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SYNTHETIC FUELS FROM U.S. OIL SHALES, A TECHNICAL AND
ECONOMIC VERIFICATION OF THE HYTORT™ PROCESS

Project 61040 Quarterly Report for January 1–March 31, 1980

June 1980
Date Published

Work Performed Under Contract No. AC01-79ET14102

Institute of Gas Technology
IIT Center
Chicago, Illinois

U. S. DEPARTMENT OF ENERGY

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EXECUTIVE SUMMARY

The following is a summary by task of the HYTORT™ Process development work conducted from January 1 through March 31, 1980.

Task 1. Laboratory Program

We completed thermobalance tests to determine the variability in shale hydroretorting behavior with location. Only slight differences were observed in behavior with New Albany shales from Kentucky and Indiana. A significant correlation was observed between shale density and organic carbon content for an Ohio shale core sample. No simple relationship between shale organic carbon content and hydroretorting yields could be observed, however, for this shale sample.

We obtained quotations from potential vendors for all long-delivery items for the laboratory-scale reactor and submitted requests to purchase. Detailed design of all major equipment is now complete.

We received the differential scanning calorimeter, and testing is under way.

Task 2. Bench-Scale Program

Four moving-bed runs were made this quarter in the bench-scale reactor and the results of two tests (with a Kentucky New Albany shale and a Cleveland member of the Ohio shale) are now available. The Ohio shale proved to be less reactive than the New Albany, but satisfactory operation was achieved with both shales.

Modifications were made in the bench-scale steam-oxygen gasification reactor to provide for feeding hydrogen and methane to the unit. A preliminary test program has been outlined for this subtask.

A set of four screening runs was made in the bench-scale hydrotreating unit with New Albany shale oil. Results of these tests will be reported in the next report.

Preliminary designs were prepared for the equipment to be used in the mist-size control studies.

No work was done on the liquid-sealed lockhopper test program this quarter. A detailed test program is being developed.

Task 3. Process Development Unit (PDU) Tests

Two runs were made this quarter in the PDU with the Kentucky New Albany shale and the Cleveland member of the Ohio shale that had been previously tested in the bench-scale unit. Satisfactory operation was achieved with both of these shales. Test results of these runs will be reported in the next report. Results of an earlier test with a Kentucky Sunbury shale, which are in good agreement with previous tests with this shale, are reported here.

Task 4. Process Environmental Assessment

The Pace Company has been selected to assist IGT in environmental assessment of the HYTORT Process. Meanwhile, IGT is designing and constructing sampling equipment and is ordering some additional analytical equipment; samples are being taken for analysis during the PDU tests. Results of these analyses will be presented in the next report.

Task 5. Process Design and Economics

A process design for manufacture of syncrude from Western oil shale has been completed and cost estimate preparation is now about half completed. A set of equations was developed to describe moving-bed retorts. We are now working on a method of solution.

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PROGRAM OBJECTIVE

The objective of this program is to fully demonstrate the technical and economic feasibility of the HYTORT Process concept as it applies to both Eocene and Devonian shales. Achievement of this objective will significantly widen the Nation's synthetic fuels resource base by adding a new resource — Devonian shale — to the list of possible feedstocks for a synthetic fuels industry. It will also establish a high-efficiency alternative to conventional retorting of Western oil shales.

INTRODUCTION

Until recently, many U.S. oil shales (e.g., the Devonian shales of the Eastern United States) were considered to be unsatisfactory feedstocks for synthetic oil production because of their relatively low oil yields in the Fischer Assay test and in conventional thermal retorting. Because oil shales that are chemically more similar to Devonian shale than to Eocene shale actually constitute the bulk of the Nation's oil shale resources, and because many of these shales have organic carbon contents comparable with much of the Eocene shale deposits, there is a need for processes capable of economically processing both of these types of shale.

Research at the Institute of Gas Technology (IGT) has led to the development of the HYTORT Process concept, which can be applied to the resources of Devonian shales of the Eastern United States as well as to Western shales, to produce oil or combustible gas at costs competitive with or less than those for retorting of Colorado shales. The HYTORT Process concept has been successfully scaled up through small-scale laboratory equipment, a bench-scale unit capable of processing 100 pounds of shale per hour, and a Process Development Unit (PDU) with a shale capacity of 1 ton/hr. In addition, preliminary process design and economic analysis work shows that the HYTORT Process exhibits attractive efficiency and economics. The main areas that require further research and that will be studied in this program are as follows:

- Hydrotretorting kinetics of those Devonian and Eocene shales not previously tested in the HYTORT Process and the nature of primary products of hydrotretorting
- Analysis of process heat effects (both chemical and physical) in the shale hydrotretorting step
- H₂ manufacture by steam-oxygen gasification of raw shale fines or spent shale
- Fluidized-bed hydrotretorting of raw shale fines
- Upgrading of raw HYTORT shale oil
- Control of oil mist size in the hydrotretorting reactor
- Performance of liquid-sealed lockhoppers on Eastern and Western shale feed

- Assessment of the environmental aspects of the HYTORT Process
- Process design and economics for previously untested shales.

The above process development work is covered by five major task areas. The objectives of these tasks and subtasks and the technical progress during the last quarter (January 1 through March 31, 1980) are presented in this report.

TECHNICAL PROGRESS REPORT

Task 1. Laboratory ProgramSubtask 1.1. Thermobalance TestsObjective

The objective of this subtask is to evaluate the chemical reactivity and determine the kinetics of reactions of selected Eastern and Western oil shales under a variety of operating conditions.

Discussion

Several samples of New Albany shale from different locations have now been tested in thermobalance runs in hydrogen at 35 atmospheres and at heat-up rates of 20°F/min. The purpose of these runs is to examine the range of variability with location in hydrotreating yield for various shale samples within a particular rock unit. For New Albany shales, four samples were available from Location 64, in Kentucky, obtained at different depths. An Indiana New Albany sample (NA-2a, Location 89) had been studied earlier at the same conditions. The yields reported in Table 1 are based on ultimate analysis of feed and residue shales and the measured hydrocarbons in the product gas. Liquid yield is by difference.

Table 1. COMPARISON OF NEW ALBANY SHALE YIELDS
(500-psig H₂, 20°F/min)

<u>Shale Source, Location No.</u>	<u>Run No.</u>	<u>Feed Organic C, wt %</u>	<u>Total Organic Conversion, %</u>	<u>Liquid Yield, % of Feed C</u>
64 (4.5 ft)*	S 79-39	13.2	88.2	66.5
64 (7.5 ft)	S-79-38	11.4	87.8	61.3
64 (18.0 ft)	S-79-7	14.5	86.9	63.3
64 (22.0 ft)	S-79-37	15.5	87.9	63.5
Clark Co. Ind.	S-79-22	13.7	83.0	57.6

* Distance from top of rock unit.

The range of variation in test results from the same source at different depths is probably within the experimental uncertainty. The sample from a different area appears to have a yield potential about 10% lower in liquid

and 5% lower in total conversion. Comparable variation was noted for Sunbury shales from different sources. It had been noted in earlier studies¹ that among differences in hydroretorting behavior noted in geologically different shales, the liquid yield varies more than the total yield.

To examine the effect of shale richness on hydroretorting yield, a sample of Ohio shale (Location 139) taken from a narrow section of a test coring (22 to 27 feet from the surface) was divided into several fractions by a sink-float technique. Particle density intervals of 0.05 g/cm^3 for the density range of 2.00 to 2.35 g/cm^3 were achieved through the use of mixtures of carbon tetrachloride and sym-tetrabromoethane.

In Figure 1 the carbon content of the different fractions is shown as a function of the particle density deduced from the sink-float operation. This simple relation is convenient for separation purposes. However, these samples are relatively dry (maximum 2.3% moisture), and the moisture is approximately monotonic with the carbon content (increasing with decreasing carbon). If the samples were extremely wet and had no correlation between moisture and organic content, this close correlation would be destroyed.

In Figure 2, samples from the same coring are examined for a correlation of carbon with helium or true density. Here the moisture content never exceeded 3.3% and showed little correlation with the carbon content. Although, more scattered, this correlation appears significant, particularly in view of the range in depth which covers geologically different shales.

For the separated sample, Table 2 presents the yields in the standard hydroretorting runs.

Table 2. YIELDS FROM SINK-FLOAT SEPARATED OHIO SHALE
(500 psig H_2 , 20°F/min)

<u>Feed Carbon,</u> <u>wt %</u>	<u>Total</u> <u>Conversion</u> <u>% of Feed Carbon</u>	<u>Liquid</u> <u>Yield</u>
18.8	74.8	57.4
16.9	78.5	58.9
16.2	74.6	56.5
11.8	68.8	49.2
10.7	67.8	49.6
8.9	70.5	44.4

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Figure 1. CARBON CONTENT OF OHIO SHALE
(Location 139, 22 to 27 Feet) AS A
FUNCTION OF PARTICLE DENSITY

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Figure 2. CORRELATION OF CARBON CONTENT OF OHIO SHALE (Location 139) WITH HELIUM DENSITY

There appears to be a decline in yield (on a relative basis) with decreasing organic content. But the fluctuations in conversion are too great to suggest a simple relationship. There are qualitative differences in the different fractions. Figure 3 shows the weight loss rate curves for three of the samples. One notable difference is the increase in weight-loss rate near 400°F with decreasing carbon content. We have no direct evidence of the nature of the product at this temperature and believe it to be primarily water, probably chemically bound to the mineral matter. If so, its significance lies in the energy required to remove it during retorting.

The second difference is in the qualitative nature of the main weight loss peak. The richest shale shows essentially a single peak. If there is an additional peak, it is too small to be differentiated within experimental variations. But the leaner shales show the onset of a 'bump' on the low-temperature side and the leanest shale shows a double peak. A kinetic description of these curves is being attempted.

Future Work

As supplied, samples of different shales will be evaluated. Systematic studies will be made to establish the effect of operating conditions and particle size on kinetics of the reactions of interest.

