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

MASTER

**Project 61040 Quarterly Report
For the Period April 1 Through June 30, 1980**

**Prepared by
Institute of Gas Technology
IIT Center, 3424 S. State Street
Chicago, Illinois 60616**

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EXECUTIVE SUMMARY

The following is a summary by task of the HYTORT Process development work conducted from April 1 through June 30, 1980.

Task 1. Laboratory Program

Thermobalance tests have been conducted on samples of shale from each large multiton sample prior to large-scale tests. We have fit these test results and others with specific kinetic expressions.

Approximately 80% of the instrumentation for the laboratory-scale reactor has been received. Fabrication of the reactor, feed hopper, and residue receiver is about 95% complete.

We are now working with the manufacturer of the DSC (differential-scanning calorimeter) to improve its operation in high-pressure nitrogen and in hydrogen atmospheres. Meanwhile, we will continue testing in nitrogen at low pressures.

Task 2. Bench-Scale Program

Two successful moving-bed tests were conducted in the bench-scale reactor during this quarter. A large, 50-ton sample of the Lower Huron member of the Ohio Shale was mined and readied for shipment to IGT.

Modification of the bench-scale steam-oxygen unit was completed. Spent shale from PDU tests was prepared for use in these tests.

We conducted a set of five screening runs on New Albany shale oil and a set of four screening runs on Sunbury shale oil during this quarter. We were able to reduce the nitrogen content of these oils to the 0.16 to 0.30 weight percent range in the bench-scale hydrotreating unit.

Design of the laboratory test system for mist-size control studies was completed. We are studying methods for measuring mist particle size.

Shakedown and initial testing of the liquid-sealed lockhopper were performed during this quarter.

Task 3. Process Development Unit (PDU) Tests

Two runs were made in the PDU with Kentucky shales using a sample of the Cleveland member of the Ohio shale and a sample of New Albany shale. Both runs were made under gas-making conditions.

Task 4. Process Environmental Assessment

An initial draft report was completed by the Pace Company, summarizing its work of Phase 1 of its contract. A second, revised draft is now in preparation. Samples for environmental analysis were taken during the PDU runs discussed above. On-line sampling equipment was installed prior to the PDU run with New Albany shale and samples were taken of the Stage 2 raw product gases.

Task 5. Process Design and Economics

We completed the cost estimate for manufacture of syncrude from Western oil shale and the results are presented in this report. Work continued on development of the one-dimensional model for a moving-bed retort. We also incorporated preliminary hydroretorting kinetics into the model.

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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:

- Hydroretorting kinetics of those Devonian and Eocene shales not previously tested in the HYTORT Process and the nature of primary products of hydroretorting
- Analysis of process heat effects (both chemical and physical) in the shale hydroretorting step
- H₂ manufacture by steam-oxygen gasification of raw shale fines or spent shale
- Fluidized-bed hydroretorting of raw shale fines
- Upgrading of raw HYTORT shale oil
- Control of oil mist size in the hydroretorting 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 (April 1 through June 30, 1980) are presented in this report.

TECHNICAL PROGRESS REPORT

Task 1. Laboratory Program

Subtask 1.1. Thermobalance Tests

Objective

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

Thermobalance runs were made on each large shale sample prior to BSU and PDU tests. Each shale was tested in two atmospheres: 500-psig H_2 , and 500-psig N_2 . In all runs, the gas flow rate was approximately 25 SCF/hr and a 12 to 14-g shale sample was heated from room temperature to $1400^\circ F$ at a nominal heating rate of $20^\circ F/min$ and held at $1400^\circ F$ for 10 minutes. Experimental conditions and test results are given in Tables 1 and 2.

The CH_4 , CO, and CO_2 were measured with infrared-type (IR) analyzers. The CO_2 analyzer went onstream in time for only the final run of Utah shale in 500-psig N_2 . The carbon conversion to liquid is found by the difference -

$$\begin{array}{l} \% \text{ Conversion} \\ C \rightarrow \text{liq} \end{array} = \begin{array}{l} \% \text{ Total Carbon} \\ \text{Conversion} \end{array} - \begin{array}{l} \% \text{ Conversion} \\ C \rightarrow \text{Light Hydrocarbons} \end{array} - \begin{array}{l} \% \text{ Conversion} \\ C \rightarrow CO + CO_2 \end{array} \quad (1)$$

In the case of the Eastern shales, the mineral carbon is sufficiently low that the lack of information on CO_2 yield affects the liquid yield estimate by less than 2%. Although the conclusions are based on unreproduced runs, it appears that the light hydrocarbon gases are essentially methane during hydroretorting of this Cleveland shale while about 40% of the light hydrocarbon gases are heavier than methane for the Antrim shale. For the latter, the relatively low liquid yield appears associated with a relatively high non-methane hydrocarbon gas yield.

In the case of the Western shale, the product gas analyzers were not operating and only total conversions are reported. The gas analyzers have since been put onstream and a CO_2 IR analyzer has been added.

Table 1. FEED AND RESIDUE COMPOSITIONS

Material	Proximate Analysis		Ultimate Analysis (moisture free)					
	Moisture	High-Temperature H ₂ O	Ash	Total C	Organic C	Mineral C	Hydrogen	Sulfur
				%				
Cleveland Feed	5.8	2.3	83.22	10.01	9.85	0.17	1.06	0.98
S-80-9 Residue	0.0	NA*	95.85	3.62	3.56	0.06	0.22	0.22
S-80-10 Residue	0.0	NA	90.91	7.88	7.85	0.03	0.21	0.77
Antrim Feed	2.7	2.1	85.86	7.87	7.49	0.38	0.94	2.61
S-80-15 Residue	0.1	1.3	96.25	2.75	2.71	0.04	0.25	1.28
S-80-16 Residue	0.0	1.1	93.56	4.40	4.35	0.05	0.18	1.90
Utah Feed	0.3	1.9	62.44	18.99	13.56	5.43	1.85	0.46
S-80-17 Residue	0.0	2.5	96.02	1.48	1.36	0.12	0.33	1.04
S-80-19 Residue	0.1	0.9	84.03	6.32	3.10	3.21	0.11	0.39

* NA means not available

Table 2. CARBON CONVERSIONS

Thermobalance Run No.	Shale	Gas	Total Carbon Conversion	Organic Carbon Conversion	C → LHC [†] %	C → liq	C → CH ₄	C → CO
S-80-9	Cleveland	H ₂	68.6	68.8	27.2	40.9	29.7	0.5
S-80-10	Location 139	N ₂	27.9	26.7	6.2	19.5	6.1	2.2
S-80-15	Antrim	H ₂	69.5	68.6	32.7	32.5	18.5	4.3
S-80-16	Location 147	N ₂	48.9	46.7	5.4	40.7	6.4	2.8
S-80-17	Utah	H ₂	95.1	93.7	NA [*]	NA	NA	NA
S-80-19	Location 142	N ₂	76.3	83.8	NA	NA	NA	NA

* NA means not available.

† LHC means light, gaseous hydrocarbons.

In the previous quarterly report (January through March 1980) carbon conversion results were given for Runs S-80-1 through S-80-8. For these, a Cleveland shale had been separated by density into fractions of different kerogen content. Each fraction was used to form a sample large enough for a series of thermobalance experiments, and all runs were made under the same conditions. The test conditions were 500 psig of H_2 with an H_2 flow rate of approximately 20 SCF/hr, a controlled heating rate of approximately $20^\circ\text{F}/\text{min}$ from room temperature to 1400°F , and a 10-minute hold at 1400°F .

During this quarter, an effort was made to fit the test results with specific kinetic expressions. During the thermobalance runs five distinct products were noted. These consisted of -

- 1) Low-temperature weight loss (assumed to be mostly H_2O), 350° to 400°F
- 2)
- 3) Two oil formation stages, 725° to 925°F
- 4) First CH_4 production, 850° to 950°F
- 5) Second CH_4 production, $1300^\circ\text{F} +$.

Information used to fit the low-temperature weight loss and oil formation peaks was obtained from the thermobalance trace. The thermobalance trace continuously records actual sample weight vs. temperature. Information to describe the CH_4 formation is obtained from the CH_4 IR analyzer. Analysis of the CH_4 (and other gaseous products) data requires definition of the age distribution developed while the gas travels between the shale sample and the detector. The occurrence of the different products is shown by the weight loss vs. temperature in a typical run (Figure 1).

Much of the weight lost between 1000° and 1400°F in these runs does not correspond to the five noted products. Parts of this weight loss result from the evolution of carbon oxides and sulfur products.

In the kinetic equations developed this quarter to describe oil production, the total weight loss recorded by the thermobalance was used instead of the weight loss adjusted for the methane observed. We used this simplification because we had not yet developed the CH_4 analysis method and the weight of carbon going to CH_4 in this region at no time exceeded 6% of the weight lost during the oil-forming temperature range and therefore could only slightly affect the kinetic estimates.

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Figure 1. EXAMPLE OF TYPICAL THERMOBALANCE RESULTS OF $dW/d\theta$ vs. $T(^{\circ}F)$ [Cleveland Shale (Location 139)]

The kinetic expressions chosen were first-order Arrhenius equations; and, by combining the two oil equations, these can be given as -

Oil Yield

$$\frac{dW_0}{d\theta} = \frac{dW_{01}}{d\theta} + \frac{dW_{02}}{d\theta} \quad (2)$$

$$\frac{dW_0}{d\theta} = -W_{01}k_{01} \exp(-A_{01}/T) - W_{02}k_{02} \exp(-A_{02}/T) \quad (3)$$

For constant heat-up rate, an accurate approximation to the integral is -

$$W_{01} = \frac{W_{01}^0}{\exp \left[\frac{k_{01} T^2}{\alpha (A_{01} + 2T)} \exp(-A_{01}/T) \right]} \quad (4)$$

$$W_{02} = \frac{W_{02}^0}{\exp \left[\frac{k_{02} T^2}{\alpha (A_{02} + 2T)} \exp(-A_{02}/T) \right]} \quad (5)$$

Low-Temperature Weight Loss

$$\frac{dW_w}{d\theta} = -W_w k_w \exp(-A_w/T) \quad (6)$$

$$W_w = \frac{W_w^0}{\exp \left[\frac{k_w T^2}{\alpha (A_w + 2T)} \exp(-A_w/T) \right]} \quad (7)$$

where -

- θ = time, min
- T = temperature, $^{\circ}\text{R}$
- α = heat-up rate, $^{\circ}\text{R}/\text{min}$
- k_{01}, k_{02}, k_w = first order rate constants, min^{-1}
- A_{01}, A_{02}, A_w = Arrhenius temperature parameter, $^{\circ}\text{R}$
- $W_{01}^0, W_{02}^0, W_w^0$ = species weight fraction initially in feed
- W_0, W_{01}, W_{02}, W_w = species weight fraction

The expression for the low-temperature weight loss peak was found to suitably describe these runs with a constant value of k_w and A_w and a value of W_w^o dependent on the total feed carbon content. This dependency must be assumed peculiar to this shale source (Table 3 and Figure 2).

Table 3. KINETICS OF LOW-TEMPERATURE WEIGHT LOSS

Run	Density	Total Feed C (wet basis), wt %	$\ln k_w$	$A_w, ^oR$	W_w^o	σ (dw/d θ), g/min
S-80-1	-2.05	18.64	11.0	10,400	1.093	0.019
S-80-2	2.05-2.1	16.76			1.110	0.012
S-80-3	2.1-2.15	14.87			1.320	0.020
S-80-4	2.15-2.2	12.84			1.602	0.016
S-80-5	2.2-2.25	11.61			1.888	0.024
S-80-6	2.25-2.3	10.54			2.447	0.028
S-80-8	2.3+	8.69			3.044	0.034

The expression for oil production, (Equations 2 through 5) was found to suitably fit the experimental data with constant values of the k 's and A 's. The values of W_{01}^o and W_{02}^o are presented as a function of the total feed carbon weight percent in Table 4 and Figure 3.

Table 4. KINETIC ESTIMATES FOR OIL PRODUCTION IN CLEVELAND SHALE (Location 139)

Run	Density	Total Feed C (wet basis), wt %	$\ln k_{01}$	$A_{01}, ^oR$	W_{02}^o	$\ln k_{02}$	$A_{02}, ^oR$	W_{02}^o , wt %	W_0^o , wt %
S-80-1	-2.05	18.64	20.732	27,148	1.000	18.779	27,062	16.575	17.575
S-80-2	2.05-2.1	16.76			1.196			13.644	14.840
S-80-3	2.1-2.15	14.87			1.537			11.238	12.775
S-80-4	2.15-2.2	12.84			1.951			9.277	11.228
S-80-5	2.2-2.25	11.61			2.437			7.668	10.105
S-80-6	2.25-2.3	10.54			3.038			6.327	9.365
S-80-8	2.3+	8.69			3.785			5.239	9.024

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Figure 2. LIMITING LOW-TEMPERATURE WEIGHT LOSS FOR CLEVELAND SHALE
(Location 139)

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Figure 3. LIMITING WEIGHT LOSSES IN OIL PEAKS FOR CLEVELAND SHALE
(Location 139)

In 1979 a series of thermobalance runs had been made with a New Albany shale (NA-2a) and the oil production described with a single first-order rate equation, and values of W_0^o were dependent on heat-up rate and hydrogen pressure. The results for 13 runs are given in Table 5.

