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

Project 61040 Annual Report, October 1, 1979—September 30, 1980

March 1981
Date Published

Work Performed Under Contract No. AC20-79ET14102

Institute of Gas Technology
IIT Center
Chicago, Illinois

U. S. DEPARTMENT OF ENERGY

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**Prepared by
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Chicago, Illinois 60616**

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EXECUTIVE SUMMARY

The following is a summary by task of the HYTORT process development work conducted during the last year (October 1, 1979, through September 30, 1980).

Task 1. Laboratory Program

Thermobalance tests were conducted, prior to bench-scale and PDU tests, on samples from each large multiton shale sample obtained. Several samples of New Albany shale from different locations were tested to show the variation in hydrotorting behavior with location for shales from the same rock unit. We studied the effect of shale richness on hydrotorting yield on an Ohio shale core sample. Specific kinetic expressions have been developed to describe the hydrotorting behavior of three of the shales tested thus far.

A small laboratory-scale integral reactor to determine oil shale hydrotorting product properties and distribution was designed and constructed. The unit is being installed in the laboratory space provided for it.

A DuPont Model 990 differential scanning calorimeter (DSC) was purchased and provided with a gas-feed system to allow controlled purging of the DSC cell at high pressures. The equipment and operating procedures were modified to improve accuracy in the data obtained.

Task 2. Bench-Scale Program

Nine tests on three different Eastern shales were conducted in the 4-inch bench-scale unit. During this time period, we acquired six additional multiton samples of oil shale for testing: five Eastern and one Western shale.

The 6-inch-diameter bench-scale unit was modified for tests to determine the feasibility of gasifying spent shale with steam-oxygen mixtures within moving-bed retorts. Three tests were conducted with spent shale from PDU tests. Future tests, investigating the feasibility of generating hydrogen by steam-oxygen gasification of raw shale fines in a fluidized bed, will be conducted.

Bench-scale hydrotreating tests were conducted on three shale-oil types: Kentucky Sunbury, Kentucky New Albany and Colorado (Piceance Basin). Acceptable reductions in nitrogen and sulfur content were achieved with all three oils using commercially available catalysts.

A test system for evaluating techniques to enhance fog formation under hydroretorting conditions was designed, and its construction was essentially completed. Testing of major equipment and instrumentation is under way.

A series of tests has been conducted with three Eastern shales in the solids feeding test unit at 500 psig with minus 1/2-inch-diameter material. Net water gains ranged from about 2 weight percent to 6 weight percent of the dry shale feed rate.

Task 3. Process Development Unit (PDU) Tests

Six PDU runs were made during this year with three of the Eastern shale samples obtained in multiton quantities. Satisfactory operation was achieved with each of these shales. Shale organic carbon conversions in these tests agreed with earlier thermobalance-test results.

Task 4. Process Environmental Assessment

A draft Phase 1 report has been completed by the Pace Company, which has been retained to assist IGT in the compilation and interpretation of the data base. Samples for environmental analysis have been taken during all PDU runs. A sampling train was designed and installed on the PDU. Samples of the Stage 2 raw product gases are being taken for analysis.

Task 5. Process Design and Economics

A process design and cost estimate for production of syncrude from Western oil shale has been prepared. Eastern shale test data are being analyzed so that an Eastern shale design and estimate can be prepared.

A one-dimensional mathematical model has been developed to describe moving-bed retorts. Preliminary hydroretorting kinetics have been incorporated 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 this year (October 1, 1979, through September 30, 1980) are presented in this report.

TECHNICAL PROGRESS REPORT

Task 1. Laboratory ProgramSubtask 1.1. Thermobalance TestsObjective

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

Discussion

The test program to study the effects of temperature, total pressure, hydrogen partial pressure, and heat-up rate on the rate and extent of kerogen removal is being carried out with a thermobalance. A schematic diagram of the thermobalance itself is shown in Figure 1. A flow diagram of the entire test unit is given in Figure 2.

In a run, the shale sample is contained in a stainless-steel wire-screen basket, 3/8 inch in diameter and 3 inches in height. The reactor section is brought to the desired initial temperature with a stabilized gas flow stream at 20 to 30 SCF/hr. The sample is lowered into the reactor, and the power into the heating elements is adjusted to achieve the desired temperature-rise rate. The heat-up rates can be varied over a range of values from 5° to 40° F/min. For very rapid heat-up, the sample is lowered quickly into a preheated reactor. In the last case, it is estimated that about 40 seconds are required for the sample to attain reactor temperature. After a prescribed time or upon reaching a prescribed temperature, the sample is raised into the cool region above the reactor, effectively stopping any reaction.