Subtask 1.2. Laboratory-Scale Reactor Tests

Objective

The objective of this subtask is to design, construct, and operate a small integral reactor to determine oil shale hydroretorting product distribution and properties under integral reactor conditions.

Discussion

Work this quarter was directed primarily towards design of the reactor, feed hopper, and residue receiver. Detailed design calculations for these units were completed and the units are ready for fabrication.

Quotations from potential vendors were obtained for "long-delivery" equipment, including the instrument panel and the continuous-bed-level gauge. Vendors were selected based upon competitive bidding. We have submitted requests for approval to purchase these items.

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Figure 3. WEIGHT LOSS RATES FOR OHIO SHALE
(Location 139, 22 to 27 Feet)(500-psig H₂, 20°F/min)

The laboratory in which the test unit will be installed is nearing completion. Drawings for the equipment layout in the laboratory are complete.

Future Work

Future work will be directed towards equipment construction. Our efforts will be concentrated in supervising fabrication of the reactor, feed hopper, residue receiver, and instrument panel. Equipment will be installed in the laboratory space prepared as it is received.

Subtask 1.3. Calorimetric Studies

Objective

The objective of this subtask is to determine the heat capacities and heats of reactions of selected Eastern and Western oil shales under hydro-retorting conditions.

Discussion

The differential scanning calorimeter that had been ordered during the last quarter was received during this quarter. Preliminary runs to achieve familiarity with the equipment were made at low pressures. A downstream system is being designed to allow controlled purging of the DSC cell at high pressures and venting of reactive gases.

Future Work

The downstream system will be completed and the operating characteristics of the system at reaction conditions of interest will be studied.

Task 2. Bench-Scale Program

Subtask 2.1. Bench-Scale Reactor Tests

Objective

The purpose of these tests is to determine the effect of initial scale-up from laboratory- to bench-scale equipment. With this 4-inch, electrically heated reactor, sufficient oil shale is processed that complete material and elemental (carbon, hydrogen, and oxygen) balances can be performed, and sufficient oil is produced that its many properties may be determined and it can be used for further testing.

Discussion

During this quarter, four moving-bed runs were made, 80BSU-1, 80BSU-2, 80BSU-3, and 80BSU-4. Run 80BSU-1 was terminated after 1.75 hours of unsteady-state operation because of a shale plug in the upper part of the reactor. Run 80BSU-4 was terminated after about 1 hour of shale feeding time because of a bed-level indicator malfunction.

In Run 80BSU-2, a Cleveland member of the Ohio shale was retorted under moderately severe conditions to maximize oil production. Shale was fed for a total of 2.75 hours including 1.50 hours of steady-state operation. The average hydrogen partial pressure during this run was calculated to be 414 psig. In addition, the average bed temperature was 1094°F, which is approximately 200°F lower than the target value of the run program.

Earlier thermobalance tests with Cleveland shale containing 10.7 weight percent organic carbon resulted in a total conversion of 67.8% with 49.6% conversion to liquid products. In these tests, the Cleveland shale was processed at 500 psig hydrogen partial pressure with a heat-up rate of 20°F/min (to a maximum temperature of 1400°F). Run 80BSU-2 (using a comparably rich shale) resulted in a total organic carbon conversion to gaseous and liquid products of 56.1% including 37.4% conversion to liquid products.

Taking into consideration the differences in test conditions between the thermobalance and bench-scale tests, the expected bench-scale conversion based on thermobalance data would be approximately 61%. The actual conversion of 56%, therefore, falls within the previously established $\pm 10\%$ range of agreement between thermobalance and bench-scale results. The results for this run are summarized in Table 3; the complete test results are contained in Appendix A.

The test results of Run 79BSU-2, which was made last quarter, are summarized in Table 4; complete test results are contained in Appendix B. This run was also made (using Kentucky New Albany shale) under process conditions of moderate severity to enhance oil production. The total conversion of organic carbon to gaseous and liquid products was 70.9% with 40.3% conversion to liquid products. The average hydrogen partial pressure during this run was 480 psig. The average bed temperature was 1151°F with a maximum bed temperature of 1259°F. Prior thermobalance work the New Albany shales, adjusted to these

Table 3. SUMMARY OF BSU MOVING-BED TEST 80BSU-2

<u>Run No.</u>	80BSU-2
Shale Type	Cleveland
Bed Height, ft	9.0
Pressure, psig	498
Average Bed Temp., °F	1094
Maximum Bed Temp., °F	1305
Oil Shale Space Velocity, lb/ft ³ -hr	95.1
Oil Shale Mass Rate, lb/ft ² -hr	860
Hydrogen/Shale Feed Ratio, SCF/lb	7.4
Organic Carbon Distribution in Products, %	
Gas	19.8
Oil	37.4
Residue*	43.9
Material Balance	110.5
Elemental Balances*	
Carbon	104.3
Hydrogen	119.5
Oxygen**	211.6

* Using residue shale weight calculated by ash balance.

** Oxygen balance is high due to unmeasured high-temperature water in the feed shale, resulting in a low oxygen value for the feed shale.

conditions, suggests that an organic carbon conversion of approximately 75% should be realized. Therefore, the results of Run 79BSU-2 agree to within 10% of the conversion predicted from the thermobalance studies on New Albany shale.

The reactor tube temperature profiles are shown in Figures 4 and 5 for Runs 80BSU-2 and 79BSU-2 respectively. Figure 4 shows a shallow, near-linear temperature gradient throughout the entire length of the reaction zone. Figure 5 shows a substantial temperature gradient in the empty reactor tube, but a nearly uniform temperature profile in the shale bed itself. Both of these runs were made to maximize oil production during the retorting process.

Table 4. SUMMARY OF BSU MOVING-BED TEST 79BSU-2

<u>Run No.</u>	79BSU-2
Shale Type	Kentucky New Albany
Bed Height, ft	9.0
Pressure, psig	527
Average Bed Temp., °F	1151
Maximum Bed Temp., °F	1260
Oil Shale Space Velocity, lb/ft ³ -hr	98.8
Oil Shale Mass Rate, lb/ft ² -hr	893
Hydrogen/Shale Feed Ratio, SCF/lb	17.8
Organic Carbon Distribution in Products, %	
Gas	23.7
Oil	40.4
Residue*	29.1
Material Balance*	101.1
Elemental Balances*	
Carbon	93.6
Hydrogen	91.2
Oxygen**	156.3

* Using residue shale weight calculated by ash balance.

** Oxygen balance is high due to unmeasured high-temperature water in the feed shale, resulting in a low oxygen value for the feed shale.

To best achieve this, the shale bed must be taken through a linear rise in temperature at a controlled, slow (approximately 20° to 30°F/min) rate. Both profiles indicate conditions of a rapid temperature rise of the shale in the upper, empty portion of the reactor tube. Little or no temperature rise is evident in the shale bed itself. The profiles shown in Figures 4 and 5 along with the relatively low maximum temperatures may have been responsible in part for the slightly-lower-than-anticipated levels of organic carbon conversion.

With the failure of the bed-level gauge during Run 80BSU-4, the bench-scale unit was temporarily taken out of service for modification. A new bed-level gauge was installed and calibrated.

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Figure 4. REACTOR TEMPERATURE PROFILE FOR CLEVELAND SHALE — RUN 80BSU-2

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Figure 5. REACTOR TEMPERATURE PROFILE FOR NEW ALBANY SHALE — RUN 79BSU-2

In addition, flow recording controllers were installed on the feed hydrogen, purge hydrogen, and an alternate feed gas line. Prior to this addition, the hydrogen flows were controlled manually.

Future Work

The modifications of the 4-inch bench-scale unit have now been completed. Further tests with a Kentucky New Albany and other Eastern shales will be made. Tests will be conducted to maximize oil production during the next quarter in the bench-scale unit, prior to testing in the PDU.

Subtask 2.2. Hydrogen Production Studies

Objective

The purpose of these studies is to determine the technical and economic feasibility of producing at least a portion of the hydrogen requirement of the HYTORT Process using either the spent shale, which contains a residual organic carbon from the process, or the raw shale fines from the crushing plant. Steam and oxygen are used to supply the hydrogen produced and the heat duty of the process, respectively.

Discussion

Current Work

We began adapting the bench-scale gasification unit (6-inch diameter reactor) for the study of hydrogen generation by the gasification of the organic carbon remaining on spent shale with steam and oxygen. Tests in this bench-scale unit would attempt to simulate a middle zone of the hydroretorting reactor. Recovery of heat from the hot gasified oil shale requires the addition of a simulated recycle gas to the hydroretort reactor. Methane plus hydrogen will be used as recycle gas.

Storage facilities were prepared for storing methane (natural gas) and hydrogen in separate gas cylinders at pressures up to 2000 psig to serve as a feed source for these gases in the bench-scale tests. High-pressure piping was installed to transfer both gases from the storage cylinders to the area of the test unit. Shut-off valves, gas filters, and pressure regulators were installed near the bench-scale unit. Gas feed lines were installed from the outlet of the pressure regulators through separate gas-metering systems and

panel-board-mounted flow control valves. The metering systems consist of orifice plates, bellows-type differential pressure transmitters for sensing the pressure-drops across the orifice plates, and transmitting them to a chart recorder, and bourdon-tube pressure gauges for sensing the static pressure at the orifice plate. The gas feed lines will be extended to the bottom of the reactor when the bench-scale equipment becomes available upon completion of the current test program.

Program

A preliminary program for this subtask has been developed. Basically, this program involves two different types of runs in the 6-inch unit, the purpose of which is to produce at least part of the hydrogen requirement of the HYTORT Process internally within the HYTORT reactor. This is accomplished by gasifying the feed material using steam and oxygen.

The first set of runs will utilize spent shale from previous PDU runs. The spent shale is processed in a countercurrent, moving-bed mode. The purpose here is to simulate, as closely as possible, an added zone, located approximately in the middle of the retort, wherein the residual organic carbon is gasified to produce carbon monoxide and hydrogen.

Three moving-bed tests using spent shale are planned. Since no previous work on this chemistry exists for Eastern shale, they are exploratory in nature. The tentative run conditions are given in Table 5.