Table 5. KINETIC ESTIMATES (1979) OF OIL PRODUCTION FOR NEW ALBANY SHALE (NA-2a)

Run	atm	Heating Rate, °F/min	Pressure, psig	$\ln k_o$	$A_o, ^\circ R$	W_0^o , wt %	σ ($dW/d\theta$), g/min
S-79-36	H ₂	5	50	17.34	25,328	9.9576	0.1159
S-79-35		5	100			12.3611	
S-79-34		5	200			14.8446	
S-79-33		5	500			17.0834	
S-79-32		10	50			10.2268	
S-79-28		10	100			12.2181	
S-79-27		10	200			14.0161	
S-79-21		10	500			16.6876	
S-79-22		20	500			16.3953	
S-79-26		35	50			10.3865	
S-79-25		35	100			11.3431	
S-79-23		35	200			12.8215	
S-79-20		35	500			16.4925	

An equally good fit of the NA-2a shale runs test results can also be achieved with the parameters corresponding to the second oil path of the Cleveland shale. This simplified one-path description is expressed as —

$$\frac{dW_0}{d\theta} = -W_{02}^o k_2 \exp(-A_{02}/T) \quad (8)$$

$$W_0 = \frac{W_{02}^o}{\exp \left[\frac{k_{02} T^2}{\alpha (A_{02} + 2T)} \exp(-A_{02}/T) \right]} \quad (9)$$

In the earlier work, the standard deviation of the weight loss rate was calculated considering all data points in all runs. In Table 6, σ of $dW_o/d\theta$ was calculated for each run using only data points from the specific run.

Table 6. KINETIC ESTIMATES FOR OIL PRODUCTION IN NEW ALBANY SHALE (NA-2a) BASED ON CLEVELAND SHALE

Run	atm	Heating Rate, °F/min	Pressure, psig	$\ln k_{O_2}$	$A_{O_2}, ^\circ R$	W_o	$\sigma (dW/d\theta),$ g/min
S-79-36		5	50	18.779	27,062	8.190	0.050
S-79-35		5	100			10.417	0.035
S-79-34		5	200			11.350	0.111
S-79-24		5	500			13.411	0.060
S-79-33		5	500			14.097	0.103
S-79-32	H ₂	10	50	18.779	27,062	8.207	0.025
S-79-28		10	100			9.977	0.052
S-79-27		10	200			11.816	0.078
S-79-21		10	500			13.262	0.100
S-79-22		20	500			12.719	0.107
S-79-26		35	50			8.561	0.189
S-79-25		35	100			9.199	0.114

With the Cleveland shale parameters the estimated limiting yields are lower than with the 1979 set. This is in the appropriate direction to correspond to reported liquid yield estimates.

A series of runs with a New Albany shale hydrotreated in H₂-N₂ mixtures is currently in progress to establish the hydrogen partial pressure dependence. Twelve runs in this series have been made to date and are being analyzed.

Future Work

The study of the dependence on H₂ partial pressure will continue to cover the full range of interest: partial pressures up to 500 psig varied independently from total pressures up to 500 psig.

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 distributions and properties under integral reactor conditions.

Discussion

During this quarter, work was directed toward equipment construction. Approximately 80% of the instrumentation has now been received by the instrument panel supplier/fabricator and assembly of the instrument panel is now under way. Meanwhile, the materials for fabrication of the reactor, feed hopper, and residue receiver were received and construction of these items is now about 95% complete. The laboratory area is now ready for installation of equipment and utilities. We are also working on installation of utilities for the lab area.

Future Work

Equipment construction will be completed by the various suppliers and we will install it, along with necessary utilities, in the laboratory area provided.

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 hydroretorting conditions.

Discussion

The gas feed system with its pressure and flow controls was constructed and integrated with the operation of the DSC. Initial tests with nitrogen and with calibrating solids indicated reasonable operation at pressures up to 500 psig and temperature to 600°C. Higher temperatures (up to the design limit of 725°C) require special sample cups. The currently used aluminum cups allow the study of shale past the region of the oil production but not quite to the region of high-temperature methane production.

Severe difficulties were encountered, however, in the use of hydrogen atmospheres. Because of the high rates of heat transfer with hydrogen, controlled operation was achieved only up to 400°C and maximum temperatures were only of the order of 500°C. Initial attempts to reduce the heat loss by insulation made only minor improvements. We are consulting with the manufacturer to solve the problem. In the meantime, studies of the retorting of shales in nitrogen and of the specific heats of shales will be made. The use of H₂-N₂ mixtures to achieve hydrotretorting with less heat loss will be investigated.

Future Work

Methods to allow use of the DSC in hydrogen atmospheres at retorting temperatures will be investigated. Data will be taken at conditions currently achievable.

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 such that complete material and elemental (carbon, hydrogen, and oxygen) balances can be performed, and sufficient oil is produced so that its many properties may be determined and it can be used for further testing.

Discussion

Five run attempts (80BSU-6, 80BSU-7, 80BSU-8, 80BSU-9, and 80BSU-10) were made during this quarter. The data for the successful runs (80BSU-8 and 80BSU-10) are being analyzed and the results will be reported later. Run 80BSU-6 on Utah shale was terminated after 1.4 hours of shale feeding and Run 80BSU-7 was stopped 1 hour after shale feeding was initiated. Run 80BSU-8, on the Cleveland member of the Ohio shale under gas producing conditions, was performed with 4 hours of steady-state operation. Run 80BSU-9 on Utah shale was terminated early. The feed screw was stopped 1.5 hours after start of the run because of bridging in the reactor, which may be a result of the shale being relatively rich. A successful run was carried out on Sunbury shale, Run 80BSU-10, having 3.7 hours of steady-state operation.

Run 80BSU-3 with the Cleveland member of the Ohio shale and Run 80BSU-5 with a Kentucky New Albany shale were made during the last quarter, and the results are included in this report. Results of these tests are summarized in Tables 7 and 8.

Table 7. SUMMARY OF BSU MOVING-BED TEST 80BSU-3

Run No.	80BSU-3
Shale Type	Cleveland
Bed Height, ft	9.0
Pressure, psig	507
Average Bed Temperature, °F	1050
Maximum Bed Temperature, °F	1169
Oil Shale Space Velocity, lb/ft ³ -hr	107
Oil Shale Mass Rate, lb/ft ² -hr	972
Hydrogen/Shale Feed Ratio, SCF/lb	6.87
Organic Carbon Distribution in Products, %	
Gas	15.6
Oil	15.8
Residue*	51.0
Material Balance, %*	101.0
Elemental Balances, %	
Carbon	83.9
Hydrogen	99.0
Oxygen	136

* Using residue shale weight calculated by ash balance.

Table 8. SUMMARY OF BSU MOVING-BED TEST 80BSU-5

Run No.	80BSU-5
Shale Type	New Albany
Bed Height, ft	9.0
Pressure, psig	506
Average Bed Temperature, °F	1470
Maximum Bed Temperature, °F	1515
Oil Shale Space Velocity, lb/ft ³ -hr	88
Oil Shale Mass Rate, lb/ft ² -hr	784
Hydrogen/Shale Feed Ratio, SCF/lb	7.08
Organic Carbon Distribution in Products, %	
Gas	44.1
Oil	25.4
Residue*	16.1
Material Balance, %*	99.9
Elemental Balances, %	
Carbon	86.0
Hydrogen	100.1
Oxygen	219

* Using residue shale weight calculated by ash balance.

Run 80BSU-3 had a shale feed rate of 85.9 lb/hr and the H_2 to feed shale ratio was 6.9. Reactor conditions were set to maximize oil production. The pressure was maintained at 507 psig and the maximum temperature was 1169°F. This run was made under conditions similar to Run 80BSU-2, using the same shale. The data show only 15.8% of the organic carbon fed was converted to liquids, 15.6% to gases, and 51.0% remained in the residue for a total of 82.4%. The total conversion of 49.0% is lower than expected, judging from thermobalance studies (about 61%) and from Run 80BSU-2 (56.1%). This result can probably be attributed to the fact that the run was made at a lower temperature than the thermobalance test or Run 80BSU-2. A fairly linear temperature profile was maintained as shown in Figure 4. The results of this run are summarized in Table 7.

More severe conditions were used for Run 80BSU-5 than for Run 79BSU-2 in order to increase the gas yield. The pressure was 505 psig and the maximum temperature 1515°F. Shale was fed at 69.3 lb/hr, and the hydrogen/oil shale ratio was maintained at 7.08. Results from Run 80BSU-5 showed that 16.1% remained in the residue and 69.5% (83.9% if the overall balance is adjusted to 100%) was converted to products, including 44.1% to gases. Thermobalance studies on Kentucky New Albany shale at 1400°F gave an organic carbon conversion of 83% to oil plus gas and 17% remained in the residue. It should be pointed out that the 4-inch reactor was run at a maximum temperature about 100°F hotter than that of the thermobalance test (Figure 5). A summary of the test results is given in Table 8.

Complete test results for bench-scale tests reported this quarter are presented in Appendix A of this report. Complete analytical data are given there for feed and residue shales, product oil, and product gases.

Future Work

The next scheduled shale to be tested will be the Sunbury (under oil producing condition), with — possibly — a test with Antrim shale following.

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

Figure 4. TEMPERATURE PROFILE FOR RUN 80BSU-3

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Figure 5. TEMPERATURE PROFILE FOR RUN 80BSU-5

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

Adaptation of 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 is now essentially complete. Two gas feed nozzles were fabricated, one for feeding steam and oxygen at a point 2 feet above the bottom of the oil shale bed, the other for feeding a mixture of methane and hydrogen to the bottom of the bed. The methane and the hydrogen feed lines are being extended to the bottom of the reactor and joined to the feed nozzle. A thermocouple bundle consisting of six thermocouples was assembled and positioned for sensing temperatures at the center of the shale bed in the reactor. These thermocouples will sense temperatures at fixed height intervals through a 4-foot-high shale bed, and between the two gas feed nozzles. Spent oil shale from recent tests in the PDU is being screened to a -1/8-inch size to prepare the shale for feed to the 6-inch unit.

Future Work

A series of moving-bed spent shale gasification tests will be conducted, to be followed by a series of fluidized-bed raw shale gasification tests.

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 this quarter, a set of five screening runs on New Albany shale oil and a set of four screening runs on Sunbury shale oil were performed. The hydrotreated shale oil was analyzed for sulfur and nitrogen content for each test. The oil was then washed with a 1:1 volume ratio of oil to water

and the sulfur and nitrogen contents were determined. This was followed by an acid wash of a 1:1 volume ratio of oil to 1N HCl with sulfur and nitrogen again being determined as the acid-washed material.

The results of the New Albany series are summarized in Table 9. The denitrification is shown as a function of the average catalyst bed temperature in Figure 6. The results of the Sunbury series are summarized in Table 10, and the denitrification as a function of average catalyst bed temperature is shown in Figure 7.

It appears that the original target of 500 to 1000 ppm nitrogen in the acid-washed shale may have been somewhat optimistic using this catalyst at the operating conditions shown. A value of 1000 to 2000 ppm may be more realistic with the shale oils tested thus far.

Future Work

The IGT hydrotreating unit will be further renovated and upgraded by use of new reactor temperature controllers and a new reactor. The reactor will be a 1-1/2 inch schedule 160 pipe with a 72-inch heated zone. This will allow use of a 2000 cc catalyst bed, double the present size, and will allow closer temperature monitoring so that any catalyst deactivation can be observed. This should also improve oil flow distribution throughout the bed and enable higher oil throughputs for the extended runs. The next scheduled series of runs will be with Colorado shale oil.

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 hydrotreating conditions and to eventually incorporate the most promising techniques into the PDU studies.

Discussion

A laboratory test system for evaluation of techniques of enhancing mist formation has been designed. The components have been ordered, and construction is being carried out as materials arrive. Figure 8 shows a schematic diagram of the apparatus. Nitrogen gas is heated by an electrically heated furnace to a predetermined temperature before it enters the reactor. Band heaters

Table 9. NEW ALBANY SHALE OIL UPGRADING TESTS
(Catalyst: Shell 324 Ni/Mo; Catalyst Volume: 1000 cc)

Run No.	<u>HTNA-1</u>	<u>HTNA-2</u>	<u>HTNA-3</u>	<u>HTNA-4</u>	<u>HTNA-5</u>
Duration, hr	4	4	4	4	4
Pressure, psig	1995	2014	2014	2002	1992
Average Catalyst Temperature, °F	774	753	799	776	825
Oil Feed Rate, g/hr	603	609	595	609	600
H ₂ Feed Rate, SCF/hr	12.3	12.2	12.5	11.5	11.2
Product Gas Rate, SCF/hr	11.5	12.5	11.9	11.2	10.0
H ₂ /Oil Ratio, SCF/bbl	3240	3180	3330	3000	2960
Liquid Hourly Space Velocity, hr ⁻¹	0.6	0.6	0.6	0.6	0.6
Product Oil					
Sulfur, wt %	0.14	0.13	0.19	--	0.09
Nitrogen, wt %	0.55	0.58	0.43	0.65	0.27
Water-Washed Oil					
Sulfur, wt %	0.06	0.08	0.05	0.12	0.04
Nitrogen, wt %	0.46	0.51	0.27	0.73	0.32
Acid-Washed Oil					
Sulfur, wt %	0.07	0.08	0.07	0.11	0.04
Nitrogen, wt %	0.38	0.42	0.23	0.50	0.16

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Figure 6. DENITRIFICATION OF NEW ALBANY SHALE OIL

Table 10. SUNBURY SHALE OIL UPGRADING TESTS
(Catalyst: Shell 324 Ni/Mo; Catalyst Volume: 1000 cc)

Run No.	HTS-1	HTS-2	HTS-3	HTS-4
Duration, hr	3	3	3	2.5
Pressure, psig	2016	2015	1987	2010
Average Catalyst Temperature, °F	801	779	824	802
Oil Feed Rate, g/hr	603	603	600	602
H ₂ Feed Rate, SCF/hr	11.3	11.2	11.5	12.0
Product Gas Rate, SCF/hr	10.7	10.6	9.9	11.5
H ₂ /Oil Ratio, SCF/bbl	2970	2950	3040	3160
Liquid Hourly Space Velocity, hr ⁻¹	0.6	0.6	0.6	0.6
Product Oil				
Sulfur, wt %	0.11	0.15	0.11	0.10
Nitrogen, wt %	0.57	0.67	0.37	0.75
Water-Washed Oil				
Sulfur, wt %	0.09	0.11	0.09	0.10
Nitrogen, wt %	0.51	0.44	0.35	0.42
Acid-Washed Oil				
Sulfur, wt %	0.09	0.11	0.09	0.10
Nitrogen, wt %	0.34	0.38	0.30	0.44

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Figure 7. DENITRIFICATION OF SUNBURY SHALE OIL

TRC = TEMP RECORDING CONTROLLER
 FI = FLOW INDICATOR
 P = PRESSURE GAUGE
 PRC = PRESSURE REDUCING CONTROLLER
 SV = SOLENOID VALVE
 PS = PRESSURE SWITCH

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Figure 8. SCHEMATIC DIAGRAM OF LABORATORY TEST SYSTEM

provide enough heat to keep the bottom of the reactor at a desired temperature. Hot nitrogen gas passes through the shale and heats it; the oils are driven off and eventually cool, condense, and form mist. Foreign nuclei can be introduced from the side of the reactor about 1 foot above the bottom of the shale bed. Six thermocouples inserted into the reactor are used to measure the temperature throughout the bed. Furnace temperature is controlled by a temperature controller and reactor temperatures are recorded. The bottom portion of the reactor, which is exposed to high temperatures, is stainless steel but the top portions are made of pyrex glass to make visual observation of mist possible. Both the inside and outside of the hot portion of the reactor are to be insulated with densely packed refractory fiber insulation to minimize heat losses and channeling of the gas inside the reactor. Near the end of a run, when heat losses are at their maximum, a small amount of air can be added to the nitrogen stream to cause combustion in the reactor to make up for the additional heat losses. In the alternate mode of operation inert rocks would be used, and an oil vapor and inert gases would be introduced into the reactor. Oil vapor is provided by pumping the desired amount of oil into the hot nitrogen stream to be vaporized. Oil mist coming out of the reactor will be collected by two coalescing filters in series where 99.9% of the mist is collected, gas and vapor then pass through a condenser for further condensation of vapors. The system pressure is limited by a pressure switch that is connected to a solenoid valve that shuts off the feed gases automatically if pressure builds up in the reactor beyond an acceptable level.

