluidized-bed mini-bench unit (MBU). All six shales were gasified in steam, and Indiana shale

was also gasified in synthesis gas. MBU tests, like the thermobalance tests, showed that high organic carbon conversions can be achieved in steam (greater than 90% after 30 minutes at 1750°F) and that organic carbon conversion is significantly greater in steam than in synthesis gas. The results from the MBU tests were not used in the development of the gasification model.

The general form of the gasification model was based on shale weight losses in the thermobalance and the known behavior of various shale species under gasification conditions. Shale, on an ash-free basis, was described as being composed of moisture, organic carbon, mineral carbonates, organic hydrogen, high-temperature water, sulfur and nitrogen. Gasification conversions and reactions of each species were assumed to be independent and simultaneous.

The sum of the gasification weight losses from the shale species gives the overall ash-free weight loss. Figures 32 and 33 show the effects of temperature and different gas environments on the moisture, ash-free weight loss of Indiana shale. The thermobalance data in these figures show, and the rest of the thermobalance data supports, the same general gasification behavior of Eastern shales. A significant amount of weight is lost very rapidly (in less than one minute). The remaining, slow weight loss occurs over at least a 30-minute period and is strongly affected by temperature and gas partial pressures.

Fast gasification reactions include some conversion by all shale species. Thermobalance data show that species conversions by fast reactions are the same for all six shales and are unaffected by temperature and gas pressures. Fast reactions include 100% conversion of moisture and mineral carbonates to steam and carbon dioxide. Other fast reactions result in the conversion of 85% of the high-temperature water to steam, 90% conversion of the organic hydrogen, and 92% of the nitrogen. The organic hydrogen and nitrogen conversions are approximations because of their low concentrations in the feed and residue shales. The six shales on a moisture-, ash-free basis contain less than 5% organic hydrogen and 2% nitrogen.

Sulfur in Eastern shales has been shown to be mostly pyritic.⁵ Other researchers have demonstrated that pyrite in coal will be gasified in two independent reactions.⁶ Yergey *et al.*⁷ have shown the first step of pyrite gasification to form iron sulfide and hydrogen sulfide, and to be complete at temperatures below 1480°F. Shale retorting MBU tests (in Subtask 1.2) at 900°

Figure 32. THE EFFECT OF TEMPERATURE ON THE DRY, ASH-FREE CONVERSION OF INDIANA NEW ALBANY SHALE

Figure 33. THE EFFECT OF GAS ENVIRONMENTS ON THE DRY, ASH-FREE CONVERSION OF INDIANA NEW ALBANY SHALE

to 1100°F suggest that the conversion of half the feed sulfur will occur at even lower temperatures. Based on MBU data for shale and the pyrite decomposition data of Yergey and others, the model assumes 50% of shale feed sulfur is converted by a fast reaction to hydrogen sulfide.

The final fast reaction identified was the conversion of 10% of shale organic carbon to hydrocarbon gas, mostly methane. Thermobalance data with a flame ionization detector showed that hydrocarbons were produced only at the start of each test. Fluidized-bed MBU tests indicated a 10% conversion of organic carbon to methane for all six shales. Other researchers, working with Swedish Ranstad shale,⁸ have also noted that hydrocarbon gas production is relatively constant with reference to gasification temperature and shale residence time. The shale gasification model developed in this project assumes the production of hydrocarbon gas from Eastern shales is complete within one minute under the gasification conditions studied.

Slow gasification reactions, taking more than one minute to complete, were identified for sulfur and organic carbon. The slow sulfur conversion was assumed to be predominantly the production of hydrogen sulfide from iron sulfide. The data are best fit in the model with a first order reaction in feed sulfur that is dependent on the feed steam pressure. The slow sulfur gasification of all six shales is described by a kinetic expression with a pre-exponential factor of $12.2 \text{ atm}^{-1} \text{ s}^{-1}$ and an activation energy of 41,000 Btu/mol. Yergey *et al.*⁷ also used a first order expression for this reaction, but determined an activation energy of 75,700 Btu/mol.

The conversion of organic carbon by slow gasification reactions is described in the shale gasification model by two reactions. The first reaction is complete in under 5 minutes and is described only as a fraction of the organic carbon for each shale. The other slow organic carbon reaction is the carbon-steam reaction. The kinetic expression in the model for carbon-steam gasification is first order in feed organic carbon and dependent on steam pressure. Thermobalance data show (Figure 33) that the rate of organic carbon conversion is enhanced by higher steam pressures, but inhibited by increases in hydrogen and carbon monoxide pressures. Rate constants for the retardation effects of hydrogen and carbon monoxide are included in the carbon-steam kinetic expression. The Eastern shales studied are described with different

rate constants for steam but the same rate constants for hydrogen and carbon monoxide.

The form of the kinetic expression used for the carbon-steam reaction is similar to expressions used by other researchers. Bjerle *et al.*,⁹ working with Swedish Ranstad shale char, Feng and Hatcher,¹⁰ working with Alabama Chattanooga shale, and McCarthy and Close,¹¹ working with Australian Yaamba lignite shale char use similar expressions for the carbon-steam rate expression. The rate expressions used by other researchers specify an additional rate constant for steam retardation of the reaction. Including a rate constant for steam inhibition did not improve the fit of the calculated organic carbon conversion compared to the experimental thermobalance data. Therefore, the rate expression in the model for the carbon-steam reaction was simplified and does not contain a steam inhibition term.

The effects of gas pressures on the rate of carbon-steam gasification are different in the rate expressions used by various workers. The gasification tests conducted in this project were conducted over wider ranges of steam and hydrogen pressures than were used by other researchers. Therefore, the carbon-steam rate expression developed in this project is valid over the range of gasification conditions studied.

All gasification tests conducted in this program were made in gas environments with steam-to-carbon dioxide molar ratios above 2.4. Due to the high relative steam pressures used, the Boudouard reaction of carbon with carbon dioxide was not included in the model developed in this project. Other researchers⁹⁻¹¹ have shown that this reaction must be included when large amounts of carbon dioxide are present.

Gasification Model: The gasification of Eastern shales has been described by a model based on thermobalance data. Correlations apply only within the range of gasification conditions studied. Ranges of temperature, shale residence time, and gas pressures are presented in Table 39. The hydrogen pressure and shale residence time must be above the minimum values of 0.5 atmospheres and 3 minutes for the model to be valid. The presence of steam during gasification is required because all tests were conducted with steam present, and steam pressure is an integral part of the kinetic expressions. Conversions determined for shale residence times of less than

Table 39. RANGES OF GASIFICATION CONDITIONS FOR SHALE KINETIC MODEL

Temperature, °F	1600 - 1900
H ₂ O Pressure, atm	0.5 - 18
H ₂ Pressure, atm	0 - 18
CO Pressure, atm	0 - 1.5
CO ₂ Pressure, atm	0 - 1.5
Shale Residence Time, min	3 - 30

3 minutes are unreliable because thermobalance data are not available for species conversions at short residence times.

Shale weight loss has been described on an ash-free basis in terms of the weight losses of various shale species. All reactions of the shale species are assumed to be independent and simultaneous. The model distinguishes between two sets of reactions: fast reactions and slow reactions. Fast reactions are assumed to be complete in less than one minute. The conversions from species exhibiting fast reactions were not affected by temperature, partial pressures, or shale source (within the ranges studied) and have therefore been described only in terms of the fractions of the species converted. Kinetic expressions were not developed for the fast reactions due to the absence of species conversion data at short residence times.

Slow reactions take significantly longer than one minute to complete under the gasification conditions studied. Two slow reactions have been identified. Sulfur and organic carbon not converted in the fast reactions are assumed to be converted to hydrogen sulfide and carbon monoxide. The formation of hydrogen sulfide is described by a kinetic expression which is first order in feed sulfur. The sulfur conversion rate increases with increasing steam pressure. Carbon conversion is by the steam-carbon reaction which forms carbon monoxide and hydrogen. The reaction, first order in feed organic carbon, is enhanced by higher steam pressure, but inhibited by higher hydrogen and carbon monoxide partial pressures. Gas partial pressures can be used instead of concentrations because gas concentrations are constant in thermobalance tests because of the large excess of gas used.

The weight loss (W) of ash-free shale at any time during gasification is defined as the sum of the feed shale weight lost by fast and slow reactions.

$$W = W_{\text{fast}} + W_{\text{slow}} \quad (1)$$

The weight lost by fast reactions is given by —

$$W_{\text{fast}} = W_{\text{H}_2\text{O}} + W_{\text{CO}_2} + W_{\text{OH}} + W_{\text{N}_2} + W_{\text{HTW}} + W_{\text{S},f} + W_{\text{OC},f} \quad (2)$$

The weights of the shale species are on an ash-free basis. The species conversions by fast reactions were the same for the six shales studied and are equal to —

$$\begin{aligned} W_{\text{H}_2\text{O}} &= 1.0 W_{\text{H}_2\text{O},o} = 100\% \text{ of moisture} \\ W_{\text{CO}_2} &= 1.0 W_{\text{CO}_2,o} = 100\% \text{ of mineral carbonates} \\ W_{\text{OH}} &= 0.90 W_{\text{OH},o} = 90\% \text{ of organic hydrogen} \\ W_{\text{N}_2} &= 0.92 W_{\text{N}_2,o} = 92\% \text{ of nitrogen} \\ W_{\text{HTW}} &= 0.85 W_{\text{HTW},o} = 85\% \text{ of high-temperature water} \\ W_{\text{S},f} &= 0.50 W_{\text{S},o} = 50\% \text{ of sulfur} \\ W_{\text{OC},f} &= 0.10 W_{\text{OC},o} = 10\% \text{ of organic carbon} \end{aligned}$$

The organic hydrogen, nitrogen, and high-temperature water not lost in fast reactions remain with the shale even after gasification at the most extreme conditions studied. A 50% sulfur conversion assumes that most feed sulfur is pyritic and that pyrite conversion to FeS is rapid at gasification conditions. Organic conversion in the fast reactions is due to the rapid conversion of 10% of the feed organic carbon to hydrocarbon gases.

The ash-free weight loss by slow reactions is given by —

$$W_{\text{slow}} = W_{\text{S},s} + W_{\text{OC},s} \quad (3)$$

Sulfur and organic carbon that can be lost by slow reactions are defined by

$$W_{\text{S},s} = W_{\text{S},o} - W_{\text{S},f} = 0.50 W_{\text{S},o} \quad (4)$$

$$W_{\text{OC},s} = W_{\text{OC},o} - W_{\text{OC},f} = 0.90 W_{\text{OC},o} \quad (5)$$

The sulfur rate expression is —

$$-\frac{dW_{S,s}}{dt} = p_{H_2O}^{0.25} k_s W_{S,s} \quad (6)$$

Integration and substitution of Equation 4 gives the sulfur weight loss by the slow reaction

$$W_{S,s} = 0.50 W_{S_o} \times [1 - \exp(-p_{H_2O}^{0.25} k_s t)] \quad (7)$$

Total sulfur weight loss is the sum of the weight loss by the fast and slow reactions and is given by

$$W_S = W_{S_o} - 0.5 W_{S_o} \times \exp(-p_{H_2O}^{0.25} k_s t) \quad (8)$$

Organic carbon conversion by slow reactions is described by two reactions.

$$W_{OC,s} = W_{OC,s1} + W_{OC,s2} = 0.90 W_{OC_o}$$

The first slow organic carbon reaction goes to completion in less than 3 minutes, and the weight loss is

$$W_{OC,s1} = (0.9 - X_{OC}) W_{OC_o} \quad (0 < X_{OC} < 0.9) \quad (9)$$

The rate expression for the second, and slower, slow organic carbon reaction is

$$-\frac{dW_{OC,s2}}{dt} = \frac{p_{H_2O}^{0.5} k_1}{1 + p_{H_2}^{0.5} k_2 + p_{CO}^{0.5} k_3} W_{OC,s2} \quad (10)$$

Integration and substitution of Equations 5 and 9 give organic conversion by the second slow reaction.

$$W_{OC,s2} = X_{OC} W_{OC_o} \times \left[1 - \exp\left(\frac{-p_{H_2O}^{0.5} k_1}{1 + p_{H_2}^{0.5} k_2 + p_{CO}^{0.5} k_3} t\right) \right] \quad (11)$$

Organic carbon conversion by slow reactions is given by

$$W_{OC,s} = (0.9 - X_{OC}) W_{OC_o} + X_{OC} W_{OC_o} \left[1 - \exp \left(\frac{- p_{H_2O}^{0.5} k_1}{1 + p_{H_2}^{0.5} k_2 + p_{CO}^{0.5} k_3} t \right) \right] \quad (12)$$

Total organic carbon weight loss is the sum of the weight loss by the fast and slow reactions and is given by —

$$W_{OC} = W_{OC_o} - X_{OC} W_{OC_o} \times \exp \left(\frac{- p_{H_2O}^{0.5} k_1}{1 + p_{H_2}^{0.5} k_2 + p_{CO}^{0.5} k_3} t \right) \quad (13)$$

The rate constants k_s , k_1 , k_2 , and k_3 have the typical Arrhenious form

$$k = A \exp (- E/RT)$$

The model allows the calculation of ash-free weight loss, sulfur conversion, and organic conversion at any time. Sulfur and organic carbon conversion are defined by Equations 8 and 13. Ash-free weight loss is found by combining Equations 2, 3, 7, and 12.

$$\text{Sulfur Conversion, \%} = 100 \times [1 - 0.5 \exp (- p_{H_2O}^{0.25} k_s t)] \quad (14)$$

$$\text{Organic Conversion, \%} = 100 \times [1 - X_{OC} \exp \left(\frac{- p_{H_2O}^{0.5} k_1}{1 + p_{H_2}^{0.5} k_2 + p_{CO}^{0.5} k_3} t \right)] \quad (15)$$

$$\text{Ash-Free Weight Loss, \%} = 100 \times [W_{fast} + 0.50 W_{S_o} \times \exp (1 - \exp \{- p_{H_2O}^{0.25} k_s t\})]$$

$$+ (0.90 - X_{OC}) W_{OC_o} + X_{OC} W_{OC_o} \times \left[1 - \exp \left(\frac{- p_{H_2O}^{0.5} k_1}{1 + p_{H_2}^{0.5} k_2 + p_{CO}^{0.5} k_3} t \right) \right] \quad (16)$$

Parameters in the shale gasification model are defined in a consistent set of units.

T = temperature, °R

p_{H_2O} , p_{H_2} , p_{CO} = pressure, atm

W	= ash-free weight loss, lb
W_x	= species weight loss, lb
W_{x_0}	= initial species weight (ash-free), lb
X_{OC}	= fraction of organic carbon, dimensionless
k_S, k_1, k_2, k_3	= rate constants, $\text{atm}^{-1}\text{s}^{-1}$
A_S, A_1, A_2, A_3	= pre-exponential factors, $\text{atm}^{-1}\text{s}^{-1}$
E_S, E_1, E_2, E_3	= activation energies, Btu/lb mol
R	= gas constant, 1.9872 Btu/lb mol, °R
t	= time, s

The rate constants for sulfur and organic carbon reactions and the split of organic carbon between the two slow reactions were determined by a weighted least squares fit for each shale. The parameters for the shale gasification model are given in Table 40.

Gasification Model Calculations: The gasification model was used to calculate organic carbon conversion, sulfur conversion, and moisture-, ash-free weight loss at the gasification conditions used in thermobalance tests with the six Eastern shales. Tables 41 and 42 present the calculated and experimental conversions for all thermobalance tests.

Indiana New Albany shale was the most extensively-studied shale and was used to develop the kinetic expressions in the gasification model. The overall description of shale gasification was better for Indiana shale than for the other five shales. Calculated organic carbon conversion at 30 minutes was within 6% of the experimental value for 21 of the 22 tests. Calculated sulfur conversion at 30 minutes was within 4% of the experimental value for 18 of 22 tests. The model also describes conversions and overall weight loss accurately for shorter residence times between 3 and 30 minutes. Figure 34 shows a close fit between the experimental and calculated moisture-, ash-free weight loss for a typical test (1700°F and 135 psig in steam:hydrogen).

The gasification model fit to the gasification results with shales other than Indiana New Albany was based on fewer tests. Calculated fits, while good, were not as good as those obtained for Indiana shale. The kinetic

Table 40. PARAMETERS FOR SHALE GASIFICATION MODEL

Shale	Indiana	Alabama	Tennessee	Kentucky	Michigan	Ohio
K_S Parameters,						
$A_S, \text{atm}^{-1}\text{s}^{-1}$	----- 12.2 -----					
$E_S, \text{Btu/lb-mole}$	----- 4.11×10^4 -----					
$X_{OC}, \% \text{ Org C}$	41	52	50	52	41	41
k_1 Parameters,						
$A_1, \text{atm}^{-1}\text{s}^{-1}$	6.62×10^6	5.90×10^6	4.80×10^6	5.20×10^6	3.20×10^6	7.10×10^6
$E_1, \text{Btu/lb-mole}$	----- 9.605×10^4 -----					
k_2 Parameters						
A_2, atm^{-1}	----- 712.5 -----					
$E_2, \text{Btu/lb-mole}$	----- 2.38×10^4 -----					
k_3 Parameters						
A_3, atm^{-1}	----- 7.28×10^9 -----					
$E_3, \text{Btu/lb-mole}$	----- 8.68×10^4 -----					

Table 41. COMPARISON OF EXPERIMENTAL AND CALCULATED GASIFICATION CONVERSIONS

Test 4.1.1-	Shale	Temperature, °F	Pressure, psig	Gasification Atmosphere	Residence Time, min	Shale Conversion, maf, %		Sulfur Conversion, %		Org. Carbon Conversion, %	
						Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
1	Indiana	1600	500	Steam/H ₂	30	81.1	80.4	93.0	92.7	73.4	69.9
2	Indiana	1700	500	Steam/H ₂	30	85.8	86.7	97.1	97.7	81.9	80.1
3	Indiana	1600	135	Steam/H ₂	30	78.1	79.0	87.3	87.7	68.1	69.1
4	Indiana	1700	135	Steam/H ₂	30	84.1	85.8	92.6	94.8	75.1	79.5
5	Indiana	1600	15	Steam/H ₂	30	77.9	76.7	81.0	80.4	67.4	67.5
6	Indiana	1700	15	Steam/H ₂	30	84.1	83.6	92.6	89.0	75.6	77.4
7	Indiana	1800	15	Steam/H ₂	30	95.2	91.0	97.2	95.0	95.1	89.2
8	Indiana	1900	15	Steam/H ₂	30	96.3	96.0	97.8	98.4	96.6	97.5
9	Indiana	1800	135	Steam/H ₂	30	94.4	92.3	98.7	98.4	95.3	90.5
10	Indiana	1600	15	Syn. Gas	30	73.3	74.5	67.5	78.3	63.8	64.0
12	Indiana	1900	135	Steam/H ₂	30	96.3	96.0	99.9	99.6	98.0	97.0
14	Indiana	1700	15	Syn. Gas	30	77.5	77.8	81.0	87.5	67.7	67.0
15	Indiana	1790	250	Steam/H ₂	30	89.5	92.0	95.2	98.9	79.5	89.7
48	Indiana	1710	135	Syn. Gas	30	81.0	78.8	91.1	93.5	68.7	66.6
49	Indiana	1750	135	Syn. Gas	30	79.1	79.4	93.3	95.5	65.6	67.1
51	Indiana	1750	15	Steam/H ₂	30	84.6	87.2	95.7	92.3	77.9	83.1
52	Indiana	1710	135	Steam	30	97.7	96.9	96.5	96.4	99.9	100.0
55	Indiana	1710	135	Steam/H ₂	30	81.9	85.9	94.4	95.0	75.6	79.5
56	Indiana	1710	135	Steam/H ₂	15	81.1	79.4	85.2	84.2	72.9	71.1
57	Indiana	1700	135	Steam/H ₂	5	73.0	71.7	53.8	65.5	61.4	63.3
58	Indiana	1600	135	Steam	30	97.2	92.8	94.9	89.5	96.1	94.7
59	Indiana	1890	15	Steam/H ₂	15	95.4	89.7	93.2	90.2	91.5	88.4

maf = Moisture-, ash-free basis.

NA = Not available.