Table 5. TENTATIVE RUN CONDITIONS

	<u>Run 1</u>	<u>Run 2</u>	<u>Run 3</u>
$T_{g_4}, ^\circ\text{F}$	1800	~ 1800	~ 1800
$\hat{T}_{s_3}, ^\circ\text{F}$	1600	~ 1600	~ 1600
O_2 in Steam, %	8		
C_{hr}	1.9		
C_G	0.8	~ 0.8	~ 0.6
Steam in M_4 , %	55	~ 20	~ 20

A schematic diagram of the unit is given in Figure 6. T_{g4} and M_4 refer to the temperature and moles per hours, respectively, for the gas stream that will gasify the shale. $\hat{T}_{s3}$ refers to the bulk shale temperature at the exit of the gasification zone. As these temperatures are not directly measured, the maximum temperature at a point just above the point of introduction of the steam and oxygen will be specified. For example, in Run 1, the maximum temperature will be in the region of 1700°F.

The second set of runs will utilize raw shale fines (produced in shale crushing operations). These will be fluidized-bed tests, using steam or oxygen as the gasifying agent. Other than to use a size range of -10+80 mesh, no run condition has been specified.

Future Work

The program outlined above will be performed as soon as the 6-inch unit becomes available. The moving-bed tests using spent shale will be performed first. These will be followed by the fluidized-bed tests using raw shale fines.

Subtask 2.3. Shale Oil Upgrading

Objective

The purpose of this subtask is to determine the hydrogen consumption and yield distributions associated with hydrotreating the raw whole shale oils produced in the other subtasks (PDU and bench-scale units). Although it is possible to reduce the nitrogen level to very low values (approximately 1 ppm), 500 to 1000 ppm nitrogen will be the level normally used as a target value.

Discussion

During the first quarter of 1980, the IGT hydrotreating unit was renovated and upgraded. A new hydrogen feed delivery system including a flow-recording controller was installed. The chosen catalyst, Shell 324, a Ni/Mo hydrotreating catalyst initially developed for treating heavy feedstocks, was loaded and pre-sulfided.

A set of four screening runs on New Albany shale oil has now been completed. Test results will be reported in the next project quarterly report.

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Figure 6. 6-INCH BENCH-SCALE UNIT

The run conditions for this test set were as follows:

Catalyst Volume, cm ³	1000
Average Catalyst Temperature, °F	775, 750, 800, 775
Pressure, psig	2000
H ₂ Feed Rate, SCF/bbl	3000
Liquid Hourly Space Velocity*	0.6

A steady-state period of 4 hours was maintained for each of the runs. The hydrotreated oil produced will be subjected to a water wash and an acid wash, and sulfur and nitrogen levels will be measured at each step. At this time analytical results are not complete.

When the results of these screening runs are available, conditions for hydrotreating shale oils produced in the future will be determined.

Future Work

A screening test will be made on oil from each of the shales tested at conditions determined by results of the tests conducted this quarter. The purpose of these screening tests is to determine the minimum level required to produce a whole liquid product of 500 to 1000 ppm nitrogen. Given sufficient raw shale oil from the PDU runs (Task 3), an extended run will be made in order to determine hydrogen consumption and yield distribution at a product nitrogen level of from 500 to 1000 ppm.

Subtask 2.4. Mist-Size Control Studies

Objective

The objective of this subtask is to design, construct, and operate a laboratory test system to evaluate techniques of enhancing fog formation under retorting conditions and to eventually incorporate the most promising techniques into the PDU studies.

Discussion

Possible laboratory test systems to evaluate techniques of enhancing mist formation have been studied for appropriateness to hydrotreating conditions.

* Defined as volume of feed/hr per unit volume of catalyst.

Generation of mist in a steady-state system appropriate to conditions of interest does not appear to be practical at the present time. It appears more practical to generate mist in an unsteady-state batch system.

Two possible modes of operation are -

1. To place raw shale in a tube to which a hot inert gas can be fed from the bottom, closely simulating a retorting system. The hot gas heats the shale to an appropriate temperature where oil vapor is drawn off the shale and eventually cools, condenses, and forms mist. The amount of mist and its size would be determined after the gas stream leaves the reactor.
2. To place some cold inert rock in the tube to which a superheated mixture of inert gas and oil vapor is introduced from the bottom. The gas mixture becomes saturated and condenses as it moves upward. This experiment can be done at lower temperatures than the shale retort.

To estimate the performance of the proposed system a solution was obtained to the equations governing the heat transfer through the bed. The major simplifications in the description include that it is adiabatic, one-dimensional, and has no intra-particle heat transfer resistance and no reaction. The primary purpose of this analysis is to estimate the run length in such a system.

Some preliminary plots of temperature profiles generated at some fixed point as a function of time are given in Figure 7 for values of $v_g = 2$ ft/s and $v_g = 1$ ft/s where v_g is the gas velocity at inlet condition. The presumed diameter of the bed is 3 inches and the bed length is 2 feet. Other values used in determining these profiles are 16 Btu/hr-ft²-°F for the gas-film coefficient, 0.25 inch for the equivalent spherical particle diameter, 0.35 Btu/lb-°F for the shale heat capacity, 135 lb/ft³ for the shale density, 7 Btu/lb mole-°F for the gas heat capacity and 0.5 for the void fraction of the bed. If we allow an exit temperature rise of 20% to 30% of the possible values to assure condensation of the vapor, a run would be about 100 minutes in duration.

The pressure drop was estimated to be 0.5 psia when the inlet gas pressure is 15 psia. Heat losses have also been estimated. Overall heat transfer coefficient (neglecting radiation) is about 1.2 Btu/hr-ft²-°F. At temperatures higher than 800°F radiation becomes more important. To supply the heat that will be lost at very high temperatures when shale is

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Figure 7. TEMPERATURE HISTORY AT BED EXIT

being retorted, a small amount of air may be added to the inert gas so that combustion may supply some of the energy. For operation with inert solid, lighter oil will be used and heat losses will be significantly less.

The power requirement for this system has been estimated to be 1.5 kW, which can be supplied electrically. The design pertaining to collection of mist and determination of mist size is currently being carried out.

Future Work

The design will be completed and construction begun.

Subtask 2.5. Liquid-Sealed Lockhopper Tests

Objective

The purpose of these tests is to determine the effect of 1) the raw shale feed rate, 2) the particle size distribution, and 3) the discharge pressure on the amount of water carry-over to the retort. This amount of water must be known accurately in order to effectively design a continuously operating retort using this feed mechanism. That is, the heat duty caused by this excess surface water must be accounted for in the upper portion of the retorting zone.

Discussion

No experimental work has been done during this quarter on the existing test unit. A test program is being developed.

Future Work

We will complete the test program and begin testing.

Task 3. Process Development Unit (PDU) Tests

Objective

The objective of this task is to demonstrate the technical feasibility of the hydrotreating process with various Eastern and Western shales under the adiabatic (thermally balanced) operating conditions that are encountered in large-scale equipment. The effects of major operating variables on product yields and properties as well as on mechanical operability of the system will be established.

Discussion

Test Results

Five PDU run attempts, including two long successful runs, were made this quarter. In 80PDU-1 a Cleveland member of the Ohio shale was fed at a rate of approximately 1000 lb/hr for 8.25 hours including 6.00 hours of steady-state operation. A Kentucky New Albany shale was fed for 8.00 hours with 6.50 hours of steady-state operation in 80PDU-2. Both runs were voluntarily terminated. Test results for these two successful runs will be reported in the next quarterly report when analytical data become available.

The first two PDU runs of this quarter were terminated before shale feed was initiated. Mechanical problems with the level transmitter for the Stage 2 quench tower and the back-pressure control valve for the Stage 1 off-gas system forced early run terminations. New level transmitters have been ordered to replace the failed transmitter, and the back-pressure control valve was repaired. A leaking Grayloc clamp during heat-up caused early run termination of our other unsuccessful test. The leaking Grayloc will be replaced by a welded pipe section for our next run.

Analytical data are now available for 79PDU-1, a test made with Kentucky Sunbury shale during the previous quarter. The Kentucky Sunbury shale test was performed first since it was the first large sample of Eastern shale received and it had been tested previously in the laboratory- and bench-scale units. Run 79PDU-1 was made to obtain information on product yield and quality of Kentucky Sunbury shale using preheated hydrogen as the hydro-retorting gas under oil-making conditions. The product oil obtained from Run 79PDU-1 also produced sufficient shale oil for the bench-shale hydro-treating tests described in Subtask 2.3, above.

A summary of test results and operating conditions is presented in Table 6. In 79PDU-1 we fed shale at a rate of 1095 lb/hr for 8.00 hours including 6.00 hours of steady-state operation, before the run was voluntarily terminated. A feed-hydrogen-to-shale ratio of 20.4 SCF/lb was used in Stage 1 while a feed-hydrogen-to-shale ratio of 12.5 SCF/lb was maintained in Stage 2. The hydrogen-to-shale ratios were chosen so that the enthalpy of the shale would nearly equal the enthalpy of the feed gas for each respective stage. The Stage 2 feed-hydrogen-to-shale ratio is lower than the ratio for Stage 1 because air is added to Stage 2, which increases the

Table 6. SUMMARY OF TEST RESULTS USING KENTUCKY SUNBURY SHALE

Run No.	79 PDU-1
Shale Type	Kentucky Sunbury
Bed Height, ft	10.0
Pressure, psig	403
Average Bed Temp., °F*	1281
Maximum Bed Temp., °F*	1381
Oil Shale Space Velocity, lb/ft ³ -hr*	125.5
Oil Shale Mass Rate, lb/ft ² -hr*	1255
Hydrogen/Shale Feed Ratio, SCF/lb*	12.5
Organic Carbon Distribution in Products, %	
Gas	24.4
Oil	29.9
Residue†	35.0
Material Balance†	103.0
Elemental Balances†	
Carbon	87.0
Hydrogen	103.9
Oxygen††	198.1

* Stage 2.

† Using residue shale weight calculated by ash balance.