The sample is weighed before and after the run, and an ultimate analysis of the residue is made. During the run, the sample weight and the temperatures of four thermocouples surrounding the sample are continuously recorded. Buoyancy corrections, particularly in nitrogen-rich atmospheres, are necessary in the data analysis.

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Figure 1. SCHEMATIC DIAGRAM OF THERMOBALANCE ASSEMBLY

Figure 2. FLOW DIAGRAM FOR THERMOBALANCE UNIT

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Light hydrocarbon gases passing through the cold trap in the gas stream were measured with a Beckman hydrocarbon analyzer. During the past year, infrared CH_4 , CO , and CO_2 analyzers have been put on line upstream of the hydrocarbon analyzer. The infrared CH_4 and CO analyzers were put on line in December 1979 and have been operational in all subsequent runs with the Cleveland (Location 139) series of sink-float separated samples, the BSU material samples, and the New Albany HK-1 (Location 64) series. The infrared CO_2 analyzer was put on line in April 1980 and was operational in the final BSU material run of Utah UB-13 shale (Run S-80-19) and the New Albany HK-1 (Location 64) series.

The original shale samples were crushed and sieved; for these studies the shale used was -6 to +20 U.S. sieve size. About 11 to 15 gram samples were used in typical runs.

To determine whether carbon conversion calculations can be based on an ash balance, the ash recovery was examined. In the sixteen runs analyzed to date for the New Albany HK-1 (Location 64) runs, a small amount of ash was lost. The average amount of ash lost was 0.6% of the feed (0.75% of the feed ash), and did not depend on the gas compositions. The ash losses observed in other shales are of the order of 1% to 2%. One unusual shale, Sunbury SS-1 (Location 142) in six runs over the last 2 years in H_2 , N_2 , and H_2O atmospheres consistently showed a much greater ash loss with an average value of 4.8% of the feed (6.2% of the feed ash). The consistency of these numbers implies the loss is characteristic of the shale and not the result of random sample material losses. All calculations for thermobalance runs, therefore, have been made on the measured weight and ultimate analysis rather than assuming complete ash recovery.

Several samples of New Albany shale from different locations have now been tested in runs in hydrogen at 35 atmospheres and at heat-up rates of $20^\circ\text{F}/\text{min}$. A comparison of these runs can be used to find the range of variability of hydroretorting yield with location for various shale samples within a particular rock unit. For New Albany shales, four samples were available from Location 64, in Kentucky, obtained at different depths. An Indiana New Albany sample (NA-2b, Location 89) had been studied earlier at the same conditions, and another New Albany sample from Location 64 has

also been studied at the same conditions during the recent study of HK-1 shale. The yields reported in Table 1 are based on ultimate analysis of the feed and residue shales. Liquid yield is by difference assuming that all organic C is converted to either liquids or light hydrocarbon gases (LHC).

$$\begin{array}{ccccc} \% \text{ Conversion} & = & \% \text{ Total Organic} & - & \% \text{ Conversion} \\ \text{C} \rightarrow \text{Liq} & & \text{C Conversion} & & \text{C} \rightarrow \text{LHC} \end{array} \quad (1)$$

The assumptions were made that all mineral C formed carbon oxides, and no carbon oxides were formed from organic C during the hydroretorting process.

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

Shale Source Location No.	Run	Feed Organic C, wt %	Total Organic C Conversion, %	Liquid Yield, % of feed C
64 (4.5 ft)*	S-79-39	13.2	88.2	66.5
64 (7.5 ft)	S-79-38	11.4	87.8	61.3
64 (18.0 ft)	S-79-7	14.5	86.9	63.3
64 (22.0 ft)	S-79-37	15.5	87.9	63.5
89 (NA-2b)	S-79-22	13.7	83.0	57.6
64 (HK-1)	S-80-24	14.3	87.9	68.7

* Distance from top of rock unit.

The range of variation in total conversion for shales from the same source (Location 64) is within the experimental uncertainty. The range of variation of liquid yields is greater and is believed to be significant. The sample from a different location (Location 89) shows a yield potential about 10% lower in liquid and 5% lower in total conversion. Comparable variation was noted for Sunbury shales from different sources.¹ It has been noted in earlier studies that among differences in hydroretorting behavior in geologically different shales, the liquid yield varies more than the total yield.