Table 42. COMPARISON OF EXPERIMENTAL AND CALCULATED GASIFICATION CONVERSIONS

Test 4.1.1-	Shale	Temperature, °F	Pressure, psig	Gasification Atmosphere	Residence Time, min	Shale Conversion, maf, %		Sulfur Conversion, %		Org. Carbon Conversion, %	
						Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
16	Alabama	1620	15	Steam/H ₂	30	71.3	71.5	37.8	82.6	60.2	60.2
17	Alabama	1760	15	Steam/H ₂	30	86.1	83.7	99.6	92.8	82.8	77.7
18	Alabama	1900	15	Steam/H ₂	30	96.2	94.8	99.2	98.4	97.9	95.7
20	Alabama	1610	500	Steam/H ₂	30	64.4	75.9	68.8	93.7	56.5	62.7
21	Alabama	1815	500	Steam/H ₂	30	89.0	91.9	98.8	99.7	88.6	89.6
22	Alabama	1750	135	Syn. Gas	30	77.2	73.6	85.8	96.0	56.9	57.0
30	Alabama	1750	135	Steam/H ₂	30	80.8	85.8	94.4	97.0	73.4	79.5
32	Alabama	1750	15	Syn. Gas	30	70.0	71.3	73.6	90.2	59.7	55.8
34	Alabama	1690	15	Steam/H ₂	30	81.7	77.5	NA	88.4	NA	68.5
23	Tennessee	1755	135	Syn. Gas	30	66.8	73.5	86.4	96.2	56.3	57.1
24	Tennessee	1605	15	Steam/H ₂	30	68.2	70.3	84.4	81.1	57.0	58.4
25	Tennessee	1755	15	Steam/H ₂	30	74.9	82.1	91.6	92.7	67.6	75.0
26	Tennessee	1895	15	Steam/H ₂	30	90.9	92.3	98.2	98.2	94.1	92.6
28	Tennessee	1605	500	Steam/H ₂	30	70.9	74.6	81.7	93.1	63.3	60.6
29	Tennessee	1750	500	Steam/H ₂	30	84.3	84.9	98.4	98.9	79.7	77.3
31	Tennessee	1750	135	Steam/H ₂	30	80.8	83.6	97.3	96.9	75.3	75.9
33	Tennessee	1750	15	Syn. Gas	30	68.2	71.4	80.2	90.1	57.6	56.2
35	Tennessee	1825	15	Steam/H ₂	30	92.4	87.9	NA	96.1	NA	84.4
36	Kentucky	1690	15	Steam/H ₂	30	75.7	74.2	95.9	88.1	67.1	65.8
37	Kentucky	1810	15	Steam/H ₂	30	78.3	84.8	97.3	95.4	73.0	82.7
38	Kentucky	1900	15	Steam/H ₂	30	94.0	91.5	94.6	98.3	94.4	93.4
39	Kentucky	1750	15	Syn. Gas	30	71.0	68.0	93.7	90.2	54.8	55.0
40	Michigan	1750	15	Syn. Gas	30	87.0	74.7	95.9	90.4	79.0	61.1
41	Michigan	1710	15	Steam/H ₂	30	79.9	79.0	96.7	89.6	68.5	69.9
42	Michigan	1800	15	Steam/H ₂	30	85.2	84.4	96.1	95.0	79.1	78.3
43	Michigan	1900	15	Steam/H ₂	30	87.2	90.3	97.8	98.3	79.6	88.8
44	Ohio	1700	15	Steam/H ₂	30	81.6	82.0	98.7	88.9	73.8	78.1
45	Ohio	1800	15	Steam/H ₂	30	93.9	89.4	99.4	95.0	91.6	89.9
46	Ohio	1900	15	Steam/H ₂	30	98.0	94.1	100.0	98.3	98.9	97.7
47	Ohio	1750	15	Syn. Gas	30	81.4	76.0	98.0	90.6	73.3	66.9

maf = Moisture-, ash-free basis.

NA = Not available.

Figure 34. EXPERIMENTAL AND CALCULATED DRY, ASH-FREE CONVERSIONS OF INDIANA NEW ALBANY SHALE

expression for sulfur conversion was the same for all six shales. The kinetic expression for the carbon-steam reaction was changed to allow for the different reactivities of the shales. Indiana and Ohio shales were the most reactive, followed by the Alabama and Tennessee Chattanooga shales, with the Kentucky and Michigan shales showing the lowest reactivity. Calculated and experimental results differ significantly for some tests. Time was not available to conduct duplicate tests needed to determine if the differences were due to experimental causes or non-optimum selection of kinetic parameters.

Comparisons of the calculated and experimental organic carbon and sulfur conversions for all six shales are presented in Figures 35 to 37. Conversions are compared for the most commonly used gasification environment, 15 psig of steam:hydrogen, over the temperature ranges studied. Calculated organic carbon conversions reflect the different reactivities of the shales studied and show that the overall fit of calculated to experimental data is good despite the variations of the limited data available.

Experimental sulfur conversions appear to be higher than the calculated values for gasification at 15 psig in steam:hydrogen. The fit of calculated to experimental sulfur conversions was made over the full range of gasification conditions studied. Over the full pressure range (15 to 500 psig) and gas environment conditions examined, the calculated sulfur conversions are not lower than the experimental sulfur conversions. Calculated sulfur conversions for most tests with the six shales show good fits to the experimental values.

Subtask 4.1.5. Process Development Scale Tests

Objective: The objective of this subtask is to conduct proof-of-concept tests in the 8-inch-diameter PDU to verify and scale-up laboratory- and bench-scale data.

Experimental Equipment and Test Procedures: The PDU system, used for shale gasification tests, has been used primarily for the study of steam-oxygen gasification of coals in an ash-agglomerating fluidized bed. Detailed descriptions of the PDU in the coal configuration have been published elsewhere.^{12,13}

The PDU system consists of 10 sections that perform all the functions necessary for integrated operations: 1) feed drying, 2) dry feed handling and

Figure 35. EXPERIMENTAL AND CALCULATED ORGANIC CARBON CONVERSIONS OF INDIANA, ALABAMA, AND TENNESSEE SHALES

Figure 36. EXPERIMENTAL AND CALCULATED ORGANIC CARBON CONVERSIONS OF KENTUCKY, MICHIGAN, AND OHIO SHALES

Figure 37. EXPERIMENTAL AND CALCULATED SULFUR CONVERSIONS OF EASTERN SHALES

storage, 3) feed weigh hoppers, 4) pressurized feed lockhoppers, 5) feed injection, 6) PDU gasifier, 7) product gas quencher, 8) product gas cyclone dust collector, 9) pressurized ash lockhoppers, and 10) gasifier control system. A flow diagram of the PDU system is shown in Figure 38.

The basic component of the dryer section is a co-current, single-shell rotary drum unit with a nominal capacity of 900 lb/h when drying coal. However, the dryer is not required for shale processing. The 1/4 inch x 0 shale is conveyed by a bucket elevator to the top of a 90-ton storage silo. The silo has a built-in, 5-ton hopper at its top with a variable-speed drive feed screw to discharge shale. Because the process is initiated by using metallurgical coke as a start-up feed material, one silo is set aside for coke storage and another is used for the shale. Each feed hopper discharges to a batch weigh system, which feeds preweighed amounts of shale and coke into the PDU feed lockhoppers.

The feed lockhopper system consists of two lockhoppers, each having a capacity of more than 1100 pounds of shale. These are operated sequentially to pressurize the feed shale to the gasifier operating pressure. The system has been automated by using a programmable logic controller that senses valve position, lockhopper pressure, and shale level along with timers to automatically recharge the feed hoppers as shale is discharged by the reactor feed screw.

The feed injection uses a design based on the experience gained in the pilot plant. It incorporates a pneumatic feeder to inject the shale. The shale feed rate is controlled by a feed-screw speed controller and is set to maintain the desired fluidized-bed level in the reactor.

The PDU is a dual-diameter reactor with 8-inch-diameter and 12-inch-diameter sections of the fluidized bed with an 18-inch-diameter freeboard section. The hot inner wall is constructed of 310 stainless steel and the outer wall of pressure-vessel-grade carbon steel. (See Figure 39.)

This PDU is of a balanced-pressure design wherein the space between the inner and outer shells (approximately 5 inches) is filled with a ceramic fiber insulation. The low heat loss that results allows adiabatic operation, with all heat supplied by the char-oxygen reaction. The annular space is purged with nitrogen at a very low rate to prevent possible raw product-gas condens-

Figure 38. FLOW DIAGRAM OF HIGH-PRESSURE, ASH-AGGLOMERATING, FLUIDIZED-BED PDU

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Figure 39. HIGH-PRESSURE, ASH-AGGLOMERATING, FLUIDIZED-BED PDU REACTOR

ables from reaching the cold (185°F) outer wall. The nitrogen is added at the lower bed and freeboard sections.

At the bottom of the fluidized-bed reactor is a removable grid assembly. It is a one-place weldment accommodating a process grid. Some internal components are removable for alteration. In the same manner, the outer shell has been sectionalized to facilitate installation and dismantling for examination, modification, or repair.

Because of the high degree of thermal expansion anticipated, nozzle connections were minimized. There are two major connections, one each for the feed chute and bed sample, fabricated with 1-inch 310 SS pipe; each includes a flexible joint to allow for the radial expansion of the inner shell. These nozzles are also used as pressure-sensing locations for bed density and height and incorporate a flexible run of stainless steel tubing. This tubing exits at the outer shell through a pipe coupling, but the flexible length prevents the imposition of a force on the hot inner shell, which has a low resistance to distortion at operating temperature.

The reactor gas leaving the freeboard enters the quencher directly through a refractory-lined tee piece. The direct quench cools the gas to about 1023°F, where it then enters a refractory-lined cyclone. The cyclone and its hopper are intended to collect fines and retain them for the length of the test run. The ash lockhopper arrangement is designed to lower the ash from reactor pressure to ambient pressure and discharge it into a scale-mounted drum at grade level.

The PDU instrumentation is designed for the control of process steam, oxygen, and shale directly from the panel board at a grade-level control room. Chart-recorded steam, oxygen, nitrogen, and shale flow rates, along with locally obtained pressures and temperatures, are logged into the U-GAS pilot plant's HP9845 computer through the PDU control room terminal. The computer output provides the reactor's operating status, including superficial velocity, steam-oxygen/shale ratios, bed density, and bed height.

Discussion: Two gasification tests were made with Indiana New Albany shale in the 8-inch-diameter PDU. Both tests were conducted with minus 1/8-inch size consist shale at a bed temperature of approximately 1800°F and a pressure of 30 psig.

The operating conditions of 1800°F, 30 psig, and 30 minutes solids residence time were based on the results of laboratory-scale batch and continuous tests. The criterion for selection of the operating conditions was a desired overall carbon conversion of 95%. A solids residence time of 30 minutes and a minimum temperature of 1800°F were selected based on this criterion and thermobalance test results. On the basis of the thermobalance test at this temperature, pressure was found to have little effect on conversion. Indiana New Albany oil shale was used in both PDU tests. Feed shale was crushed, and the 6 x 0 mesh cut was used for both tests. Table 43 contains the proximate, ultimate, and sieve analyses for the feeds, steady-state elutriated fines, and steady-state residue solids. Residue solids analyses show high conversions of all non-ash species and little change in particle size during gasification.

Summaries of the operating conditions and test results for the PDU tests are presented in Table 44. In Test 4.1.5-1, a 4-hour steady-state period was achieved. During steady state, the average bed temperature was 1810°F, and no residue agglomerates were formed. In an attempt to form agglomerates, the bed temperature was increased to 1875°F by supplying additional feed oxygen. No agglomerates were formed, and the test was terminated when the bed defluidized because of sinter formation. Test 4.1.5-2 was conducted under the same nominal operating conditions as Test 4.1.5-1. A longer, 8-hour steady-state period was achieved, and the test was voluntarily terminated. Table 45 gives the ranges for the operating conditions and product gas rate during the steady-state periods.

For Tests 4.1.5-1 and 4.1.5-2, the carbon balances were reconciled from 86% and 101%, respectively. Carbon and sulfur distributions to products shown in Table 44 have been reconciled to 100%. Carbon not recovered with the fines and residue solids was assumed to form gaseous species in the same ratio as found in the average steady-state product gas. Sulfur not recovered with fines and residue solids was assumed to form hydrogen sulfide.

The main carbon-containing product gas species were carbon monoxide, carbon dioxide, and methane. Direct hydrogen production was achieved in these tests. Product gas contained about 6 mole percent hydrogen. Hydrogen plus carbon monoxide produced by steam-carbon gasification was about 11 mole percent of the product gas. The yield of hydrogen plus carbon monoxide was about 3380 SCF per ton of dry shale. Product gas contained about 1.5 mole percent

Table 43. SOLIDS ANALYSES FROM STEAM/OXYGEN FLUIDIZED-BED
PDU TESTS WITH INDIANA NEW ALBANY SHALE

Test No. Solids Stream	----- Feed	4.1.5-1 Fines	----- Residue	----- Feed	4.1.5-2 Fines	----- Residue
Proximate, wt %						
Moisture	1.78	0.16	0	0.21	0.06	0
High-Temperature Water	5.66	0.79	0.57	5.26	0.79	0.50
Ash	75.83	90.72	98.98	75.90	92.69	97.94
Ultimate, wt % dry						
Organic Carbon	11.98	6.97	1.11	11.82	5.60	1.64
Mineral Carbon	0.53	0.05	0	0.53	0.04	0.03
Hydrogen	1.52	0.13	0.07	1.78	0.15	0.09
Oxygen (by HTW)	5.12	0.71	0.52	4.68	0.70	0.44
Nitrogen	0.47	0.09	0.03	0.41	0.07	0.02
Sulfur	3.71	2.28	0.77	3.83	2.68	1.10
Ash	77.79	90.86	98.98	76.06	92.75	97.94
Sieve Analysis, wt % retained on						
6	0	0	0.1	0	0	0
12	31.8	0	37.9	47.2	0	41.1
20	30.9	0	19.8	24.2	0	28.6
40	14.8	0.9	20.8	10.4	7.4	13.2
70	8.4	1.3	14.8	7.1	2.6	11.0
140	5.2	16.1	6.1	4.9	16.3	5.8
230	--	25.3	--	--	20.1	--
270	3.9	--	0.3	2.4	--	0.3
Pan	5.0	56.4	0.2	3.8	53.6	0
HHV, Btu/lb (dry)	2329	1123	189	2363	974	257

Table 44. OPERATING CONDITIONS AND TEST RESULTS FROM STEAM/OXYGEN
FLUIDIZED-BED PDU TESTS WITH INDIANA NEW ALBANY SHALE

Test No.	4.1.5-1	4.1.5-2
Pressure, psig	31	30
Bed Temperature, °F	1794	1785
Freeboard Temperature, °F	1509	1620
Shale Feed Rate, lb/h	421.7	437.4
Steam Feed Rate, lb/h	7.76	7.98
Oxygen Feed Rate, lb/h	3.04	3.26
Fines Rate, lb/h	31.5	50.7
Residue Solids Rate, lb/h	282.8	307.5
Product Gas Rate, lb mol/h	17.31	18.10
Bed Density, lb/ft ³	59	54
Bed Height, ft	3.84	4.59
Solids Residence Time, min	31	32
Inlet Superficial Velocity, ft/s	4.49	4.79
Product Gas Composition, mol %		
CO	4.9	4.7
CO ₂	15.9	14.5
H ₂	6.2	5.8
H ₂ O	53.5	53.7
CH ₄	1.4	1.6
C ₆ ⁺	0.05	0.07
N ₂	15.9	17.5
H ₂ S	2.2	2.1
Product Gas HHV, * Btu/SCF	214	228
Product Carbon Distribution, %		
CO	19.4	19.0
CO ₂	63.5	58.5
CH ₄	5.5	6.4
C ₆ ⁺	1.1	1.7
Fines	4.3	5.3
Residue Solids	6.2	9.1
Total	100.0	100.0
Product Sulfur Distribution, %		
H ₂ S**	80.8	72.7
Fines	4.7	8.1
Residue Solids	14.5	19.2
Total	100.0	100.0

* Dry, nitrogen-free.

** By difference.

Table 45. RANGES OF OPERATING CONDITIONS AND TEST RESULTS
DURING STEADY-STATE OPERATIONS

Test No.	4.1.5-1		4.1.5-2	
	Average	Standard Deviation	Average	Standard Deviation
Bed Temperature, °F	1794	9.4	1785	6.5
Feed Rates				
Shales, lb/h	421.7	9.0	437.4	11.0
Steam, lb/h	7.76	0.011	7.98	0.026
Oxygen, lb/h	3.04	0.088	3.26	0.020
Product Rates				
Residue Solids, lb/h	282.8	5.5	307.5	19.0
Fines, lb/h	31.5	1.8	50.7	4.4
Gas, * kg lb mol/h	14.55	NA	15.30	0.46

* Nitrogen-free.

of methane, which corresponds to a methane yield of about 450 SCF per ton of dry shale. Higher hydrocarbons, observed as C_6+ compounds by gas chromatography, were 0.06 mole percent of the product gas. Methane and higher hydrocarbons produced were 6% and 1.4%, respectively, of the feed carbon. Fines contained about 5% of the feed carbon, and residue solids contained about 6.5% of the feed carbon. The major sulfur-containing gasification product was hydrogen sulfide. Trace amounts of carbonyl sulfide were also detected. Fines contained 6.5% and residue solids contained about 17.5% of the feed sulfur. Although steam is converted in the reactor, the total amount of water collected downstream of the gasifier is higher than the steam fed. This is because, in addition to the steam fed to the reactor, water is also produced in the reactor from shale moisture and high-temperature water. Oxygen was fed to provide process heat by combustion. The molar feed oxygen-to-carbon ratio was about 0.72. The higher heating value of the product gas on a dry, nitrogen-free basis was about 221 Btu/SCF. Removal of hydrogen sulfide as well as water and nitrogen from the product gas gives gas that has a higher heating value of about 192 Btu/SCF.

The conversion of the non-ash components of the fines was lower than that of the residue. Fines were significantly smaller than both feed and residue

shales. In all fines samples tested, over 50 weight percent of the sample was between 5 and 40 microns in size. The similar feed and residue solids particle sizes, the small but nonuniform size of fines particles, and the partial conversion of fines non-ash species indicate that fines are generated by abrasion during the gasification process. Reactor conditions were not severe enough to induce particle fracturing.

The residue solids from Test 4.1.5-2 were tested for the leaching of inorganics by a modified version of EP Method 1310. A residue solids sample was placed in 16 times its weight of deionized water and agitated for 24 hours. Acetic acid was added, as needed, to stabilize the aqueous phase. The solution was kept at a pH value of 4.8 to 5.2. Atomic absorption spectroscopy was used to measure the concentrations of eight metals in the leachate. Results are presented in Table 46. Concentrations were found to be low and, in all cases, below the threshold values for EP Method 1310.

Table 46. CONCENTRATION OF INORGANICS IN THE EXTRACT FROM EP METHOD 1310 LEACHATE USING TEST 4.1.5-2 RESIDUE SOLIDS

<u>Metal</u>	<u>Leachate Concentration, µg/l</u>	<u>EPA Threshold Limit, µg/l</u>
Silver	<30	5000
Arsenic	<40	5000
Barium	<700	100,000
Cadmium	<30	1000
Chromium	<80	5000
Mercury	1.9	200
Lead	<300	5000
Selenium	<40	1000

The results of the PDU gasification tests show that 75% of the oxygen reacted with carbon to form carbon dioxide. The balance of the oxygen reacts with organic hydrogen to form water. About 76% of the total sulfur in the shale was converted to hydrogen sulfide. This reaction consumes about 27% of the hydrogen produced by the steam-carbon reaction and organic hydrogen gasification.

Because of the absence of heat recovery from the exiting streams and the heat losses from the PDU, the oxygen demand in the PDU tests is higher than

that anticipated for a commercial gasifier. Results from the PDU tests were used to estimate conversions and product gas composition for a conceptual, commercial-scale, adiabatic, steam/oxygen, fluidized-bed gasifier processing Indiana New Albany shale. Bed temperature (1800°F) and pressure (30 psig) of the conceptual gasifier were assumed to be the same as those in the PDU tests. Shale residence time was raised to 60 minutes to give an overall carbon conversion of 95%. The conceptual design employs internal fines recycle, sensible heat recovery (exit streams cooled to 320°F to heat inlet streams from 77°F), and inlet steam at 300°F. A practical upper limit of 50 volume percent oxygen in the feed gas was set. Detailed results of the conceptual, commercial-scale reactor calculations have been published.¹⁰

The conceptual, commercial-scale reactor requires 0.305 moles of oxygen per mole of carbon to close the energy balance. The reduction from the 0.716 moles of oxygen per mole of carbon for the PDU tests was due to better heat recovery from the exit streams and a lower steam rate. The high steam-to-carbon ratios in the PDU tests were due to reactor geometry, not kinetic requirements. The product gas from the conceptual, commercial-scale reactor contains less carbon dioxide and has a subsequently higher heating value. The heating value of 335 Btu/SCF is 52% higher than the PDU test product-gas heating value. Hydrogen sulfide production in the conceptual case consumes only 13% of the hydrogen produced compared to 27% in the PDU tests. The total hydrogen plus carbon monoxide produced in the conceptual, commercial-scale reactor is more than three times as much as was produced in the PDU tests. Estimates show that, if 20% of the mined shale is gasified, the calculated amount of hydrogen plus carbon monoxide produced by gasification is sufficient to supply all the hydrogen required by the HYTORT reactor to process the remaining 80% of the mined shale.

Subtask 4.2. Cold-Flow-Model (CFM) Studies

Objective: The objective of this task is to determine the effect of fines concentration on the operation of a moving-packed-bed of shale with gas flowing countercurrently through it. The results of these tests will be used to establish the fines tolerance limits for high-pressure, moving-bed retorts.