Possible techniques of enhancement of mist formation are being studied. So far, it seems that practical ways of mist enhancement may be ionizing a stream of an inert gas and introducing the ionized gas into the reactor, or ionizing the gas to produce a very fine mist of a heavy oil (possibly obtained from the shale oil) prior to introduction into the reactor where it can serve as condensation nuclei for the oil vapors (as done by Sinclair and La Mer),¹ or to ionize a stream of vapor in inert gas for direct vapor injection into the reactor.

Techniques for measuring mist particle size are being studied. Initial experimental studies, however, will be based on detection of substantial improvement in the yield of the oil on the mist collectors and in visual appearance upon introduction of foreign nuclei.

Future Work

Future work will involve construction of the apparatus and more comprehensive study of possible techniques of enhancement of mist formation.

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 carryover 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

A preliminary test program has been developed to determine the effects of shale particle size and feed rate on net water gain. A two-variable three-level design set of experiments will be used initially during this program with a few shale types. The program presented in Table 11 shows the two variables with the operating pressure being held constant at 500 psig. The variables are shale feed rate and particle size range. Based on the results of the initial screening tests, we will select operating conditions for the tests with the other shales to be tested.

Table 11. INITIAL PROGRAM FOR LIQUID-SEALED LOCKHOPPER UNIT

<u>Feed Rate, rpm</u>	<u>APD₁[*] (-1/2 inch +6 mesh)</u>	<u>APD₂[*] (-1/4 inch +12 mesh)</u>
15	X ₁	X ₄
20	X ₂	X ₅
25	X ₃	X ₆

Where X_i represents the weight percent water that was observed during an eight-cycle operation of the unit. The operating pressure will be set at 500 psig.

* APD means average particle diameter.

Shakedown and initial testing of the solids feeding unit (Figure 9) were performed during this quarter. A test was performed with -1/2-inch to +6-mesh oil shale as part of a series to determine the effect of feed rate on the net water gain of the discharged oil shale.

In Run 80PF-1, all the equipment for the solids feeding device operated well with a few minor problems with the top and bottom ball valve operators, the bucket elevator (not shown in Figure 9), and instrument line plugging.

In this test (Run 80PF-1), a Michigan Antrim oil shale in the size range -1/2 inch to +6 mesh was fed to the reactor at 500 psig. Four feeding cycles were performed with 220 pounds of oil shale charged to the lockhopper during each cycle. The feed rate to the reactor was 2000 lb/hr.

A test (Run 80PF-2) was made to determine the effect of shale feed rate to the reactor on net water gain at a pressure of 500 psig. In Run 80PF-2, a Cleveland member of the Ohio shale with particle size in the range -1/2 inch to +6 mesh was used. The test consisted of 7 feeding cycles with about 220 pounds of oil shale being discharged from the lockhopper in each cycle. The feed rate to the reactor was 2000 lb/hr. Times required for key operating steps in Run 80PF-2 are presented in Table 12.

Table 12. TIMES FOR VARIOUS STEPS IN FEEDING CYCLE

Run No.	80PF-2
Operating Pressure, psig	500
Number of Feed Cycles	7
Operating Step	<u>Time, s</u>
1. Open Feed Hopper Slide Valve	8
2. Open Top Lockhopper Ball Valve	4
3. Drop Shale From Feed Hopper Into Lockhopper	35
4. Close Top Lockhopper Ball Valve	2
5. Pressurize Lockhopper With Water	2
6. Open Bottom Lockhopper Ball Valve	2
7. Discharge Oil Shale From Lockhopper With Screw Feeder	300
8. Close Bottom Lockhopper Ball Valve	2
9. Depressurize Lockhopper	4

Figure 9. SOLIDS FEEDING TEST UNIT

The results of the test, presented in Table 13, show the net water gain of the discharge sample as well as screen analyses of the feed and discharge samples. It shows the net water gain at 2000 lb/hr feed rate was about 6 weight percent with this shale. In previous testing with Colorado shale, net water gains were only about 3 weight percent.²

Table 13. RESULTS OF HIGH-PRESSURE FEEDING TESTS, VARISIZED
CLEVELAND OIL SHALE

Run No.	80PF-2	
Feed Size	-1/2 inch +6 mesh	
Pressure, psig	500	
Material	Feed	Discharge
Moisture, wt %	4.30	10.30
Net Water Gain (Dry Basis), wt %	--	6.00
Screen Analysis (U.S. Sieve), wt %		
+1/2 in.	1.1	0.0
+3/8 in.	4.3	1.5
+1/4 in.	45.6	39.9
+4	--	--
+6	45.4	48.2
+8	--	--
+12	3.6	9.6
+14	--	0.8
Total	100.0	100.0
Bulk Density, lb/ft ³	64.5	66.4

Future Work

Feeding tests will be performed with other shale types.

Task 3. Process Development Unit (PDU) Tests

Objective

The objective of this task is to demonstrate the technical feasibility of the hydroretorting 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

Two successful runs were made this quarter in the PDU. A Cleveland member of the Ohio shale was hydroretorted under gas-making conditions in Run 80PDU-3. A total of 8.00 hours of shale feeding time, including 4.50 hours of steady-state operation, was achieved. In Run 80PDU-4, a Kentucky New Albany oil shale was processed under gas-making conditions. Shale was fed for 8.50 hours, including 6.00 hours of steady-state operation. Both runs had a shale feed rate of approximately 1000 lb/hr, a reactor pressure of 400 psig, and a hydrogen-to-shale ratio in Stage 2 of approximately 17.5 SCF/lb. Both runs were completely successful and were terminated voluntarily. Test results for these two runs will be reported in the next quarterly report when sufficient analytical data become available.

Analytical data are now available for the two successful PDU Runs 80PDU-1 and 80PDU-2 made during the previous quarter. Runs 80PDU-1 and 80PDU-2 were made to obtain information on product yield and quality with hydroretorting of a Cleveland member of the Ohio shale and a Kentucky New Albany shale, respectively. Both shales were processed under oil-making conditions. Sufficient shale oils were produced from each run to conduct the bench-scale hydrotreating tests described above in Subtask 2.3.

Test results and operating conditions of both runs are summarized in Table 14. Detailed operating conditions and test results for both runs are presented in Appendix B. In Run 80PDU-1, a Cleveland member of the Ohio shale was fed at a rate of 1021 lb/hr for 8.25 hours, including 6.00 hours of steady-state operation. Reactor pressure was 402 psig. A feed-hydrogen-to-shale ratio of 19.9 was used in Stage 1, while a hydrogen-to-shale ratio of 13.0 was maintained in Stage 2. The hydrogen-to-shale ratios were

Table 14. SUMMARY OF TEST RESULTS USING EASTERN SHALES

<u>Run No.</u>	<u>80PDU-1</u>	<u>80PDU-2</u>
Shale Type	Cleveland	Kentucky New Albany
Bed Height, ft	10.0	10.0
Pressure, psig	402	406
Average Bed Temperature, °F*	1100	1224
Maximum Bed Temperature, °F*	1245	1335
Oil Shale Space Velocity, lb/ft ³ -hr*	117	121
Oil Shale Mass Rate, lb/ft ² -hr*	1171	1214
Hydrogen/Shale Feed Ratio, SCF/lb*	13.0	13.2
Organic Carbon Distribution in Products, %		
Gas	28.2	23.4
Oil	26.4	42.0
Residue	48.3	24.6
Material Balances, % [†]	103.0	99.6
Elemental Balances, % [†]		
Carbon	96.1	88.0
Hydrogen	104.5	102.7
Oxygen	155	118

* Stage 2

† Using residue shale weight calculated by ash balance.

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 total enthalpy of the feed gas. Some of the feed hydrogen is burned (with injected air) to increase the enthalpy of the Stage 2 feed gas.

We have begun using high-temperature water (HTW) analytical determinations of feed and spent shales in an attempt to improve the elemental oxygen balances. The HTW is generated by passing nitrogen over the sample at 900°C. Condensable oils are removed from the stream by adsorption on a Tenax gas-chromatograph-type packing at ambient temperature, prior to

adsorption of the water on magnesium perchlorate. Water evolved is determined by weighing the magnesium perchlorate. The total HTW is then determined by subtracting the initial shale surface moisture from the water evolved. The high-temperature water presumably includes a water-of-constitution of the inorganic material, as well as that evolved during the pyrolysis of the organic material.

The detection of hydrogen sulfide in the gas stream before and after the magnesium perchlorate proved that the high-temperature water did not include any H_2S formed during pyrolysis of the high sulfur shales. Any ammonia formed would be adsorbed by the perchlorate. However, the total nitrogen lost during inert gas pyrolysis of these shales is small compared with the HTW and is therefore neglected.

Based on the amount of product water obtained during the BSU runs and the PDU runs, we are apparently still not analyzing all of the oxygen present in the feed shales. Elemental oxygen balances are still high, 118% for Run 80PDU-2 and 155% for Run 80PDU-1. The greatest source of the oxygen in the exit system is the product water. We will continue searching for a more accurate method of determining the oxygen in the feed and spent Eastern shales.

The Stage 1 and Stage 2 bed-temperature profiles for Run 80PDU-1 are shown in Figures 10 and 11, respectively. The temperature for Stage 1 is nearly constant at a value of $300^{\circ}F$ for about the top half of the shale bed. Part of the reason for the slow shale heat-up at the top of the bed is probably the 5.0% by weight surface moisture and the additional water (4.1% by weight) collected in the Stage 1 quench tower. Some of the additional water collected in the Stage 1 quench tower results from the HTW present in the raw shale. The bottom half of the shale bed in Stage 1 shows a linear temperature gradient.

It may not be possible to obtain a linear profile for the entire shale bed in Stage 1 for some high-moisture-content shales due to the large amount of water that must be vaporized. It may, therefore, be necessary to provide an additional several feet in the retort before the hydroretorting begins to preheat the shale to approximately 250° to $300^{\circ}F$ in order to drive off surface moisture and some HTW present in the raw shale.

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Figure 10. STAGE 1 AVERAGE STEADY-STATE TEMPERATURES FOR RUN 80PDU-1

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Figure 11. STAGE 2 AVERAGE STEADY-STATE TEMPERATURES FOR RUN 80PDU-1

The Stage 2 temperature profile is nearly linear for the entire shale bed. The profile indicates that the product of shale rate times average shale heat capacity was nearly equal to that for the gas in Stage 2. No exothermic or endothermic reactions are discernible from the temperature profile. The water removed in the Stage 2 quench tower was 6.6 weight percent of the feed shale weight. The water yield from the hydrogen-air combustion used to preheat the feed gas in Stage 2 was only 1% by weight. The other 5.6% by weight water collected was probably due to HTW recovery as well as water formation by additional gas-phase chemical reactions.

Although conditions were used in Run 80PDU-1 that gave high oil yields with other shales, with this shale only 0.03 lb oil/lb shale was recovered. In addition, the conversion of organic carbon to liquids was nearly equal to that to gas. Much water was recovered from this shale, approximately 37.6 gal/ton compared with the 7.5 gal/ton of oil recovered. This high water yield was previously encountered in bench-scale testing of this shale. The maximum bed temperature in Stage 2 was only 1245°F compared with a target value of 1400°F. The 155°F lower maximum shale temperature may have contributed to the low (51.7%) total organic carbon conversion.

Runs 80PDU-1 and 80BSU-2 were both made with a Cleveland member of the Ohio shale. Run 80PDU-1 had an average hydrogen partial pressure of 331 psig, an average bed temperature of 1100°F, a maximum bed temperature of 1245°F, and a total organic carbon conversion of 51.7%. Run 80BSU-2 had an average hydrogen partial pressure of 498 psig, an average bed temperature of 1094°F, a maximum bed temperature of 1305°F, and a total organic carbon conversion of 56.1%. The hydrogen partial pressure was 167 psi greater in the BSU run than that used in the PDU run, but the higher hydrogen partial pressure in the bench-scale test resulted in only 4.4% additional organic carbon recovery. Thus the results of the two runs are comparable and indicate that we can project and scale-up BSU results to the PDU.