†† Oxygen balances are high due to unmeasured high-temperature water in the feed shales, resulting in a low oxygen value for the feed shale. Future analyses will use high-temperature water data in order to obtain more accurate oxygen balances.

total enthalpy of the feed gas. Some of the feed hydrogen is burned to provide additional heat to the hydroretorting gas in Stage 2. The reactor pressure was 403 psig while the average hydrogen partial pressure (calculated by numerically averaging the inlet hydrogen partial pressure with the exit hydrogen partial pressure) was approximately 337 psig. Complete test results are presented in Appendix C of this report.

Total organic carbon conversion to liquid plus gases was approximately 65%, by use of ash balance to calculate the yield of spent shale. The ratio of organic carbon converted to oil to that for gas was 1.2 for this run. Thermobalance tests were not made on this particular batch of shale prior to the PDU run since the shale was procured from the same area where a previous batch of Kentucky Sunbury shale was obtained. Thermobalance, bench scale, and PDU tests were conducted on an earlier sample of the same Kentucky Sunbury shale. These test results are reported elsewhere.¹

Figure 8 shows the relationship between heat-up rate and hydrogen partial pressure, with organic carbon recovery, for previous thermobalance tests performed earlier with Eastern shale.¹ Using an average heat-up rate for Run 79PDU-1 for both stages of approximately 20°F/min, an average hydrogen partial pressure of 337 psig, and previous thermobalance data,¹ one can estimate the expected organic carbon recovery to be about 65%.

A comparison of measured and calculated organic carbon conversions is graphically depicted in Figure 9. The data shown on this graph were also obtained from previous work.¹ The graph indicates the accuracy with which we are able to predict organic carbon conversion in the PDU or BSU based on organic carbon conversion data obtained in the thermobalance.

The bed temperature profiles of Stage 1 and Stage 2 for Run 79PDU-1 are shown in Figures 10 and 11, respectively. The Stage 1 temperature profile indicates that the gas/shale ratio was probably too low. That is, the product of shale rate times average shale heat capacity was higher than that for the gas. The temperature profile remains constant at a value of approximately 300°F for more than half the bed in Stage 1. Part of the reason for the slow shale heat-up at the top of the bed is probably the approximately 1% by weight surface water and approximately 5.8% by weight bound water that was driven off in Stage 1. Sensible heat from the incoming gas must supply the heat of vaporization of the water present in the shale as well as sensible-heat requirements. Also, we estimate that approximately 20% of the feed gas to Stage 1 bypassed into Stage 2. Normally, we can control gas bypassing from one stage into another to less than 5% of the feed gas rate.

There is a very rapid heat-up of the shale between the temperature range of 400°F to 1150°F as evidenced by the temperature profiles shown previously in Figures 10 and 11. The rapid heat-up of the shale, approximately 75°F/min, in the range of 400°F to 1150°F may have contributed somewhat to a lower total organic carbon conversion.

The bed-temperature profile for Stage 2 indicates that the gas/shale ratio was too high. The temperature profile is not linear as it would be if the product of shale rate times the average shale heat capacity was nearly the same as that for the gas.

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Figure 8. ORGANIC CARBON CONVERSION IN THERMOBALANCE TESTS WITH KENTUCKY NEW ALBANY SHALE

Figure 9. COMPARISON OF MEASURED ORGANIC CARBON CONVERSIONS WITH THOSE ESTIMATED FROM THERMOBALANCE RESULTS

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Figure 10. STAGE 1 BED-TEMPERATURE PROFILE FOR RUN 79PDU-1

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Figure 11. STAGE 2 BED-TEMPERATURE PROFILE FOR RUN 79PDU-1

A detailed summary of the product oil properties is shown in Appendix C of this report. Most (85.7%) of the oil was produced in Stage 2. The oil in Stage 2 had a pour point of 5°F with an API gravity of 13.4. Therefore, there should be no difficulty pumping this oil.

Shale Sample Acquisition

A 40-ton sample of Antrim (Michigan) shale, crushed to minus 1/2-inch, was received this quarter for testing in the PDU. The Antrim shale will be tested in the thermobalance and the bench-scale reactor before being tested in the PDU.

Future Work

We will continue to test those shales now available in large-tonnage quantities. We will continue to work to obtain other large-tonnage samples.

Task 4. Process Environmental Assessment

Objective

The objective of environmental assessment activities is to establish a data base that can be used to estimate the environmental effects of a commercial-scale hydroretorting plant. This data base will be established using environmental data obtained from the largest operating unit in this program - the PDU. A subcontractor, recognized in the environmental engineering field and with experience in oil-shale conversion processes, has been retained to assist IGT in the computation and interpretation of the data base. Environmental data for the HYTORT Process must be developed concurrently with process data to enable proper and economical design of wastewater and air-pollution control systems plus the determination of process environmental impacts for specific sites.

Discussion

The process of selecting a subcontractor to assist IGT in the HYTORT environmental assessment has been completed with the selection of The Pace Company from the Jacobs Engineering Group, Inc. A contract has now been negotiated, and the contract has been signed. An orientation meeting was held in Chicago on February 13, 1980, to review the IGT PDU operation and to discuss the PDU environmental test plan with Pace. Sampling re-

quirements and analytical capabilities are now being reviewed with Pace in preparation for development of an environmental test plan.

Experimental sampling and analytical equipment is now being designed, constructed, and ordered. Sampling probes and lines from the first and second stages of the PDU prior to the cyclone and gas quench are now being designed. Assorted equipment (sampling bombs, pressure regulators, valves, gas meters, tubing, fittings, support structure, etc.) have been ordered for construction of a sampling train to obtain PDU gas samples during steady-state operation. A purchase order was placed for a laboratory gas chromatograph to allow specific analyses for halogen, nitrogen, or sulfur-containing compounds in both liquid and gas samples. This instrument uses electrolytic conductivity detection for selective analysis of priority pollutants, thiophenes, and other sulfur compounds; in addition, the detector is reported to be effective for the specific detection of nitrosamines in the presence of other nitrogen compounds. This instrument will be located near the PDU to allow timely analysis of process samples in an effort to minimize the effects of sample degradation.

Samples for environmental purposes were taken from run 80PDU-1 carried out with Cleveland oil shale. Information sought includes trace elements on feed and spent shales, and organic compounds in the first- and second-stage oil and water phases.

Future Work

The immediate objective is to complete an environmental test plan that remains within budget and time restraints, yet addresses the major environmental questions concerning larger HYTORT plants. This test plan will be completed through the combined efforts of IGT and Pace staff members. Delivery of the gas chromatograph and sampling equipment is expected within 30 to 60 days. Once delivery is completed, we will prepare for the on-line sampling of PDU process streams during steady-state operation.

Task 5. Process Design and Economics

Objective

In order to evaluate the potential of various oil shales as feedstocks for oil or SNG, and to help guide the experimental program, process design and

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Figure 12. MANUFACTURE OF SYNCRUDE FROM COLORADO OIL SHALE

economics studies for the conversion of Western Eocene Shale and Eastern Devonian shale will be made. A mathematical model to predict gas and shale temperature profiles in moving-bed-type retorts will also be developed.

Discussion

Process Economics

Figure 12 presents a simplified flow diagram for the manufacture of syncrude from Western oil shale. With our usual assumption of all power generated onsite, the design produces 55,606 bbl/day of 28.7°API oil from a shale input of 87,125 tons/SD at an overall efficiency at the 70% level. The oil after hydrotreating contains only 675 ppm nitrogen and 60 ppm sulfur.

The design requires no oxygen, a moderate amount of steam (317 million Btu/hr), and 70,000 kW of power. Costing of the plant is now about half completed.

Process Design

A set of equations to describe moving-bed retorts has been developed. The key assumptions are as follows:

- The system is a steady-state one-dimensional process.
- Four different phases are considered. They are gas phase, solid phase, mist phase, and liquid phase on the solid surface.
- Mist-phase velocity is the same as gas-phase velocity.
- Liquid-phase velocity and temperature are the same as solid-phase velocity and temperature.
- The mist and gas phases may be at different temperatures.
- The system is adiabatic.
- The solid particle volume is constant.
- An average solid particle diameter and an average mist particle diameter can represent all respective particles.
- The densities of liquid and mist phases are equal and constant throughout the bed.
- The gas phase obeys the ideal gas law.
- The system pressure variation is negligible compared with the total pressure. No hydrodynamic equations are considered.
- Ash is inert and remains with the particle. Ash is used as a tracer in formulating solid-phase continuity equations.
- The shale particle consists of p species. The gas phase consists of m species. Liquid and mist phases consist of n species.

- The rates of formation of mist and liquid film are mass-transfer limited.
- The rate of mist deposition on the liquid film is first order.
- Raoult's Law is applicable for multicomponent vapor-liquid equilibrium relationships.
- Each solid particle can be described in terms of its average temperature. An effective solid-gas heat transfer coefficient could be made to take into account the heat transfer resistance inside the particles. The Final Report for Hydrogasification of Oil Shale¹ showed that the average solid temperature profile along the bed for 1/2-inch-diameter particles does depend upon the heat transfer resistance inside the particle under the conditions of interest. However, a similar average temperature profile can be obtained by modifying the mathematical heat transfer analysis and applying an effective heat transfer coefficient ($h = 15.92$ compared with $20 \text{ Btu/hr-ft}^2 \text{ } ^\circ\text{F}$) and the isothermal particle assumption.