Experimental Equipment: A schematic diagram of the equipment used to conduct the cold-flow-modeling studies is shown in Figure 40. The 6-foot-diameter test vessel is the "heart" of the CFM unit and was modularly designed

Figure 40. SCHEMATIC DRAWING OF THE OIL-SHLE COLD FLOW MODEL

to allow equipment changes to be made with a minimum of time and effort. The test vessel consisted of six separate flanged sections, designed for easy removal and replacement, as required. Both the storage silo and the test vessel were 6 feet in diameter and approximately 82.5 feet tall. The test equipment was housed in a 34-foot-long by 45-foot-wide building, which was about 140 feet tall. The control room and motor control center were contained in a two-story block building attached to the main structure.

Shale was added to the CFM via an outside feed hopper, which in turn was fed using a front-end loader. After leaving the feed hopper, the shale passed through a vibrating screener and then to a bucket elevator, which transferred the shale to the top of the unit. The shale exiting the bucket elevator could be routed to either the silo for storage or the CFM test vessel. Hydraulically driven, 18-inch-diameter screw conveyors were located at the bottom of both the silo and the test vessel to discharge the shale at a controlled flow rate. Shale could be recirculated in the solids handling loop at rates of up to 40 tons/h.

Shale leaving the test vessel then flowed onto a belt conveyor. This conveyor passed under a nuclear density gauge, which was used to measure the shale flow rate. The belt conveyor transferred the shale to a diverter valve, which routed the shale either back into the screener (for recirculation tests) or onto a belt conveyor that transferred the shale out of the building.

Air was supplied at rates of up to 2000 ft³/min to the test vessel from a blower. The air flow rate was measured with an orifice meter and controlled with a butterfly valve. Nitrogen could also be added to the test vessel from a low-pressure storage tank.

The test vessel consisted of six separate flanged sections, as shown in Figure 41. Section A, at the top of the unit, contained a solids distributor which utilized a series of cones to minimize shale particle-size segregation in the test vessel. This section also contained a gas outlet port.

Section B was a 22-foot-long cylindrical section that contained two, 24-inch-diameter manways which allowed access to the interior of the test vessel. This section simulated the preheat section of a commercial HYTORT retort.

Section C was 6 feet long and contained both a gas inlet and a gas exit port. Twelve 2-inch-diameter ports were distributed around the circumference

Figure 41. COLD FLOW MODEL TEST VESSEL

of the vessel at both the gas inlet and gas exit locations. A manifold around the outside of the test vessel allowed equal gas flow out of each of the gas entrance and exit ports.

Section D was an 11-foot-long section that contained another entrance manway. This section generally simulated the retorting section of the commercial retort.

Section E was another 6-foot-long section that contained gas ports, similar to those in Section C. It also contained a solids collection device used to sample solids as they flowed in the column.

Section F consisted of a wedge-shaped mass flow hopper. The hopper had a slot discharge opening 6 feet long and 18 inches wide. The mass flow hopper, in conjunction with the variable-pitch discharge screw, provided uniform shale drawdown across the vessel cross-section.

The gas flow distribution across the shale bed was measured using the CFM configuration shown in Figure 42. The gas flow distribution in the bed was determined by measuring the flow of air from a four-nozzle distributor through sixteen equal-area collectors placed on the surface of the packed bed of shale. The sixteen 9-inch-wide air collectors were arranged in a circular pattern, as illustrated in Figure 43. Each collector covered an area of 1.76 square feet. Gas exited the top of each collector through a short, 6-inch-diameter tube, which was fitted with a totalizing anemometer to measure the flow over a period of time. A sectional view of a collector and anemometer is shown in Figure 44.

Shale entrainment rate measurements were made using the test configuration shown in Figure 45. The exit gas stream was routed through a four-point gas collector approximately 15 feet above the air inlet nozzles, and then out through a cyclone separator. The gas collectors consisted of 2-inch pipes pointed downward, with 6-inch by 2-inch bell-shaped pipe reducers on the end of the pipe. The area ratio of the CFM vessel to the four gas collectors was approximately 33-to-1, so that a gas velocity of 1.0 ft/s in the vessel corresponded to 33 ft/s in the 6-inch-diameter collectors, and 323 ft/s in the 2-inch pipes.

The air/solids streams from the four gas collectors were directed to the cyclone through an air plenum which encircled the CFM test vessel. The

Figure 42. CFM CONFIGURATIONS FOR GAS-FLOW TESTS

Figure 43. GAS COLLECTOR CONFIGURATION

Figure 44. SECTIONAL VIEW OF GAS COLLECTOR/ANEMOMETER ASSEMBLY

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Figure 45. SCHEMATIC DRAWING OF GAS DRAW-OFF CONFIGURATION

cyclone was a "powered" type, with a solids-handling blower on the air outlet to draw dust-laden air through the cyclone. The air flow rate through the cyclone was determined by averaging several pitot-tube pressure-drop readings taken in the cyclone blower discharge line during each test.

Test Procedures: Two types of tests were conducted in the 6-foot-diameter cold-flow-model to determine the effect of fines content on the gas-solids contacting in moving-packed-beds of oil shale. In the first series of tests, the concentration of fines (defined here as material smaller than 1/8 inch) in the bed was increased in stages to determine its effect on gas distribution across the packed bed. The entrainment rate of shale in the gas outlet stream was also measured at each fines concentration. In the second type of test, the bed was "doped" with fines to determine if fines can be held up (or collect) above a gas inlet distributor and cause gas maldistribution in the packed bed.

Fines-concentration testing consisted of measuring the gas velocity distribution across the shale bed at various fines concentrations in the bed material. The first test was conducted at the lowest natural fines concentration of the system (approximately 2% by weight) to determine the gas velocity distribution at this base condition, using a nominal gas velocity through the bed of 1.2 ft/s. A description of the test sequence is given below.

1. Raw shale of approximately 1-1/4 inch by 1/8 inch in size was added to the CFM test vessel.
2. The shale was then recirculated around the CFM test loop twice to mix the shale with the solids distributor in vessel Section A.
3. Shale was then recirculated around the test loop at approximately 30 tons/h while gas was added to the bed through the gas inlet ports in vessel Section E (Figure 41) at a constant flow rate. The entrainment rate of solids in the outlet gas line of Section C was then determined by weighing the solids collected by the cyclone and filter bags (Figure 45) over short time intervals.
4. The shale was then recirculated at approximately 30 tons/h for 2 hours (once through) and then drawn down to a level just below the top manway in the CFM while now withdrawing gas through Section A. The surface of the shale bed was then leveled off, and the anemometer assembly (Figures 43 and 44) placed on the bed surface.
5. Gas was then passed through the stationary bed at a nominal superficial velocity of 1.2 ft/s for short time intervals. The individual anemometer

readings were recorded after each time interval and used to determine the radial gas velocity distribution in the shale bed.

6. The surface of the shale bed was then lowered to an intermediate level in vessel Section B with gas again flowing through the bed, and Step 5 was repeated.
7. The shale level was then lowered to a third level just below the lower manway in Section D with gas flowing, and Step 5 was again repeated.
8. A sample of the shale bed was then taken utilizing the solids sampler in vessel Section E while the bed was moving. The sample was analyzed to determine fines concentration and bed voidage as functions of radial position in the bed.

For subsequent tests, the fines concentration in the bed was increased. This was accomplished using the natural attrition of the shale particles as they were transported around the recirculation loop. Naturally, the fines were not removed from the shale at the screener during this fines-generation step.

Crushing tests on Eastern oil shales, reduced in size to the range tested here, have shown that about 9.5% of the original shale is produced as fines.¹⁶ Mining and handling the shale add approximately another 10% fines to the above value.¹⁶ Thus, the maximum fines concentration expected in the feed shale to a commercial retort is approximately 20%.

The second fines-concentration test was conducted at a nominal fines concentration of 7% by weight. Once the measured fines content of the shale being discharged from the CFM reached this level, Steps 3 through 8 in the test sequence described above were repeated.

The third fines concentration test was conducted at a nominal fines concentration of about one-half the maximum expected value, or 10% by weight. Once the measured fines content of the material being discharged from the CFM reached this level, Steps 3 through 8 in the test sequence described above were repeated.

The fines concentration of the shale bed was again increased by moving the shale around the test loop. The rate of attrition of the shale particles decreased as the fines content increased, reaching a practical limit of approximately 16% by weight. The fourth test was then conducted at this fines concentration by again repeating Steps 3 through 8.

The fines doping test consisted of filling a specific region of the shale bed with material containing a high concentration of fines. The remainder of the bed had a fines concentration equal to the base fines concentration. A test was then conducted to determine whether the accumulation of fines would permanently stay in one location as gas flowed through the bed. The test sequence for this test is described below.

1. A region of high fines-concentration material was added to the CFM vessel, as shown in Figure 46. (This region of fines was approximately 4 feet deep and extended roughly 2 feet from the vessel wall. The fines concentration in this region was 30% by weight.)
2. The anemometer assembly was placed on top of the shale bed.
3. Gas was then passed through the stationary bed at a nominal superficial velocity of 1.2 ft/s for several short time intervals. The individual anemometer readings were recorded after each time interval and used to determine the radial gas velocity distribution in the shale bed.
4. The shale was drawn down at a rate of 30 tons/h, with gas flowing through the bed at a nominal velocity of 1.2 ft/s, to an intermediate level in the CFM vessel.
5. Step 3 was repeated.
6. The shale was drawn down with gas flowing, to a level just below the bottom manway in Section D, and Step 3 was repeated.
7. A sample of the shale bed was then taken utilizing the solids sampler in vessel Section E while the bed was moving. The sample was analyzed to determine fines concentration as a function of radial position in the bed.

Discussion: In general, reactors of the moving-bed type have not processed fines. The term "fines" is a relative term, but typically, particle sizes 0.05 to 0.1 times the largest particle in the distribution are usually considered "fines." Attempts to operate with high fines concentrations have resulted in gas maldistribution (which leads to "hot" and "cold" spots in the reactor) and high pressure drops in the reactor. Pressure-drop considerations are much more important for processes which operate near atmospheric pressure than at high pressure. For a high-pressure oil shale retorting process, gas distribution is a more important consideration than pressure drop.

There are strong economic reasons to try to process fines along with larger particles in a moving-bed retorting process. In a feasibility study funded by Phillips Petroleum Company in the early 1980's, it was found that

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Figure 4b. SCHEMATIC DRAWING OF CFM CONFIGURATION
FOR THE FINES MIGRATION TESTS

about 20% of the raw Eastern oil shale that was mined would not be processed because it was considered too fine by traditional criteria. The "fines" in this case were arbitrarily considered to be any oil shale less than 0.125 inches in diameter. The top size of shale to be processed in the retort was 1.25 inches in diameter.

Of the 20% of the raw mined shale generated as fines, approximately half of the fines were produced in the mine and the other half generated during crushing. For a moving-bed hydroretorting plant processing 50,000 barrels per day of oil from an Indiana New Albany shale, the total energy contained in the fines represented about 126×10^9 Btu, or an oil equivalent of 21,000 barrels per day — a significant amount of unutilized resource. It is evident that if a substantial portion of the raw shale fines can be processed, the efficiency of the process can be increased significantly.

Therefore, to see if operation with increased fines concentration is possible, tests were conducted in this subtask to determine the effect of fines concentration on the operation of a moving-packed bed. Separate studies were conducted to determine the effect of fines concentration in moving-packed beds on —

1. radial gas and solids distributions,
2. entrainment of fines in the off-gas,
3. fines migration, and
4. oil yield.

Radial Gas and Solids Distribution: The ability of a moving-bed retort to process shale fines (considered to be shale smaller than 0.125 inch) depends on the uniformity of gas-solids contacting throughout the bed. A significant maldistribution of gas flow or variation in bed packing can lead to "cold" and "hot" spots in the bed, and result in a decrease in overall conversion. Therefore, tests with -1.25/+0.125-inch Indiana New Albany shale were conducted in the 6-foot-diameter, cold-flow model (CFM) to determine the radial particle-size and gas-velocity distributions in the shale bed. From the data obtained in these tests, calculations of the expected oil yield from the process were then made.

Radial particle-size distribution tests were conducted with four fines concentrations — 2.35%, 6.3%, 9.8%, and 15.6% by weight. These fines concentrations were given nominal fines concentration designations of 3%, 7%, 10%, and 16% by weight, respectively. The distribution of the shale fines in the moving-packed bed was determined by collecting a sample of the solids in the solids sampler located in Section E of the vessel (Figure 41). Each solids sample was taken while the bed was moving.

The shale sampler was essentially a cylinder that rotated inside another cylinder (Figure 47). It was positioned in the center of the CFM and oriented perpendicularly to the flow of the solids. The inner cylinder was actuated pneumatically, and could be closed within about one second. The flow opening in the sampler was 12 inches wide and 6 feet long. The sampler had a volume of approximately 9.3 ft³. After the solids sample had been "captured," the bed was drawn down to a level several feet below the sampler. Solid collection bags were then attached to the bottom of the sampler and the sampler was opened, allowing the shale to fall into the bags.

Each bed sample was divided into 12 equally spaced segments across the bed diameter. The particle-size distribution of each sample was then determined by sieve analysis. The net weight of each sample was also used to calculate the bed voidage, assuming that each sample completely filled an equal-volume segment of the solids sampler at the time it was closed.

Sampling of the shale bed for the base-case fines concentration of 3% was unsuccessful, because of failure of the solids sampler to fully close. However, after cleaning and adjusting the sampler, shale bed samples were successfully collected at nominal fines concentrations of 7%, 10%, and 16% by weight.

The distribution of fines in the moving-packed bed was strongly affected by the solids mixing cone at the top of the CFM (Figure 48). The highest concentration of fines was always found in the samples directly under the outer edge of the internal cone. The high fines contents resulted in small average particle sizes in these samples. Therefore, the average particle-size profiles across the CFM had a consistent "W" shape, with peaks at the walls and in the center of the bed under the internal solids antisegregation cone. This can be seen in Figure 49. In this figure, the average particle-size profiles from tests with nominal fines concentrations of 7%, 10%, and 16% by weight are

Solids Sampler Internal Dimensions

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Figure 47. SCHEMATIC DRAWING OF SOLIDS SAMPLER

Figure 48. SCHEMATIC DRAWING OF SOLIDS FEEDER AND ANTISEGREGATION CONE

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Figure 49. MEASURED AVERAGE PARTICLE-SIZE PROFILES IN THE CFM

shown for comparison. The average particle size used in this analysis was the surface/mean volume particle size, i.e.,

$$\frac{1}{D_p} = \sum \frac{X_i}{D_{p_i}}$$

Voidage in the packed bed is the volumetric fraction of the bed not occupied by solids. The bed voidage, calculated from individual sample weights and the particle density of the shale (136 lb/ft³), also varied with radial position in the CFM. In general, bed voidages varied between 0.35 and 0.5, with the lower values occurring in the high-fines regions of the bed. This variation in voidage, combined with the variation in the average particle size, had a strong effect on the gas-velocity distribution in the bed.

Radial Gas-Velocity Distribution: Uniform distribution of reactant gas is necessary to achieve optimum gas-solids contacting and high conversions in moving-packed-bed hydroretorting. Therefore, tests were conducted to determine the effect of increasing the overall fines concentration in the shale on the gas-velocity profile across the bed. This was accomplished by measuring the air flow rates through 16 equal-area gas collectors placed on the surface of the packed bed, as shown in Figure 43. The air flow rates were measured by calibrated anemometers placed in the outlet conduit of each collector. Gas-flow measurements were made for nominal fines concentrations of 3%, 7%, 10%, and 16% by weight. At each fines concentration, air-flow measurements were made at packed-bed heights of approximately 6, 22, and 40 feet above the gas-inlet nozzles.

Based on the design of the concentric, static solids distributor, and the essentially equal air flow rates within each concentric ring of the gas collectors, the fully developed gas-velocity profile was assumed to be symmetrical around the center of the bed. A gas-velocity profile for the 16% fines concentration case is shown in Figure 50. This profile is typical of the profiles for each of the different fines concentrations. The gas velocity was found to be highest near the walls and in the center of the bed, and lowest below the outer edge of the internal solids distribution cone. Thus, the gas velocity was highest where the average particle size was large, and lowest where the average particle size was small. The averaged gas-velocity

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Figure 50. MEASURED GAS-VELOCITY DISTRIBUTION IN THE CFM

profiles for each fines concentration also showed no significant variation with bed height.

From the results of the gas-velocity and particle-size distribution tests, the measured gas velocity, average particle-size, and bed-voidage profiles were used to calculate the corresponding pressure-drop-per-unit-length ($\Delta P/L$) profile using the Ergun Equation.¹⁴ The resulting $\Delta P/L$ profile varied from 0.02 to 0.13 psi/ft for the nominal 16% fines-concentration test, as shown in Figure 51. However, the $\Delta P/L$ profile should really be flat, with gas redistributing itself across the bed based on relative resistance to flow. Therefore, the Ergun Equation¹⁴ was used to adjust the gas-velocity profile across the bed to match the measured bed $\Delta P/L$, using the measured bed-voidage and particle-size profiles and the overall superficial gas velocity in the CFM. The calculations were performed by dividing the column into six concentric, equal-width annuli. For the 6-foot-diameter column, each annulus was 0.5 feet wide. The gas-velocity profile in each annulus was then calculated assuming that the pressure-drop per unit length was the same in each annulus.

The calculated gas-velocity profile from the Ergun Equation for the 16-percent-nominal-fines-concentration case, varied from 0.34 ft/s in the high-fines region to 1.95 ft/s in the center of the bed. The measured and calculated gas-velocity profiles for the 16-percent-nominal-fines-concentration case are shown in Figure 52 for comparison. Similar gas-velocity profiles were calculated for the nominal fines concentrations of 7% and 10%. No gas-velocity calculations were made for the 3-percent-nominal-fines-concentration case because solids sampling was not successful in that test.

Effect of Fines Concentration on Oil Yield: To evaluate the effect of increasing fines concentration on oil yield in a moving-packed-bed retort, a mathematical model was used. Temperature profiles and oil yields based on the measured packed-bed properties from the 7%, 10%, and 16% fines-concentration tests were obtained from the model. The model equations used for calculating the temperature profiles and oil yields are presented in Appendix E. Gas and shale flow rates and inlet temperatures were, in general, taken from HYCRUDE Retort Calculation Run MBU5-86.¹⁵ A schematic flow diagram of the retort configuration used in the calculation is shown in Figure 53. The model was also applied separately to the preheat zone in order to determine a realistic shale temperature profile at the top of the retort zone. Oil

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Figure 51. CALCULATED CFM $\Delta P/L$ PROFILE FROM GAS-VELOCITY MEASUREMENTS

Figure 52. MEASURED AND CALCULATED GAS-VELOCITY PROFILE

Figure 53. RETORT FLOW CONFIGURATION AND CONDITIONS ASSUMED FOR KINETIC MODEL CALCULATIONS

yields were also calculated for the ideal case in which an even distribution of fines and a flat gas-velocity profile across the bed were assumed. The ideal oil yield was then compared to the non-ideal oil yield to determine if increasing the fines concentration in the retort would be beneficial or detrimental to the process.

The kinetic model was used to calculate average heat-transfer coefficients assuming constant gas velocity, gas density, gas viscosity, and thermal conductivity over the height of each zone. These assumptions were made to facilitate application of the existing kinetic equations, and should not have a significant effect on the relative results for the fines concentrations analyzed. Zone heights were determined from the solids fluxes, bed voidages, and the shale residence times set for each case. The 12-segment average-particle-size and bed-voidage profiles measured in the CFM were used to define six annular areas of the packed bed. The gas-velocity profiles calculated using the Ergun Equation for the packed-bed pressure drop were used to set the relative gas flow rates in each annular area. The surface/mean volume average particle size was used in these calculations.

The kinetic model was then applied to each equal-width annulus as if it were a separate retort operating in parallel with the other annuli. This method assumed that there was no heat or mass transfer between adjacent annuli, even though a considerable temperature difference may have existed between them. A summation of the oil yields in each annuli was then made on a solids-flux, area-weighted basis to obtain the overall yield for each retort fines concentration studied. In this calculation, the weighted average particle size was used, i.e.,

$$D_{pw} = \sum X_i D_{pi}$$

From the results of the yield calculations made, using the average particle-size profile, it is evident that the calculated oil yield is a strong function of the final temperature of the shale particles leaving the retort zone. This relationship is shown graphically in Figure 54 in the form of temperature and oil yield profiles for the nominal 7% fines-concentration case. The low bed voidage and the small average particle size, together with the low calculated gas velocity, resulted in a very low heat-up rate, and a maximum shale temperature of less than 700°F in the high-fines region of the

Figure 54. CALCULATED TEMPERATURE AND OIL-YIELD PROFILES IN THE RETORT

bed. Based on the conversion model developed from bench-scale studies, less than 5% of the kerogen in the shale would be converted to oil in this annulus.

Table 47 summarizes the predictions of the model for both the uniform (ideal) and non-uniform (measured) particle-size profiles for nominal fines concentrations of 7%, 10%, and 16%. Also included in the table are calculations for a fines concentration from average particle-size data from a previous study with the same size of shale, and with a fines concentration of 4% by weight. The latter material closely approximated the shale fines concentration in the "base" fines-concentration case.