To examine the effect of shale richness on hydroretorting yield, a sample of Ohio shale (Location 139) taken from a narrow section of a test coring (22 to 27 feet from the surface) was divided into several fractions by a sink-float technique. Particle density intervals of 0.05 g/cm³ from the density range of 2.00 to 2.35 g/cm³ were achieved through the use of mixtures of carbon tetrachloride and sym-tetrabromoethane.

Figure 3 shows the shale carbon content as a function of the sink-float determined density for the separated sample. This simple relationship is convenient for separation purposes. However, the samples are relatively dry (maximum 2.3% moisture), and the moisture content values approximately monotonic with the carbon content (increasing with decreasing carbon). This close correlation would be destroyed if the samples were extremely wet and had no correlation between moisture and organic carbon content.

Samples from the same coring are examined for a correlation of carbon with helium or true density in Figure 4. Here the moisture content never exceeded 3.3% and showed little correlation with the carbon content. Although more scattered than the correlation shown in Figure 3, this correlation appears significant, particularly in view of the range in depth, which includes shales from different geological periods.

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

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

<u>Feed Carbon</u> <u>wt % (dry)</u>	<u>Total</u> <u>Conversion</u> <u>———— % of Feed Carbon ————</u>	<u>Liquid</u> <u>Yield</u> <u>————</u>
18.8	74.8	57.4
16.9	78.5	58.9
15.1	72.6	53.0
11.8	68.8	49.2
10.7	67.8	49.6
8.9	70.5	44.4

There appears to be a decline in yield (on a relative basis) with decreasing organic carbon content. But the fluctuations in conversion are too great to suggest a simple relationship. Figure 5 shows the weight loss rate curves for three of the samples. One notable qualitative correlation in the behavior of all of the samples is the increase in weight loss rate near 400°F with decreasing carbon content. We have no direct evidence of the nature of the product at this temperature, but CO and light hydrocarbon gases (including CH_4) were not produced at temperatures below 500°F. This weight loss is believed to be primarily water, probably chemically bound to the mineral matter. If so, its significance lies in the energy required to remove it during retorting.

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Figure 3. CARBON CONTENT OF OHIO SHALE (Location 139, 22 to 27 Feet) AS A FUNCTION OF PARTICLE DENSITY

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Figure 4. CORRELATION OF CARBON CONTENT OF OHIO SHALE (Location 139) WITH HELIUM DENSITY

Figure 5. WEIGHT LOSS RATES FOR OHIO SHALE (Location 139, 22 to 27 Feet)
(500-psig H_2 , $20^\circ F/min$)

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

An effort has been made to fit the test results of these sink-float samples with specific kinetic expressions. During the thermobalance runs, five distinct products (excluding carbon oxides) were noted. These consisted of -

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

The thermobalance trace continuously records actual sample weight vs. temperature and is the basis for the description of the low-temperature loss and the oil formation. The CH_4 IR analyzer data accounts for the CH_4 formation. The occurrence of the different products is shown by the rate of weight loss in a typical run (Figure 6).

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 age distribution of a gas is a mathematical description of the physical effects acting on the gas between its formation and detection: for example, time delays, mixing, etc. If the age distribution of a gas is known, the formation of that gas can be described from the detected gas and the age distribution without knowing the actual physical effects on the gas. A systematic procedure has been developed to describe the age distribution, and calculations using this procedure are under way.

Much of the weight loss between 1000° and $1400^{\circ}F$ 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, as well as some water.

The total weight loss recorded by the thermobalance was used instead of the weight loss adjusted for the methane observed in developing the kinetic equations to describe oil production. This simplification was used because the CH_4 analysis method has not been fully developed and the weight of carbon going to CH_4 in this region at no time exceeded 6% of the weight loss during

Figure 6. EXAMPLE OF TYPICAL THERMOBALANCE RESULTS OF $dW/d\theta$ vs. $T(^{\circ}F)$
 [Cleveland Shale (Location 139)]

the oil-forming temperature range. This simplification, therefore, could only slightly affect the kinetic estimates.