Nomenclature

a_ℓ	=	contact area between solid and gas per unit reactor volume, ft^2/ft^3
a_m	=	contact area between mist particles and gas per unit reactor volume, ft^2/ft^3
B_j	=	rate of production of gas species due solely to solid-gas reaction, per unit reactor volume, $\text{lb}/\text{ft}^3/\text{s}$
C_{pgj}	=	heat capacity of gas species j, $\text{Btu}/\text{lb-}^\circ\text{R}$
C_{pmj}	=	heat capacity of mist species j, $\text{Btu}/\text{lb-}^\circ\text{R}$
C_{plj}	=	heat capacity of liquid species j, $\text{Btu}/\text{lb-}^\circ\text{R}$
C_{psi}	=	heat capacity of solid species i, $\text{Btu}/\text{lb-}^\circ\text{R}$
C_{pg}	=	gas mixture specific heat, $\text{Btu}/\text{lb-}^\circ\text{R}$
D_m	=	average diameter of mist particles, ft
D_p	=	average diameter of solid particles, ft
D_v	=	volumetric vapor diffusivity, ft^2/hr
h_{gj}	=	total enthalpy of gas species j, Btu/lb
h_{mj}	=	total enthalpy of mist species j, Btu/lb

$h_{\ell j}$	=	total enthalpy of liquid species j, Btu/lb
$h_{s i}$	=	total enthalpy of solid species i, Btu/lb
$h_{s g}$	=	solid-gas heat transfer coefficient, Btu/ft ² -°R-s
$h_{s m}$	=	mist-gas heat transfer coefficient, Btu/ft ² -°R-s
K_g	=	mass transfer coefficient, lb mole/ft ² -hr-mole fraction
k_g	=	gas mixture thermal conductivity, Btu/ft-s-°R
M_j	=	molecular weight of j th component, lb/lb mole
$\bar{M}$	=	average molecular weight, lb/lb mole; $\bar{M} = \sum_{j=1}^m y_j M_j$
$\dot{m}_{\text{cond}, m_j}$	=	rate that mist species j is condensed from vapor per unit reactor volume, lb/ft ³ -s
$\dot{m}_{\text{cond}, \ell_j}$	=	rate that liquid species j is condensed from vapor per unit reactor volume, lb/ft ³ -s
$\dot{m}_{\text{dep}, j}$	=	rate that liquid species j is deposited from mist phase per unit reactor volume, lb/ft ³ -s
N_m	=	number flux of mist particles, No./ft ² -s
Nu	=	Nusselt number, $h_{s g} D_p / k_g$ or $h_{s m} D_m / k_g$
P	=	system pressure, atm
P_j	=	partial pressure of j th component in gas phase, atm
P_j^o	=	vapor pressure of pure j th species, atm
$P_{j, \text{eq}}(T_\ell, Z)$	=	equilibrium pressure of j th component at liquid temperature $T_\ell (= T_s)$ and compositions Z_1 through Z_n , atm
$P_{j, \text{eq}}(T_m, X)$	=	equilibrium pressure of j th component mist temperature T_m and compositions X_1 through X_n , atm
Pr	=	Prandtl number, $C_{p g} \mu / k_g$
Q_{ash}	=	ash flow rate per unit reactor cross-sectional area, lb/ft ² -s

R	=	universal gas constant, 1546 ft-lbf/lb mole- $^{\circ}R$
$\dot{R}_i$	=	reaction rate for i^{th} reaction, sec $^{-1}$
Re	=	Reynolds number, $\epsilon_g \rho_g (v_s - v_g) D_p / \mu_g$
$(S_j)_g$	=	mass rate of gas species j produced per unit reactor volume, lb/ft 3 -s
$(S_j)_l$	=	mass rate of liquid species j produced per unit reactor volume, lb/ft 3 -s
$(S_j)_m$	=	mass rate of mist species j produced per unit reactor volume, lb/ft 3 -s
$(S_i)_s$	=	mass rate of solid species i produced per unit reactor volume, lb/ft 3 -s
Sc	=	Schmidt number, $\mu_g / \rho_g D_v$
Sh	=	Sherwood number, $K_g D \bar{M} / \rho_g D_v$
T_g	=	gas-phase temperature, $^{\circ}R$
T_m	=	mist-phase temperature, $^{\circ}R$
T_s	=	solid-phase temperature, $^{\circ}R$
v_g	=	gas velocity, ft/s (negative for upward flow)
v_s	=	solid velocity, ft/s (positive for downward flow)
X_j	=	weight fraction of j^{th} species in mist phase
x_j	=	mole fraction of j^{th} species in mist phase
Y_j	=	weight fraction of j^{th} species in gas phase
y_j	=	mole fraction of j^{th} component in gas phase
$y_{j,eq}(T_m, X)$	=	j^{th} component mole fraction in equilibrium with mist phase temperature, T_m , and compositions X_1 through X_n
$y_{j,eq}(T_s, Z)$	=	j^{th} component mole fraction in equilibrium with the liquid phase at $T_l = T_s$ and compositions Z_1 through Z_n
Z_j	=	weight fraction of j^{th} species in liquid phase
z_j	=	mole fraction of j^{th} species in liquid phase

ρ_{ash}	= ash density, lb/ft ³
ρ_g	= gas density, lb/ft ³
ρ_l	= liquid density, lb/ft ³
ρ_m	= mist density, lb/ft ³
ϵ_g	= gas-phase volume fraction
ϵ_l	= liquid-phase volume fraction
ϵ_m	= mist-phase volume fraction
ϵ_s	= solid-phase volume fraction
μ_g	= gas mixture viscosity, lb/ft-s
ω_i^o	= lb of solid species i in raw shale per lb of ash, dimensionless
ξ_i	= fraction of solid species i converted, dimensionless.

Total Gas Phase Mass Balance

$$\frac{d}{dx} [\rho_g \epsilon_g v_g] = \sum_{j=1}^m (S_j)_g \quad (1)$$

Total Mist Phase Mass Balance

$$\frac{d}{dx} [\rho_m \epsilon_m v_g] = \sum_{j=1}^n (S_j)_m \quad (2)$$

Total Liquid Phase Mass Balance

$$\frac{d}{dx} [\rho_l \epsilon_l v_s] = \sum_{j=1}^n (S_j)_l \quad (3)$$

Gas Phase Species Mass Balance

$$\frac{d}{dx} [\rho_g \epsilon_g v_g Y_j] = (S_j)_g \quad j = 1, \dots, m \quad (4)$$

Mist Phase Species Mass Balance

$$\frac{d}{dx} [\rho_m \epsilon_m v_g X_j] = (S_j)_m \quad j = 1, \dots, n \quad (5)$$

Liquid Phase Species Mass Balance

$$\frac{d}{dx} [\rho_l \epsilon_l v_s Z_j] = (S_j)_l \quad j = 1, \dots, n \quad (6)$$

Solid Phase Species Mass Balance

$$\frac{d}{dx} [Q_{ash} \omega_i^o (1 - \xi_i)] = (S_i)_s \quad i = 1, \dots, p \quad (7)$$

Gas Phase Energy Balance

$$\begin{aligned} & \frac{d}{dx} \left[\sum_{j=1}^m \epsilon_g \rho_g v_g Y_j (h_{gj})_{T_g} \right] \\ &= h_{mg} a_m (T_m - T_g) + h_{sg} a_l (T_s - T_g) + \sum_{j=1}^m B_j (h_{gj})_{T_s} \\ &- \sum_{j=1}^n \dot{m}_{cond, m_j} (h_{mj})_{T_g} - \sum_{j=1}^n \dot{m}_{cond, l_j} (h_{lj})_{T_g} \end{aligned} \quad (8)$$

Mist Phase Energy Balance

$$\begin{aligned}
 & \frac{d}{dx} \left[\sum_{j=1}^m \epsilon_m \rho_m v_g X_j (h_{mj})_{T_m} \right] \\
 &= h_{mg} a_m (T_g - T_m) - \sum_{j=1}^n \dot{m}_{dep,j} (h_{lj})_{T_m} \\
 &+ \sum_{j=1}^n \dot{m}_{cond,mj} (h_{mj})_{T_g}
 \end{aligned} \tag{9}$$

Solid and Liquid Phases Energy Balance

$$\begin{aligned}
 & \frac{d}{dx} \left[\sum_{i=1}^p Q_{ash} \omega_i^o (1 - \xi_i) (h_{si})_{T_s} + \sum_{j=1}^n \epsilon_l \rho_l v_s Z_j (h_{lj})_{T_s} \right] \\
 &= h_{sg} a_l (T_g - T_s) - \sum_{j=1}^m B_j (h_{gj})_{T_s} + \sum_{j=1}^m \dot{m}_{cond,lj} (h_{lj})_{T_g} \\
 &+ \sum_{j=1}^n \dot{m}_{dep,j} (h_{lj})_{T_m}
 \end{aligned} \tag{10}$$

Gas Phase Density (Ideal Gas Law Assumption)

$$\rho_g = \frac{P}{RT_g} \left(\sum_{j=1}^m Y_j / M_j \right)^{-1} \tag{11}$$

Constant Voidage Assumption

$$\epsilon = \epsilon_g + \epsilon_m + \epsilon_l = \text{constant} = 1 - \epsilon_s \tag{12}$$

From the definitions of the variables, the above equations could be arranged as a set of first order ordinary differential equations.