In Run 80PDU-2, a Kentucky New Albany shale was fed at a rate of 1059 lb/hr for 8.00 hours, including 6.50 hours of steady-state operation. A feed-hydrogen-to-shale ratio of 19.0 SCF/lb was used in Stage 1 while a feed-hydrogen-to-shale ratio of 13.2 SCF/lb was maintained in Stage 2. The run conditions for Run 80PDU-2 were chosen for the same reasons as those given earlier in this section for Run 80PDU-1.

The bed-temperature profiles of Stage 1 and Stage 2 for Run 80PDU-2 are shown in Figures 12 and 13, respectively. The temperature profile for Stage 1 is nearly linear throughout the entire bed. There is a slight exotherm (or possibly two endotherms) that occurs at a point 3 feet down from the top of the Stage 1 shale bed. The temperature profile is substantially different from that of Run 80PDU-1. The lack of an initially flat temperature profile was probably due to the fact that there was only one-half as much water present in the Kentucky New Albany shale as was present in the Cleveland member of the Ohio shale. Approximately 20.6 gal/ton of water was recovered in Run 80PDU-2 along with 16.0 gal/ton of oil. The Stage 2 bed-temperature profile for 80PDU-2 is nearly linear for the top half of the shale bed. The temperature rises gradually from 1000°F to a maximum of approximately 1350°F.

Runs 80PDU-2 and 79BSU-2 were made with a Kentucky New Albany shale. Run 80PDU-2 had an average hydrogen partial pressure of 339 psig, an average bed temperature (Stage 2) of 1224°F, a maximum bed temperature of 1335°F, and a total organic carbon conversion of 75.4%. Run 79BSU-2 had an average hydrogen partial pressure of 480 psig, an average bed temperature of 1151°F, a maximum bed temperature of 1259°F, and a total organic carbon conversion of 70.9%. The beneficial effect of a higher (141 psi) hydrogen partial pressure in the bench-scale run than in the PDU run was probably offset by a 100°F lower maximum shale temperature in the BSU run. Consequently, the BSU run had a 5.5% lower total organic carbon conversion than occurred in the PDU. Run 79BSU-2 had a carbon selectivity of 63% to liquids while Run 80PDU-2 had a selectivity of 64% to liquids. Total organic carbon converted to liquids was 42% in 80PDU-2 and 40.3% in 80BSU-2. Thus, operating conditions and results are nearly the same for the two runs.

Using an average heat-up rate for Run 80PDU-2 for both stages of approximately 22°F/min, an average hydrogen partial pressure of 339 psig, and previous thermobalance data, one can estimate the expected organic carbon recovery to be about 77%. This compares remarkably well with the 75.4% conversion actually obtained for this PDU run.

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Figure 12. STAGE 1 BED-TEMPERATURE PROFILE FOR RUN 80PDU-2

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Figure 13. STAGE 2 BED-TEMPERATURE PROFILE FOR RUN 80PDU-2

Approximately 89% of the total oil recovered in Run 80PDU-2 was collected from the Stage 2 quench system. The oil had a pour point of -15°F , an API gravity of 14.4 and a carbon-to-hydrogen weight ratio of 8.66. The oil contained 1.0 weight percent nitrogen and 1.1 weight percent sulfur. The gasoline fraction ($\text{C}_5 - 400^{\circ}\text{F}$) was split nearly equally among saturates, olefins, and aromatics (36%, 30%, and 34%, respectively). As with all shale oils, this oil will require some hydrotreating to bring the sulfur and nitrogen levels down to acceptable limits before the oil can be processed in conventional petroleum refining equipment.

Future Work

A Kentucky Sunbury shale will be tested next in the PDU under gas-making conditions. Some routine, annually scheduled maintenance will be performed on the PDU during the next quarter. Work will be continued to obtain additional large-tonnage oil shale 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. The Pace Company from the Jacobs Engineering Group, Inc., has been retained as a subcontractor 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

An initial draft report summarizing the efforts of Pace for completion of Phase 1 of its contract has been completed and reviewed by IGT, and a second draft is in preparation. In Phase 1, the HYTORT Process concept is reviewed for both Eastern and Western shales and questions about environmental effects are formulated for commercial HYTORT plant operations. Major areas for review include spent shale leaching and process wastewater treatment.

Additionally, Phase 1 includes a review of the IGT experimental work for completeness, cost-effectiveness, and feasibility. Pace has formulated a detailed test program to complement the IGT experimental plan and help answer major questions about commercial HYTORT operation.

The laboratory gas chromatograph has been received, installed, and checked-out. It has also been calibrated and adjusted and is considered to be operational. It will be used initially for analysis of sulfur compounds in both liquid and gaseous PDU samples. This instrument is located near the PDU which allows timely analysis of PDU samples to minimize any effects of sample degradation.

Samples for environmental purposes were taken from Runs 80PDU-2, with Kentucky New Albany shale, and 80PDU-3, with Cleveland oil shale. Information sought includes trace elements in feed and spent shales plus organic compounds in the first and second stage oil and water phases.

A sampling probe has been placed into the second stage of the PDU, upstream of the cyclone and quench tower, to collect samples and improve our ability to accurately characterize the HYTORT Process gases for possible pollutants. This direct sampling system is required because samples can be taken from the recirculating quench system only after completion of a run and not during steady-state operation. Also, the collection efficiency of the quench system for such species as NH_3 , HCN , and H_2S is not completely known, some species collected in the quench waters may be lost because of reaction to other species (for example, CN^- to SCN^-) and because of volatilization losses upon sample depressurization. Additionally, the correlation of stream loadings with process conditions is difficult because of the dampening effects and unknown response times for the PDU quench system.

The sampling probe provides filtration and bulk solids removal at operating temperature and pressure in the reactor prior to any pressure release. The sampled reactor gases are then introduced into a sampling train where they are cooled, condensed, and scrubbed with specific preservative solutions to prevent loss of species of environmental interest. Volumetric gas flow measurements are made during each sample collection and the exit gas from the train can be sampled and analyzed to evaluate the sampling efficiency.

The on-line sampling equipment was completed, installed, and placed into operation for Run 80PDU-4 with Kentucky New Albany Shale. During the 6 hours of steady-state operation for this run, three complete sets of environmental samples were taken: that is, a set consisted of raw condensate samples, samples scrubbed with acid, samples scrubbed with base, samples scrubbed with organic solvents, and the four respective exit-gas samples. These samples are now being analyzed.

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 is being completed through the combined efforts of IGT and Pace engineers. Although there were no apparent problems with the sampling train, the inlet line operated at 130° to 140°F and there may have been some condensation and refluxing of oil and water before the sample reached the condenser and sampling bombs. Consequently, the sampling train will be moved down one deck from its present location so that the inlet line will slope steeply from the reactor probe position to the top of the condenser on the sampling train. Additionally, the inlet line will be heat-traced in an effort to maintain high temperatures and prevent condensation.

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 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 Design and Cost Estimate for Conversion of Colorado Oil Shale to Synthetic Crude Oil

This report presents the process description and cost estimate for the conversion of Western Eocene (Colorado) oil shale to synthetic crude oil. The oil produced in the HYTORT reactor is hydrotreated to remove sulfur and

nitrogen. During the process the oil is upgraded to 44^oAPI and a C/H weight ratio of approximately 6.0. This oil is of much higher quality than conventionally produced shale oils or crude petroleum, so it is expected that refining this oil to gasoline and fuel oil should cost less. Consequently, from the standpoint of a refinery which would receive this product, this oil has a higher market value than heavier shale oils or crudes. The process design and cost bases used in this design are considered to represent a base case for future estimates for the conversion of Western as well as Eastern oil shales to syncrude and SNG.

Process Description

Figure 14 is a flow diagram for the process. Table 15 gives compositions and flow rates for process streams. The process design for syncrude is based on a feed rate of 87,125 tons/SD of crushed oil shale, containing 2.91 weight percent water to the HYTORT reactors. The average hourly mine production rate is 96,000 tons/SD, based on the assumption of 10,500 tons/day of fines production during mining and shale preparation.

Four shale reactor systems are used, each with a liquid-sealed type lockhopper feed and discharge system. Each reactor has a 34-foot refractory ID and 56-foot tan-to-tan length. Adding the hemispherical head and bottom cone gives an overall length of 102 ft. Operating pressure is 400 psig.

Overall shale organic carbon conversion in the reactor is 89.5%. Hydrogen conversion is 89.0%. The HYTORT net yields include oil, gas, and water, amounting to 46.9%, 25.6%, and 27.4%, respectively, of the feed shale weight.

The raw effluent is cooled to 234^oF by countercurrent heat exchange with the incoming shale. The oil is assumed to be present primarily as a mist, much of which is extracted in the primary separator along with dust and 55% of the water, which is also present as a mist. The scrubbed gas is then sent to a direct contact washer-cooler where water is used to cool the gas and condense the remaining water vapor. All of the ammonia plus small amounts of H₂S and CO₂ that are dissolved in the water streams are recovered via the Chevron process.

Figure 14. PRODUCTION OF 50,727 bbl/SD OF SYNCRUDE FROM WESTERN OIL SHALE BY THE HYTORT PROCESS

Table 15. COMPOSITIONS AND FLOW RATES FOR PROCESS STREAMS IN FIGURE 14

Stream No.	1		2		3A		3B	
Stream Name	Raw Shale to HYTORT		Spent Shale		Raw Shale Oil to Hydrotreater		Product Oil	
Temperature, °F	100		123		100		100	
Pressure, psig	400		390		375		50	
Component	lb/hr	wt %	lb/hr	wt %	lb/hr	wt %	lb/hr	wt %
Organic C	782,438	11.10	82,337	1.42	605,160	84.55	587,914	85.63
Mineral C	344,701	4.89	254,892	4.41	--	--	--	--
H	120,573	1.71	13,814	0.24	82,015	11.46	98,088	14.29
N	22,581	0.32	5,771	0.10	12,019	1.68	504	0.07
S	38,736	0.55	20,715	0.36	4,072	0.57	32	--
O	1,094,880	15.53	757,248	13.10	12,448	1.74	64	0.01
Mineral Matter	4,645,083	65.90	4,645,083	80.37	--	--	--	--
Subtotal (Dry)	7,048,992	100.00	5,779,860	100.00	715,714	100.00	686,602	100.00
H ₂ O* (2.91%)	211,470	--	--	--	--	--	--	--
Total	7,260,462		5,779,860	100.00	715,714	100.00	686,602	100.00

Stream No.	4		5		6		7		8		9		10	
Stream Name	Retort Offgas		Quench System Effluent		Retort Recycle Gas		Recycle Gas to Furnace		Preheated H ₂ + Recycle to Retort		Acid Gas Removal Feed		Acid Gas Removal Effluent	
Temperature, °F	234		100		100		100		1285		100		100	
Pressure, psig	400		390		390		425		410		390		375	
Component	mol/hr	mol %	mol/hr	mol %	mol/hr	mol %	mol/hr	mol %	mol/hr	mol %	mol/hr	mol %	mol/hr	mol %
CO	41,207	19.78	41,207	22.54	27,884	22.54	9,749	22.54	9,918	16.42	3,574	22.54	3,574	24.55
CO ₂	33,796	16.22	33,716	18.44	22,815	18.44	7,977	18.44	8,045	13.31	2,924	18.44	1,998	13.74
H ₂	45,945	22.06	45,949	25.13	31,093	25.13	10,871	25.13	27,377	45.31	3,985	25.13	3,985	27.42
CH ₄	28,563	13.71	28,563	15.62	19,328	15.62	6,758	15.62	7,121	11.79	2,477	15.62	2,477	17.04
C ₂ H ₆	12,186	5.85	12,186	6.66	8,246	6.66	2,883	6.66	2,883	4.77	1,057	6.66	1,057	7.27
C ₃ H ₈	2,702	1.30	2,702	1.48	1,828	1.48	639	1.48	639	1.06	235	1.48	235	1.62
C ₄ H ₁₀	4,062	1.95	4,062	2.22	2,749	2.22	961	2.22	961	1.59	352	2.22	352	2.42
C ₃ H ₆	6,764	3.25	6,764	3.70	4,577	3.70	1,600	3.70	1,600	2.65	587	3.70	587	4.04
C ₄ H ₈	2,702	1.30	2,702	1.48	1,828	1.48	639	1.48	639	1.06	235	1.48	235	1.62
H ₂ S	4,609	2.21	4,571	2.50	3,093	2.50	1,081	2.50	1,081	1.79	397	2.50	--	--
NH ₃	342	0.16	--	--	--	--	--	--	--	--	--	--	--	--
Raw Shale Oil	2,196	1.05	--	--	--	--	--	--	--	--	--	--	--	--
H ₂ O	23,243	11.16	421	0.23	285	0.23	100	0.23	152	0.25	36	0.23	35	0.24
Total	208,321	100.00	182,843	100.00	123,726	100.00	43,258	100.00	60,416	100.00	15,859	100.00	14,535	100.00

Stream No.	11		12		13		14		15		16		17	
Stream Name	Hydrogen Plant Feed		Hydrogen Plant Fuel Gas		Total H ₂ Plant Effluent		Makeup H ₂ to HYTORT		H ₂ Plant Effluent to Methanation		Makeup H ₂ to Hydrotreater		Hydrotreater Offgas	
Temperature, °F	100		100		100		100		100		410		100	
Pressure, psig	375		375		300		300		300		2500		2000	
Component	mol/hr	mol %	mol/hr	mol %	mol/hr	mol %	mol/hr	mol %	mol/hr	mol %	mol/hr	mol %	mol/hr	mol %
CO	3,049	24.59	525	24.59	319	0.98	169	0.98	150	0.98	--	--	--	--
CO ₂	1,704	13.74	294	13.74	128	0.40	68	0.40	60	0.40	--	--	--	--
H ₂	3,400	27.42	585	27.42	31,169	96.20	16,506	96.20	14,663	96.20	13,973	95.98	1734	58.46
CH ₄	2,113	17.04	364	17.04	685	2.12	363	2.12	322	2.12	532	3.65	815	27.48
C ₂ H ₆	902	7.27	155	7.27	--	--	--	--	--	--	--	--	189	6.37
C ₃ H ₈	200	1.62	35	1.62	--	--	--	--	--	--	--	--	137	4.62
C ₄ H ₁₀	300	2.42	52	2.42	--	--	--	--	--	--	--	--	91	3.07
C ₃ H ₆	501	4.04	86	4.04	--	--	--	--	--	--	--	--	--	--
C ₄ H ₈	200	1.62	35	1.62	--	--	--	--	--	--	--	--	--	--
H ₂ S	--	--	--	--	--	--	--	--	--	--	--	--	--	--
H ₂ O	30	0.24	5	0.24	98	0.30	52	0.30	46	0.30	54	0.37	--	--
Total	12,399	100.00	2,136	100.00	32,399	100.00	17,158	100.00	15,241	100.00	14,559	100.00	2966	100.00

* Added to shale in water-pressured lockhoppers.