The kinetic expressions chosen were first-order Arrhenius equations; and, assuming two independent paths, the total weight loss rate is —

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

Subscripts

- 0 = oil
- w = water

In the kinetic expressions, W_w^0 , W_{01}^0 , and W_{02}^0 represent the species weight fraction in the raw shale feed that can be lost by a given path. W_w , W_{01} , and W_{02} are the weight fractions relative to the raw feed. The kinetic parameters were determined using a non-linear least-square fit of the experimental rate data and temperatures to the kinetic expressions (Equations 3 through 6). Care was taken to correct the weight loss data for the change in buoyancy as a function of temperature and to use rate of weight loss data in Equations 3 and 6 such that there was no overlap of low-temperature and oil-formation regimes.

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^0 dependent on the total feed carbon content. This dependency must be assumed peculiar to this shale source (Table 3 and Figure 7).

Table 3. KINETICS OF LOW-TEMPERATURE WEIGHT LOSS SINK-FLOAT CLEVELAND SHALE SAMPLES (Location 139)

Run	Density, g/cm ³	Total Feed C (wet basis), wt %	ln k_w	$A_w \cdot 10^4$	W_w^0 , wt %	Std. Dev. dW/dθ, g/min
S-80-1	-2.05	18.64	11.0	10,400	1.1	0.019
S-80-2	2.05-2.1	16.76			1.1	0.012
S-80-3	2.1-2.15	14.87			1.3	0.020
S-80-4	2.15-2.2	12.84			1.6	0.016
S-80-5	2.2-2.25	11.61			1.9	0.024
S-80-6	2.25-2.3	10.54			2.4	0.028
S-80-8	2.3+	8.69			3.0	0.034

The expression for oil production, (Equations 2 through 5) was found to fit the experimental data adequately using uniform values of k and A . The values of W_{01}^0 and W_{02}^0 are presented as a function of the total feed carbon weight percent in Table 4 and Figure 8. As in Table 3, the units of k are min^{-1} .

Thermobalance runs were made on each large shale sample prior to BSU and PDU tests. Each shale was tested in 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°F at a nominal heating rate of 20°F/min and held at 1400°F for 10 minutes. Experimental conditions and test results are given in Tables 5 and 6.

Figure 7. LIMITING LOW-TEMPERATURE WEIGHT LOSS FOR CLEVELAND SHALE
(Location 139)

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Figure 8. LIMITING WEIGHT LOSSES IN OIL PEAKS FOR CLEVELAND SHALE
(Location 139)

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

Run	Density, g/cm ³	Total Feed C (wet basis), wt %	$\ln k_{01}$	$A_{01}, ^\circ R$	W_{01}^o , wt %	$\ln k_{02}$	$A_{02}, ^\circ R$	W_{02}^o , wt %	W_0^o , wt %
S-80-1	-2.05	18.64	20.73	27,150	1.0	18.78	27,060	16.6	17.6
S-80-2	2.05-2.1	16.76			1.2			13.6	14.8
S-80-3	2.1-2.15	14.87			1.5			11.2	12.7
S-80-4	2.15-2.2	12.84			1.9			9.3	11.2
S-80-5	2.2-2.25	11.61			2.4			7.7	10.1
S-80-6	2.25-2.3	10.54			3.0			6.3	9.3
S-80-8	2.3+	8.69			3.8			5.2	9.0

Table 5. FEED AND RESIDUE COMPOSITIONS

Material	Proximate Analysis		Ultimate Analysis (moisture free)					
	Moisture	High-Temperature	Ash	Total C	Organic C	Mineral C	Hydrogen	Sulfur
		H ₂ O						
				%				
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	85.85	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	93.55	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 6. 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.

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 —

$$\% \text{ Conversion }_{\text{C} \rightarrow \text{liq}} = \frac{\% \text{ Total Carbon}}{\text{Conversion}} - \frac{\% \text{ Conversion}}{\text{C} \rightarrow \text{Light Hydrocarbons}} - \frac{\% \text{ Conversion}}{\text{C} \rightarrow \text{CO} + \text{CO}_2} \quad (8)$$

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. Runs have been repeated for this shale with the analyzers on stream but their analysis is not yet complete.

A series of thermobalance runs has been made using a New Albany shale, designated HK-1, from Location 64. A comparison of the ultimate analysis of raw HK-1 shale and the average composition (ultimate analysis) of raw NA-2b shale (Location 89) tested extensively in 1979 is shown in Table 7.