$$\frac{dY_j}{dx} = \frac{1}{\epsilon_g \rho_g v_g} \left[(S_j)_g - Y_j \sum_{j=1}^m (S_j)_g \right] \tag{13}$$

$$\frac{dX_j}{dx} = \frac{1}{\epsilon_m \rho_m v_g} \left[(S_j)_m - X_j \sum_{j=1}^n (S_j)_m \right] \tag{14}$$

$$\frac{dz_j}{dx} = \frac{1}{\epsilon_{\ell} \rho_{\ell} v_s} \left[(S_j)_{\ell} - z_j \sum_{j=1}^n (S_j)_{\ell} \right] \quad (15)$$

$$\frac{d\epsilon_{\ell}}{dx} = \frac{1}{\rho_{\ell} v_s} \left[\sum_{j=1}^n (S_j)_{\ell} \right] \quad (16)$$

$$\frac{d\epsilon_m}{dx} = \frac{1}{\rho_m v_g} \left[\sum_{j=1}^n (S_j)_m - \rho_m \epsilon_m \left(\frac{dv_g}{dx} \right) \right] \quad (17)$$

$$\frac{d\epsilon_g}{dx} = - \frac{d\epsilon_m}{dx} - \frac{d\epsilon_{\ell}}{dx} \quad (18)$$

$$\frac{d\xi_i}{dx} = \frac{1}{v_s} \dot{R}_i \quad (19)$$

$$\frac{d\rho_g}{dx} = - \frac{\rho_g}{T_g} \frac{dT_g}{dx} - \frac{R\rho_g^2 T_g}{P} \left(\sum_{j=1}^m \frac{1}{M_j} \frac{dY_j}{dx} \right) \quad (20)$$

$$\frac{dv_g}{dx} = \frac{1}{\epsilon_{g\mu} v_g} \left[\sum_{j=1}^m (S_j)_g - \rho_g v_g \left(\frac{d\epsilon_g}{dx} \right) - \epsilon_{g\mu} v_g \frac{d\rho_g}{dx} \right] \quad (21)$$

$$\begin{aligned} \frac{dT_g}{dx} = & \{ h_{mg} a_m (T_m - T_g) + h_{sg} a_{\ell} (T_s - T_g) + \sum_{j=1}^m B_j (h_{gj})_{T_s} \\ & - \sum_{j=1}^n \dot{m}_{cond, mj} (h_{mj})_{T_g} - \sum_{j=1}^n \dot{m}_{cond, \ell j} (h_{\ell j})_{T_g} \\ & - \sum_{j=1}^m (h_{gj})_{T_g} (S_j)_g \} / \left[\sum_{j=1}^m \epsilon_{g\mu} \rho_{g\mu} v_{gj} C_{pgj} \right] \end{aligned} \quad (22)$$

$$\begin{aligned}
\frac{dT_m}{dx} = & \{ h_{mg} a_m (T_g - T_m) - \sum_{j=1}^n \dot{m}_{dep,j} (h_{lj})_{T_m} \\
& + \sum_{j=1}^n \dot{m}_{cond,mj} (h_{mj})_{T_g} - \sum_{j=1}^n (h_{mj})_{T_g} (S_j)_m \} \\
& / [\sum_{j=1}^n \epsilon_m \rho_m v_{g,j} X_j C_{Pmj}]
\end{aligned} \quad (23)$$

$$\begin{aligned}
\frac{dT_s}{dx} = & \{ h_{sg} a_g (T_g - T_s) - \sum_{j=1}^m B_j (h_{gj})_{T_s} + \sum_{j=1}^n \dot{m}_{cond,lj} (h_{lj})_{T_g} \\
& + \sum_{j=1}^n \dot{m}_{dep,j} (h_{lj})_{T_m} - \sum_{j=1}^n (h_{lj})_{T_s} (S_j)_l + Q_{ash} \sum_{j=1}^p \omega_i^o (h_{si})_{T_s} \left(\frac{d\xi_i}{dx} \right) \} \\
& / [(\sum_{j=1}^n \epsilon_l \rho_l v_{s,j} Z_j C_{Plj}) + Q_{ash} (\sum_{j=1}^p \omega_i^o (1 - \xi_i) C_{ps_i})]
\end{aligned} \quad (24)$$

The above set of first order, nonlinear differential equations describes the one-dimensional moving-bed-type retorts. This set also requires some auxiliary algebraic equations as component model parts, which are described below.

The Solid Species Production Rate

$$(S_i)_s = \frac{-Q_{ash}}{v_s} \omega_i^o \dot{R}_i \quad (25)$$

The Gas Phase Species Production Rate

(i) Non-Condensable Gases

$$(S_j)_g = -(S_j)_s + \text{Secondary production in gas phase reactions} \quad (26)$$

(ii) Condensable Gases

$$\begin{aligned}
(S_j)_g - -(S_j)_s = & \dot{m}_{cond,mj} - \dot{m}_{cond,lj} + \text{secondary production in} \\
& \text{gas phase reactions}
\end{aligned} \quad (27)$$

The Mist Phase Species Production Rate

$$(S_j)_m = \dot{m}_{\text{cond},mj} - \dot{m}_{\text{dep},j} \quad (28)$$

The Liquid Phase Species Production Rate

$$(S_j)_l = \dot{m}_{\text{cond},lj} + \dot{m}_{\text{dep},j} \quad (29)$$

Rate of Condensation - Liquid

$$\dot{m}_{\text{cond},lj} = a_l k_{g,j} M_j (y_j - y_{j,\text{eq}}(T_l, Z)) \quad (30)$$

or -

$$\dot{m}_{\text{cond},lj} = a_l \frac{k_{g,j} M_j}{p} [P_j - P_{j,\text{eq}}(T_l, Z)] \quad (31)$$

where, for nonflooding conditions -

$$a_l \approx \frac{6\epsilon_s}{D_p}$$

$$P_{j,\text{eq}}(T_l, Z) = z_j P_j^0(T_l) \quad [\text{Raoult's Law}]$$

$$\text{and } z_j = \frac{Z_j/M_j}{\sum_{i=1}^n Z_i/M_i}$$

Rate of Condensation - Mist

$$\dot{m}_{\text{cond},mj} = a_m k_{g,j} M_j (y_j - y_{j,\text{eq}}(T_m, X)) \quad (32)$$

or -

$$\dot{m}_{\text{cond},mj} = a_m \frac{k_{g,j} M_j}{p} (P_j - P_{j,\text{eq}}(T_m, X)) \quad (33)$$

where -

$$P_{j,\text{eq}}(T_m, X) = x_j P_j^0(T_m) \text{ and } x_j = \frac{X_j/M_j}{\sum_{i=1}^n X_i/M_i}$$

$$a_m = \frac{6\epsilon_m}{D_m}$$

and —

$$\frac{d}{dx} (\epsilon_m v_g) = \frac{d}{dx} (\pi N_m D_m^3 / 6) \quad (34)$$

Two possible alternatives could be used to determine the contact area between gas and mist particles, a_m .

- (i) Assume that the number flux of mist particles (N_m) is constant and that the size of the particles varies along the bed.
- (ii) Assume that the size of mist particles remains the same and that the number flux of mist particles is increasing along the bed.

Heat Transfer Coefficient

An empirical correlation for the Nusselt Number (Nu) for flow through a bed of particles (Ranz and Marshall, 1952) is —

$$Nu = 2.0 + 0.6 Pr^{1/3} Re^{1/2} \quad (35)$$

or —

$$\left(\frac{hD_p}{k_g} \right) = 2.0 + 0.6 \left(\frac{C_{pg} \mu_g}{k_g} \right)^{1/3} \left[\frac{\epsilon_g \rho_g (v_s - v_g) D_p}{\mu_g} \right]^{1/2} \quad (36)$$

Mass Transfer Coefficient

An empirical correlation for the Sherwood Number (Sh) for flow through a bed of particles (Ranz and Marshall, 1952) is used to calculate the mass transfer coefficient.

$$Sh = 2.0 + 0.6 (Sc^{1/3}) (Re^{1/2}) \quad (37)$$

or —

$$\left(\frac{K D_p \bar{M}}{\rho_g D v} \right) = 2.0 + 0.6 \left(\frac{\mu_g}{\rho_g D v} \right)^{1/3} \left(\frac{\epsilon_g \rho_g (v_s - v_g) D_p}{\mu_g} \right)^{1/2} \quad (38)$$

At present, the same heat and mass transfer correlations will be used for mist and solid particles. However, since the mist and gas velocity are assumed equal, the limiting Nusselt number and Sherwood number will be the resulting value for gas-mist transfer.

Future Work

Future work will involve estimation of the economics of the above design plus process designs and economic studies for SNG from Western shale and for syncrude and SNG from Eastern shale.

A method of solution of the proposed reactor model system of equations will be developed and programmed.

REFERENCE CITED

1. Feldkirchner, H.L., et al., "Hydrogasification of Oil Shale" Final report for the period 1972-1979, GRI(A.G.A.) Project IU-4-7. Chicago: Institute of Gas Technology, in preparation.

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APPENDIX A. Bench-Scale Test Results
for Run 80BSU-2

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Table A-1, Part 1. BENCH-SCALE OPERATING CONDITIONS AND TEST RESULTS —
COUNTERCURRENT MOVING-BED OPERATION WITH CLEVELAND SHALE

Oil Shale Type	Cleveland Member
Source	Kentucky
Oil Shale Particle Size (U.S. Sieve)	-10+30
Run No.	80BSU-2
Test Duration, hr	2.75
Steady-State Operating Period, hr	1.50
<u>Operating Conditions</u>	
Bed Height, ft	9.0
Reactor Pressure, psig	498
Average Bed Temperature, °F ^a	
Zone 1	957
Zone 2	1078
Zone 3	1084
Zone 4	1070
Zone 5	1016
Zone 6	1025
Zone 7	1198
Oil Shale Feed Rate, lb/hr	76.0
Oil Shale Space Velocity, lb/ft ³ -hr	95.1
Oil Shale Residence Time, min	44.1
Hydrogen Feed Gas Rate, SCF/hr	559.6
Hydrogen Feed Gas Superficial Velocity, ft/s ^b	0.17
Hydrogen Feed Gas Residence Time, s ^c	24.7
Feed Gas/Oil Shale Ratio, SCF/lb shale fed	7.36
Shale Feed Hopper Hydrogen Purge Rate, SCF/hr	49.7

Table A-1, Part 2. BENCH-SCALE OPERATING CONDITIONS AND TEST RESULTS —
COUNTERCURRENT MOVING-BED OPERATION WITH CLEVELAND SHALE

<u>Run No.</u>	80BSU-2
<u>Test Results</u>	<u>Residue Weight by Ash Balance</u>
Product Gas Rate, SCF/hr ^d	621.6
Product Gas Yield, SCF/lb shale fed ^d	8.18
Residue Shale Rate, lb/hr ^e	64.6
Residue Shale Yield, lb/lb shale fed ^{b,e}	0.60
Liquid Product Rate, lb/hr ^f	3.20
Liquid Product Yield, lb/lb shale fed ^f	0.042
Water Product Rate, lb/hr	12.8
Water Product Yield, lb/lb shale fed	0.169
Organic Carbon Distribution in Products	
Gaseous Hydrocarbons	19.8
Liquid Products	37.4
Solid Residue	<u>43.9</u>
Total	101.1
Overall Material Balance, %	110.5
Total Carbon Balance, %	104.1
Hydrogen Balance, %	120.5
Oxygen Balance, % ^g	211.6

Table A-1, Part 3. BENCH-SCALE OPERATING CONDITIONS AND TEST RESULTS
COUNTERCURRENT MOVING-BED OPERATION WITH CLEVELAND SHALE

<u>Run No.</u>	80BSU-2
Product Gas Properties	
Gas Composition, mol % ^h	
Hydrogen Sulfide	0.00
Nitrogen	2.00
Carbon Monoxide	0.37
Carbon Dioxide	0.70
Hydrogen	92.44
Methane	2.93
Ethane	0.92
Propane	0.23
Butane+	0.08
Ethylene	0.05
Propylene	0.11
Butenes+	0.16
Benzene	<u>0.01</u>
Total	100.00
Heating Value, Btu/SCF ^h	357
Specific Gravity (Air = 1.00)	0.134

^a Outer tube wall temperature, averaged values.