Table 47 shows that the fractional oil yield (i.e., the fraction of kerogen in the shale converted to oil) generally decreased as the fines concentration was increased. This is because the fines concentration in the annulus immediately below the outer edge of the solids distribution cone was very high. This high fines concentration resulted in less gas flowing in that region, which in turn resulted in less heat transfer to the particles in that annulus. Therefore, the solids did not get heated to a temperature high enough for significant reaction to take place, and the yield was very poor. In some cases, the yield was essentially zero. For example, in the 16-percent-fines-concentration case, the fractional oil yield in annulus 3 was only 0.003.

At each fines concentration, the uniform (ideal) particle-size distribution resulted in a uniform gas-velocity distribution, and equal conversion of the kerogen across the packed bed. These results are presented in Figure 55, along with the calculated oil yield from the above analysis. The numbers in parentheses in this figure denote the predicted oil yields for the measured average particle-size distributions as a percentage of the yield calculated for a bed with a uniform particle-size distribution.

The calculated fraction of the kerogen converted to oil decreased as the fines concentration was increased, as shown in Table 47. However, more shale is being processed when the fines are utilized in the process. Thus, even though the fractional yield is reduced, does the actual amount of oil produced increase when the fines are used? To answer this question, a calculation of the amount of oil produced as a function of fines concentration was made. The calculation was based on 100 tons of raw shale from the mine. As discussed above, approximately 20% by weight of this shale is produced as fines either

Table 47. SUMMARY OF OIL YIELD CALCULATIONS

Fines Concentration, wt %	Annulus (-)	Particle Size, in.	Voidage, (-)	V _{rel} , ft/s	Area, ft ²	Inlet Temperature, °F	Outlet Temperature, °F	Annular Oil Yield, (-)	Weighted Fractional Yield, (-)
4	Ideal	0.494	0.416	5.74	28.27	516	894	0.561	0.561
	1	0.529	0.420	6.11	12.37	516	892	0.561	0.2438
	2	0.471	0.431	5.65	8.84	531	908	0.564	0.1717
	3	0.450	0.398	4.84	5.30	491	875	0.520	0.1005
	4	0.528	0.419	5.41	1.77	501	879	0.540	0.0336
	Total								0.5496
7	Ideal	0.467	0.405	5.90	28.27	521	900	0.564	0.564
	1	0.557	0.443	7.79	8.64	549	916	0.563	0.1610
	2	0.393	0.407	5.50	7.07	536	917	0.564	0.1405
	3	0.307	0.332	2.56	5.50	329	691	0.023	0.0050
	4	0.395	0.376	4.54	3.93	480	896	0.489	0.7120
	5	0.563	0.379	6.95	2.36	496	870	0.521	0.0453
	6	0.654	0.509	10.74	0.79	580	937	0.564	0.0129
	Total								0.4361
10	Ideal	0.388	0.392	6.09	28.27	544	922	0.564	0.5640
	1	0.436	0.380	6.79	8.64	533	910	0.564	0.1757
	2	0.399	0.378	6.46	7.07	538	916	0.564	0.1442
	3	0.260	0.334	3.07	5.50	384	777	0.112	0.0239
	4	0.305	0.413	6.23	3.93	592	960	0.564	0.0756
	5	0.416	0.435	8.57	2.36	597	956	0.564	0.0437
	6	0.518	0.433	10.05	0.79	576	937	0.564	0.0146
	Total								0.4777
16	Ideal	0.347	0.404	5.91	28.27	560	937	0.564	0.5640
	1	0.440	0.468	7.99	8.64	600	958	0.563	0.1536
	2	0.407	0.407	6.21	7.07	548	925	0.562	0.1398
	3	0.256	0.309	2.19	5.50	276	599	0.003	0.0007
	4	0.203	0.374	2.77	3.93	406	816	0.187	0.0273
	5	0.339	0.430	6.52	2.36	593	959	0.564	0.0449
	6	0.495	0.434	8.94	0.79	574	937	0.563	0.0149
	Total								0.3811

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Figure 55. EFFECT OF FINES CONCENTRATION ON CALCULATED OIL YIELD

in mining or in sizing. Therefore, a moving-packed-bed retort processing no fines would utilize only 80 tons of this material. However, a retort processing shale containing 16% fines would process 96 tons of the material.

The results of the calculation are shown in Table 48. The results indicate that, in general, it is better to operate with no or reduced fines in the retort rather than with a high fines concentration. The reduction in the oil yield reduces the amount of kerogen converted to oil more than the increased use of fines increases the amount of oil product. Therefore, it appears that if the type of solids feeder used in this study is used to distribute shale to a retort, the fines should not be processed in the retort. However, if a solids feeder could be developed which distributed the fines evenly over the entire retort surface, fines could (and probably should) be processed in the retort. In the last column of Table 48, the calculated amount of oil produced (assuming perfect mixing of the fines throughout the shale) is shown. This value increases with increasing fines concentration in the retort.

Table 48. OIL PRODUCED AS A FUNCTION OF FINES CONCENTRATION
BASIS: 100 TONS OF 20-WEIGHT-PERCENT-KEROGEN SHALE

Fines Concentration, wt %	Shale Processed, tons	Fractional Yield, (-)	Kerogen In Shale, tons	Oil Produced, tons	Oil Produced, Ideal Case, tons
4	84	0.550	16.8	9.24	9.5
7	87	0.436	17.4	7.60	9.8
10	90	0.478	18.0	8.60	10.2
16	96	0.381	19.2	7.30	10.8

Fines Carryover in the Off-Gas: The HYTORT moving-bed shale retort consists of three zones (Figure 56). At the top of the retort is the shale pre-heat zone where the raw feed shale is preheated by the gas flowing from the retort zone. The retort zone is where the actual reaction of the preheated shale with hydrogen occurs. Below the retorting zone is the shale cooldown zone where the hot shale from the retorting zone is cooled by countercurrent contacting with the cool feed gas.

In the Hot-Top type of retort design, the gas from the top of the retorting zone is removed from the retort and cooled to condense oil vapors from the

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Figure 56. SCHEMATIC DRAWING OF RETORT ZONES IN MOVING-BED HOT-TOP DESIGN

gas. The removal of the oil vapors prevents refluxing of oil in the preheat zone as the off-gas is cooled. The cooled gas is then reheated and reinjected back to the bottom of the preheat zone.

There is much uncertainty about the amount and size distribution of the solids that will be carried out of the moving packed bed in the off-gas stream from the retorting zone in the Hot-Top design. This uncertainty impacts the design of the cyclone to remove the entrained solids from the off-gas stream. Therefore, a series of tests was conducted as part of the solids distribution tests, to determine the carryover rate and the particle-size distribution of the entrained solids in the off-gas stream from the retorting zone. The tests were designed to determine solids carryover rate as a function of 1) the concentration of fines in the shale, and 2) the superficial gas velocity through the shale bed. Solids carryover rates were measured at four fines concentrations in the shale bed: 2.35%, 6.3%, 9.8%, and 15.6% by weight. These concentrations were referred to nominally as 3%, 7%, 10%, and 16% by weight, respectively. The tests at the fines concentrations of 7%, 10%, and 16% were conducted at a superficial gas velocity through the bed of approximately 0.74 ft/s. The superficial gas velocity used in the 3% fines test was 0.83 ft/s. To determine the effect of superficial gas velocity on the solids carryover rate, additional tests at superficial gas velocities of 0.67 and 0.56 ft/s were conducted at the fines concentration of 10% by weight.

A schematic drawing of the gas draw-off system used in the investigation is shown in Figure 45. Shale entrainment-rate measurements were made by separating solids from the exit gas stream which was routed through a gas collector located approximately 15 feet above the air inlet nozzles. The gas collector consisted of four 2-inch-diameter pipe nozzles directed downward, with a 6-inch-diameter by 2-inch-diameter bell-shaped reducer on the end of each nozzle.

The entrained solids stream passed through the gas collector and then through an air plenum which encircled the CFM test vessel. The cyclone was a powered type which used a solids-handling blower on the air outlet to draw dust-laden air through it. The separated solids were collected in a 55-gallon drum placed directly below the cyclone. The air flow rate through the cyclone was determined by averaging several pressure-drop readings from a pitot tube located in the cyclone discharge line.

A typical entrainment-rate test consisted of 1) establishing a solids recirculation rate of 30 tons/h through the CFM, 2) quickly setting the air flow to its desired rate, 3) turning on the cyclone blower, 4) recording the pitot tube pressure-drop readings after the static pressure in the shale bed had been stabilized, and 5) quickly stopping the air flow through the CFM and cyclone after the desired time interval. The total shale entrainment rate was taken to be the sum of the material collected by the cyclone and the filter bags located downstream of the cyclone. Multiple determinations of the shale entrainment rate were made at each fines concentration. The average of the multiple measurements was taken as the actual shale entrainment rate.

The maximum solids-flow rate attainable with the solids recirculation system was 40 tons/h. Therefore, in order to not operate the system at its limit in all tests, a solids flow rate of 30 tons/h was selected as the solids flow rate in all of the tests. This corresponded to a mass flux of 2123 lb/s-ft^2 through the CFM.

The gas used in all of the entrainment tests was air. The gas in a commercial retort would be essentially hydrogen. At a retort temperature of 1100°F and a pressure of 600 psig (the approximate conditions in the retorting zone), the density and viscosity of hydrogen are essentially the same as that of air at 70°F and 0 psig (the conditions under which the entrainment tests were conducted). This is shown in Table 49. Therefore, the shale carryover rates measured in the tests should be what would be expected in the hot retort at the same actual superficial gas velocity.

Table 49. DENSITIES AND VISCOSITIES OF HYDROGEN AND AIR

<u>Gas</u>	<u>Temperature, °F</u>	<u>Pressure, psig</u>	<u>Density, lb/ft³</u>	<u>Viscosity, lb/ft-h</u>
Air	70	0	0.075	0.044
Hydrogen	1100	600	0.073	0.044

The effect of fines concentration on the entrainment rate from the moving packed bed is shown in Figure 57. The shale carryover rate was found to increase dramatically with fines concentration up to nominal fines concentration of 10%, and then level off. The flattening in the curve above the fines concentration of 10% is probably due to the fact that the gas had reached its

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Figure 57. THE EFFECT OF FINES CONCENTRATION ON SHALE ENTRAINMENT RATE

carrying capacity saturation for solids of that size. If so, a higher gas velocity would result in a significant increase in the carryover rate at those fines concentrations.

As is indicated in the figure, the gas velocity used for the 7%, 10%, and 16% nominal fines concentration tests was maintained constant at 0.74 ft/s. However, for the 3-percent-fines-concentration test, the superficial gas velocity through the CFM was 0.83 ft/s. This resulted from the fact that the maximum flow of gas was used in each test. The 3% nominal fines concentration test was the first one made and the maximum gas flow in the unit resulted in a superficial gas velocity of 0.83 ft/s. At the higher fines concentrations, the pressure drop through the system increased and resulted in a decrease in the maximum gas flow possible in the system.

The maximum shale entrainment rate measured in these tests was approximately 47.5 lb/min, or 2850 lb/hr. This corresponded to approximately 4.8% of the shale flowing through the bed. This is a relatively high number, and indicates that shale carryover could be a potential problem for the Hot-Top design.

The effect of gas velocity on the shale entrainment rate in the system is shown in Figure 58.. In this figure, the shale entrainment rate is plotted as a function of superficial gas velocity through the shale bed with a nominal fines concentration of 10%. Three gas velocities (0.74, 0.67, and 0.56 ft/s) were used in this test. As expected, it was found that the shale carryover rate increased with increasing gas velocity. Also indicated in Figure 58 is the gas velocity at the entrance of the 6-inch-diameter "bells" at the bottom of the gas collector. For superficial gas velocities of 0.74, 0.67, and 0.56 ft/s, the entrance velocities to the gas collector were 24.7, 22.7, and 19.0 ft/s, respectively. These entrance or "pick-up" velocities correspond to terminal velocities for particles of 0.2, 0.17, and 0.132 inches in size. Some particle sizes in the cyclone catch were even larger than this (as much as 0.5 inches) although the particles were generally elongated and flat. With this shape, the particle shape factor would be approximately 0.5, resulting in a much smaller effective particle size. Thus, the results seem to be consistent with theory.

The entrainment rate of the shale decreased rapidly with a decrease in superficial gas velocity in the bed. At a superficial gas velocity of

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Figure 58. THE EFFECT OF GAS VELOCITY ON SHALE ENTRAINMENT RATE

0.74 ft/s, the shale carryover rate was approximately 47.5 lb/min. At the lowest superficial gas velocity (0.56 ft/s), the shale carryover rate was only about 2 lb/min. Thus, there was a decrease in the shale carryover rate by a factor of over 23, when the gas velocity was only decreased by about 30%. The particle-size distribution of the cyclone catch also varied greatly with gas velocity. The particle-size distributions of the cyclone catch for the tests with a nominal 10% fines concentration and different superficial gas velocities are shown in Table 50. As can be seen in the table, the particle-size distribution of the cyclone catch for the 0.56-ft/s test was much smaller than the particle-size distribution of the cyclone catches for the other two test velocities. The reason for this is not entirely clear. Perhaps it is related to the actual gas velocity profile at the entrance to the gas collectors. More research needs to be conducted to determine the actual mechanism of shale entrainment from such a bed. However, it is evident that unless the gas velocity is reduced, substantial shale carryover can occur from a shale bed of this particle size — especially if the fines concentration in the bed is significant.

Table 50. PARTICLE SIZE DISTRIBUTIONS OF CYCLONE CATCH MATERIAL AS A FUNCTION OF SUPERFICIAL GAS VELOCITY

Gas Velocity, ft/s	0.74	0.67	0.56
Size	<u>Wt %</u>	<u>Wt %</u>	<u>Wt %</u>
+1/2 inch	0.9	0.4	--
+1/4 inch	22.3	15.8	0.1
+1/8 inch	37.7	40.2	0.5
+10 mesh	12.3	16.3	3.5
+20 mesh	13.0	13.9	10.2
+40 mesh	6.6	6.4	17.5
+80 mesh	4.3	3.9	32.1
+200 mesh	2.2	2.0	27.9
Pan	1.0	1.1	8.2

The shale carryover rate can obviously be reduced if the velocity through the gas collectors is reduced. This can be accomplished by increasing the number of collectors, or by increasing the diameter of the "bell" on the end of a collection nozzle. These improvements either increase the amount, or the size, of the internals in a retort, both of which are not desirable. However, just adding one more gas collector would decrease the gas velocity through each gas collector by 20%. This would have resulted in a gas velocity of

0.8 (0.74 ft/s) = 0.59 ft/s in this study. If this had been done, the predicted carryover would have been reduced tremendously — from 47.5 to about 5 or 6 lb/min from the curve shown in Figure 58. This amount of decrease in the entrainment rate would appear to be a good trade-off for the relatively small amount of increased steel required in the retort.

Fines Migration: The tests described above have shown the effect of increasing fines concentration on gas distribution in the bed, and its resulting effect on oil yield. However, it is possible that another problem related to fines movement in the bed may occur. If fines can move through the bed through the interstices of the larger particles, it may be possible for them to preferentially migrate laterally to one spot in the bed. If this would occur, gas channeling may result, leading to "cold" and "hot" spots in the retorting zone. This would also lead to a decrease in the oil yield in the retorting zone.

A test to determine whether an accumulation of fines would stay in one relative location as solids move through the bed, or whether the fines would migrate laterally, was conducted. The test was carried out by first "doping" a region of the bed with shale containing a high concentration of fines. The shale was then drawn down at a rate of approximately 30 tons/h with gas flowing through the bed, until the high-fines region was at the level of the solids sampler. The distribution of solids across the bed was then determined by particle-size analysis of the shale taken from the solids sampler.

In the actual test, a pocket of material containing 30% by weight of fines was placed near the surface of the shale bed. The shale outside of the high-fines region had a fines concentration of approximately 4% by weight. A schematic drawing of the position and configuration of the fines "pocket" is shown in Figure 46. The "pocket" was approximately 6 feet long, and extended 2 feet away from the wall at its midpoint. The "pocket" was oriented symmetrically about the solids sampler.

The shale was then drawn down a distance of 32 feet at a rate of approximately 30 tons/h, with gas flowing through the bed at a superficial velocity of 1.1 ft/s. The gas flow profile at the top of the bed, measured with the anemometers, indicated that the gas profile was stable and that the gas flow through the fines "pocket" was only approximately one-third of that through the remainder of the bed.

No measurable movement of the fines out of the "pocket" was noted. This can be seen in Figure 59. In this figure, the fines concentration across the bed (obtained from 12 samples) was essentially flat at approximately 4% except for the "pocket" region. The concentration of fines in the high-fines region was essentially the same as the concentration of fines in the original doped material. Only a minor decrease in fines concentration at the interface of the high-fines region was measured. Thus, it would appear that lateral fines migration in the moving packed-bed is minimal, and that the fines concentration profile imposed at the top of the bed will be the profile occurring at the bottom of the bed.

Conclusions and Recommendations

1. The existing solids feeder configuration in the CFM produced an average particle-size distribution profile which had a "W" shape, with larger material at the walls and the center of the bed, and smaller material directly under the solids distribution cone.
2. The measured gas-velocity profile also had a "W" shape, with higher gas flows measured at the walls and at the center of the bed (where the particle-size distribution was large) and lower gas flows measured directly under the solids distribution cone (where the particle-size distribution was small).
3. The spread between the minimum and maximum gas velocities in the "W" was greater for the higher fines concentrations tested.
4. Calculated oil yields obtained from measured particle-size and calculated gas-velocity profiles, showed that oil yield decreased with increasing fines concentration.
5. The decrease in oil yield with fines concentration was a result of the nonuniformity of the fines distribution in the bed.
6. The total amount of oil produced per ton of oil shale mined also decreased with increasing fines concentration. However, the total amount of oil produced per ton of oil shale mined would increase with fines concentration if the fines could be distributed uniformly throughout the bed. This would occur if a more effective solids distributor were used to feed the shale into the retort.
7. The entrainment rate of shale fines from the shale bed increased significantly with both fines concentration and gas velocity.
8. The maximum entrainment rate of oil shale amounted to approximately 4.8% of the material flowing through the CFM. This is a relatively high value and indicates that gas-collector design will be important in a Hot-Top retort operating with a relatively high fines concentration.

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Figure 59. FINES CONCENTRATION VERSUS DISTANCE
(Fines Migration Test)

9. Shale entrainment rates can be reduced by decreasing the gas velocity in the gas collectors. This can be accomplished by increasing the number of collectors and/or the diameter of the collectors.
10. Shale entrainment rates can also be reduced by locating the gas collectors in low-fines region of the retort.
11. Measurements indicated that lateral fines movement in moving-packed beds with countercurrent gas flow was minimal.
12. The model used to calculate oil yields could be refined further to more accurately reflect changing conditions in the retort.

Task 5. Sample Procurement

Objective: The objective of this task is to prepare samples for all the small-scale (laboratory-scale and mini-bench-scale) tests in this program from the six states that contain the Eastern Devonian oil shale resources. These states are Alabama, Indiana, Kentucky, Michigan, Ohio, and Tennessee.

Discussion: Shale samples were procured from Alabama, Indiana, Kentucky, Michigan, Ohio, and Tennessee. The Alabama shale was taken from a location in Madison County, Alabama, utilized by the Mineral Resource Institute (MRI) at the University of Alabama. The Indiana New Albany shale was available at run-of-mine (ROM) size at IGT from a previous test program. The Kentucky, Michigan, Ohio, and Tennessee shales were obtained from sites in Fleming County, Kentucky; Alpena County, Michigan; Delaware County, Ohio; and Putnam County, Tennessee.

The Alabama shale was obtained from MRI in a nitrogen-blanketed, 55-gallon, epoxy-lined drum. The entire contents of 500 pounds was crushed to size and screened for testing. Two drums of ROM size (approximately minus 8 inches) Indiana New Albany shale were crushed to minus 6 mesh through a Jodal impact crusher. Nearly 200 pounds of product were screened for testing. Approximately one 55-gallon drum (400 to 600 pounds) of each of the shales from Kentucky (Sunbury), Michigan (Antrim), and Ohio (Cleveland Member) was also crushed to minus 6 mesh through the impact crusher, screened, and stored in a nitrogen atmosphere prior to testing.

A 2-3/8 inch-diameter core-drilled sample of Tennessee Chattanooga shale obtained from Putnam County, Tennessee was utilized for testing. A split of the first core sample containing both Gassaway and Doweltown members was sent to Tennessee Technological University for storage and reference. The

remaining core samples contained only the Gassaway member that was utilized for testing. Approximately 320 pounds of crushed and screened Tennessee shale were prepared for testing. All samples used in this test program were crushed, screened, and stored in an inert atmosphere prior to testing.

A detailed discussion of sample and site selection is contained in the R. D. Matthews, Inc., report for sample procurement.

NOMENCLATURE

D_p = surface/mean volume particle size, in.

D_{p_i} = particle size of material collected between two adjacent mesh sizes, in.

D_{p_w} = weighted average particle size

X_i = weight fraction of material collected between two adjacent mesh sizes, dimensionless

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29WP/65072f13/RPP

APPENDIX A. Summary of Operating Conditions and Results
for Kentucky Sunbury HAU Tests

SUMMARY OF OPERATING CONDITIONS AND RESULTS FOR KENTUCKY SUNBURY HAU TESTS

Previously reported HAU data on oil yields and elemental conversions for the Kentucky Sunbury shale were revised; the revised data are included in this Appendix A and reflect a more representative feed shale composition.