Table 7. ANALYSIS OF NEW ALBANY SHALE FEEDS (DRY BASIS) HK-1 (Location 64) AND NA-2b (Location 89)

	Shale Feed	
	HK-1	NA-2b
	%	
Organic Carbon	14.42	13.80
Hydrogen	1.64	1.60
Sulfur	5.51	5.86
Nitrogen	0.36	0.50
CO_2	0.82	0.34
Oxygen (From High-Temperature H_2O)	3.0	3.2
Ash	76.3	76.9
Total	102.0	102.2

The ultimate analyses of these New Albany shales are quite similar. The rates of feed weight loss (in percent of feed/min) vs. temperature for thermobalance runs of HK-1 and NA-2b shale made under the same conditions are shown in Figure 9. The area under each curve is related to the weight loss in percent of feed weight. The difference in weight loss under the main peak of the HK-1 sample is about 0.5% of the sample, in rough agreement with the difference in organic carbon. Initially at least, the two samples appear sufficiently similar to consider together.

For the series of thermobalance runs with HK-1 shale the same LHC, CO, CO₂, and CH₄ analyzers were again used, and all instruments, including the infrared CO₂ analyzer, were operational for each run. The liquid yield was found by difference, using the total carbon conversion, the conversion of carbon to LHC and carbon oxides, and Equation 8. Feed and residue carbon (Table 8), and therefore all carbon conversions (Table 9), were based on an overall weight balance. The ash was not used as a tracer.

To date, 21 runs have been made using HK-1 (Location 64) shale. Sixteen have been analyzed. Three runs, two in nitrogen and one in hydrogen, consisted of "dropping" the sample basket into a 1500°F pre-heated thermobalance. Six runs in hydrogen and nitrogen atmospheres consisted of heating the sample from room temperature to 1400°F at 20°F/min and holding the 1400°F temperature for 10 minutes. Seven runs were made in two hydrogen/nitrogen mixtures, 66.6/33.4 (mole %) and 35.0/65.0 (mole %). Samples tested in the mixture atmospheres were heated to 1200°F at 20°F/min and then held at 1200°F for 10 minutes. By heating the samples to only 1200°F in the mixtures, it was possible to make more runs with each specific mixture, and the entire liquid-forming regime was included in the test.

For each of the three "drop" tests, there was a 20°F/min heat-up rate run in the same atmosphere and at the same pressure. Although the sample weight loss was too rapid to fit kinetic analysis, the overall carbon conversions, except $C \rightarrow CH_4$, were determined. For the 35.0 atmosphere "drop" H₂ run, S-80-28, comparison with the heat-up run S-80-24 shows that in the "drop" run 17.6% less total carbon was converted to products, 3.8% less carbon formed LHC, total conversion to carbon oxides was equal but with 0.5% more carbon forming CO and 0.4% less carbon forming CO₂, and 13.9% less feed carbon

Figure 9. RATE OF WEIGHT LOSS FOR SAMPLES S-79-22 (NA-2b) AND S-80-24 (HK-1)
HEATED AT $20^{\circ}\text{F}/\text{min}$ IN 35.0 atm H_2

Table 8. FEED AND RESIDUE COMPOSITIONS

Run No.	Proximate Analysis		Ultimate Analysis (Moisture Free)					
	Moisture	High	Ash	Total C	Organic C	Mineral C	Hydrogen	Sulfur
		Temperature H ₂ O						
				wt %				
HK-1 Feed	0.9	3.4	76.26	14.65	14.22	0.22	1.64	5.51
S-80-20 Residue	0.1	1.2	87.27	9.88	9.81	0.07	0.23	3.85
S-80-21 Residue	0.0	1.5	86.98	9.26	9.11	0.14	0.32	4.34
S-80-22 Residue	0.2	0.9	88.55	8.14	8.08	0.06	0.22	4.44
S-80-23 Residue	0.7	0.5	88.44	9.16	9.10	0.06	0.19	3.84
S-80-24 Residue	0.6	0.6	97.35	2.32	2.23	0.09	0.17	2.69
S-80-25 Residue	0.6	0.6	93.61	5.07	5.02	0.05	0.24	2.91
S-80-26 Residue	0.5	0.9	91.12	7.06	7.00	0.06	0.28	3.05
S-80-27 Residue	1.4	1.1	90.70	8.02	8.02	0.00	0.21	3.29
S-80-28 Residue	1.1	0.3	93.61	5.44	5.44	0.00	0.14	3.21
S-80-29 Residue	1.3	0.5	93.74	4.72	4.65	0.07	0.18	3.36
S-80-30 Residue	0.6	0.8	90.78	6.72	6.54	0.19	0.37	3.24
S-80-31 Residue	0.5	1.0	89.55	7.61	7.42	0.19	0.39	3.41
S-80-32 Residue	0.3	1.2	88.69	8.16	7.94	0.21	0.41	3.76
S-80-33 Residue	0.8	0.8	90.99	6.55	6.40	0.15	0.33	3.57
S-80-34 Residue	1.3	0.5	90.51	7.69	7.56	0.13	0.29	3.41
S-80-35 Residue	1.0	1.0	88.43	8.44	8.31	0.14	0.46	3.26