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Of the scrubbed gas 90.3% is recycled to the HYTORT reactor. Two-thirds enters the bottom of the reactor to extract heat by countercurrent cooling of the spent shale, cooling it to 123°F, and 23.7% combines with the makeup hydrogen and is preheated to 1285°F. Total makeup hydrogen is 156 million SCF/day, or 1720 SCF/ton of feed.

All of the net gas make from the HYTORT reactor is used for the manufacture of hydrogen used in the plant. The gas is first scrubbed in a Selexol system which removes the H₂S and 32% of the CO₂. The hydrogen plant produces 294.3 million SCF/day of 96.2% hydrogen. A little over one-half of the hydrogen, 53%, is sent to the HYTORT reactor; the rest is methanated to convert carbon oxides and is then used for hydrotreating the oil. Fuel for the hydrogen plant is supplied by HYTORT offgas, offgas from hydrotreating, plus a small amount of fuel oil.

Raw shale oil, at a rate of 55,606 bbl/SD, is sent to the hydrotreater. The operating requirements and plant costs are based on the report by Chevron on the upgrading of Paraho Shale Oil.³ Hydrotreating is carried out at 2000 psig and 750°F over a cobalt-molybdate catalyst. Net hydrogen consumption amounts to 2000 SCF/bbl. The recycle plus net hydrogen give a total hydrogen-to-oil feed ratio of approximately 5000 SCF/bbl. Feed and product oil properties are summarized in Table 16.

Table 16. FEED AND PRODUCT PROPERTIES

	<u>HYTORT Oil</u>	<u>Hydrotreated Oil</u>
°API	28.7	44
C/H	7.38	6.0
<u>Wt %</u>		
C	84.55	85.62
H	11.46	14.29
N	1.68	0.08
S	0.57	<0.01
O	1.74	0.01
	<u>100.00</u>	<u>100.00</u>
lb/hr	715,714	686,602
bbl/SD	55,606	58,472

The oil is very light and has such a low C/H ratio that it seems inaccurate to call it a crude oil. The heating value, based on correlations, is considered to be 5.64 million Btu/bbl. Hydrotreater offgas supplies 158.9 bbl/hr F.O.E. to the reformer furnace augmented by 16.3 bbl/hr of fuel oil. A total of 322.8 bbl/hr of product oil is used as plant fuel (7745 bbl/SD). Net product is 50,727 bbl/SD, or 286 billion Btu equivalent. By-products are 220.8 tons/day of ammonia and 190.3 long tons/day of sulfur.

Plant Utilities and Overall Efficiency

Table 17 summarizes power requirements for the plant. A total of 119,250 hp is estimated. Hydrotreating, including the makeup hydrogen compressor, amounts to 30% to the total. Since it is necessary to burn product oil for boiler fuel, it was decided to purchase power at 5¢/kWhr rather than generate it onsite in a relatively small power plant using expensive product oil as fuel. A rough calculation indicated that the cost of power generated onsite would exceed 7¢/kWhr.

Table 17. SUMMARY OF POWER REQUIREMENTS FOR CONVERSION OF WESTERN SHALE TO 50,727 bbl/SD SYNCRUDE

<u>Section</u>	<u>Horsepower</u>
Shale Handling	2,000
Shale Crushing	9,000
Shale Feed System	9,030
Reactor Effluent Scrubber	1,210
Retort Recycle Gas Compressor	9,000
Preheat Recycle Gas Compressor	6,200
Hydrogen Plant	17,180
Retort Recycle H ₂ Compressor	5,200
Hydrotreater Make-Up H ₂	26,000
Hydrotreater	10,330
Acid-Gas Removal (Selexol)	3,930
Shale Disposal	2,000
Sulfur Recovery	830
Waste-Water Treatment	1,340
Boiler Feed Water Pumps	1,000
Cooling-Water Pumps	5,000
Miscellaneous	<u>10,000</u>
Total Power Required	119,250

(90,000 kW purchased)

Table 18 summarizes steam requirements. These are relatively small, but boiler fuel is 13.7% of hydrotreated product.

Table 18. SUMMARY OF STEAM REQUIREMENTS FOR CONVERSION OF WESTERN OIL SHALE TO 50,727 bbl/SD SYNCRUDE

	<u>lb/hr</u>	<u>10⁶ Btu/hr</u>
<u>50 psig, 298°F</u>		
Acid Gas Scrubbing	96,446	111.0
Waste-Water Treatment	<u>120,960</u>	<u>139.2</u>
Total	217,406	250.2
<u>150 psig, 367°F</u>		
Hydrotreating	73,000	85.2
Waste-Water Treatment	<u>39,850</u>	<u>46.5</u>
Total	112,850	131.7
Total Requirements	330,256	381.9
Less Waste Heat From Sulfur Recovery		<u>49.3</u>
Net Boiler Duty		332.6

Cooling water requirements are summarized in Table 19. The 75,000 gpm is supplied by a cooling tower operating in the range of 85° to 115°F.

Table 19. SUMMARY OF COOLING-WATER REQUIREMENTS FOR CONVERSION OF WESTERN SHALE TO 50,727 bbl/SD SYNCRUDE

<u>Section</u>	<u>Gallons per Minute</u>
Retort Effluent Cooling	27,740
Acid-Gas Removal	4,800
Hydrogen Plant	27,450
Hydrotreating	6,000
Waste-Water Treatment	1,710
Sulfur Recovery	660
Miscellaneous	<u>5,000</u>
Total Process Cooling Water	73,360
Total Cooling Tower Capacity; Sized for	75,000

Table 20 summarizes the overall plant efficiency, which calculates out at 63.3%. By-products constitute only a small portion, 1.3%. If all the shale mined (including fines produced in mining plus those generated in crushing and grinding operations) could be utilized, then the overall efficiency would be increased and could approach 71%. The heating value plus sensible heat of the spent shale is only 4.2% of the heating value of the mined shale and is 4.75% of that of the shale actually fed to the reactor. Net product yield amounts to 25.2 gal/ton of dry oil shale fed to the reactor.

Table 20. OVERALL PLANT EFFICIENCY

<u>In</u>	<u>10⁶ Btu/hr</u>
Oil Shale H.H.V. 96,000 tons/SD (1.0% H ₂ O) 2317 Btu/lb dry	18,350.6
Electricity 90,000 kW generated at 35% efficiency	<u>877.6</u> 19,228.2
<u>Products</u>	
Synthetic "Crude," 50,727 bbl/SD 5.64 X 10 ⁶ Btu/bbl	11,920.9
Sulfur, 190 long tons/SD	70.6
Ammonia, 220 tons/SD	<u>177.2</u>
	12,168.7
Efficiency = 63.3%	

Process Economics

Estimates have been made of the plant investment, annual operating costs, revenue requirements, and product prices. Four different cases for private investor financing were developed:

1. 100% equity financing with 12% DCF rate of return
2. A debt-to-equity ratio of 25/75, with 12% DEF rate of return for the equity portion and 9% interest rate on the debt portion
3. A debt-to-equity ratio of 50/50 with 12% DCF rate of return for the equity portion and 9% interest rate on the debt portion
4. 100% equity financing with a 15% DCF rate of return.

Investment and Operating Costs

Total capital requirements (Table 21) for the plant vary from \$1242.5 million to \$1344.5 million, depending upon the financial factors used to derive it from the total plant investment of \$961.3 million. Hydrotreating (including the makeup compressor and methanation) and hydrogen manufacture are the two most expensive sections, representing 17.1% and 14.6%, respectively of the total plant investment. The sum of HYTORT reactor, solids handling, hydrogen compression, and preheat is 17.8%. Shale storage and preparation (12.9%) and HYTORT effluent cooling and scrubbing (6.7%) are the other major items.

The major item of the annual operating costs (Table 22) is that for oil shale, which varies from \$3.80/ton to \$5.25/ton for different financing methods. The basis for deriving the shale costs is explained below.

Shale Costs

The cost of oil shale can be presented either as a raw material input or incorporated into the capital and operating costs of the entire operation. By making a separate calculation for the shale cost, we then know the contribution of this raw material to the product price and provide a basis for showing the sensitivity of the product price to the raw material cost.

The estimation of the details of investment and operating costs of mined Western oil shale is beyond the scope of this study. However, published estimates have been made, and these have been used to provide a basis for the cost of shale to this plant.

Two published estimates of the cost of mining Western oil shale were used.^{4,5} Costs given in these references are for mid 1977 and September 1977, respectively. After capital and operating costs for nominal 66,000 ton/day mining rates were extracted, costs were calculated per ton of shale and then inflated to January 1980 by cost indexing. Capital costs were calculated from each reference using the four different financial methods discussed above. The costs, adjusted to 1980 from each source plus the intermediate value used in this study, are summarized in Table 23.

Table 21. SUMMARY OF PLANT INVESTMENT COST FOR THE PRODUCTION OF 50,727 bbl/DAY OF SYNCRUDE FROM WESTERN OIL SHALE USING HYTORT PROCESS AND PRIVATE INVESTOR FINANCING
(90% Stream Factor, January 1980 Cost Basis)

Financing Method	Private Financing, Discounted Gas Flow			
	0/100	25/75	50/50	0/100
Debt/Equity Ratio		12		15
Discounted Cash Flow Rate of Return, %		9		9
Interest on Debt, %	--			--
<u>Components of Plant Investment</u>				
Shale Storage			\$10 ⁶	
Shale Preparation			15.2	
Shale Retort Feed and Discharge Systems			81.8	
Shale Hydroretorts			28.4	
Hydroretort Effluent Scrubbing, Cooling, and Oil-Gas Separation			42.6	
Acid Gas Removal			50.4	
Sulfur Recovery, Tail Gas Treating			27.0	
Hydrogen Plus Recycle Gas Preheat			17.9	
Hytort Make-up Hydrogen Compressor			51.5	
Hytort Recycle Gas Compressor			3.0	
Preheated Hytort Recycle Gas Compressor			4.7	
Hydrotreater Make-up Hydrogen Compressor			3.6	
Methanation			4.8	
Hydrogen Plant			1.7	
Hydrotreating Section			110.0	
Steam Generation			122.0	
Electric Power Distribution			24.0	
Cooling Water Supply			22.0	
Raw Water and Boiler Feed Water Treatment			5.5	
Blowdowns Water Treatment			11.2	
Waste Water Treatment			22.0	
Particulate Emission Control			18.0	
General Facilities, 12% of Above			5.0	
Installed Plant Cost Excluding Contingencies			80.7	
Contingencies, 15%			753.0	
Installed Plant Cost			113.0	
Contractor's Overhead and Profits (11% of above)			866.0	
Total Plant Investment (T.P.I.)			95.3	
			961.3	
Return on Investment During Construction (Return rate* X 1.875 years X T.P.I.)	216.3	202.8	189.3	270.4
Start-Up Cost† (20% of Gross Operating Costs)	54.4	51.5	49.4	58.5
<u>Working Capital</u>				
30 Days Raw Materials	18.9	17.5	16.5	20.7
Supplies (O.S.Y. of T.P.I.)	8.7	8.7	8.7	8.7
1/24 of Annual Revenue Required	21.0	19.0	17.3	24.9
Total Capital Required (C)	1280.6	1260.8	1242.5	1344.5

* Return rate is the weighted average of return on equity and interest on debt.

† A nondepreciated item treated as an expense before the first year of operation as part of the cash flow.

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Table 22. SUMMARY OF ANNUAL OPERATING COSTS AND REVENUE REQUIREMENTS FOR PRODUCTION OF 50,727 bbl/DAY OF SYNCRUDE FROM WESTERN OIL SHALE USING HYTORT PROCESS AND PRIVATE INVESTOR FINANCING
(90% Stream Factor, January 1980 Cost Basis)

Financing Method	Private Financing Discounted Cash Flow			
Debt/Equity Ratio	0/100	25/75	50/50	0/100
Discounted Cash Flow Rate of Return, %		12		15
Interest on Debt, %	--	9	9	--
Raw Shale Cost, \$/ton	4.60	4.14	3.80	5.25
<u>Annual Operating Costs</u>	<u>\$10⁶/year</u>			
<u>Raw Materials</u>				
Oil Shale 96,000 Tons/Day	145.06	130.55	119.83	165.55
Catalysts and Chemicals		24.10		
Make-Up Water at \$1/1000 gal		1.77		
Electric Power, 90,000 kW at 5¢/kWhr		35.48		
<u>Labor</u>				
Direct Operating Labor, 55 Men/Shift at \$9.25/hr		4.46		
Supervision, 20% of Direct Operating Labor		0.89		
Administrative and General Overhead, 60% of Direct Operating Labor and Supervision		3.21		
<u>Supplies</u>				
Operating, 30% of Direct Operating Labor		1.34		
Maintenance, 3% of Total Plant Investment		28.84		
Local Taxes and Insurance, 1.5% of Total Plant Investment		14.42		
Shale Fines Disposal at \$3.60/ton		12.44		
Gross Operating Costs	272.01	257.50	246.78	292.50
<u>By-Product Credits</u>				
Sulfur, 190 Long Tons/Day at \$20/Long Ton		-1.25		
Ammonia, 220 Tons/Day at \$100/Ton		-7.23		
Net Operating Costs (N)	263.53	249.02	238.30	284.02
Depreciation (20-Year Equivalent Average)*	58.88	58.20	57.53	61.59
Net Income	93.40	76.52	60.24	129.72
Federal Income Tax	86.22	70.63	55.60	119.75
1/20 of Initial Start-Up Expense	2.72	2.57	2.47	2.93
Total Revenue Required	504.75	456.94	414.14	598.01
Annual Syncrude Production, 10 ⁶ /bbl		16.664		
Syncrude Price, \$/bbl	30.29	27.42	24.85	35.89

* Total plant investment plus interest during construction depreciated over 20 years.