HAU results and operating conditions as well as analyses of product solids, oils, and gases from hydrotretorting Kentucky Sunbury shale are presented in Tables A-1, A-2, and A-3.

The effect of hydrotretorting temperature on the oil yield from Kentucky Sunbury shale is shown in Figure A-1. Oil yield increases with increasing temperature at a given pressure and also increases with increasing pressure for the same temperature.

The effects of hydrotretorting temperature on the feed shale organic carbon, hydrogen, nitrogen, and sulfur conversions for the Kentucky Sunbury shale are shown in Figures A-2, A-3, A-4, and A-5, respectively. The effect of temperature on organic carbon conversion for three pressures, as presented in Figure A-2, shows that the organic carbon conversion increases with increasing temperature for a given pressure and conversion increases with increasing pressure for the same temperature. The effect of hydrotretorting temperature on the feed shale hydrogen conversion for three pressures, as shown in Figure A-3, indicates that hydrogen conversion increases with increasing temperature for a given pressure. The data points which were obtained at reactor pressures of 600 and 1000 psig appear reversed. One would expect the conversion at 1000 psig to be higher than the conversion at 800 psig for the same temperature, and likewise, one would expect the conversion at 600 psig to be lower than the conversion at 800 psig for the same temperature. The effect of hydrotretorting temperature on feed shale nitrogen conversion for Kentucky Sunbury shale, shown in Figure A-4, indicates that for 400 and 800 psig, the conversion increases with increasing temperature. The effect of hydrotretorting temperature on the feed shale sulfur conversion of Kentucky Sunbury shale shown in Figure A-5, shows no effect of temperature in the range of 900° to 1200°F and no effect of pressure at 400 and 800 psig. The data indicate a slightly lower feed shale sulfur conversion for operation at 1000°F and 1000 psig and an anomalously low conversion (approximately 14.5%) for operation at 950°F and 600 psig.

Sour water yields as a function of temperature for three pressures for the Kentucky Sunbury shale are shown in Figure A-6. The sour water yield increases slightly with temperature but does not show any effect of pressure for the ranges investigated. The product water obtained from hydroretorting comes from moisture that was present in the feed shale and high-temperature water product that is derived during retorting. This high-temperature water may be generated by the dehydration of mineral compounds or may come from oxygen in the shale reacting with the hydrogen. Moisture in the feed shale from Kentucky accounts for approximately 15 gallons per ton of the total sour water yield.

The effect of hydroretorting temperature on the calorific value of the spent shale from the Kentucky Sunbury shale is shown in Figure A-7. The data show, as expected, that the gross calorific value of the shale decreases with increasing temperature at a given pressure and the calorific value decreases with increasing hydrogen pressure at a given temperature.

Table A-1. ANALYSES OF KENTUCKY SHALE FEED AND PRODUCTS FROM HAU HYDRORETORTING TESTS

Run Identification	Feed	122872	12387	12687	12887	12987	13087	20287	120487
Maximum Temperature, °F	--	899	1050	1214	1002	1054	903	1209	957
Pressure, psig	--	402	402	401	999	801	797	808	591
Proximate Analysis Moisture, wt %	5.89	0.03	0.08	0	0.14	0.08	0.14	0	0.26
Ultimate Analysis, wt % (dry basis)									
Ash*	82.34	92.00	93.40	95.03	94.64	95.07	93.07	96.69	93.17
Organic Carbon	9.65	4.66	4.14	3.72	2.96	3.13	3.80	2.61	3.91
Mineral Carbon	0.01	--	--	--	--	--	--	--	--
Hydrogen	1.14	0.55	0.38	0.23	0.41	0.33	0.47	0.19	0.38
Sulfur	1.20	1.03	1.05	1.07	1.09	1.07	1.05	1.08	1.16
Nitrogen	0.51	0.24	0.17	0.11	0.07	0.07	0.14	0.06	0.34
Gross Calorific Value, Btu/lb	1672	783	670	596	481	481	635	416	649
Shale Oil Ultimate Analysis, wt %									
Carbon	--	85.45	85.45	83.50	86.86	87.25	86.70	86.60	--
Hydrogen	--	9.60	9.68	9.41	9.79	9.81	9.61	9.62	--
Sulfur	--	1.12	1.03	1.09	1.14	1.05	1.11	0.97	1.06
Nitrogen	--	1.87	1.68	1.83	1.72	1.41	1.73	1.78	1.80
Ash	--	0	0	0	0	0	0	0	0
Oxygen (by difference)	--	1.96	2.16	4.17	0.49	0.48	0.85	1.03	--
Total	--	100.00	100.00	100.00	100.00	100.00	100.00	100.00	--
C/H Ratio	--	8.90	8.83	8.87	8.87	8.89	9.02	9.00	--
Specific Gravity (60/60°F), gm/mL	--	0.938	0.988	0.997	0.975	0.976	0.977	0.982	1.01
Gravity, °API	--	11.7	11.7	10.4	13.6	13.5	13.3	12.6	8.6

*Oxygen is present as mineral oxides and high-temperature water included as ash; because the high-temperature (925°C) ashing procedure alters the composition of mineral matter existing in the original raw shale, e.g., the conversion of CaCO_3 plus pyrites to CaSO_4 and Fe_2O_3 , the sum of the elements may exceed 100%.

Table A-2. HAU RESULTS AND CONDITIONS FROM HYDRORETORTING KENTUCKY SHALE

Run Identification	122872	12387	12687	12887	12987	13087	20287	120487
Maximum Temperature, °F	899	1050	1214	1002	1054	903	1209	957
Pressure, psig	402	402	401	999	801	797	808	591
Heat-Up Rate, °F/min	21.1	23.4	25.1	23.1	23.9	22.2	25.4	22.1
Shale Feed, gm	100.68	100.51	100.28	100.72	100.87	92.90	100.68	99.58
Shale Residue, gm	82.51	81.29	80.37	80.29	80.01	74.81	78.75	81.50
Hydrogen Feed, SCFH	3.92	3.92	3.92	3.93	3.93	3.93	3.93	4.02
Component Conversions, ^a % of Feed Shale								
Total Carbon	56.8	62.2	66.6	73.3	71.9	65.2	77.0	64.2
Organic Carbon	56.8	62.2	66.6	73.3	71.9	65.2	77.0	64.2
Hydrogen	56.8	70.6	82.5	68.7	74.9	63.5	85.8	70.5
Sulfur	23.2	22.9	22.7	21.0	22.8	22.6	23.4	14.6
Nitrogen	57.9	70.6	81.3	88.1	88.1	75.7	90.0	41.1
Spent Shale Gross Calorific Value, ^b Btu/lb								
	783	670	596	481	481	635	416	649
Recovered Oil Yield, lb/lb ^c								
Recovered Oil Yield, GPT ^c	0.054	0.054	0.055	0.061	0.058	0.053	0.064	0.054
	13	13	13	15	14	13	16	13
Reconciled Oil Yield, lb/lb ^d								
Reconciled Oil Yield, GPT ^d	0.055	0.059	0.062	0.075	0.073	0.067	0.079	0.067
	13	14	15	18	18	16	19	16
Water Yield, GPT ^e								
	28.6	28.9	34.3	32.4	32.3	15.9 ^f	33.4	25.3

^aElemental conversions based on solids ash balance.

^bFeed shale gross calorific value is 1672 Btu/lb.

^cRecovered yields based on laboratory data (dry feed shale basis).

^dDry shale basis. Carbon balance adjusted to 100% by adding 15% (relative) carbon to gas phase and then the rest to oil. This method gives a conservative oil yield.

^eWater not analyzed for NH₃, H₂S, CO₂ or hydrocarbons. Moisture accounts for 15.0 GPT of total.

^fWater yield is low based on feed moisture content. Feed shale sample probably dried before this test.

Table A-3. HAU PRODUCT GAS COMPOSITION FROM HYDRORETORTING KENTUCKY SHALE

Run Identification	<u>122872</u>	<u>12387</u>	<u>12687</u>	<u>12887</u>	<u>12987</u>	<u>13087</u>	<u>20287</u>	<u>120487</u>
Maximum Temperature, °F	899	1050	1214	1002	1054	903	1209	957
Pressure, psig	402	402	401	999	801	797	808	591
Composition,* mol %								
Carbon Dioxide	45.4	31.1	18.0	25.3	18.3	28.1	29.2	37.3
Carbon Monoxide	4.6	2.2	2.9	2.3	2.2	5.3	0	13.5
Methane	24.1	35.7	49.5	42.7	46.0	35.0	9.2	27.0
Ethane	11.1	13.3	15.7	17.2	19.4	10.5	37.0	11.5
Ethene	0	2.2	1.2	1.1	1.1	1.8	3.1	0
Propane/Propene	8.3	7.8	5.2	8.0	9.7	12.3	12.3	6.7
Butane/Butenes	3.7	4.4	5.2	2.3	2.2	3.5	4.6	2.0
C ₅ ⁺	<u>2.8</u>	<u>3.3</u>	<u>2.3</u>	<u>1.1</u>	<u>1.1</u>	<u>3.5</u>	<u>4.6</u>	<u>2.0</u>
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

*Hydrogen- nitrogen- and helium-free basis. Detection limit approximately 0.5%.

BDL = Below detection limit.

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Figure A-1. THE EFFECT OF HYDRORETORTING TEMPERATURE ON THE OIL YIELD FROM KENTUCKY SHALE

Figure A-2. THE EFFECT OF HYDRORETORTING TEMPERATURE ON THE FEED ORGANIC CARBON CONVERSION FOR KENTUCKY SHALE

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Figure A-3. THE EFFECT OF HYDRORETORTING TEMPERATURE ON THE FEED HYDROGEN CONVERSION FOR KENTUCKY SHALE

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Figure A-4. THE EFFECT OF HYDRORETORTING TEMPERATURE ON THE FEED NITROGEN CONVERSION FOR KENTUCKY SHALE

Figure A-5. THE EFFECT OF HYDRORETORTING TEMPERATURE ON THE FEED SULFUR CONVERSION FOR KENTUCKY SHALE

Figure A-6. THE EFFECT OF HYDRORETORTING TEMPERATURE ON THE SOUR WATER YIELD FOR KENTUCKY SHALE

Figure A-7. THE EFFECT OF HYDRORETORTING TEMPERATURE ON THE HEATING VALUE OF SPENT KENTUCKY SHALE

APPENDIX B. Summary of Operating Conditions and Results
for Indiana New Albany BSU Test, 87BSU-3

BENCH-SCALE OPERATING CONDITIONS AND TEST RESULTS —
COUNTERCURRENT MOVING-BED OPERATION WITH EASTERN SHALE

Oil Shale Type	New Albany
Source	Indiana
Oil Shale Particle Size (U.S. Sieve)	-6+20
Run No.	87BSU-3
Test Duration, hrs	3.10
Total Shale Feed Time, hrs	3.10
Steady-State Operating Period, hrs	1.00
<u>Operating Conditions</u>	
Bed Height, ft	6.0
Shale Preheat Height, ft	3.5
Reactor Pressure, psig	594
Average Bed Temperature, °F ^a	
Zone 1	630
Zone 2	683
Zone 3	720
Zone 4 Bed Level →	747
Zone 5	896
Zone 6	1079
Zone 7	986
Oil Shale Feed Rate, lb/h ^b	86.0
Oil Shale Space Velocity, lb/ft ³ -h	162
Oil Shale Residence Time, min ^c	29.3
Hydrogen Feed Gas Rate, SCF/h ^d	1108
Feed Gas Superficial Velocity, ft/s ^e	0.25
Feed Gas Residence Time, s ^f	9.7
Hydrogen/Oil Shale Ratio, SCF/lb shale fed ^j	13.2
Shale Feed Hopper Purge Rate, SCF/h	260
Total Hydrogen Feed Gas Rate, SCF/h	1355
Helium Tracer Gas Rate, SCF/h	70.0

See NOTES on page B-5.

BENCH-SCALE OPERATING CONDITIONS AND TEST RESULTS --
COUNTERCURRENT MOVING-BED OPERATION WITH EASTERN SHALE

Run No.	----- 87BSU-3 -----	
Test Results	Residue Weight By Weight Measurement	Residue Weight By Ash Balance
Product Gas Rate (as measured), SCF/h ^m		1333
Product Gas Rate, SCF/h ^{g,m}		1016
Product Gas Yield, SCF/lb Shale Fed ^{g,j,m}		12.1
Residue Shale Rate, lb/h	72.73	71.29
Residue Shale Yield, lb/lb Shale Fed ^b	0.845	0.829
Product Oil Rate, lb/h ^h		7.15
Product Oil Yield, lb/lb Shale Fed ⁱ		0.0849
Product Oil Yield, gal/ton ⁱ		20.6
Product Water Rate (as measured), lb/h ^s		4.50
Water Product Rate, lb/h ⁿ		4.25
Water Product Yield, lb/lb Shale Fed ^j		0.0504
Water Product Yield, gal/ton ^j		12.1
Organic Carbon Distribution in Products, %		
Gaseous Hydrocarbons		15.2
Liquid Products		58.6
Solids Residue	<u>25.4</u>	<u>24.9</u>
Total	99.2	98.7
Overall Material Balance, %	102.0	100.5
Total Carbon Balance, %	102.1	101.5
Hydrogen Balance, %	97.2	97.1
Oxygen Balance, % ^k	140.7	139.3
Sulfur Balance, %	96.9	95.9
Nitrogen Balance, % ^t	90.5	89.9
Selectivity to Oil, % ^q		79.4

See NOTES on page B-5.

NOTES

- a. Outer tube wall temperature, averaged values.
- b. Measured on a "wet" basis, i.e., includes moisture.
- c. Based on feed shale bulk density.
- d. Excluding He tracer flow and excluding purge gas flow.
- e. At maximum reactor bed temperature, including helium tracer gas.
- f. Based on void fraction calculated from feed shale bulk density.
- g. On a nitrogen- and helium-free, and purge-free basis.
- h. On a water-free and solids-free basis.
- i. Product oil on a water-free and solids-free basis; shale on moisture-free basis.
- j. On a dry shale basis.
- k. Based on revised analytical oxygen measurement technique and includes O₂ as HTW and CO₂.
- l. Calculated, based on exit gas rate minus purge gas rate, on a nitrogen-free basis.
- m. Gross, gas saturated at 60°F, 30-in. Hg pressure. SCF; dry gas volume in SCF at 60°F, 30-in. Hg pressure.
- n. Excluding the dissolved gases in the water.
- o. Hydrogen.
- p. Based on gas meter readings.
- q. Selectivity defined as
$$\frac{\text{Carbon} + \text{Oil}}{\text{carbon to oil} + \text{carbon to gas}} \times 100$$
- r. Moisture from Fischer Assay Report.
- s. Includes dissolved gases, CO₂, H₂S, and NH₃.
- t. Only bound nitrogen in feed shale is used for total nitrogen fed. Free nitrogen is assumed to be inert.

BENCH-SCALE OPERATING CONDITIONS AND TEST RESULTS --
COUNTERCURRENT MOVING-BED OPERATION WITH EASTERN SHALE

Run No.	87 BSU-3			
	Feed Gas	Product Gas*		
		As Metered	H ₂ S Adj.	N ₂ & He Free
Gas Composition, mol %				
Hydrogen Sulfide		1.26	1.26	1.33
Nitrogen		0.00	0.00	0.00
Carbon Monoxide		0.22	0.22	0.23
Carbon Dioxide		0.39	0.39	0.41
Hydrogen	95.11	91.01	91.01	95.96
Helium	4.89	5.16	5.16	0.00
Methane		1.12	1.12	1.18
Ethane		0.34	0.34	0.36
Propane		0.13	0.13	0.14
n-Butane		0.06	0.06	0.06
Iso-Butane		0.00	0.00	0.00
Pentanes		0.03	0.03	0.03
Hexanes		0.11	0.11	0.12
Heptanes				
Ethylene		0.06	0.06	0.06
Propylene		0.06	0.06	0.06
Butene		0.05	0.05	0.05
Pentene		0.00	0.00	0.00
Hexene				
Heptene				
Butadiene				
Pentadiene				
Cyclopentadiene				
Acetylene				
M. Acet./Propadiene				
Benzene				
Toluene				
Xylene				
Ethyl Benzene				
Styrene				
Total		100.00	100.00	100.00
Specific Gravity (Air = 1.00)	0.073	0.113	0.113	0.111

* Since the product gas was analyzed by a gas chromatograph, the as-metered and H₂S adjusted compositions are the same. When the product gas is analyzed by the mass spectrograph, an adjustment for the concentration of sulfur species in the product is usually necessary.

ANALYSES OF EASTERN SHALE FEED AND RESIDUE — BENCH-SCALE TEST

Run No.	87BSU-3	
Sample	Feed	Residue
Lab No.	870701506	870701507
Moisture, wt %	2.11	0.00
Modified Ultimate Analysis	Wt % Feed (dry basis)	Residue
Ash	78.47	92.71
HTW in Ash	0.41	0.64
MOX Oxygen in Ash	2.73	3.74
Residual Mineral Oxides	75.33	88.33
Organic Carbon	12.33	3.63
Organic Hydrogen	1.09	0.19
Sulfur	4.06	2.36
Nitrogen	0.43	0.17
Carbon Dioxide	1.20	1.50
High Temperature Water	3.88	1.79
MOX Oxygen	0.87	1.70
Oxygen (by difference)	0.81	2.12
Total	100.00	100.00
Screen Analysis, U.S. Sieve, wt %		
3	0.0	0.0
6	0.0	0.0
12	47.4	57.4
20	46.9	35.2
30	4.5	3.8
40	0.8	1.0
Pan	0.4	2.6
Total	100.0	100.0
Gross Heating Value, Btu/lb	2437	725
Bulk Density, lb/ft ³	79.2	66.8
Helium Density, g/cc	2.28	2.65
Mercury Density, g/cc	2.11	1.72

LIQUID PRODUCT PROPERTIES — BENCH-SCALE TEST WITH EASTERN SHALE

Run No.	87BSU-3
Lab No.	
Ultimate Analysis, wt % (dry and solids-free basis)	
Carbon	85.11
Hydrogen	9.96
Sulfur	1.37
Nitrogen	1.92
Ash	0.00
Oxygen (by difference)	1.64
C/H Weight Ratio	8.54
Viscosity, SSU at 100°F	123.5
Specific Gravity (60/60°F)	0.986
API Gravity, °API	12.1
Distillation, °F	
IBP	200
5%	296
10%	344
20%	438
30%	522
40%	602
50%	658
60%	696
70%	718
80%	739
90%	--
95%	--
End Point	742
% Recovery	83.0
% Residue	15.5
Heating Value, Btu/lb	16,680
Pour Point, °F	-40
Sour Water Analysis, wt %	
Carbon	0.53
Nitrogen	1.49
Sulfur	1.72

ELEMENTAL DISTRIBUTIONS FOR 87BSU-3, Part 1

Element	Inlet		Outlet (by ash)		Outlet (adjusted)	
	lb/h	%	lb/h	%	lb/h	%
Total Carbon						
Raw Shale	10.663	100.0	--	--	--	--
Spent Shale	--	--	2.880	27.0	2.880	27.0
Hydrocarbon Gas	--	--	1.582	14.8	1.621	15.2
Carbon Oxides	--	--	0.258	2.4	0.258	2.4
Dissolved Gas in Sour Water	--	--	0.024	0.2	0.024	0.2
Product Oil	--	--	6.083	57.1	5.880	55.2
Total	10.663	100.0	10.827	101.5	10.663	100.0
Hydrogen						
Raw Shale (dry basis)	1.280	14.7	--	--	--	--
Moisture	0.203	2.3	--	--	--	--
Feed Gas	7.196	83.0	--	--	--	--
Spent Shale	--	--	0.278	3.2	0.278	3.2
Product Gas	--	--	6.944	80.0	7.218	83.2
Product Oil	--	--	0.712	8.2	0.688	7.9
Dissolved Gas in Sour Water	--	--	0.019	0.2	0.019	0.2
Product Water	--	--	0.476	5.5	0.476	5.5
Total	8.679	100.0	8.429	97.1	8.679	100.0
Oxygen						
Raw Shale	5.053	75.8	--	--	--	--
Moisture	1.612	24.2	--	--	--	--
Spent Shale	--	--	4.634	69.5	2.016	30.2
Product Gas as Carbon Oxides	--	--	0.699	10.5	0.699	10.5
Dissolved Gas in Sour Water	--	--	0.064	1.0	0.064	1.0
Product Water	--	--	3.773	56.6	3.773	56.6
Product Oil	--	--	0.117	1.8	0.113	1.7
Total	6.665	100.0	9.287	139.4	6.665	100.0
Sulfur						
Raw Shale	3.420	100.0	--	--	--	--
Spent Shale	--	--	1.682	49.2	1.682	49.2
Product Gas	--	--	1.423	41.6	1.566	45.8
Product Oil	--	--	0.098	2.9	0.095	2.8
Dissolved Gas in Sour Water	--	--	0.077	2.2	0.077	2.2
Total	3.420	100.0	3.280	95.9	3.420	100.0