Table 9. CARBON CONVERSIONS FOR HK-1 SHALE
(Location 64)

Thermobalance Run No.	Nominal Heating Rate, °F/min	Total Pressure, atm	Gas	Total C Conversion	Organic C Conversion	C + LHC	C + Lig wt %	C + CH ₄	C + CO	C + CO ₂
S-80-20	20	35.0	N ₂	41.3	39.9	7.9	28.6	7.4	1.8	3.0
S-80-21	20	3.0	N ₂	44.9	44.2	4.9	37.1	7.1	1.0	1.9
S-80-23	∞*	35.0	N ₂	46.2	45.0	14.1	25.4	NA†	4.2	2.5
S-80-22	∞	3.0	N ₂	52.7	51.6	12.5	31.1	NA	5.1	4.0
S-80-24	20	35.0	H ₂	87.6	87.7	19.2	66.5	13.1	0.9	1.0
S-80-25	20	14.6	H ₂	72.0	71.4	13.0	60.9	7.0	0.6	0.5
S-80-26	20	7.8	H ₂	59.9	59.0	3.3	49.3	6.3	0.8	0.5
S-80-27	20	4.4	H ₂	54.5	53.1	3.5	44.7	4.5	0.8	0.5
S-80-28	∞	35.0	H ₂	70.0	69.1	13.4	52.6	NA	1.4	0.6
S-80-29	20	35.0	2/3 H ₂ - 1/3 N ₂	73.8	73.4	16.6	55.8	9.4	0.6	0.8
S-80-30	20	21.7	2/3 H ₂ - 1/3 N ₂	61.9	61.8	14.4	46.2	11.1	0.6	0.7
S-80-31	20	11.5	2/3 H ₂ - 1/3 N ₂	56.0	55.8	12.4	42.4	9.7	0.5	0.7
S-80-32	20	6.4	2/3 H ₂ - 1/3 N ₂	52.5	52.4	11.4	39.6	8.1	0.6	0.9
S-80-33	20	35.0	1/3 H ₂ - 2/3 N ₂	62.9	62.7	13.5	48.2	9.5	0.6	0.6
S-80-34	20	23.4	1/3 H ₂ - 2/3 N ₂	56.3	56.0	11.7	43.4	7.7	0.5	0.7
S-80-35	20	13.2	1/3 H ₂ - 2/3 N ₂	51.0	50.2	10.1	39.4	8.8	0.7	0.8

* ∞ means the sample basket was dropped into a pre-heated 1500°F furnace.

† NA means not available.

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was converted to liquid. Both N_2 -atmosphere "drop" runs showed a greater total carbon conversion than their heat-up counterparts, a result in qualitative agreement with other studies. In the N_2 "drop" runs greater LHC and carbon oxides conversions were noticed, and in both cases the conversion of feed carbon to liquid was at least 3% less. By using a controlled heating rate, the liquid yield was enhanced in both hydrogen and nitrogen atmospheres, but this may be the result of the greater chance of secondary reaction to lighter materials in the drop runs. In the heat-up runs, in an atmosphere of H_2 , the conversion of C to CO and CO_2 did not vary greatly with pressure, (1.1% to 1.9%) but the largest conversion to both CO and CO_2 was shown at the greatest pressure. In nitrogen atmospheres the total conversion of carbon to carbon oxides appeared to increase with pressure, from 2.9% to 4.8%, and was significantly greater than in runs in hydrogen. Since in the runs in H_2/N_2 mixtures the shale samples were heated to only 1200°F, a direct comparison cannot be made with the runs in H_2 and N_2 , but the yield of carbon oxides did not vary with pressure or mixture (1.2% to 1.5%).