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Table 23. SHALE COST SUMMARY, ADJUSTED TO 1980

Financing Method		Shale Cost, \$/Ton	
Source of Cost Data	Tosco	Ashland-Shell	Intermediate Value Used In This Work
12% DCF, 100% Equity	4.80	4.33	4.60
15% DCF, 100% Equity	5.65	4.90	5.25
12% DCF, 9% Interest, 25/75 D/E	4.25	3.98	4.14
12% DCF, 9% Interest, 50/50 D/E	3.91	3.73	3.80
Utility — 15% Equity, 9% Interest, 75/25 D/E	3.60	3.62	3.60*

* Not used in calculating product oil prices.

Shale cost ranges from 49% to 57% of gross operating costs and from 28% to 29% of total revenue.

The other major operating costs are for catalysts and chemicals and electric power. Hydrotreater catalyst replacement costs account for about 75% of the catalyst and chemicals costs. These are summarized in Table 24.

Table 24. ANNUAL COST OF CATALYSTS AND CHEMICALS

	<u>\$/Year</u>
Hydrotreating Catalyst	21,600,000
Hydrogen Manufacture	735,300
Methanation Catalyst	120,000
Acid Gas Removal	130,000
Water Treatment	<u>1,510,000</u>
Total	24,095,300

As discussed above in the section, Plant Utilities and Overall Efficiency, it was determined that purchase of electric power at 5¢/kWhr is cheaper than onsite generation. Direct operating labor was estimated at 55 men/shift with an hourly rate of \$9.25. Other operating cost factors for estimating overhead,

supplies, maintenance, local taxes, and insurance are based on the modified guidelines given to C. F. Braun for evaluating processes for SNG from Eastern coal.⁶ Sulfur and ammonia are the only two by-products, and are credited to the plant at \$20/long ton and \$100/ton, respectively. The by-product credits are subtracted from the gross operating costs to obtain the net operating costs.

Start up costs (shown in Table 21) are assumed to be 20% of the gross operating costs. The net operating costs (Table 22) are part of annual revenue requirements and syncrude prices.

Calculation of Revenue Requirement and Product Prices

Product prices are based on annual revenues calculated for private investor financing. The method used is based on a DCF return on equity for varying debt/equity ratios. The basic approach is adapted from the DCF method for 100% equity financing of the Supply-Technical Advisory Task Force — Synthetic Gas Coal of the FPC. Financial factors are summarized below:

Project Life	20 years
Depreciation	16-year sum-of-the-years'-digits
Debt/Equity Ratio	0/100, 25/75, 50/50
% Return	Equity, 12% and 15% DCF; Interest, 9%
Federal Income Tax	48%
Return on Investment During Construction	Average return rate X 1.875* years X total plant investment
Plant Stream Factor	90%
Contingencies	15% of installed plant cost
Contractor's Overhead and Profit	11% of total plant cost
Start-up Cost †	20% of gross operating costs
Working Capital	Raw materials inventory (30-day feed at full rate) Material and supplies (0.9% of total plant investment) Net receivables (1/24 X annual revenue received)

* 10% for 3 years, 90% for 1.75 years.

† This cost is not depreciated but is expensed immediately before the first operating year as part of net cash flow.

The 20-year average annual revenue (REV) required is basically the sum of the following components:

- a. Net operating cost (gross operating cost less by-product credit), N
- b. Annual depreciation of plant investment, I
- c. 20-year average net income after Federal Income Tax (FIT), X
- d. Federal Income Tax, $(48/52)$, X
- e. $1/20$ of initial start-up cost, distributed over the 20-year plant life.

Once net income is known, Federal income tax is calculated as $48/52$ times net income. The sum of the 20-year equivalent average depreciation, net income, Federal income tax, and $1/20$ th of the start-up cost equals the 20-year average annual revenue required.

To calculate the components of annual revenue as presented in Table 22, the following basic equation was used:

$$\text{Revenue} = N + 20 \text{ yr-average depreciation} + X + (48/52) X + S/20 \quad (10)$$

For the calculations in this study, the return on investment during construction was capitalized and included in the depreciation schedule. Thus, depreciation is calculated as follows:

	Case			
	1	2	3	4
Debt/Equity	0/100	25/75	50/50	0/100
20-Year Average Depreciation	$\frac{1.225I}{20}$	$\frac{1.2109I}{20}$	$\frac{1.1969I}{20}$	$\frac{1.28125I}{20}$
	0.06125I	0.06055I	0.05985I	0.06406I

Substituting the values of the 20-year equivalent average depreciation in Equation 10 and solving for the net income, Equations 11 through 14 are obtained for calculating net annual income:

Case 1

(12% DCF, 100% Equity)

$$X = 0.52 (\text{REV} - N) - 0.0319I - 0.026S \quad (11)$$

Case 2

(12% DCF, 25% Debt, 75% Equity)

$$X = 0.52 (\text{REV} - N) - 0.0315I - 0.026S \quad (12)$$

Case 3

(12% DCF, 50% Debt, 50% Equity)

$$X = 0.52 (\text{REV} - N) - 0.0311I - 0.026S \quad (13)$$

Case 4

(15% DCF, 100% Equity)

$$X = 0.52 (\text{REV} - N) - 0.0333I - 0.026S \quad (14)$$

The 20-year average syncrude price (Table 22) varies from a low of \$24.85/bbl for a debt-to-equity ratio of 50/50 using a 12% DCF rate of return on equity and a 9% interest rate on debt to a high of \$35.89/bbl for 100% equity using a 15% DCF rate of return.

Based on calculations made for each year of the 20-year plant life, equations have been derived that permit the calculation of constant annual product price as a function of annual operating costs, initial investment factors, and annual production rate. Table 25 gives the equations used in calculating prices for the four different financial cases given in Table 22.

Sensitivities to Changes in Shale Cost and Plant Investment

Figure 15 shows the effect of shale cost on syncrude price. The sensitivity to a \$1/ton change in shale cost is about a \$2/bbl change in syncrude price for all financing methods.

The effect of plant cost on syncrude price is shown in Figure 16. The primary variable is the installed plant cost, excluding contingencies and other factors. This allows one to estimate the effect of changes in the cost of individual sections of the plant on the syncrude price. The sensitivity of syncrude price to a \$1 million change in installed cost, excluding contingencies and other factors, varies from 1.67¢ and 2.71¢ per barrel of syncrude depending upon the method of financing. The total capital required ranges from 1.63 to 1.81 times the installed plant cost excluding contingencies and other factors. The sensitivity of syncrude price to the change in total capital required is thus 55% to 61% of that of the sensitivity for the installed plant cost excluding contingencies and other factors. As both the percentage and return on equity increase, the effects on product price and total capital become more pronounced.

Table 25. SUMMARY OF EQUATIONS USED TO CALCULATE SYNCRUDE PRICES
USING DCF METHOD

Case 1 12% DCF Rate of Return, 100% Equity Financing

$$P = \frac{N + 0.2317I + 0.1339S + 0.2305W}{G} = \frac{\text{Revenue}}{G} \quad (15)$$

Case 2 12% DCF Rate of Return, 9% Interest Rate on Debt, 25/75
Debt/Equity Ratio

$$P = \frac{N + 0.1992I + 0.1339S + 0.2128W}{G} = \frac{\text{Revenue}}{G} \quad (16)$$

Case 3 12% DCF Rate of Return, 9% Interest Rate on Debt, 50/50
Debt to Equity Ratio

$$P = \frac{N + 0.1674I + 0.1339S + 0.1949W}{G} = \frac{\text{Revenue}}{G} \quad (17)$$

Case 4 15% DCF Rate of Return, 100% Equity Financing

$$P = \frac{N + 0.3006I + 0.1598S + 0.2885W}{G} = \frac{\text{Revenue}}{G} \quad (18)$$

where —

P = 20-year average product price, \$/bbl

N = Annual net operating costs, \$

I = Total plant investment, \$

S = Start-up cost, \$

W = Working capital, \$

G = Annual product output, bbl of Syncrude

These are derived equations arranged for the calculation of total annual revenue. They are very convenient for this purpose, but do not show the four components of capital cost (b to e above) given in Table 22.

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Figure 15. EFFECT OF SHALE COST AND FINANCING ARRANGEMENTS ON SYNCRUDE PRICE, USING 12% AND 15% DCF RATES OF RETURN ON EQUITY AND 9% INTEREST RATE ON DEBT

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Figure 16. EFFECT OF INSTALLED PLANT COST EXCLUDING CONTINGENCIES AND ALL OTHER CHARGES ON SYNCRUDE PRICE, USING 12% AND 15% DCF RATES OF RETURN ON EQUITY AND 9% INTEREST RATE ON DEBT

Moving-Bed Retort Model

The preliminary hydroretorting kinetics are used in the development of the one-dimensional model for a moving-bed retort. The program allows for ready extension in the number of chemical components, but at present the shale is assumed to consist of 6 solid species and the gas of 7 species (Table 26). The liquid and mist phases are assumed to consist of a single pseudocomponent with a single molecular weight. The gas species (CH_2) represents gaseous light hydrocarbons other than CH_4 , while (CH_M) represents the vaporized shale oil. The properties of $\text{C}_{17}\text{H}_{36}$ were chosen to characterize shale oil (CH_M) because its boiling point corresponds closely to the mass-averaged boiling point of shale oil derived from IGT tests on Eastern shale.

Figure 17 shows the scheme of preliminary kinetics. Shale is assumed to react in two steps: 1) primary devolatilization reactions and 2) secondary gas phase reactions. The primary devolatilization step consists of various reactions that form water vapor, light gaseous hydrocarbons, shale oil vapor, and char. In the secondary stage, light hydrocarbons may be hydrogenated to form methane and the carbon oxides may react with hydrogen. The rates of the reactions are based on the preliminary analysis of thermo-balance runs.

By using these kinetics, the moving-bed retort is described by 41 simultaneous nonlinear first order differential equations. The 41 variables are summarized in Table 27. The general equations were presented in the March 31, 1980 Quarterly Report for January 1 through March 31, 1980.

The boundary conditions needed for the model are inlet solid and liquid compositions and temperatures at the top of the bed, and the gas and mist compositions and temperatures at the bottom of the bed.

The system of equations forms a 41st-order two-point boundary value problem that must be solved iteratively to match the boundary conditions. The following preliminary solution procedure will be used. To begin the solution, the exit gas and mist fluxes, compositions, and temperatures are estimated; and, with the known composition and temperature for the inlet solid and liquid stream, the 41 differential equations are integrated from the top to the bottom of the reactor. The integration uses the variable-step GEAR Method, which is particularly well suited for stiff systems of equations.⁷ If the calculated inlet gas and mist

Table 26. SOLID, GAS, LIQUID, AND MIST SPECIES USED IN THE PRELIMINARY KINETIC MODEL

Solid Species Gas Species Liquid Species Mist Species

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Figure 17: PRELIMINARY SHALE HYDRORETORTING SCHEME

Table 27. SUMMARY OF THE VARIABLES

<u>No.</u>	<u>Variable</u>	<u>Description</u>
1	x	Position from top to the bottom of the bed
2	v_g	Gas phase velocity
3	v_s	Solid phase velocity
4	ϵ_g	Gas phase volume fraction
5	ϵ_l	Liquid phase volume fraction
6	ϵ_m	Mist phase volume fraction
7	ϵ_s	Solid phase volume fraction
8	ζ_g	Gas density
9	ζ_s	Solid density
10	ζ_m	Mist density
11	ζ_l	Liquid density
12	T_g	Gas phase temperature
13	T_m	Mist phase temperature
14	T_s	Solid phase temperature
15	P	System pressure
16	V_r	Relative volume of solid particles
17	D_p	Average diameter of solid particles
18	D_m	Average diameter of mist particles
19	θ_g	Gas residence time
20	θ_s	Solid residence time
21	G	Gas phase mass flux
22	F	Solid phase mass flux
23	R	Mist phase mass flux
24	S	Liquid phase mass flux

Table 27, Cont. SUMMARY OF THE VARIABLES

<u>No.</u>	<u>Variable</u>	<u>Description</u>
25	N_m	Number of mist particles
26	Y_{H_2}	Weight fraction of H_2 in gas phase
27	Y_{H_2O}	Weight fraction of H_2O in gas phase
28	Y_{CO}	Weight fraction of CO in gas phase
29	Y_{CO_2}	Weight fraction of CO_2 in gas phase
30	Y_{CH_4}	Weight fraction of CH_4 in gas phase
31	Y_{CH_2}	Weight fraction of CH_2 in gas phase
32	Y_{CH_M}	Weight fraction of CH_M in gas phase
33	Y_{Inert}	Weight fraction of inert gas in gas phase
34	X_{CH_M}	Weight fraction of CH_M in mist phase
35	Z_{CH_M}	Weight fraction of CH_M in liquid phase
36	ξ_{H_2O}	Fraction of solid H_2O converted
37	ξ_{CO_2}	Fraction of solid CO_2 converted
38	ξ_{CH_x}	Fraction of solid CH_x converted
39	ξ_{CH_M}	Fraction of solid CH_M converted
40	ξ_{CH_y}	Fraction of solid CH_y converted
41	ξ_{Ash}	Fraction of solid ash converted

fluxes, compositions, and temperatures do not match the given boundary conditions, new estimates are made, and the calculations are repeated until the bottom inlet boundary conditions are met within a reasonable tolerance. The exit gas and mist fluxes, compositions, and temperatures are adjusted by the Newton-Raphson gradient-type procedure.