ELEMENTAL DISTRIBUTIONS FOR 87BSU-3, Part 2

<u>Element</u>	<u>Inlet</u>		<u>Outlet (by ash)</u>		<u>Outlet (adjusted)</u>	
	<u>lb/h</u>	<u>%</u>	<u>lb/h</u>	<u>%</u>	<u>lb/h</u>	<u>%</u>
Nitrogen						
Raw Shale	0.362	100.0	--	--	--	--
Spent Shale	--	--	0.121	33.4	0.162	44.8
Product Oil	--	--	0.137	37.9	0.133	36.7
Dissolved Gas in Sour Water	--	--	0.067	18.5	0.067	18.5
Total	0.362	100.0	0.325	89.8	0.362	100.0

COMBINED HYDROGEN DISTRIBUTION

<u>Appearance of Combined Hydrogen</u>	<u>Outlet (by ash)</u>		<u>Outlet (adjusted)</u>	
	<u>lb/h</u>	<u>%</u>	<u>lb/h</u>	<u>%</u>
Product Gas (HC + H ₂ S)	0.482	32.4	0.504	34.0
Product Oil	0.712	47.9	0.688	46.3
Dissolved Gas in Sour Water	0.019	1.3	0.019	1.3
Net Product Water (total product water - feed moisture)	0.273	18.4	0.273	18.4
Total	1.486	100.0	1.484	100.0

BENCH-SCALE UNIT STATISTICAL ANALYSIS DATA FOR 87BSU-3

DEPENDENT VARIABLES

Hydrogen Consumption, SCF/ton	2150
Oil Yield, gal/ton	
Measured	20.6
Reconciled	19.9
Oil Properties	
Pour Point, °F	-40
API, @ 60°F	12.1
C/H Ratio	8.54
S, wt %	1.37
N, wt %	1.92
Viscosity, SUS	123.5
Distillate Fractions Temperature, °F	
10% -	344
50% -	658
80% -	739
Organic Carbon Conversion, % (adjusted by ash balance)	75.1
Selectivity to Oil, % (adjusted)	79.4
Hydrocarbon Gas Yield, MM Btu/ton (methane equivalent - adjusted)	1.23
Percent Organic Carbon to Gas, %	15.6
Oil, %	59.5
Residue, %	24.9
Percent Sulfur to Gas, %	48.0
Oil, %	2.8
Residue, %	49.2
Water Production, lb/h	4.25
Water Production, lb/h (less shale moisture)	2.43

INDEPENDENT VARIABLES

Maximum Bed Temperature, °F	1079
Run Type (high, center, low)	--
Total Pressure, psia	609
Hydrogen Partial Pressure, psia	540
Run Type (high, center, low)	--
Shale Residence Time, min	29.3
Run Type (high, center, low)	--

METHOD AND SEQUENTIAL STEPS USED FOR ADJUSTING
MATERIAL BALANCE FOR RUN 87BSU-3

1. Based on previous experience and data from operation of the Flash Gas (FG) system and the Freeze-Out (Cold Finger [CF] apparatus), approximately 0.1 to 0.15 weight percent of carbon is lost in the FG during liquid draining and 0.2 to 0.25 weight percent of carbon (mainly C₇, C₈, C₉ and C₁₀) is not analyzed in the product gas. Therefore, the total carbon balance is first adjusted by adding approximately 0.4 weight percent carbon to the product gas stream as hydrocarbons; then —
2. After closing the total carbon balance by adjusting product oil make rate, then —
 - a. Adjust S balance in proportion to amount of oil added in 2.
 - b. Adjust N₂ balance in proportion to amount of oil added in 2.
 - c. Adjust O₂ balance in proportion to amount of oil added in 2.
 - d. Adjust H₂ balance in proportion to amount of oil added in 2.

(Assume that the lost or missing oil has the same ultimate analysis as that of the oil which was actually recovered and analyzed.)
3. After adjusting the product sulfur rate (based on the revised product oil rate), adjust the H₂S concentration in the product gas to close the sulfur balance. The greatest uncertainty for sulfur detection occurs in the analysis of the product gas.
4. After adjusting the product nitrogen (as combined nitrogen) rate (based on the revised product oil rate), adjust the nitrogen in the spent shale. Because the amount of nitrogen present in the spent shale is quite small, the relative error associated with its measurement may be quite large.
5. After adjusting the product oxygen rate based on the revised product oil rate, adjust the oxygen present in the spent shale. The two major sources of oxygen in the outlet streams are product water and oxygen in the spent shale. Although the moisture in the feed shale is only known to the nearest 0.1 weight percent (ASTM) and therefore has an uncertainty of 5% relative, the reported shale oxygen analysis has an uncertainty which is the sum of all the other uncertainties of analyses performed.
6. After adjusting the product hydrogen rate based on the reconciled product oil rate, on the revised H₂S product rate, and the estimated amount of hydrogen in the FG and CF systems, close the hydrogen balance by adjusting the "free" product hydrogen rate.

APPENDIX C. Summary of Operating Conditions and Results
for Indiana New Albany MBU Syngas Test, 88MBU-3

c-1/c-2

MINI-BENCH OPERATING CONDITIONS AND TEST RESULTS
COUNTER-CURRENT MOVING-BED OPERATION WITH EASTERN SHALE

Oil Shale Type	New Albany
Source	Indiana
Oil Shale Particle Size (U.S. Sieve)	-6+40
Run No.	88MBU-3
Run Date	2/11/88
Test Duration, h	4.75
Total Shale Feed Time, h	4.50
Steady State Operating Period, h	2.00
Bed Height, ft	1.67
Shale Preheat Height, ft	0.92
Reactor Pressure, psig	942.0
Average Bed Temperature, °F	
Zone 7 Bed Height -->	620
Zone 6	875
Zone 5	1035
Zone 4	1055
Zone 3	1075
Zone 2	1060
Zone 1	825
Oil Shale Feed Rate, lb/h	2.09
Oil Shale Space Velocity, lb/ft ³ -h	73.40
Oil Shale Residence Time, min	56.9
Syngas Feed Gas Rate, SCF/h	7.14
Hydrogen Feed Gas Rate, SCF/h	17.32
Feed water rate, lb/h	0.431
(Feed Syngas + Hydrogen + Steam) Superficial Velocity, ft/s	0.0208
(Feed Syngas + Hydrogen + Steam) Residence Time, s	31.4
(Syngas + Hydrogen + Steam)/ Oil Shale Ratio, SCF/lb Feed Shale	16.02
Feed Hopper Syngas Purge Rate, SCF/h	1.04
Total Feed + Purge Gas Rate, SCF/h	34.34

MINI-BENCH OPERATING CONDITIONS AND TEST RESULTS
COUNTER-CURRENT MOVING-BED OPERATION WITH EASTERN SHALE

Run No.	----- 88MBU-3 -----	
Test Results	Residue Weight by Weight Measurement	Residue Weight by Ash Balance
Product Gas Rate (as measured), ¹ SCF/h		29.00
Product Gas Rate, ¹ SCF/h		27.96
Product Gas Yield, ¹ SCF/lb Shale Fed		13.4
Residue Shale Rate, lb/h	--	1.714
Residue Shale Yield, lb/lb Shale Fed	--	0.820
Product Oil Rate, lb/h		0.1628
Product Oil Yield, lb/lb Shale Fed		0.0787
Product Oil Yield, gal/ton		19.8
Product Water Rate (as measured), lb/h		0.4905
water Product Rate, ² lb/h		0.0367
Water Product Yield, lb/lb Shale Fed		0.0178
Water Product Yield, gal/ton		4.3
Organic Carbon Distribution in Product,* %		
Gaseous Hydrocarbons		14.7
Liquid Products		52.0 <53.0>
Solid Residue	--	18.5
Total	-- < -->	85.2 <86.2>
Overall Material Balance, %	-- (--)	98.3 (98.3)
Total Carbon Balance	--	90.0
Hydrogen Balance	-- (--)	111.0 (110.5)
Oxygen Balance	--	99.5
Sulfur Balance	--	92.4
Nitrogen Balance	--	93.7
Selectivity to Oil, %		78.0 <78.3>

1 - Dry Basis.

2 - Feed water and Moisture Free.

Numbers in < > include organic carbon in water phase liquids.

Numbers in () indicate balances have been corrected for accumulated gases in new shale pores formed by hydroretorting.

*Based on organic carbon in the feed shale.

MINI-BENCH OPERATING CONDITIONS AND TEST RESULTS
COUNTER-CURRENT MOVING-BED OPERATION WITH EASTERN SHALE

Run No.	88MBU-3			
	Feed Gas*	Product Gas		
		(dry)	Metered	H ₂ S Adj.
Gas Composition, mol %				
Hydrogen Sulfide	0.00	1.66	1.66	1.67
Nitrogen	0.00	0.00	0.00	0.00
Carbon Monoxide	8.30	7.32	7.32	7.35
Carbon Dioxide	7.92	8.06	8.06	8.09
Hydrogen	81.04	77.67	77.67	78.00
Helium	0.43	0.42	0.42	0.00
Methane	2.24	3.86	3.86	3.88
Ethane	0.00	0.52	0.52	0.52
Propane	0.00	0.17	0.17	0.17
n-Butane	0.00	0.05	0.05	0.05
iso-Butane	0.00	0.00	0.00	0.00
Pentanes	0.00	0.03	0.03	0.03
Hexanes	0.00	0.03	0.03	0.03
Heptanes	0.00	0.00	0.00	0.00
Ethylene	0.00	0.08	0.08	0.08
Propylene	0.00	0.06	0.06	0.06
Butene	0.00	0.04	0.04	0.04
Pentene	0.00	0.00	0.00	0.00
Hexene	0.00	0.00	0.00	0.00
Heptene	0.00	0.00	0.00	0.00
Butadiene	0.00	0.00	0.00	0.00
Pentadiene	0.00	0.00	0.00	0.00
Cyclopentadiene	0.00	0.00	0.00	0.00
Acetylene	0.00	0.00	0.00	0.00
M. Acetylene/Propadiene	0.00	0.00	0.00	0.00
Benzene	0.00	0.00	0.00	0.00
Toluene	0.00	0.00	0.00	0.00
Xylene	0.00	0.00	0.00	0.00
Ethyl benzene	0.00	0.00	0.00	0.00
Styrene	0.00	0.00	0.00	0.00
Sulfur Compounds	0.00	0.00	0.00	0.00
Total	100.00	100.00	100.00	100.00

* Composition of dry synthesis gas only, does not include the 9.04 SCFH of added feed steam.

ANALYSES OF EASTERN SHALE FEED AND RESIDUE MINI-BENCH TEST

Run No.	88MBU-3	
Sample	Feed	Residue
Lab No.	880105401	880206401
Moisture	1.12	0.00

Modified Ultimate Analysis, wt % Dry Basis

Ash	77.10	93.00	
HTW in Ash	0.10	0.19	
MOX Oxygen in Ash	3.47	4.17	
Residual Mineral Oxides	74.42		88.79
Organic Carbon	12.94		2.89
Organic Hydrogen	1.10		0.11
Sulfur	4.80		2.87
Nitrogen	0.54		0.33
Carbon Dioxide	1.82		1.52
High-Temperature Water	3.24		1.71
MOX Oxygen	0.28		1.32
Oxygen (by difference)	<u>0.86</u>		<u>0.46</u>
Total	100.00		100.00

Screen Analysis, wt %, U.S. Sieve

8	11.9	2.7
12	12.6	11.1
16	12.0	14.1
18	4.8	5.9
20	9.6	3.6
30	28.8	14.3
40	16.5	12.7
60	3.7	12.9
80	0	14.5
Pan	<u>0.1</u>	<u>8.2</u>
Total	100.0	100.0

Gross Heating Value, Btu/lb	2601.4	584.6
Bulk Density, g/cc	1.115	1.03
Mercury Density, g/cc	2.07	1.48
Helium Density, g/cc	--	2.72

LIQUID PRODUCT PROPERTIES MINI-BENCH TEST WITH EASTERN SHALE

Run No.

88MBU-3

Lab No.

880206002, 880206003

Stream Identification

Oil Phase

Ultimate Analysis, wt %,
dry and solids free basis

Carbon	85.47
Hydrogen	10.30
Sulfur	0.85
Nitrogen	1.22
Asn	0.00
Oxygen, by difference	2.16
C/H Weight Ratio	8.30

Viscosity, SSU at 100°F
Specific Gravity, 60/60°F
API Gravity, °API

52.7
0.953
17.0

Distillation, °F

ASTM D86

IBP	163
5%	242
10%	288
20%	378
30%	461
40%	543
50%	606
60%	667
70%	713
80%	742
90%	--
95%	--
End Point	745
% Recovery	85.5
% Residue	15.5

Heating Value, Btu/lb
Pour Point, °F

17619
-10

Stream Identification

Water Phase

Mineral Carbon, wt %	0.16
Organic Carbon, wt %	0.52
Nitrogen, wt %	0.58
Sulfur, wt %	0.07

ELEMENTAL DISTRIBUTION FOR 88MBU-3

	Inlet		Outlet (by ash)		Outlet (adjusted)	
	lb/hr	%	lb/hr	%	lb/hr	%
Total Carbon						
Raw Shale	0.2778	66.0	0.0000	0.0	0.0000	0.0
Feed Hydrocarbon Gas	0.0174	4.1	0.0000	0.0	0.0000	0.0
Feed Carbon Oxides	0.1259	30.0	0.0000	0.0	0.0000	0.0
Spent Shale	0.0000	0.0	0.0566	13.4	0.0566	13.4
Product Hydrocarbon Gas	0.0000	0.0	0.0567	13.5	0.0649	15.4
Product Carbon Oxides	0.0000	0.0	0.1232	29.3	0.1283	30.5
Dissolved Gas in Sour Water	0.0000	0.0	0.0034	0.8	0.0034	0.8
Product Oil	0.0000	0.0	0.1391	33.0	0.1679	39.9
Total	0.4211	100.0	0.3790	90.0	0.4211	100.0
Organic Carbon						
Raw Shale	0.2675	93.9	0.0000	0.0	0.0000	0.0
Feed Hydrocarbon Gas	0.0174	6.1	0.0000	0.0	0.0000	0.0
Spent Shale	0.0000	0.0	0.0495	17.4	0.0495	17.4
Product Hydrocarbon Gas	0.0000	0.0	0.0567	19.9	0.0649	22.8
Dissolved Gas in Sour Water	0.0000	0.0	0.0026	0.9	0.0026	0.9
Product Oil	0.0000	0.0	0.1391	48.8	0.1679	58.9
Total	0.2849	100.0	0.2479	87.0	0.2849	100.0
Mineral Carbon						
Raw Shale	0.0103	7.6	0.0000	0.0	0.0000	0.0
Feed Carbon Oxides	0.1259	92.4	0.0000	0.0	0.0000	0.0
Spent Shale	0.0000	0.0	0.0071	5.2	0.0071	5.2
Product Carbon Oxides	0.0000	0.0	0.1232	90.5	0.1283	94.2
Dissolved Gas in Sour Water	0.0000	0.0	0.0008	0.6	0.0008	0.6
Total	0.1362	100.0	0.1311	96.3	0.1362	100.0
Hydrogen						
Raw Shale (dry basis)	0.0302	15.7	0.0000	0.0	0.0000	0.0
Moisture	0.0026	1.4	0.0000	0.0	0.0000	0.0
Feed Steam	0.0482	25.1	0.0000	0.0	0.0000	0.0
Feed Gas (dry basis)	0.1114	57.9	0.0000	0.0	0.0000	0.0
Spent Shale	0.0000	0.0	0.0051	2.7	0.0051	2.7
Product Gas	0.0000	0.0	0.1369	71.2	0.1123	58.4
Dissolved Gas in Sour Water	0.0000	0.0	0.0010	0.5	0.0010	0.5
Product Water	0.0000	0.0	0.0537	27.9	0.0537	27.9
Product Oil	0.0000	0.0	0.0168	8.7	0.0203	10.6
Total	0.1924	100.0	0.2135	111.0	0.1924	100.0
Oxygen						
Raw Shale (dry basis)	0.1100	14.4	0.0000	0.0	0.0000	0.0
Moisture	0.0208	2.7	0.0000	0.0	0.0000	0.0
Feed Steam	0.3822	50.1	0.0000	0.0	0.0000	0.0
Feed Carbon Oxides	0.2495	32.7	0.0000	0.0	0.0000	0.0
Spent Shale	0.0000	0.0	0.0755	9.9	0.0682	8.9
Product Carbon Oxides	0.0000	0.0	0.2510	32.9	0.2614	34.3
Dissolved Gas in Sour Water	0.0000	0.0	0.0028	0.3	0.0028	0.3
Product Water	0.0000	0.0	0.4259	55.9	0.4259	55.9
Product Oil	0.0000	0.0	0.0035	0.5	0.0042	0.6
Total	0.7625	100.0	0.7587	99.5	0.7625	100.0
Sulfur						
Raw Shale	0.0992	100.0	0.0000	0.0	0.0000	0.0
Spent Shale	0.0000	0.0	0.0492	49.6	0.0492	49.6
Product Gas	0.0000	0.0	0.0408	41.1	0.0480	48.4
Dissolved Gas in Sour Water	0.0000	0.0	0.0003	0.3	0.0003	0.3
Product Oil	0.0000	0.0	0.0014	1.4	0.0017	1.7
Total	0.0992	100.0	0.0917	92.4	0.0992	100.0
Nitrogen						
Raw Shale	0.0112	100.0	0.0000	0.0	0.0000	0.0
Spent Shale	0.0000	0.0	0.0051	50.9	0.0060	53.6
Dissolved Gas in Sour Water	0.0000	0.0	0.0028	25.0	0.0028	25.0
Product Oil	0.0000	0.0	0.0020	17.8	0.0024	21.4
Total	0.0112	100.0	0.0105	93.7	0.0112	100.0

COMBINED HYDROGEN DISTRIBUTION FOR 88MBU-3

Appearance of Combined Hydrogen	Outlet (by ash)		Outlet (Adjusted)	
	<u>lb/h</u>	<u>%</u>	<u>lb/h</u>	<u>%</u>
Product Gas (HC + H ₂ S)	0.0130	38.6	0.0158	39.5
Product Oil	0.0168	49.9	0.0203	50.7
Dissolved Gas in Sour Water	0.0010	3.0	0.0010	2.5
Net Product Water	<u>0.0029</u>	<u>8.6</u>	<u>0.0029</u>	<u>7.3</u>
Total	0.0337	100.0	0.0400	100.0

HYDROGEN CONSUMPTION, SCF/TON

1. Direct Measurement	2720
2. Appearance of Combined Hydrogen	2706
3. Forced Oxygen Balance	2815

MINI-BENCH UNIT TEST 88MBU-3 STATISTICAL ANALYSIS DATA

Dependent Variables

1.	Hydrogen Consumption, SCF/ton	2760
2.	Oil Yield, gal/ton - Recovered	19.8
	Reconciled	23.9
3.	Oil Properties: Pour Point, °F	-10.0
	API, @ 60°F	17.0
	C/H Ratio	8.30
	S, wt %	0.85
	N, wt %	1.22
	Viscosity, SSU	52.7
	Distillate Fractions	
	Temperature, °F - 10%	288
	50%	606
	E.P.	745
4.	Organic Carbon Conversion, % (adjusted by ash balance)	81.5
5.	Selectivity to Oil, % (adjusted)	77.1
6.	Hydrocarbon Gas Yield, MMBTU/ton	
	Methane Equivalent - adjusted	1.47
7.	Organic Carbon to Gas, %	18.7
	Oil, %	62.8
	Residue, %	18.5
8.	Sulfur Conversion to Gas, %	48.7
	Oil, %	1.7
	Residue, %	49.6
9.	Water Production, lb/hr	0.4905
	Water Production, lb/hr (less shale moisture)	0.0367

Independent Variables

1.	Maximum Bed Temperature, °F	1075
2.	Total Pressure, psia	957
	Hydrogen Partial Pressure, psia	557
3.	Shale Residence time, min	57

Hydrogen consumption is average of combined hydrogen and forced oxygen methods.
Sulfur to gas is 48.4% to product gas and 0.3% to dissolved gas.