The total carbon conversion based on the weight of the feed and residue shale and analytic carbon determinations has been found to be a function of both the type of gas and total pressure (Figure 10). In a nitrogen atmosphere the total conversion decreased slightly with increasing pressure. In hydrogen-containing atmospheres the total carbon conversion increased with total pressure. The difference in maximum temperatures does not affect the qualitative characteristics. At constant pressure the total conversion increases with H_2 partial pressure. At the highest pressures, the total carbon conversion appears to approach a limiting value.

The yield of liquid shows the same pattern as the total carbon conversion (Figure 11). Since all liquid was produced before 1200°F, the liquid yield given by Equation 8 is independent of whether the sample is heated to 1200°F or 1400°F and the results can be considered on the same basis for all four gas systems. In a nitrogen atmosphere, the conversion of carbon to liquid decreases with increasing pressure, while in hydrogen-containing atmospheres the liquid yield increases with increasing pressure but it is not simply related to the partial pressure of hydrogen. At the higher hydrogen pressure the liquid yield appears to approach a limiting value. Future tests will include

Figure 10. TOTAL CARBON CONVERSION FOR NEW ALBANY HK-1 (Location 64) SHALE

Figure 11. LIQUID YIELD FOR NEW ALBANY HK-1 (Location 64) SHALE

runs in H_2/N_2 mixtures with between 67% and 100% H_2 in order to find the necessary H_2 content to produce the enhanced liquid yield shown by the runs made in pure hydrogen.

The yield of LHC (light hydrocarbon gases) has also been shown as a function of total pressure (Figure 12). Notice that the LHC yield in the H_2/N_2 mixtures was lower than would be observed if the samples had been raised to $1400^\circ F$. From the qualitative CH_4 data available, a mechanism yielding CH_4 at temperatures above $1200^\circ F$ can be clearly seen. Quantitative values have not yet been determined for this high-temperature CH_4 -forming reaction. A similar high-temperature CH_4 -producing path was present in the Cleveland shales (Figure 6).

In both H_2/N_2 mixtures (and possibly pure N_2) the LHC yield is linear with total pressure between 10 and 35 atmospheres and increases with hydrogen partial pressure at any given total pressure. In H_2 the conversion of carbon to LHC is nonlinear at the higher pressure. By virtue of the method of analysis, the light hydrocarbon yield is strongly related to the liquid yield.

A first-order Arrhenius equation was used to describe the product in the main weight loss region for the HK-1 shale. The simplification, made earlier in fitting the results in the Cleveland sink-float series, of using the recorded weight loss (instead of the weight loss corrected for observed methane) was again adopted. The data for the HK-1 shale series and the NA-2b shale series (made in 1979) were found to be well-described by a single oil-producing path. This simplification of Equation 3 is expressed as -

$$\frac{dW_o}{d\theta} = -W_o^o k_o \exp(-A_o/T) \quad (9)$$

$$W_o = \frac{W_o^o}{\exp \left[\frac{k_o T^2}{\alpha(A_o + 2T)} \exp(-A_o/T) \right]} \quad (10)$$

Figure 12. LHC YIELD FOR NEW ALBANY HK-1 (Location 64) SHALE

Solving for the best fit of Equation 9 to the experimental rate values, the value of A_0 was found to be essentially constant and independent of total pressure, H_2 partial pressure, or even type of New Albany shale (NA-2b or HK-1). Table 10 gives the oil-production kinetic determination results for 27 thermobalance runs using various heating rates, different pressures, varying H_2/N_2 feed gas ratios, and NA-2b (Location 89) and HK-1 shale (Location 64). Values listed for each run are k_0 (min^{-1}), A_0 ($^{\circ}\text{R}$), W_0° (weight percent), σ (standard deviation of the experimental and calculated values of $dW/d\theta$), and W_c (feed weight percent lost at temperatures below those of the oil-producing weight loss peak). As the rate of weight loss was used to obtain the kinetic parameters, the average difference between the recorded weight losses and the values of W_0 given by Equation 10 was used to find W_c . Examples of the fit of these kinetic parameters are given in Figures 13 and 14.