A preliminary computer program for the model using this solution procedure has been developed and is being tested.

Future Work

Further process designs and economic studies for SNG from Western shale and for syncrude and SNG from Eastern shale will be prepared.

The efficiency and accuracy of the preliminary program for the model will be tested. If the rate of convergence is not adequate, alternative solution procedures will also be studied.

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APPENDIX A. Bench-Scale Unit Test Results

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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-3
Test Duration, hr	5.25
Steady-State Operating Period, hr	4.00
<u>Operating Conditions</u>	
Bed Height, ft	9.0
Reactor Pressure, psig	507
Average Bed Temperature, °F ^a	
Zone 1	911
Zone 2	914
Zone 3	952
Zone 4	925
Zone 5	947
Zone 6	1081
Zone 7	1128
Oil Shale Feed Rate, lb/hr	85.9
Oil Shale Space Velocity, lb/ft ³ -hr	107
Oil Shale Residence Time, min	39
Hydrogen Feed Gas Rate, SCF/hr	590
Hydrogen Feed Gas Superficial Velocity ft/s ^b	0.16
Hydrogen Feed Gas Residence Time, s ^c	30
Feed Gas/Oil Shale Ratio, SCF/lb shale fed	6.87
Shale Feed Hopper Hydrogen Purge Rate, SCF/hr	114

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

Run No.

80BSU-3

<u>Test Results</u>	<u>Residue Weight</u>	
	<u>By Weight</u>	<u>By Ash Balance</u>
Product Gas Rate, SCF/hr ^d	641	
Product Gas Yield, SCF/lb shale fed ^d	7.5	
Residue Shale Rate, lb/hr ^e	71.8	72.8
Residue Shale Yield, lb/lb shale fed ^{b,e}	0.836	0.847
Liquid Product Rate, lb/hr ^f	1.45	
Liquid Product Yield, lb/lb shale fed ^f	0.0168	
Water Product Rate, lb/hr	7.69	
Water Product Yield, lb/lb shale fed	0.096	
Organic Carbon Distribution in Products		
Gaseous Hydrocarbons	15.6	
Liquid Products	15.8	
Solid Residue	50.2	51.0
Total	81.6	82.4
Overall Material Balance, %	99.9	101.0
Total Carbon Balance, %	83.2	83.9
Hydrogen Balance, %	99.0	99.0
Oxygen Balance, % ^g	136	136

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

Run No.	80BSU-3
<u>Product Gas Properties</u>	
Gas Composition, mol % ^h	
Hydrogen Sulfide	0.00
Nitrogen	4.50
Carbon Monoxide	0.27
Carbon Dioxide	0.70
Hydrogen	91.29
Methane	2.09
Ethane	0.60
Propane	0.18
Butane +	0.08
Ethylene	0.06
Propylene	0.09
Butenes +	0.13
Benzene	0.01
Total	100.00
Heating Value, Btu/SCF ^{h,i}	340
Specific Gravity (Air = 1.00)	0.147

- 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 Liquid hydrocarbons 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 SCR at 60°F, 30-in. Hg pressure.

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

Run No.	80BSU-3	
Sample	<u>Feed</u>	<u>Residue</u>
Lab No.	119492	119491
Moisture, %	5.8	0.0
Ultimate Analysis (Dry Basis), wt %		
Organic Carbon	9.85	5.58
Mineral Carbon	0.17	0.0
Hydrogen	1.06	0.35
Nitrogen	0.48	0.27
Oxygen (By High-Temperature Water)	2.14	1.42
Sulfur	0.98	0.88
Ash	<u>83.22</u>	<u>92.52</u>
Total	97.90	101.02
Mineral Carbon Dioxide	0.61	0.0
Screen Analysis, U.S. Sieve, wt %		
+4	0.0	0.0
+6	0.0	0.0
+8	13.0	13.8
+16	75.8	72.9
+30	7.2	6.6
+40	0.8	1.4
+60	0.7	1.2
+80	0.2	0.5
+100	0.2	0.4
+325	0.7	1.4
Pan	<u>1.4</u>	<u>1.8</u>
Total	100.0	100.0
Gross Heating Value, Btu/lb	1779	912
Bulk Density, lb/ft ³	69.7	59.5
Helium Density, g/cc	2.40	2.57

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

Run No.	80BSU-3
Lab No.	42569
Ultimate Analysis, wt % (Dry and Solids-Free Basis)	
Carbon	87.18
Hydrogen	9.61
Sulfur	1.16
Nitrogen	2.04
Ash	0.0
C/H Weight ratio	9.07
Viscosity, SSU at 100°F	--
SSU at 210°F	--
Specific Gravity (60/60°F)	0.973
API Gravity, °API	13.9
Distillation, °F	
IBP	168
5%	220
10%	301
20%	380
30%	434
40%	510
50%	580
60%	634
70%	672
80%	724
90%	--
95%	--
End Point	760
% Recovery	88.0
% Residue	11.0
Bromine Number ^a	72.5
Free Carbon, wt %	--
Free Solids, wt %	0.14
Pour Point, °F	0
Conradson Carbon Residue, wt %	--
Heating Value, Btu/lb	17,630
Fractional Distillation, %	--
C ₅ -400°F	27.5
400°-600°F	30.2
600°-692°F	23.7
+692°F	15.6

^a For C₅-400°F fraction only.

Table A-4, 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)	-6+10 Mesh
Run No.	80BSU-5
Test Duration, hr	5.50
Steady-State Operating Period, hr	4.00
<u>Operating Conditions</u>	
Bed Height, ft	9.0
Reactor Pressure, psig	506
Average Bed Temperature, °F ^a	
Zone 1	1149
Zone 2	1162
Zone 3	1278
Zone 4	1345
Zone 5	1480
Zone 6	1484
Zone 7	1461
Oil Shale Feed Rate, lb/hr	69.3
Oil Shale Space Velocity, lb/ft ³ -hr	88
Oil Shale Residence Time, min	47.4
Hydrogen Feed Gas Rate, SCF/hr	490
Hydrogen Feed Gas Superficial Velocity, ft/s ^b	0.17
Hydrogen Feed Gas Residence Time, s ^c	28
Feed Gas/Oil Shale Ratio, SCF/lb shale fed	7.08
Shale Feed Hopper Hydrogen Purge Rate, SCF/hr	58

Table A-4, Part 2. BENCH-SCALE OPERATING CONDITIONS AND TEST RESULTS —
COUNTERCURRENT MOVING-BED OPERATION WITH NEW ALBANY SHALE

Run No.

80BSU-5

<u>Test Results</u>	<u>Residue Weight</u>	
	<u>By Weight</u>	<u>By Ash Balance</u>
Product Gas Rate, SCF/hr ^d	449	
Product Gas Yield, SCF/lb shale fed ^d	6.49	
Residue Shale Rate, lb/hr ^e	53.1	54.7
Residue Shale Yield, lb/lb shale fed ^{b,e}	0.77	0.79
Liquid Product Rate, lb/hr ^f	3.01	
Liquid Product Yield, lb/lb shale fed ^f	0.043	
Water Product Rate, lb/hr	4.47	
Water Product Yield, lb/lb shale fed	0.065	
Organic Carbon Distribution in Products		
Gaseous Hydrocarbons	44.1	44.1
Liquid Products	25.4	25.4
Solid Residue	<u>15.7</u>	<u>16.1</u>
Total	85.2	85.6
Overall Material Balance, %	97.7	99.9
Total Carbon Balance, %	85.6	86.0
Hydrogen Balance, %	100.0	100.1
Oxygen Balance, % ^g	219	219

Table A-4, Part 3. BENCH-SCALE OPERATING CONDITIONS AND TEST RESULTS —
COUNTERCURRENT MOVING-BED OPERATION WITH NEW ALBANY SHALE

Run No.	80BSU-5
<u>Product Gas Properties</u>	
Gas Composition, mol % ^h	
Hydrogen Sulfide	2.63
Nitrogen	1.41
Carbon Monoxide	1.04
Carbon Dioxide	0.46
Hydrogen	69.49
Methane	19.41
Ethane	4.72
Propane	0.49
Butane +	0.07
Ethylene	0.03
Propylene	0.11
Butenes +	0.07
Benzene	0.07
Total	100.00
Heating Value, Btu/SCF ^{h,i}	523
Specific Gravity (Air = 1.00)	0.249

- 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 Liquid hydrocarbons 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 SCR at 60°F, 30-in. Hg pressure.

Table A-5. ANALYSES OF NEW ALBANY SHALE FEED
AND RESIDUE — BENCH-SCALE TEST

Run No. Sample Lab No.	80BSU-5	
	Feed	Residue
Moisture, %	120035 0.7	120036 0.0
Ultimate Analysis (Dry Basis), wt %		
Organic Carbon	14.90	3.03
Mineral Carbon	0.21	0.02
Hydrogen	1.68	0.11
Nitrogen	0.44	0.04
Oxygen (By High-Temperature Water)	2.38	0.41
Sulfur	5.71	3.38
Ash	75.94	96.24
Total	101.26	103.23
Mineral Carbon Dioxide	0.76	0.08
Screen Analysis, U.S. Sieve, wt %		
+4	--	--
+6	2.3	0.8
+8	46.5	25.6
+16	45.9	53.1
+30	3.7	8.7
+40	0.6	2.6
+60	0.3	3.2
+80	0.1	1.7
+100	0.1	0.7
+200	0.1	1.8
+325	0.1	0.9
Pan	0.3	0.9
Total	100.0	100.0
Gross Heating Value, Btu/lb	3023	732
Bulk Density, lb/ft ³	68.4	56.9
Helium Density, g/cc	2.30	2.74

Table A-6. LIQUID PRODUCT PROPERTIES —
BENCH-SCALE TEST WITH NEW ALBANY SHALE

Run No.	80BSU-5
Lab No.	42929
Ultimate Analysis, wt % (Dry and Solids-Free Basis)	
Carbon	86.43
Hydrogen	6.69
Sulfur	1.49
Nitrogen	1.29
Ash	0.00
C/H Weight ratio	12.91
Viscosity, SSU at 100°F	7.9
Specific Gravity (60/60°F)	1.071
API Gravity, °API	0.7
Distillation, °F	
IBP	168
5%	220
10%	242
20%	292
30%	392
40%	464
50%	530
60%	620
70%	690
80%	--
90%	--
95%	--
End Point	711
% Recovery	75.5
% Residue	22.2
Bromine Number ^a	28.2
Free Carbon, wt %	0.0
Free Solids, wt %	0.1
Pour Point, °F	-55
Conradson Carbon Residue, wt %	11.0
Heating Value, Btu/lb	16,280
Fractional Distillation, %	
C ₅ -400°F	29.8
400°-600°F	27.5
600°-711°F	2.6
+711°F	39.6

^a For C₅-400°F fraction only.

APPENDIX B. Process Development Unit Test Results

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Table B-1. PDU OPERATING CONDITIONS AND TEST RESULTS —
COUNTERCURRENT OPERATION WITH CLEVELAND SHALE

Oil Shale Type	Cleveland Member		
Oil Shale Source	Ohio Shale		
Oil Shale Particle Size (U.S. Sieve)	-1/2 in. +6 Mesh		
Run No.	80PDU-1		
Test Duration, hr	8.25		
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	400	400	
Oil Shale Bed Temperature, °F ^a			
No. 1	Bed Level → 88	→ 879	
No. 2	273	966	
No. 3	274	1004	
No. 4	273	1050	
No. 5	274	1101	
No. 6	277	1146	
No. 7	333	1168	
No. 8	536	1164	
No. 9	776	1245	
No.10	795	--	
Oil Shale Feed Rate, lb/hr ^b	1021	--	
Oil Shale Space Velocity, lb/ft ³ -hr ^b	118.7	117.1	
Oil Shale Residence Time, min ^b	33.6	34.0	
Hydrogen Feed Gas Flow Rate, SCF/hr	20,135	13,005	
Nitrogen Purge Gas Flow Rate, SCF/hr	287	574	
Feed Gas Superficial Velocity, ft/s ^c	0.328	0.450	
Feed Gas Residence Time, s ^d	16.44	11.98	
Feed Gas/Oil Shale Ratio, SCF/lb shale fed ^b	19.86	13.02	
Air Flow Rate, SCF/hr	--	468	
Air/Oil Shale Ratio, SCF/lb shale fed	--	0.46	
<u>Test Results</u>			
Product Gas Rate, SCF/hr ^e	17,725	14,815	14,450 ⁱ
Product Gas Yield, SCF/lb shale fed ^e	17.36	14.51	14.15
Residue Shale Rate (From Stage 2), lb/hr			
By Direct Weight Measurement		761	
(By Ash Balance Calculation)		(862)	
Residue Shale Yield, lb/lb shale fed			
By Direct Weight Measurement		0.746	
(By Ash Balance Calculation)		(0.844)	
Liquid Hydrocarbon Product Rate, lb/hr ^f	0.7	29.3	
Liquid Hydrocarbon Product Yield, lb/lb shale fed ^f	0.001	0.029	
Water Product Rate, lb/hr	92.6	57.5	
Water Product Yield, lb/lb shale fed	0.091	0.066	
Water Product Rate From H ₂ -Air Combustion, lb/hr ^g	--	9.32	
Water Product Yield from H ₂ -Air Combustion, lb/lb shale fed ^g		0.009	
Overall Material Balance, % ^h			
Residue Shale by Weight Measurement	95.8		
(Residue Shale by Ash Balance)	(103.0)		

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Table B-1, Cont. PDU OPERATING CONDITIONS AND TEST RESULTS —
COUNTERCURRENT OPERATION WITH CLEVELAND SHALE

Run No.	80PDU-1			
	Stage 1		Stage 2	
Total Carbon Balance, %				
Residue Shale by Weight Measurement		92.4		
(Residue Shale by Ash Balance)		(96.1)		
Total Hydrogen Balance, %				
Residue Shale by Weight Measurement		104.4		
(Residue Shale by Ash Balance)		(104.5)		
Total Oxygen Balance, %				
Residue Shale by Weight Measurement		153.9		
(Residue Shale by Ash Balance)		(155.3)		
Organic Carbon Distribution in Products, %				
Gaseous Hydrocarbons	1.0		27.2	
Liquid Hydrocarbons	0.6		25.8	
Residue Shale (From Stage 2)		42.7		
By Weight Measurement		(48.3)		
(By Ash Balance)				
<u>Gas Properties</u>				
	<u>Feed</u>	<u>Product^e Stage 1</u>	<u>Product^e Stage 2</u>	<u>Product^f Stage 2</u>
Gas Composition, mol %				
Hydrogen Sulfide	--	--	--	--
Nitrogen + Argon	0.70	0.00	4.30	1.77
Carbon Monoxide	3.00	2.63	1.46	1.49
Carbon Dioxide	--	--	0.21	0.21
Hydrogen	94.40	95.08	87.75	90.08
Methane	1.90	2.12	5.61	5.76
Ethane	--	0.03	0.42	0.43
Propane	--	0.01	0.09	0.10
n-Butane	--	--	0.03	0.03
i-Butane	--	--	--	--
Pentanes	--	--	0.02	0.02
Hexanes	--	--	0.01	0.01
Ethylene	--	--	0.05	0.05
Propylene	--	0.01	0.02	0.02
Butenes	--	0.01	0.01	0.01
Petenes	--	0.01	0.02	0.02
Acetylene	--	--	--	--
Butadiene	--	--	--	--
Cyclopentadiene	--	--	--	--
Benzene	--	--	--	--
Toluene	--	--	--	--
Total	100.00	100.00	100.00	100.00
Heating Value, Btu/SCF ^j	330	335	355	364
Specific Gravity (Air = 1.00)	0.112	0.106	0.160	0.138

^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 purge-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; SCF: dry gas volume in SCF at 60°F, 30-inch-Hg pressure.