APPENDIX D. Summary of Operating Conditions and Results
for Indiana New Albany MBU Mist Test, 88MBU-14

MINI-BENCH OPERATING CONDITIONS AND TEST RESULTS
COUNTERCURRENT MOVING-BED OPERATION WITH EASTERN SHALE

Oil Shale Type	Indiana - No Ions
Source	New Albany
Oil Shale Particle Size (U.S. Sieve)	-6+40
Run No.	88MBU-14
Run Date	4/15/88
Test Duration, hrs	3.00
Total Shale Feed Time, hrs	2.95
Steady State Operating Period, hrs	1.50
Operating Conditions	
Bed Height, ft	1.67
Shale Preheat Height, ft	0.92
Reactor Pressure, psig	670.0
Average Bed Temperature, F	
Zone 1	896.
Zone 2	939.
Zone 3	937.
Zone 4	847.
Zone 5	782.
Zone 6	650.
Zone 7 Bed Height -	542.
Oil Shale Feed Rate, lb/hr	2.041
Oil Shale Space Velocity, lb/ft(3)-hr	60.89
Oil Shale Residence Time, min	68.5
Hydrogen Feed Gas Rate, SCF/hr	19.15
Feed Gas Superficial Velocity, ft/s	.0159
Feed Gas Residence Time, s	42.5
Hydrogen/Oil Shale Ratio, SCF/lb shale fed	9.5
Shale Feed Hopper Purge Rate, SCF/hr	1.20
Total Hydrogen Feed Gas Rate, SCF/hr	20.35

MINI-BENCH OPERATING CONDITIONS AND TEST RESULTS
COUNTERCURRENT MOVING-BED OPERATION WITH EASTERN SHALE

Run No.	88MBU-14	
Test Results	Residue Weight By Weight Measurement	Residue Weight By Ash balance
Product Gas Rate (as measured), SCF/hr		19.55
Product Gas Rate, SCF/hr		18.35
Product Gas Yield, SCF/lb shale fed		9.1
Residue Shale Rate, lb/hr	1.680	1.731
Residue Shale Yield, lb/lb shale fed	0.823	0.848
Product Oil Rate, lb/hr		0.1254
Product Oil Yield, lb/lb shale fed		0.0621
Product Oil Yield, gal/ton		16.3
Product Water Rate (as measured), lb/hr		0.0866
Water Product Rate, lb/hr		0.0798
Water Product Yield, lb/lb shale fed		0.0395
Water Product Yield, gal/ton		9.5
Organic Carbon Distribution in Products, %		
Gaseous Hydrocarbons		13.4
Liquid Products		41.0<41.3>
Solid Residue	31.4	32.4
Total	85.8< 86.2>	86.8< 87.2>
Overall Material Balance, %	96.7(96.7)	99.1(99.1)
Total Carbon Balance, %	86.6	87.6
Hydrogen Balance, %	99.7(99.4)	99.9(99.6)
Oxygen Balance, %	120.6	122.5
Sulfur Balance, %	98.2	99.9
Nitrogen Balance, %	92.8	94.7
Selectivity to Oil, %		75.3<75.4>

Numbers in < > include organic carbon in water phase liquids
Numbers in () indicate balances have been corrected for accumulated
gases in new shale pores formed by hydrotreating

MINI-BENCH OPERATING CONDITIONS AND TEST RESULTS
COUNTERCURRENT MOVING-BED OPERATION WITH EASTERN SHALE

Run No.

88MBU-14

Gas Composition, mol %	Feed Gas	Product Gas		
		Metered	H(2)S Adj	N(2) Free
Hydrogen Sulfide	0.00	2.54	2.54	2.54
Nitrogen	0.00	0.00	0.00	0.00
Carbon Monoxide	0.00	0.00	0.00	0.00
Carbon Dioxide	0.00	0.00	0.00	0.00
Hydrogen	100.00	94.51	94.51	94.51
Helium	0.00	0.00	0.00	0.00
Methane	0.00	1.58	1.58	1.58
Ethane	0.00	0.59	0.59	0.59
Propane	0.00	0.22	0.22	0.22
n-Butane	0.00	0.13	0.13	0.13
Iso-Butane	0.00	0.00	0.00	0.00
Pentanes	0.00	0.07	0.07	0.07
Hexanes	0.00	0.10	0.10	0.10
Heptanes	0.00	0.00	0.00	0.00
Ethylene	0.00	0.09	0.09	0.09
Propylene	0.00	0.10	0.10	0.10
Butene	0.00	0.06	0.06	0.06
Pentene	0.00	0.01	0.01	0.01
Hexene	0.00	0.00	0.00	0.00
Heptene	0.00	0.00	0.00	0.00
Butadiene	0.00	0.00	0.00	0.00
Pentadiene	0.00	0.00	0.00	0.00
Cyclopentadiene	0.00	0.00	0.00	0.00
Acetylene	0.00	0.00	0.00	0.00
M. Acet./Propadiene	0.00	0.00	0.00	0.00
Benzene	0.00	0.00	0.00	0.00
Toluene	0.00	0.00	0.00	0.00
Xylene	0.00	0.00	0.00	0.00
Ethyl Benzene	0.00	0.00	0.00	0.00
Styrene	0.00	0.00	0.00	0.00
Total	100.00	100.00	100.00	100.00
Specific Gravity (Air = 1.00)	0.070	0.125	0.125	0.125

ANALYSES OF EASTERN SHALE FEED AND RESIDUE - MINI-BENCH TEST

Run No.	88MBU-14	
Sample	Feed	Residue
Lab No.	880105401	880404701
Moisture	1.12	0.00
Modified Ultimate Analysis		
(wt %, dry basis)		
Ash	77.10	89.88
HTW in Ash	0.00	0.00
MOX Oxygen in Ash	0.00	0.00
Residual Mineral Oxides	74.42	85.97
Organic Carbon	12.94	4.89
Organic Hydrogen	1.10	0.23
Sulfur	4.80	3.02
Nitrogen	0.54	0.40
Carbon Dioxide	1.82	1.93
High Temperature Water	3.24	1.77
MOX Oxygen	0.28	1.69
Oxygen (by difference)	0.86	0.10
Total	100.00	100.00
Screen Analysis, U.S. Sieve, wt %		
6	--	0.0
8	11.9	12.4
12	12.6	17.8
16	12.0	17.1
18	4.8	7.6
20	9.6	7.7
30	28.8	16.5
40	16.5	9.6
60	3.7	5.2
80	0.0	1.7
Pan	0.1	4.4
Total	100.0	100.0
Gross Heating Value, BTU/lb	2601.0	961.0
Bulk Density, g/cc	1.12	0.97
Mercury Density, g/cc	2.07	1.63
Helium Density, g/cc	--	2.63

LIQUID PRODUCT PROPERTIES - MINI-BENCH TEST WITH EASTERN SHALE

Run No.	88MBU-14
Lab No.	880404401, 880404402
Stream Identification	Oil Phase

Ultimate Analysis, wt %
(dry and solids free basis)

Carbon	85.32
Hydrogen	10.80
Sulfur	1.30
Nitrogen	1.40
Ash	0.00
Oxygen (by difference)	1.18
C/H Weight Ratio	7.90

Viscosity, SSU at 100 F	37.6
Specific Gravity (60/60 F)	0.915
API Gravity, degrees API	23.1

Distillation, F	ASTM D86	GC Sim.
IBP	--	250.
5%	--	250.
10%	--	263.
20%	--	349.
30%	--	422.
40%	--	481.
50%	--	540.
60%	--	596.
70%	--	651.
80%	--	704.
90%	--	765.
95%	--	818.
End Point	--	900.
% Recovery	--	****
% Residue	--	0.0

Heating Value, BTU/lb	18085.
Pour Point, F	-35.

Stream Identification

	Water Phase
Mineral Carbon, wt %	0.90
Organic Carbon, wt %	1.10
Nitrogen, wt %	1.89
Sulfur, wt %	0.87

ELEMENTAL DISTRIBUTION FOR 88MBU-14

	Inlet		Outlet (by ash)		Outlet Adjusted	
	lb/hr	%	lb/hr	%	lb/hr	%
Total Carbon						
Raw Shale	0.271	100.0	0.000	0.0	0.000	0.0
Spent Shale	0.000	0.0	0.094	34.6	0.094	34.6
Hydrocarbon Gas	0.000	0.0	0.035	12.9	0.036	13.3
Carbon Oxides	0.000	0.0	0.000	0.0	0.000	0.0
Dissolved Gas in Sour Water	0.000	0.0	0.002	0.6	0.002	0.6
Product Oil	0.000	0.0	0.107	39.4	0.139	51.4
Total	0.271	100.0	0.238	87.6	0.271	100.0
Hydrogen						
Raw Shale (dry basis)	0.029	21.0	0.000	0.0	0.000	0.0
Moisture	0.003	1.8	0.000	0.0	0.000	0.0
Feed Gas	0.108	77.2	0.000	0.0	0.000	0.0
Spent Shale	0.000	0.0	0.007	5.3	0.007	5.3
Product Gas	0.000	0.0	0.109	77.9	0.106	75.4
Dissolved Gas in Sour Water	0.000	0.0	0.001	0.4	0.001	0.4
Product Water	0.000	0.0	0.009	6.4	0.009	6.4
Product Oil	0.000	0.0	0.014	9.6	0.018	12.6
Total	0.140	100.0	0.140	99.6	0.140	100.0
Oxygen						
Raw Shale (dry basis)	0.108	84.2	0.000	0.0	0.000	0.0
Moisture	0.020	15.8	0.000	0.0	0.000	0.0
Spent Shale	0.000	0.0	0.083	64.4	0.053	41.5
Product Gas as Carbon Oxides	0.000	0.0	0.000	0.0	0.000	0.0
Dissolved Gas in Sour Water	0.000	0.0	0.002	1.6	0.002	1.6
Product Water	0.000	0.0	0.071	55.3	0.071	55.3
Product Oil	0.000	0.0	0.001	1.2	0.002	1.5
Total	0.128	100.0	0.157	122.5	0.128	100.0
Sulfur						
Raw Shale	0.097	100.0	0.000	0.0	0.000	0.0
Spent Shale	0.000	0.0	0.052	54.0	0.052	54.0
Product Gas	0.000	0.0	0.042	43.4	0.042	43.1
Dissolved Gas in Sour Water	0.000	0.0	0.001	0.8	0.001	0.8
Product Oil	0.000	0.0	0.002	1.7	0.002	2.2
Total	0.097	100.0	0.097	99.9	0.097	100.0
Nitrogen						
Raw Shale	0.011	100.0	0.000	0.0	0.000	0.0
Spent Shale	0.000	0.0	0.007	63.5	0.007	64.0
Dissolved Gas in Sour Water	0.000	0.0	0.002	15.0	0.002	15.0
Product Oil	0.000	0.0	0.002	16.1	0.002	21.0
Total	0.011	100.0	0.010	94.7	0.011	100.0

COMBINED HYDROGEN DISTRIBUTION FOR 88MBU-14

Appearance of Combined Hydrogen	Outlet (by ash)		Outlet (Adjusted)	
	lb/hr	%	lb/hr	%
Product Gas (HC + H(2)S)	0.011	35.6	0.012	32.2
Product Oil	0.014	42.6	0.018	48.7
Dissolved Gas in Sour Water	0.001	1.8	0.001	1.5
Net Product Water				
(total product water - feed moisture)	0.006	20.0	0.006	17.6
Total	0.032	100.0	0.036	100.0

HYDROGEN CONSUMPTION SCF/TON

1. Direct Measurement	1929.
2. Appearance of Combined Hydrogen	2651.
3. Forced Oxygen Balance	1965.

MINI-BENCH UNIT TEST 88MBU-14 STATISTICAL ANALYSIS DATA - PHASE TWO

Dependent Variables

1. Hydrogen Consumption (SCF/ton)	2308.
2. Oil Yield (gal/ton) Recovered	16.3
Reconciled	21.2
3. Oil Properties	
Pour Point (F)	-35.
API (@ 60 F)	23.1
C/H Ratio	7.90
S (wt %)	1.30
N (wt %)	1.40
Viscosity (SSU)	37.6
Distillate Fractions	
Temp. (F) 10 %	--
50 %	--
E.P.	--
4. Organic Carbon Conversion (%)	67.6
(Adjusted by Ash Balance)	
5. Selectivity to Oil (%)	79.5
(Adjusted)	
6. Hydrocarbon Gas Yield (MM BTU/ton)	1.14
Methane Equivalent - Adjusted	
7. Organic Carbon to Gas (%)	13.9
Oil (%)	53.7
Residue (%)	32.4
8. Sulfur Conv. to Gas (%)	43.8
Oil (%)	2.2
Residue (%)	54.0
9. Water Production (lb/hr)	0.0798
Water Production (lb/hr)	0.0570
(less shale moisture)	

Independent Variables

1. Maximum Bed Temperature (F)	939.
2. Total Pressure (psia)	685.
Hydrogen Partial Pressure (psia)	630.
3. Shale Residence Time (min)	69.

Hydrogen Consumption is Average of Combined Hydrogen and Forced Oxygen methods

Sulfur in gas is 43.1 % to product gas and 0.8 % to dissolved gas

MINI-BENCH OPERATING CONDITIONS AND TEST RESULTS
COUNTERCURRENT MOVING-BED OPERATION WITH EASTERN SHALE

Oil Shale Type	Indiana - With Ions
Source	New Albany
Oil Shale Particle Size (U.S. Sieve)	-6+40
Run No.	88MBU-14
Run Date	4/15/88
Test Duration, hrs	3.00
Total Shale Feed Time, hrs	2.95
Steady State Operating Period, hrs	1.50
Operating Conditions	
Bed Height, ft	1.67
Shale Preheat Height, ft	0.92
Reactor Pressure, psig	615.0
Average Bed Temperature, F	
Zone 1	898.
Zone 2	944.
Zone 3	949.
Zone 4	913.
Zone 5	807.
Zone 6	718.
Zone 7 Bed Height -	530.
Oil Shale Feed Rate, lb/hr	1.843
Oil Shale Space Velocity, lb/ft(3)-hr	54.98
Oil Shale Residence Time, min	75.9
Hydrogen Feed Gas Rate, SCF/hr	19.15
Feed Gas Superficial Velocity, ft/s	.0173
Feed Gas Residence Time, s	41.4
Hydrogen/Oil Shale Ratio, SCF/lb shale fed	10.5
Shale Feed Hopper Purge Rate, SCF/hr	1.20
Total Hydrogen Feed Gas Rate, SCF/hr	20.35

MINI-BENCH OPERATING CONDITIONS AND TEST RESULTS
COUNTERCURRENT MOVING-BED OPERATION WITH EASTERN SHALE

Run No.	88MBU-14	
Test Results	Residue Weight By Weight Measurement	Residue Weight By Ash balance
Product Gas Rate (as measured), SCF/hr	19.66	
Product Gas Rate, SCF/hr	18.46	
Product Gas Yield, SCF/lb shale fed	10.1	
Residue Shale Rate, lb/hr	1.509	1.555
Residue Shale Yield, lb/lb shale fed	0.819	0.844
Product Oil Rate, lb/hr	0.1127	
Product Oil Yield, lb/lb shale fed	0.0619	
Product Oil Yield, gal/ton	16.2	
Product Water Rate (as measured), lb/hr	0.0880	
Water Product Rate, lb/hr	0.0802	
Water Product Yield, lb/lb shale fed	0.0440	
Water Product Yield, gal/ton	10.6	
Organic Carbon Distribution in Products, %		
Gaseous Hydrocarbons	11.0	
Liquid Products	40.6<41.1>	
Solid Residue	31.5	32.4
Total	83.1< 83.6>	84.1< 84.6>
Overall Material Balance, %	96.5(96.5)	98.9(98.9)
Total Carbon Balance, %	83.8	84.8
Hydrogen Balance, %	99.6(99.3)	99.7(99.5)
Oxygen Balance, %	121.9	123.6
Sulfur Balance, %	98.2	99.8
Nitrogen Balance, %	100.9	103.0
Selectivity to Oil, %	78.7<78.9>	

Numbers in < > include organic carbon in water phase liquids
Numbers in () indicate balances have been corrected for accumulated
gases in new shale pores formed by hydrotreating

MINI-BENCH OPERATING CONDITIONS AND TEST RESULTS
COUNTERCURRENT MOVING-BED OPERATION WITH EASTERN SHALE

Run No.

88MBU-14

	Feed Gas	Product Gas		
		Metered	H(2)S Adj	N(2) Free
Gas Composition, mol %				
Hydrogen Sulfide	0.00	2.33	2.33	2.33
Nitrogen	0.00	0.00	0.00	0.00
Carbon Monoxide	0.00	0.00	0.00	0.00
Carbon Dioxide	0.00	0.00	0.00	0.00
Hydrogen	100.00	95.61	95.61	95.61
Helium	0.00	0.00	0.00	0.00
Methane	0.00	1.06	1.06	1.06
Ethane	0.00	0.39	0.39	0.39
Propane	0.00	0.19	0.19	0.19
n-Butane	0.00	0.09	0.09	0.09
Iso-Butane	0.00	0.00	0.00	0.00
Pentanes	0.00	0.06	0.06	0.06
Hexanes	0.00	0.10	0.10	0.10
Heptanes	0.00	0.00	0.00	0.00
Ethylene	0.00	0.06	0.06	0.06
Propylene	0.00	0.07	0.07	0.07
Butene	0.00	0.04	0.04	0.04
Pentene	0.00	0.00	0.00	0.00
Hexene	0.00	0.00	0.00	0.00
Heptene	0.00	0.00	0.00	0.00
Butadiene	0.00	0.00	0.00	0.00
Pentadiene	0.00	0.00	0.00	0.00
Cyclopentadiene	0.00	0.00	0.00	0.00
Acetylene	0.00	0.00	0.00	0.00
M. Acet./Propadiene	0.00	0.00	0.00	0.00
Benzene	0.00	0.00	0.00	0.00
Toluene	0.00	0.00	0.00	0.00
Xylene	0.00	0.00	0.00	0.00
Ethyl Benzene	0.00	0.00	0.00	0.00
Styrene	0.00	0.00	0.00	0.00
Total	100.00	100.00	100.00	100.00
Specific Gravity (Air = 1.00)	0.070	0.115	0.115	0.115

ANALYSES OF EASTERN SHALE FEED AND RESIDUE - MINI-BENCH TEST

Run No.	88MBU-14	
Sample	Feed	Residue
Lab No.	880105401	880404702
Moisture	1.12	0.00
Modified Ultimate Analysis		
(wt %, dry basis)		
Ash	77.10	90.35
HTW in Ash	0.00	0.00
MOX Oxygen in Ash	0.00	0.00
Residual Mineral Oxides	74.42	86.44
Organic Carbon	12.94	4.92
Organic Hydrogen	1.10	0.18
Sulfur	4.80	2.98
Nitrogen	0.54	0.43
Carbon Dioxide	1.82	1.75
High Temperature Water	3.24	1.92
MOX Oxygen	0.28	1.07
Oxygen (by difference)	0.86	0.31
Total	100.00	100.00
Screen Analysis, U.S. Sieve, wt %		
6	--	3.0
8	11.9	10.1
12	12.6	20.0
16	12.0	18.5
18	4.8	7.9
20	9.6	5.5
30	28.8	14.9
40	16.5	9.9
60	3.7	6.0
80	0.0	1.7
Pan	0.1	5.5
Total	100.0	103.0
Gross Heating Value, BTU/lb	2601.0	959.0
Bulk Density, g/cc	1.12	0.94
Mercury Density, g/cc	2.07	1.64
Helium Density, g/cc	--	2.62

LIQUID PRODUCT PROPERTIES - MINI-BENCH TEST WITH EASTERN SHALE

Run No.	88MBU-14
Lab No.	880404403, 880404404
Stream Identification	Oil Phase

Ultimate Analysis, wt % (dry and solids free basis)

Carbon	85.04
Hydrogen	10.92
Sulfur	1.27
Nitrogen	1.34
Ash	0.00
Oxygen (by difference)	1.43
C/H Weight Ratio	7.79

Viscosity, SSU at 100 F	37.0
Specific Gravity (60/60 F)	0.914
API Gravity, degrees API	23.3

Distillation, F

	ASTM D86	GC Sim.
IBP	--	250.
5%	--	250.
10%	--	262.
20%	--	347.
30%	--	419.
40%	--	476.
50%	--	533.
60%	--	588.
70%	--	640.
80%	--	689.
90%	--	749.
95%	--	795.
End Point	--	900.
% Recovery	--	****
% Residue	--	0.0

Heating Value, BTU/lb	18108.
Pour Point, F	-30.