^b At maximum reactor bed temperature.

^c Based on void fraction calculated from feed shale bulk density.

^d Minus purge hydrogen.

^e Measured.

^f On a water and solids-free basis.

^g Oxygen balance is high due to unmeasured high-temperature water in the feed shale, resulting in a low oxygen value for the feed shale.

^h Calculated, based on exit gas rate minus purge gas rate.

ⁱ Gross, gas saturated at 60°F, 30-in. Hg pressure. SCF; dry gas volume in SCF at 60°F, 30-in. Hg pressure.

Table A-2. ANALYSES OF CLEVELAND SHALE FEED
AND RESIDUE — BENCH-SCALE TEST

<u>Run No.</u>	80BSU-2	
<u>Sample</u>	<u>Feed</u>	<u>Residue</u>
Lab No.	119473	119474
Moisture, %	3.1	0.0
Ultimate Analysis (Dry Basis), wt %		
Organic Carbon	10.08	5.05
Mineral Carbon	0.00	0.00
Hydrogen	1.15	0.23
Nitrogen	0.47	0.14
Oxygen (By Difference)	4.81	0.00
Sulfur	0.91	0.74
Ash	<u>82.58</u>	<u>94.16</u>
Total	100.00	100.32
Mineral Carbon Dioxide	0.00	0.00
Screen Analysis, U.S. Sieve, wt %		
4	0.00	0.00
6	0.00	0.00
8	15.80	12.50
16	73.00	67.60
30	5.10	10.70
40	0.80	1.80
60	0.90	2.40
80	0.40	0.90
100	0.20	0.40
325	1.40	2.10
Pan	<u>2.40</u>	<u>1.60</u>
Total	100.00	100.00
Gross Heating Value, Btu/lb	1752	802
Bulk Density, lb/ft ³	69.9	62.3
Helium Density, g/cc	2.39	2.42

Table A-3. LIQUID PRODUCT PROPERTIES —
BENCH-SCALE TEST WITH CLEVELAND SHALE

<u>Run No.</u>	80BSU-2
<u>Lab No.</u>	42546
Ultimate Analysis, wt % (Dry and Solids-Free Basis)	
Carbon	86.56
Hydrogen	9.05
Sulfur	1.42
Nitrogen	2.08
Ash	0.00
C/H Weight Ratio	9.56
Viscosity, SSU at 100°F	44.8
Specific Gravity (60/60°F)	0.985
API Gravity, °API	12.1
Distillation, °F	
IBP	163
5%	218
10%	267
20%	326
30%	393
40%	450
50%	511
60%	588
70%	640
80%	702
90%	--
95%	--
End Point	717
% Recovery	86.0
% Residue	15.0
Conradson Carbon Residue, wt %	3.7
Free Solids, wt %	0.2
Pour Point, °F	-45

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APPENDIX B. Bench-Scale Test Results for
Run 79BSU-2

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Table B-1, Part 1. BENCH-SCALE OPERATING CONDITIONS AND TEST RESULTS —
COUNTERCURRENT MOVING-BED OPERATION WITH NEW ALBANY SHALE

Oil Shale Type	New Albany
Source	Kentucky
Oil Shale Particle Size (U.S. Sieve)	-20+40
Run No.	79BSU-2
Test Duration, hr	4.50
Steady-State Operating Period, hr	2.00
<u>Operating Conditions</u>	
Bed Height, ft,	9.0
Reactor Pressure, psig	527
Average Bed Temperature, °F ^a	
Zone 1	669
Zone 2	833
Zone 3	1006
Zone 4	1172
Zone 5	1203
Zone 6	1234
Zone 7	1178
Oil Shale Feed Rate, lb/hr	79.0
Oil Shale Space Velocity, lb/ft ³ -hr	98.8
Oil Shale Residence Time, min	45.2
Hydrogen Feed Gas Rate, SCF/hr	1407
Hydrogen Feed Gas Superficial Velocity, ft/s ^b	0.40
Hydrogen Feed Gas Residence Time, s ^c	10.9
Feed Gas/Oil Shale Ratio, SCF/lb shale fed	17.8
Shale Feed Hopper Hydrogen Purge Rate, SCF/hr	194

Bed Level →

Table B-1, Part 2. BENCH-SCALE OPERATING CONDITIONS AND TEST RESULTS —
COUNTERCURRENT MOVING-BED OPERATION WITH NEW ALBANY SHALE

<u>Run No.</u>	79BSU-2
<u>Test Results</u>	<u>Residue Weight by Ash Balance</u>
Product Gas Rate, SCF/hr ^d	1187
Product Gas Yield, SCF/lb shale fed ^d	15.0
Residue Shale Rate, lb/hr ^e	63.1
Residue Shale Yield, lb/lb shale fed ^{b,e}	0.74
Liquid Product Rate, lb/hr ^f	4.79
Liquid Product Yield, lb/lb shale fed ^f	0.061
Water Product Rate, lb/hr	6.72
Water Product Yield, lb/lb shale fed	0.085
Organic Carbon Distribution in Products	
Gaseous Hydrocarbons	23.7
Liquid Products	40.4
Solid Residue	<u>29.1</u>
Total	93.2
Overall Material Balance, %	101.1
Total Carbon Balance, %	93.6
Hydrogen Balance, %	91.1
Oxygen Balance, % ^g	156.4

Table B-1, Part 3. BENCH-SCALE OPERATING CONDITIONS AND TEST RESULTS —
COUNTERCURRENT MOVING-BED OPERATION WITH NEW ALBANY SHALE

Run No.	79BSU-2
Product Gas Properties	
Gas Composition, mol % ^h	
Hydrogen Sulfide	0.04
Nitrogen	1.58
Carbon Monoxide	1.14
Carbon Dioxide	0.32
Hydrogen	93.51
Methane	2.16
Ethane	0.66
Propane	0.23
Butane+	0.07
Ethylene	0.04
Propylene	0.09
Butenes+	0.14
Benzene	0.02
Total	100.00
Heating Value, Btu/SCF ^h	355
Specific Gravity (Air = 1.00)	0.1258

- a Outer tube wall temperature, averaged values.
 b At maximum reactor bed temperature.
 c Based on void fraction calculated from feed shale bulk density.
 d Minus purge hydrogen.
 e Measured.
 f On a water and solids-free basis
 g Oxygen balance is high due to unmeasured high-temperature water in the feed shale, resulting in a low oxygen value for the feed shale.
 h Calculated, based on exit gas rate minus purge gas rate.
 i Gross, gas saturated at 60°F, 30-in. Hg pressure. SCF; dry gas volume in SCF at 60°F, 30-in. Hg pressure.

Table B-2. ANALYSES OF NEW ALBANY SHALE FEED
AND RESIDUE — BENCH-SCALE TEST

<u>Run No.</u>	79BSU-2	
<u>Sample</u>	<u>Feed</u>	<u>Residue</u>
Lab No.	42258	42259
Moisture, %	1.5	0.10
Ultimate Analysis (Dry Basis), wt %		
Organic Carbon	13.06	4.68
Mineral Carbon	1.05	0.48
Hydrogen	1.51	0.28
Nitrogen	0.46	0.16
Oxygen (By Difference)	4.45	0.00
Sulfur	4.94	3.21
Ash	<u>74.53</u>	<u>91.98</u>
Total	100.00	100.79
Mineral Carbon Dioxide	3.83	1.74
Screen Analysis, U.S. Sieve, wt %		
4	0.0	0.0
6	0.0	0.0
8	0.0	0.0
16	31.5	13.5
30	48.0	49.3
40	16.3	27.8
60	3.1	6.5
80	0.1	0.9
100	0.0	0.3
325	0.1	0.9
Pan	<u>0.9</u>	<u>0.8</u>
Total	100.0	100.0
Gross Heating Value, Btu/lb	3550	1019
Bulk Density, lb/ft ³	74.5	65.6
Helium Density, g/cc	2.31	2.66

Table B-3. LIQUID PRODUCT PROPERTIES —
BENCH-SCALE TEST WITH NEW ALBANY SHALE

Run No.	79BSU-2
Lab. No.	42222
Ultimate Analysis, wt % (Dry and Solids-Free Basis)	
Carbon	85.74
Hydrogen	8.01
Sulfur	2.17
Nitrogen	2.21
Ash	0.0
C/H Weight Ratio	10.71
Viscosity, SSU at 100°F	66.4
Specific Gravity (60/60°F)	1.036
API Gravity, °API	5.1
Distillation, °F	
IBP	172
5%	198
10%	253
20%	339
30%	410
40%	480
50%	556
60%	628
70%	685
80%	--
90%	--
95%	--
End Point	690
% Recovery	75.0
% Residue	27.5
Conradson Carbon Residue, wt %	10.0
Free Solids, wt %	0.10
Pour Point, °F	-60.0

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APPENDIX C. Process Development Unit Test Results
for Run 79PDU-1

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Table C-1, Part 1. PDU OPERATING CONDITIONS AND TEST RESULTS —
COUNTERCURRENT OPERATION WITH SUNBURY SHALE