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Table B-2. ANALYSIS OF CLEVELAND SHALE FEED AND RESIDUE —
COUNTERCURRENT OPERATION

Run No.	80PDU-1	
Sample Lab No.	Feed 119731	Residue** 119857
Moisture (Dry Basis), wt %	5.0	0.0
Ultimate Analysis (Dry Basis), wt %		
Organic Carbon	10.56	5.74
Mineral Carbon	0.11	0.04
Hydrogen	1.18	0.32
Nitrogen	0.53	0.11
Oxygen (By High-Temperature Water)	3.36	1.81
Sulfur	0.95	0.48
Ash	82.16	92.47
Total	98.85	100.97
Mineral Carbon Dioxide	0.39	0.14
Screen Analysis (U.S. Sieve), wt %		
+1/2 in.	0.4	0.0
+3/8 in.	9.0	7.2
+1/4 in.	39.2	30.0
+6 mesh	42.2	46.1
+12 mesh	8.3	13.3
+20 mesh	0.0	1.3
+40 mesh	0.0	0.4
+70 mesh	0.0	0.3
+140 mesh	0.1	0.2
+200 mesh	0.0	0.1
-200 mesh	0.8	1.1
Total	100.0	100.0
Bulk Density, lb/ft ³	66.4	59.5
Helium Density, gm/cm ³ *	2.29	2.55

* A measure of the true shale particle density.

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

Table B-3. LIQUID PRODUCT PROPERTIES — PDU TEST WITH CLEVELAND SHALE,
COUNTERCURRENT OPERATION

Run No. Lab No. Sample Source	8CPDU-1							
	42833				42834			
	Stage 1 Quench Tower				Stage 2 Quench Tower			
Sample Boiling Point Range, °F	Total	C ₅ -400	400-600	600-625	Total	C ₅ -400	400-600	600-650
Fraction of Total Oil, wt %	100	4.5	53.1	13.5	100	20.6	39.1	23.6
Ultimate Analysis (Dry and Solids-Free Basis), wt %								
Carbon	83.32	83.34	84.50	85.54	85.11	84.20	84.92	85.67
Hydrogen	10.07	11.31	11.03	10.49	9.73	11.49	10.19	9.45
Sulfur	2.70	1.55	1.75	1.49	1.50	1.49	1.14	1.22
Nitrogen	0.55	1.32	0.61	0.72	1.73	1.33	1.16	1.70
Ash	0.00	0.00	0.00	0.20	0.00	0.00	0.00	0.00
C/H Weight Ratio	8.27	7.37	7.06	8.16	8.75	7.33	8.33	9.07
Viscosity, SSU at 100°F*	23.73				6.88			
Specific Gravity (60/60 °F)	0.974	0.856	0.909	0.940	0.965	0.846	0.946	0.996
API Gravity, °API	13.8	34.2	24.7	19.0	15.1	35.8	18.1	10.5
Distillation, °F*								
IBP	208				190			
5%	211				264			
10%	212				328			
20%	234				390			
30%	540				448			
40%	576				502			
50%	608				550			
60%	640				604			
70%	665				650			
80%	700				700			
90%	--				738			
95%	--				--			
End Point	702				739			
% Recovery	89.5				94			
% Residue	11				5.5			
Hydrocarbon Types, vol %*								
Saturates		25				26		
Olefins		24				25		
Aromatics		51				49		
Bromine Number								
Free Carbon, wt %*	0.11				0.07			
Free Solids, wt %*	0.21				0.01			
Pour Point, °F*	35				15			
Conradson Carbon Residue, wt. %*	3				1.1			
Heating Value, Btu/lb*	20,570				17,620			

* This Analysis not performed on all fractions.

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Table B-4. PDU OPERATING CONDITIONS AND TEST RESULTS —
COUNTERCURRENT OPERATION WITH NEW ALBANY SHALE

Oil Shale Type	New Albany	
Oil Shale Source	Kentucky	
Oil Shale Particle Size (U.S. Sieve)	-3/8 in + 6 Mesh	
Run No.	80PDU-2	
Test Duration, hr	8.00	
Steady-State Operation, hr	6.50	
<u>Operating Conditions</u>	<u>Stage 1</u>	<u>Stage 2</u>
Bed Height, ft	10.0	10.0
Reactor Pressure, psig	406	406
Oil Shale Bed Temperature, °F ^a		
No. 1	270	1010
No. 2	317	1089
No. 3	376	1113
No. 4	539	1171
No. 5	572	1289
No. 6	608	1335
No. 7	674	1355
No. 8	783	1312
No. 9	810	1342
No. 10	798	--
Oil Shale Feed Rate, lb/hr ^b	1059	--
Oil Shale Space Velocity, lb/ft ³ -hr ^b	123.1	121.4
Oil Shale Residence Time, min ^b	36.3	36.8
Hydrogen Feed Gas Flow Rate, SCF/hr	20,080	13,950
Nitrogen Purge Gas Flow Rate, SCF/hr	290	580
Feed Gas Superficial Velocity, ft/s ^c	0.454	0.534
Feed Gas Residence Time, s ^d	10.45	8.88
Feed Gas/Oil Shale Ratio, SCF/lb shale fed ^b	18.96	13.17
Air Flow Rate, SCF/hr	--	599
Air/Oil Shale Ratio, SCF/lb shale fed	--	0.57
<u>Test Results</u>		
Product Gas Rate, SCF/hr ^e	18,230	17,590 17,120 ¹
Product Gas Yield, SCF/lb shale fed ^e	17.21	14.72
Residue Shale Rate (From Stage 2), lb/hr		
By Direct Weight Measurement	--	836
(By Ash Balance Calculation)	--	(857)
Residue Shale Yield, lb/lb shale fed		
By Direct Weight Measurement	--	0.790
(By Ash Balance Calculation)		(0.809)
Liquid Hydrocarbon Product Rate, lb/hr ^f	7.77	60.18
Liquid Hydrocarbon Product Yield, lb/lb shale fed ^f	0.007	0.057
Water Product Rate, lb/hr	37.6	52.8
Water Product Yield, lb/lb shale fed	0.036	0.050
Water Product Rate From H ₂ -Air Combustion, lb/hr ^g	--	11.94
Water Product Yield From H ₂ -Air Combustion, lb/lb shale fed ^g	--	0.011
Overall Material Balance, % ^h		
Residue Shale by Weight Measurement		98.2
(Residue Shale by Ash Balance)		(99.6)

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Table B-4, Cont. PDU OPERATING CONDITIONS AND TEST RESULTS —
COUNTERCURRENT OPERATION WITH NEW ALBANY SHALE

Run No.	80PDU-2			
	Stage 1	Stage 2		
Total Carbon Balance, %				
Residue Shale by Weight Measurement		87.6		
(Residue Shale by Ash Balance)		(88.1)		
Total Hydrogen Balance, %				
Residue Shale by Weight Measurement		102.7		
(Residue Shale by Ash Balance)		(102.7)		
Total Oxygen Balance, %				
Residue Shale by Weight Measurement		117.6		
(Residue Shale by Ash Balance)		(117.8)		
Organic Carbon Distribution in Products, %				
Gaseous Hydrocarbons	3.4		20.0	
Liquid Hydrocarbons	4.4		37.5	
Residue Shale (From Stage 2)				
By Weight Measurement		24.0		
(By Ash Balance)		(24.6)		
Gas Properties	Feed	Product ^e Stage 1	Product ^e Stage 2	Product ¹
Gas Composition, mol %				
Hydrogen Sulfide	--	0.30	0.27	0.28
Nitrogen + Argon	0.70	--	3.91	1.25
Carbon Monoxide	2.50	2.13	1.46	1.33
Carbon Dioxide	0.10	0.10	0.31	0.33
Hydrogen	95.10	95.23	88.07	90.38
Methane	1.60	2.09	5.13	5.37
Ethane	--	0.04	0.52	0.53
Propane	--	0.03	0.12	0.12
n-Butane	--	0.02	0.03	0.03
i-Butane	--	0.01	0.01	0.01
Pentanes	--	0.01	0.02	0.02
Hexanes	--	--	0.01	0.01
Ethylene	--	--	0.04	0.04
Propylene	--	0.01	0.05	0.05
Butenes	--	0.02	0.03	0.03
Petenes	--	0.01	0.01	0.01
Acetylene	--	--	--	--
Butadiene	--	--	--	--
Cyclopentadiene	--	--	--	--
Benzene	--	--	0.01	0.01
Toluene	--	--	--	--
Total	100.00	100.00	100.00	100.00
Heating Value, Btu/SCF ^j	327	335	355	365
Specific Gravity (Air = 1.00)	0.108	0.085	0.137	0.136

^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 measureable; 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 purge-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; SCF: dry gas volume in SCF at 60°F, 30-inch-Hg pressure.

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Table B-5. ANALYSES OF NEW ALBANY SHALE FEED AND RESIDUE -
COUNTERCURRENT OPERATION

Run No.	80PDU-2	
Sample	<u>Feed</u>	<u>Residue**</u>
Lab No.	121005	121035
Moisture (Dry Basis), wt %	1.9	0.0
Ultimate Analysis (Dry Basis), wt %		
Organic Carbon	14.17	4.22
Mineral Carbon	0.27	0.08
Hydrogen	1.57	0.21
Nitrogen	0.54	0.18
Oxygen (By High-Temperature Water)	4.03	0.71
Sulfur	5.19	3.56
Ash	77.22	93.59
Total	102.99	102.55
Mineral Carbon Dioxide	1.00	0.29
Screen Analysis (U.S. Sieve), wt %		
+1/2 in.	0.0	0.0
+3/8 in.	1.5	3.0
+1/4 in.	18.3	8.7
+6 mesh	50.2	25.0
+12 mesh	19.6	18.0
+20 mesh	5.2	9.1
+40 mesh	1.8	7.7
+70 mesh	0.9	8.0
+140 mesh	0.7	6.3
+200 mesh	0.3	2.3
-200 mesh	1.5	11.9
Total	100.0	100.0
Bulk Density, lb/ft ³	74.5	71.1
Helium Density, gm/cm ³ *	2.27	2.72

* A measure of the true shale particle density.

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

Table B-6. LIQUID PRODUCT PROPERTIES - PDU TEST WITH NEW ALBANY SHALE, COUNTERCURRENT OPERATION

Run No.	80PDU-2						
Lab No.	43055			43056			
Sample Source	Stage 1 Quench Tower			Stage 2 Quench Tower			
Sample Boiling Point Range, °F	Total	C ₅ -400	400-580	Total	C ₅ -400	400-600	600-620
Fraction of Total Oil, wt %	100.0		50.2	100.0		26.9	18.5
Ultimate Analysis (Dry and Solids-Free Basis), wt %							
Carbon	83.98	84.80	86.04	85.52	85.64	85.50	85.55
Hydrogen	12.06	13.07	11.89	9.88	12.26	10.82	10.33
Sulfur	1.63	1.56	1.32	1.11	0.91	1.05	1.10
Nitrogen	0.73	0.57	0.50	1.00	1.19	1.45	0.41
Ash	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C/H Weight Ratio	6.97	6.49	7.23	8.66	5.98	7.90	8.28
Viscosity, SSU at 100°F*							
Specific Gravity (60/60 °F)	0.863	0.814	0.886	0.870	0.815	0.927	0.966
API Gravity, °API	32.5	42.4	28.2	14.4	47.2	21.2	15.9
Distillation, °F*							
IBP	268			182			
5%	306			282			
10%	326			340			
20%	358			426			
30%	382			456			
40%	400			580			
50%	426			650			
60%	450			682			
70%	474			706			
80%	510			720			
90%	602			--			
95%	--			--			
End Point	625			724			
% Recovery	94.5			87.0			
% Residue	6.0			12.5			
Hydrocarbon Types, vol %*							
Saturates		49			36		
Olefins		24			30		
Aromatics		27			34		
Bromine Number		44.3					
Free Carbon, wt %*	0.01			0.07			
Free Solids, wt %*	0.01			0.00			
Pour Point, °F*	-75			-15			
Conradson Carbon Residue, wt %*	0.64			1.7			
Heating Value, Btu/lb*	18,840			17,490			

* This analysis not performed on all fractions.

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