Stream Identification

	Water Phase
Mineral Carbon, wt %	1.00
Organic Carbon, wt %	1.30
Nitrogen, wt %	2.20
Sulfur, wt %	0.86

ELEMENTAL DISTRIBUTION FOR 88MBU-14

	Inlet		Outlet (by ash)		Outlet Adjusted	
	lb/hr	%	lb/hr	%	lb/hr	%
Total Carbon						
Raw Shale	0.245	100.0	0.000	0.0	0.000	0.0
Spent Shale	0.000	0.0	0.084	34.3	0.084	34.3
Hydrocarbon Gas	0.000	0.0	0.026	10.6	0.027	11.0
Carbon Oxides	0.000	0.0	0.000	0.0	0.000	0.0
Dissolved Gas in Sour Water	0.000	0.0	0.002	0.8	0.002	0.8
Product Oil	0.000	0.0	0.096	39.1	0.132	53.9
Total	0.245	100.0	0.208	84.8	0.245	100.0
Hydrogen						
Raw Shale (dry basis)	0.027	19.4	0.000	0.0	0.000	0.0
Moisture	0.002	1.7	0.000	0.0	0.000	0.0
Feed Gas	0.108	78.9	0.000	0.0	0.000	0.0
Spent Shale	0.000	0.0	0.006	4.4	0.006	4.4
Product Gas	0.000	0.0	0.109	79.1	0.105	76.2
Dissolved Gas in Sour Water	0.000	0.0	0.001	0.5	0.001	0.5
Product Water	0.000	0.0	0.009	6.5	0.009	6.5
Product Oil	0.000	0.0	0.012	9.0	0.017	12.3
Total	0.137	100.0	0.137	99.5	0.137	100.0
Oxygen						
Raw Shale (dry basis)	0.097	84.2	0.000	0.0	0.000	0.0
Moisture	0.018	15.8	0.000	0.0	0.000	0.0
Spent Shale	0.000	0.0	0.068	58.6	0.040	34.4
Product Gas as Carbon Oxides	0.000	0.0	0.000	0.0	0.000	0.0
Dissolved Gas in Sour Water	0.000	0.0	0.002	2.0	0.002	2.0
Product Water	0.000	0.0	0.071	61.6	0.071	61.6
Product Oil	0.000	0.0	0.002	1.4	0.002	1.9
Total	0.116	100.0	0.143	123.6	0.116	100.0
Sulfur						
Raw Shale	0.087	100.0	0.000	0.0	0.000	0.0
Spent Shale	0.000	0.0	0.046	53.0	0.046	53.0
Product Gas	0.000	0.0	0.039	44.3	0.038	43.9
Dissolved Gas in Sour Water	0.000	0.0	0.001	0.9	0.001	0.9
Product Oil	0.000	0.0	0.001	1.6	0.002	2.3
Total	0.087	100.0	0.087	99.8	0.087	100.0
Nitrogen						
Raw Shale	0.010	100.0	0.000	0.0	0.000	0.0
Spent Shale	0.000	0.0	0.007	68.0	0.006	59.2
Dissolved Gas in Sour Water	0.000	0.0	0.002	19.7	0.002	19.7
Product Oil	0.000	0.0	0.002	15.3	0.002	21.1
Total	0.010	100.0	0.010	103.0	0.010	100.0

COMBINED HYDROGEN DISTRIBUTION FOR 88MBU-14

Appearance of Combined Hydrogen	Outlet (by ash)		Outlet (Adjusted)	
	lb/hr	%	lb/hr	%
Product Gas (HC + H(2)S)	0.009	30.9	0.009	27.2
Product Oil	0.012	43.3	0.017	50.8
Dissolved Gas in Sour Water	0.001	2.3	0.001	2.0
Net Product Water				
(total product water - feed moisture)	0.007	23.5	0.007	20.0
Total	0.028	100.0	0.033	100.0

HYDROGEN CONSUMPTION SCF/TON

1. Direct Measurement	1772.
2. Appearance of Combined Hydrogen	2640.
3. Forced Oxygen Balance	1915.

MINI-BENCH UNIT TEST 88MBU-14 STATISTICAL ANALYSIS DATA - PHASE TWO

Dependent Variables

1. Hydrogen Consumption (SCF/ton)	2277.
2. Oil Yield (gal/ton)	Recovered 16.2
	Reconciled 22.4
3. Oil Properties	Pour Point (F) -30.
	API (@ 60 F) 23.3
	C/H Ratio 7.79
	S (wt %) 1.27
	N (wt %) 1.34
	Viscosity (cSt) 37.0
	Distillate Fractions
	Temp. (F) 10 % --
	50 % --
	E.P. --
4. Organic Carbon Conversion (%)	67.6
(Adjusted by Ash Balance)	
5. Selectivity to Oil (%)	83.1
(Adjusted)	
6. Hydrocarbon Gas Yield (MM BTU/ton)	0.94
Methane Equivalent - Adjusted	
7. Organic Carbon to Gas (%)	11.4
	Oil (%) 56.1
	Residue (%) 32.4
8. Sulfur Conv. to Gas (%)	44.8
	Oil (%) 2.3
	Residue (%) 53.0
9. Water Production (lb/hr)	0.0802
Water Production (lb/hr)	0.0596
(less shale moisture)	

Independent Variables

1. Maximum Bed Temperature (F)	949.
2. Total Pressure (psia)	630.
Hydrogen Partial Pressure (psia)	583.
3. Shale Residence Time (min)	76.

Hydrogen Consumption is Average of Combined Hydrogen
and Forced Oxygen methods

Sulfur in gas is 43.9 % to product gas and 0.9 % to dissolved gas

APPENDIX E. Equations used for Calculating Temperature Profiles and
Oil Yields in Moving-Bed Retorts

Table E-1. EQUATIONS USED TO CALCULATE THE TEMPERATURE PROFILES
IN A COUNTERCURRENT MOVING-BED RETORT

$$M_s C_s \frac{dT_s}{dx} = h (T_g - T_s) A \quad (1)$$

$$M_g C_g \frac{dT_g}{dx} = h (T_g - T_s) A \quad (2)$$

Where

$$C_1 = \frac{T_{g, \text{in.}} - T_{s, \text{in.}}}{\left[\frac{C}{(C-1)} \exp\left(\frac{Ah}{M_g C_g} - \frac{Ah}{M_s C_s}\right) L - \frac{1}{(C-1)} \right]}$$

$$C_2 = T_{s, \text{in.}} - C_1 \frac{1}{(C-1)}$$

$$C = \frac{M_s C_s}{M_g C_g}$$

$$T_s = \frac{1}{(C-1)} C_1 \exp\left(\frac{Ah}{M_g C_g} - \frac{Ah}{M_s C_s}\right) x + C_2$$

$$T_g = T_s + C_1 \exp\left(\frac{Ah}{M_g C_g} - \frac{Ah}{M_s C_s}\right) x$$

Table E-2. EQUATIONS USED TO CALCULATE OIL AND GAS YIELDS
FOR HYDRORETORTING OF OIL SHALE

$$\frac{dO}{d\theta} = R_1 \quad (1)$$

$$\frac{dC}{d\theta} = R_2 - R_3 \quad (2)$$

$$\frac{dG}{d\theta} = R_3 \quad (3)$$

$$R_1 = (0.01429 P_{H_2} + 3.0) * 10^6 * \frac{0.1}{D_P} e^{-23000/T} K^{2/3} \quad (4)$$

$$R_2 = 48 * 10^6 e^{-26500/T} K^{2/3} \quad (5)$$

$$R_3 = 0.025 C$$

Where:

- O: Shale Oil Yield, fraction of feed organic carbon
- C: Residue Carbon Yield, fraction of feed organic carbon
- G: Light Hydrocarbon Gases Yield, fraction of feed organic
- θ : Shale Residence Time, min.
- P_{H_2} : H_2 Partial Pressure, atm
- D_P : Partial Size, inch
- T: Solid Temperature, °R
- K: Kerogen Content of Shale, fraction of feed organic carbon

APPENDIX F.

Executive Summary and Table of Contents

From

Volume 1. Project Results and Achievements

Final Project Report Prepared by

HYCRUDE Corporation
IIT Center
Chicago, Illinois 60616

PERFORM RESEARCH IN PROCESS DEVELOPMENT FOR
HYDRORETORTING OF EASTERN OIL SHALES

VOLUME 1. PROJECT RESULTS AND ACHIEVEMENTS

Final Report for the Period
October 1985-September 1988

Volume 1. Project Results and Achievements

Volume 2. Expansion of the Moving-Bed Hydro-
Retorting Data Base for Eastern
Oil Shales

Volume 3. Sample Procurement Summary Report

Prepared by

HYCRUDE CORPORATION
10 West 35th Street
Chicago, Illinois 60616

Prepared for

The United States Department of Energy
Under Cooperative Agreement
No. DE-FC21-85LC11069

November 1989

F-3/F-4

EXECUTIVE SUMMARY

This report summarizes the results of work performed under DOE Cooperative Agreement Number DE-FC21-85LC11069, "Perform Research in Process Development for Hydroretorting of Eastern Oil Shales," for the period October 1985 through September 1988.

During the course of the program, a data base was established for 6 eastern oil shales, including geological characterization and the determination of hydroretorting characteristics. Conceptual commercial plant designs were developed for each shale and the potential environmental impact of a commercial hydroretorting plant in Putnam County, Tennessee was evaluated. Various concepts for improving the process efficiency of moving-bed hydroretorting and increasing resource utilization were investigated.

When circumstances warrant, the data obtained during this program will provide an adequate basis for the design of a moving-bed hydroretorting demonstration plant for the eastern oil shales studied, which represent the major portion of the surface minable eastern oil shale resource.

The 3-year research and development program was performed by HYCRUDE Corporation (as the prime contractor), the Institute of Gas Technology, Tennessee Technological University, and R. D. Matthews, Inc. The program was divided into 5 tasks, the results of which are summarized briefly below.

Task 1. Hydroretorting Characteristics

The hydroretorting characteristics of 6 eastern U.S. oil shales: Alabama Chattanooga, Indiana New Albany, Kentucky Sunbury, Michigan Antrim, Ohio Cleveland, and Tennessee Chattanooga, were evaluated in batch mode in a custom-designed hydroretorting assay unit (HAU) and, subsequently, in a continuous mini-bench-scale laboratory unit (MBU), having nominal feed capacities of 100 grams and 1-lb/h, respectively. The data base obtained in this task was the cornerstone of the program. It provided data for the evaluation of potential environmental impacts of a hydroretorting industry, and was the basis for the conceptual process designs necessary to evaluate the methods of potential process efficiency improvement investigated in this program.

Two tests were conducted with Indiana New Albany shale in a continuous, adiabatic bench-scale unit (BSU) with a nominal feed rate of 100 lb/h to verify the data obtained in the MBU and the replicability of BSU tests. The BSU tests were conducted on Indiana New Albany shale because a large data base, including results of 19 BSU runs on this shale, was available from a prior privately-funded research program.

At least 200% of the Fischer Assay oil yield was obtained by moving-bed hydroretorting of all 6 shales in the temperature range of 900°F to 1200°F and hydrogen partial pressure range of 400 psig to 1000 psig.

Except for a few anomalies, the observed trends were the same for all six oil shales tested:

- Oil yield and conversions of organic carbon, hydrogen and nitrogen increase with increasing temperature and pressure.
- Water yield increases with increasing temperature, but is relatively insensitive to changes in pressure.
- Sulfur conversion is relatively insensitive to changes in temperature and pressure.

Task 2. Environmental Mitigation Analysis and Process Design

An assessment of the applicability of existing pollution abatement technologies was made. It was concluded that existing pollution abatement technologies are sufficient to achieve and maintain compliance with environmental regulations for a commercial moving-bed hydroretorting facility.

A site-specific study for a commercial-scale moving-bed hydroretorting plant operating in Putnam County, Tennessee on Chattanooga oil shale was made and compared to the expected impact of a conventional retorting facility with the same oil production. It was concluded that the potential environmental impact of a moving-bed hydroretorting facility in this location is expected to be less than that of a conventional retorting facility with the same oil production. This is mainly because the oil yield per ton of shale processed is greater for the moving-bed hydroretorting process than for conventional retorting processes, therefore, less shale is processed in the hydroretorting facility.

A computer program was developed to simulate the operation of a conceptual commercial moving-bed hydroretorting plant. The simulation was used to generate the quantity and composition of process streams based on adjusted material balance data obtained in Task 1 for all 6 oil shales. Subroutines were developed to calculate process plant capital cost, utility and other operating costs, and product oil costs. The product oil cost is primarily a function of oil shale grade. Based on the conceptual plant designs, the product cost estimated for each of the 6 eastern oil shales ranged from \$47 to \$71/bbl of hydrotreated oil. An energy utilization subroutine was also incorporated in the process simulation computer program. The energy conversion efficiency, defined as available energy in hydrocarbon products divided by the energy in the raw shale plus utilities, ranges from 46% to 53% for the 6 shales tested.

Task 3. Process Efficiency Improvement Tests

In this task, two process efficiency improvement methods were investigated: the effect of using synthesis gas as the retorting atmosphere, and the generation of oil mist in the retort.

The use of synthesis gas produced from oil shale fines as the retorting atmosphere could replace the hydrogen produced from natural gas. Laboratory-scale batch tests using the 100-gram capacity HAU were performed to identify

the effects of synthesis gas composition, heat-up rate, temperature and pressure on hydroretorting oil yield. It was discovered that oil yield is primarily a function of the inlet hydrogen partial pressure. There was a net consumption of water in each test presumably due to the water-gas shift reaction, which consumes carbon monoxide and water to produce carbon dioxide (CO_2) and hydrogen. An improvement of about 65% to 75% over Fischer Assay oil yields was obtained for each shale.

Continuous synthesis gas retorting tests were conducted on all 6 shales at operating conditions similar to those used to determine hydroretorting characteristics in the 1-lb/h capacity MBU in Task 1. In all cases, the oil yields obtained in synthesis gas retorting tests at similar hydrogen partial pressures were lower than those obtained in the hydrogen retorting tests in Task 1. However, the oil produced during synthesis gas retorting was lighter, less viscous, and contained lower nitrogen content than that obtained during hydrogen retorting.

A mist generation system was added to the MBU to test the hypothesis that a reduction in oil refluxing in the retort by production of an oil mist would improve the oil yield. It was believed that in the existing moving-bed hydroretorting design, large droplets of oil condense on the incoming cold raw shale and form gas during refluxing, thereby reducing the oil yield and increasing hydrogen consumption.

Four successful MBU tests, each with 2 steady-state periods of operation, were conducted using Indiana New Albany oil shale. During one steady-state period of operation, uncharged CO_2 was introduced to the retort, and during the second period, ionized CO_2 was introduced to the retort to produce an oil mist. For all 4 tests, the oil yields did not vary significantly between the 2 periods. In 3 of the tests, the oil yield increased when ionized gas was introduced to promote mist generation, but the differences were within the accuracy of the reconciled oil yield calculations. There is, therefore, no conclusive evidence that the presence of ions can reduce refluxing and, thereby, increase the oil yield for moving-bed hydroretorting.

Task 4. Fines Utilization Tests

In this task, two methods to improve the efficiency of moving-bed hydroretorting by increasing the utilization of fines were investigated: a) gasification of fines to produce synthesis gas or hydrogen for retorting, and b) increasing the concentration of fines in the feed to the retort.

The aim of the gasification tests was to develop a fluidized-bed gasification process with agglomeration of the spent shale. A fluidized-bed process was chosen for high energy efficiency. Spent shale agglomeration was investigated because agglomeration of ash in coal gasification has been shown to produce a non-leachable solids waste material.

The fines gasification portion of the program included:

- Thermobalance tests to determine differential rate kinetic data.

- Fluidization and agglomeration tests to obtain fluidized-bed gasification operating parameters.
- Fluidized-bed gasification tests in a 1-lb/h capacity mini-bench scale unit to obtain gasification operating parameters.
- Fluidized-bed gasification tests in a 400-lb/h, 8-inch-diameter process development unit to obtain the data for development of conceptual plant design, and
- The correlation of the differential rate HAU kinetic data and the integral-bed MBU kinetic data.

Differential rate kinetic data were obtained in a thermobalance unit for all 6 shales. The Indiana New Albany shale was studied more extensively than the others. The range of operating conditions included gasification temperatures of 1600°F to 1900°F and operating pressures of 15 psig to 500 psig. The gasification tests were conducted in steam/hydrogen, steam/nitrogen, and synthesis gas environments.

It was discovered that organic carbon, sulfur, and overall conversions increase with increasing temperature and steam partial pressure, and that shale reactivity decreases as the gasification environment is changed from steam/nitrogen, to a mixture of steam/hydrogen, to synthesis gas. Under similar gasification conditions, the highest organic carbon reactivity was exhibited by the Indiana New Albany and Ohio Sunbury shales. The 2 Chattanooga shales (Alabama and Tennessee) showed intermediate organic carbon reactivities. The Kentucky and Michigan shales showed the lowest organic carbon reactivities.

Fluidization tests with nitrogen as the fluidization media were conducted on all 6 shales in a 2-inch diameter Plexiglas column at ambient conditions. For the -20+40 mesh samples of the 6 shales, the complete fluidization velocity was determined to be between 1.8 and 2.2 times the minimum fluidization velocity. Ash agglomeration tests, which were performed on all six shales, were unsuccessful. The majority of the spent shale was recovered as clinkers.

In the MBU, as in the thermobalance unit, higher organic carbon conversion was observed for all shales when gasified under similar conditions in a steam/nitrogen atmosphere rather than a synthesis gas atmosphere. It was also shown that the organic carbon conversion in the MBU was significantly lower than that obtained in the thermobalance. Conversions achieved with Indiana oil shale during gasification in synthesis gas were 10% to 15% lower.

Two syngas gasification tests were performed with Indiana New Albany oil shale in the 8-inch-diameter process development unit at a feed rate of 440-lb/h. A carbon conversion of 87% was achieved and the inorganic components of the extract from a residue solids leaching test were below EP method 1310 threshold limits. A preliminary conceptual gasifier design using a carbon conversion of 95% was developed because it is believed that this conversion is achievable at a longer residence time than used in the PDU test.

Up to 20 wt % of eastern oil shale is converted to fines during mining and sizing operations. Therefore, increasing the amount of fines that can be processed in the moving-bed retort is another method to increase utilization of the resource. A high concentration of fines in a moving-bed retort can result in operating problems caused by uneven temperature distributions. Tests were conducted to determine the effect of fines concentration in the moving-bed retort on: radial gas and solids distribution, entrainment of fines in the off-gas stream, and fines migration laterally in the bed. The effect of fines concentration on oil yield was calculated using a kinetic model and gas-solids contacting data.

A 6-foot diameter cold-flow-model was used to determine the average particle-size distribution and gas-velocity profile using the existing solids feeder configuration. Both the particle-size distribution and gas-velocity profile exhibited a "W" shape. Larger material was found at the walls and at the center of the bed, which resulted in higher gas flows in these areas.

For the existing equipment configuration, the entrainment of shale fines in the off-gas increased with both fines concentration and gas velocity. It was determined that lateral movement of fines in a moving-packed bed with gas flow countercurrent to the shale flow was minimal.

Calculated oil yields obtained from a kinetic model utilizing measured particle-size and calculated gas velocity profiles showed that the total amount of oil produced per ton of mined shale decreases as the fines concentration in the retort is increased.

Task 5. Sample Procurement

Six bulk samples of eastern oil shale were taken from 5 states. The shale samples, ranging in size from 315 to 1300 pounds, were taken from the Clegg Creek Member of the New Albany shale in northwestern Kentucky, the Chattanooga shale in northern Alabama, the Gassaway Member of the Chattanooga shale in central Tennessee, the Antrim shale in northeastern Michigan, the Cleveland Member of the Ohio shale in central Ohio, and the Sunbury shale in eastern Kentucky. A seventh sample of Clegg Creek shale from southern Indiana, sampled in a previous program, was used in place of the Kentucky New Albany shale discussed above. Additionally, an 80-ton sample of Kentucky New Albany shale was procured from Skaggs Quarry for cold-flow-model testing.

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Executive Summary and Table of Contents

From

Volume 3. Sample Procurement Summary Report

Final Project Report Prepared by

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PERFORM RESEARCH IN PROCESS DEVELOPMENT FOR
HYDRORETORTING OF EASTERN OIL SHALES

VOLUME 3. SAMPLE PROCUREMENT SUMMARY REPORT

Final Report for the Period
October 1985-September 1988

Volume 1. Project Results and Achievements

Volume 2. Expansion of the Moving-Bed Hydro-
Retorting Data Base for Eastern
Oil Shales

Volume 3. Sample Procurement Summary Report

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Under a Subcontract to HYCRUDE
for Their Cooperative Agreement
No. DE-FC21-85LC11069 With the
United States Department of Energy

November 1989

G-3/G-4

EXECUTIVE SUMMARY

Six bulk samples of eastern oil shale were taken from five states during the three years of a Department of Energy cooperative agreement with HYCRUDE Corporation in support of hydroretorting research. The oil shale samples, ranging in size from 1300 pounds to 315 pounds, were taken from the Clegg Creek Member of the New Albany Shale in northwestern Kentucky, the Chattanooga Shale in northern Alabama, the Gassaway Member of the Chattanooga Shale in central Tennessee, the Antrim Shale in northeastern Michigan, the Cleveland Member of the Ohio Shale in central Ohio, and the Sunbury Shale in eastern Kentucky. A seventh sample of Clegg Creek from southern Indiana had been sampled earlier.

The stratigraphic position of all bulk samples was documented using both outcrops and subsurface control; at five sites stratigraphic test holes were cored and logged. Surface gamma was run on the cores before slabbing. Geophysical logging of on-site core holes contributed new stratigraphic knowledge linking subsurface terminology to surface exposures in Michigan, Kentucky, and Tennessee; previously unreported geological contacts - unit boundaries - were discovered in outcrops in Michigan and Ohio.

The representative character of the Tennessee sample was assured by recovering the required weight in four cores. Obtaining representative bulk samples at other sites often required adapting channel sampling techniques to earth moving equipment, reducing an initial sample by hand methods, and minimizing contamination throughout the sampling operation.

Cores were assayed for carbon and Fischer Assay oil yield both on a selected per foot basis as composites. In two of the cases where the bulk zone was represented in cores, oil yields differed, for example: in the Michigan Antrim the bulk sample assayed 14.0 gal/ton compared to a core average of 15.6 gal/ton,

in the Kentucky Sunbury the bulk sample tested 8.4 gal/ton and the core averaged 10.8 gal/ton. Bulk samples from other sites assayed as follows: Ohio Cleveland - 11.9 gal/ton, Indiana Clegg Creek - 13.8 gal/ton, Kentucky Clegg Creek - 14.6 gal/ton, Alabama Chattanooga - 13.1 gal/ton, and Tennessee Gassaway - 9.7 gal/ton.

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