Oil Shale Type	Sunbury
Oil Shale Source	Kentucky
Oil Shale Particle Size (U.S. Sieve)	-1/2 inch + 6 mesh
Run No.	79PDU-1
Test Duration, hr	8.00
Steady-State Operation, hr	6.00

<u>Operating Conditions</u>	<u>Stage 1</u>	<u>Stage 2</u>
Bed Height, ft	10.0	10.0
Reactor Pressure, psig	403	403
Oil Shale Bed Temperature, °F ^a		
No. 1	Bed Level → 263	1145
No. 2	280	1185
No. 3	288	1193
No. 4	293	1297
No. 5	306	1370
No. 6	311	1381
No. 7	319	1375
No. 8	391	1303
No. 9	594	--
No. 10	813	--
Oil Shale Feed Rate, lb/hr ^b	1095	--
Oil Shale Space Velocity, lb/ft ³ -hr ^b	127.3	125.5
Oil Shale Residence Time, min ^b	33.6	34.1
Hydrogen Feed Gas Flow Rate, SCF/hr	22,300	13,700
Nitrogen Purge Gas Flow Rate, SCF/hr	292	576
Feed Gas Superficial Velocity, ft/s ^c	0.378	0.571
Feed Gas Residence Time, s ^d	12.7	8.4
Feed Gas/Oil Shale Ratio, SCF/lb shale fed ^b	20.4	12.5
Air Flow Rate, SCF/hr	--	495
Air/Oil Shale Ratio, SCF/lb shale fed	--	0.45

Test Results

Product Gas Rate, SCF/hr ^e	18,000	17,500	17,120 ⁱ
Product Gas Yield, SCF/lb shale fed ^e	16.4	16.0	15.6
Residue Shale Rate (From Stage 2), lb/hr			
By Direct Weight Measurement	--	734	
(By Ash Balance Calculation)	--	(905)	
Residue Shale Yield, lb/lb shale fed			
By Direct Weight Measurement	--	0.670	
(By Ash Balance Calculation)	--	(0.827)	
Liquid Hydrocarbon Product Rate, lb/hr ^f	8.0	47.7	
Liquid Hydrocarbon Product Yield, lb/lb shale fed ^f	0.007	0.044	
Water Product Rate, lb/hr	74.0	74.9	
Water Product Yield, lb/lb shale fed	0.068	0.068	
Water Product Rate From H ₂ -Air Combustion, lb/hr ^g	--	9.9	
Water Product Yield from H ₂ -Air Combustion, lb/hr shale fed ^g	--	0.009	
Overall Material Balance, % ^h			
Residue Shale by Weight Measurement		91.5	
(Residue Shale by Ash Balance)		(103.0)	

Table C-1, Part 2. PDU OPERATING CONDITIONS AND TEST RESULTS —
COUNTERCURRENT OPERATION WITH SUNBURY SHALE

Run No.	79PDU-1			
	Stage 1	Stage 2		
Total Carbon Balance, %				
Residue Shale by Weight Measurement		81.8		
(Residue Shale by Ash Balance)		(87.0)		
Total Hydrogen Balance, %				
Residue Shale by Weight Measurement		103.6		
(Residue Shale by Ash Balance)		(103.9)		
Total Oxygen Balance, %				
Residue Shale by Weight Measurement		197.4		
(Residue Shale by Ash Balance)		(198.1)		
Organic Carbon Distribution in Products, %				
Gaseous Hydrocarbons	2.2		22.2	
Liquid Hydrocarbons	4.2		25.7	
Residue Shale (From Stage 2)				
By Weight Measurement		28.4		
(By Ash Balance)		(35.0)		
Gas Properties	Feed	Product ^e Stage 1	Product ^e Stage 2	Product ⁱ
Gas Composition, mol %				
Hydrogen Sulfide	--	0.01	0.01	0.01
Nitrogen + Argon	0.87	0.00	4.03	1.84
Carbon Monoxide	2.60	2.58	1.69	1.73
Carbon Dioxide	--	0.11	0.10	0.10
Hydrogen	95.48	95.88	89.13	91.16
Methane	1.05	1.22	4.19	4.29
Ethane	--	0.05	0.55	0.56
Propane	--	0.03	0.11	0.12
n-Butane	--	0.03	0.03	0.03
i-Butane	--	0.01	0.01	0.01
Pentanes	--	0.02	0.01	0.01
Hexanes	--	0.01	--	--
Ethylene	--	--	0.03	0.03
Propylene	--	0.01	0.04	0.04
Butenes	--	0.03	0.04	0.04
Pentenenes	--	0.01	0.01	0.01
Acetylene	--	--	0.01	0.01
Butadiene	--	--	--	--
Cyclopentadiene	--	--	--	--
Benzene	--	--	0.01	0.01
Toluene	--	--	--	--
Total	100.00	100.00	100.00	100.00
Heating Value, Btu/SCF ^j	323	332	349	357
Specific Gravity (Air = 1.00)	0.106	0.104	0.153	0.134

Table C-1, Part 3. PDU OPERATING CONDITIONS AND TEST RESULTS —
COUNTERCURRENT OPERATION WITH SUNBURY SHALE

- a Temperatures measured with multiple thermocouples mounted in thermowell. Measuring points equally spaced. Ten thermocouples spaced 12 inches apart in Stage 1, and 9 thermocouples spaced 13-inches apart in Stage 2. Thermowell consists of 3/8-inch I.P.S 316-SS pipe; thermocouples are 1/16-inch OD, Type K (Chromel-Alumel), with 316-SS sheath. The lowest thermocouple in both Stages 1 and 2 is approximately 12 inches above the center lines of the discharge screws.
- b Approximate for Stage 2. Feed rate to Stage 2 not measurable; therefore, estimated using feed rate to Stage 1 in calculation.
- c At center of shale bed and at conditions prevailing there.
- d Based on void fraction in the bed calculated from measured feed shale bulk density and true shale density.
- e On a pure-nitrogen-free basis.
- f On a water-and-ash-free basis.
- g Calculated, assuming all oxygen combusted with feed hydrogen.
- h Includes input and output for both stages.
- i On a purge-nitrogen-free basis and excluding nitrogen and argon fed with the combustion air.
- j Gross heating value: gas saturated at 60°F, 30-inch-Hg pressure: dry gas volume in SCF at 60°F, 30-inch-Hg pressure.

Table C-2. ANALYSES OF SUNBURY SHALE FEED AND RESIDUE -
COUNTERCURRENT OPERATION

Run No.	79PDU-1	
	Feed	Residue**
Sample Lab. No.	42465	42494
Moisture (Dry Basis), wt %	1.4	0.4
Ultimate Analysis (Dry Basis), wt %		
Organic Carbon	14.71	6.17
Mineral Carbon	0.03	0.01
Hydrogen	1.74	0.36
Nitrogen	0.56	0.25
Oxygen (By Difference)	2.66	0.00
Sulfur	3.25	1.52
Ash	77.05	92.26
Total	100.00	100.57
Mineral Carbon Dioxide	0.11	0.05
Screen Analysis (U.S. Sieve), wt %		
+1/2 in.	1.7	0.0
+3/8 in.	7.2	0.0
+1/4 in.	25.0	9.5
+6 mesh	32.3	29.3
+12 mesh	21.4	18.4
+20 mesh	9.8	15.0
+40 mesh	1.0	6.2
+70 mesh	0.5	4.1
+140 mesh	0.4	3.2
+200 mesh	0.4	1.1
-200 mesh	0.3	13.2
Total	100.0	100.0
Bulk Density, lb/ft ³	71.3	62.1
Helium Density, gm/cm ³ *	2.20	2.55

* A measure of the true shale particle density.

** From Stage 2, it was not possible to sample residue from Stage 1.

Table C-3. LIQUID PRODUCT PROPERTIES — PDU TEST WITH SUNBURY SHALE, COUNTERCURRENT OPERATION

Run No. Lab. No. Sample Source	79PDU-1							
	42466				42467			
	Stage 1 Quench Tower				Stage 2 Quench Tower			
Sample Boiling Point Range, °F	Total	C ₅ -400	400-600	600-632	Total	C ₅ -400	400-600	600-668
Fraction of Total Oil, wt %	100.0	40.8	46.9	3.3	100.0	16.2	27.5	38.5
Ultimate Analysis (Dry and Solids-Free Basis), wt %								
Carbon	84.47	84.70	85.56	85.13	85.59	85.56	85.05	85.67
Hydrogen	11.72	12.87	11.55	10.03	9.70	11.81	10.37	9.55
Sulfur	2.29	1.91	1.70	1.56	1.37	1.06	1.23	1.37
Nitrogen	0.78	0.52	0.58	1.56	2.07	1.57	1.76	1.95
Ash	0.1	0.0	0.0	0.0	0.1	0.0	0.2	0.4
C/H Weight Ratio	7.21	6.58	7.41	8.48	8.83	7.24	8.20	8.97
Viscosity, SSU at 100°F*	--	--	--	--	--	--	--	--
Specific Gravity (60/60°F)	0.875	0.811	0.893	0.973	0.977	0.829	0.942	1.076
API Gravity, °API	30.3	43.0	26.9	13.9	13.4	39.3	18.7	--
Distillation, °F*								
IBP	180				163			
5%	280				250			
10%	297				318			
20%	338				414			
30%	369				500			
40%	394				569			
50%	425				616			
60%	454				672			
70%	485				703			
80%	524				726			
90%	602				--			
95%	--				--			
End Point	602				738			
% Recovery	90.0				89.0			
% Residue	12.5				11.5			
Hydrocarbon Types, vol %*								
Saturates		45				41		
Olefins						29		
Aromatics						30		
Eromine Number								
Free Carbon, wt %*	0.09				0.07			
Free Solids, wt %*	0.00				0.00			
Pour Point, °F*	-80.0				-5			
Conradson Carbon Residue, wt %*	1.7				1.8			
Heating Value, Btu/lb*	18,360				17,560			

* This analysis not performed on all fractions.