For the series of NA-2b shale runs in pure hydrogen, the value of k_0 was found to be relatively independent of pressure at heat-up rates of $5^{\circ}\text{F}/\text{min}$ and $10^{\circ}\text{F}/\text{min}$ but greater for the $10^{\circ}\text{F}/\text{min}$ heating rate. At a heating rate of $35^{\circ}\text{F}/\text{min}$, the rate constant still increases but appears to be pressure dependent.

Much greater change in the rate constant was observed in the HK-1 series. At low pressure (5 atm), the rates appear similar. At higher pressures, the systems leaner in hydrogen exhibit greater rate enhancement; in all cases the rate increases with total pressure. While the rate change (a factor of 5) is large in the heat-up procedure, the difference is compensated by a 120°F temperature difference. That is, at the lowest reaction rate the conversion is 99% at 1060°F while at the highest rate that level is reached at 940°F . See Figure 15. For the HK-1 series the temperatures at which the main weight-loss rate was a maximum decreased in all gases with increasing pressure (Table 11).

The calculated values of W_0° for the HK-1 series proved to be a linear function of total pressure and independent of the hydrogen partial pressure except at 0 atmospheres H_2 pressure (Figure 16). A similar analysis of the NA-2b samples indicates an interaction effect of the heat-up rate and total pressure with respect to the value of W_0° . This relationship is being further studied for the HK-1 shale in the current series of thermobalance runs at different heat-up rates in H_2 and N_2 mixtures.

Table 10. KINETIC ESTIMATES FOR OIL PRODUCTION IN NEW ALBANY SHALES
(HK-1 and NA-2b)

Run	atm	Heat-up Rate, °F/min	Pressure, atm (abs)	$k_0 \times 10^{-7}$, min	A_0 , °R	W_0 , wt %	σ dW/d θ , % feed/min	W_c , wt %
NA-2b								
S-79-33	H ₂	5	35.0	2.89	25,450	14.7	0.030	2.8
S-79-24		5	35.0	2.95		14.2	0.037	3.5
S-79-34		5	14.6	2.12		12.4	0.027	3.4
S-79-35		5	7.8	3.43		10.7	0.029	1.8
S-79-36		5	4.4	2.75		8.8	0.016	1.7
S-79-21		10	35.0	3.46		13.8	0.057	2.8
S-79-27		10	14.6	3.43		12.2	0.020	1.9
S-79-28		10	7.8	3.50		10.4	0.023	2.0
S-79-32		10	4.4	3.86		8.4	0.018	1.7
S-79-22		20	35.0	4.72		13.0	0.058	2.6
S-79-20		35	35.0	5.82		12.2	0.043	2.7
S-79-23		35	14.6	3.79		11.2	0.140	1.5
S-79-25		35	7.8	3.86		9.5	0.070	1.7
S-79-26		35	4.4	3.33		9.1	0.087	1.4
HK-1								
S-80-20	N ₂	20	35.0	10.51	25,450	8.5	0.038	0.7
S-80-21	N ₂		3.0	2.02		8.0	0.060	0.9
S-80-24	H ₂		35.0	5.60		13.5	0.088	1.1
S-80-25	H ₂		14.6	2.78		11.4	0.077	0.7
S-80-26	H ₂		7.8	2.72		10.5	0.058	0.2
S-80-27	H ₂		4.4	2.54		9.7	0.112	0.7
S-80-29	H ₂ /N ₂ (67/33)		35.0	6.97		14.1	0.126	0.2
S-80-30			21.7	4.96		12.3	0.088	0.6
S-80-31			11.5	3.57		10.4	0.103	1.0
S-80-32			6.4	2.46		10.2	0.098	0.7
S-80-33	H ₂ /N ₂ (35/65)		35.0	9.04		13.1	0.118	0.5
S-80-34			23.4	7.04		12.6	0.073	1.5
S-80-35			13.2	5.22		10.7	0.090	0.3

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Figure 13. EXPERIMENTAL AND CALCULATED OIL PRODUCTION RATE DATA FOR NEW ALBANY (NA-2b) RUN S-79-25

Figure 14. EXPERIMENTAL AND CALCULATED OIL PRODUCTION RATE DATA FOR NEW ALBANY (HK-1) RUN S-80-27

Figure 15. OIL PRODUCTION RATE CONSTANT FOR NEW ALBANY HK-1 (Location 64)

Figure 16. TOTAL PRESSURE DEPENDENCE AT W_O FOR NEW ALBANY HK-1 (Location 64)

Table 11. EXPERIMENTAL MAXIMUM WEIGHT LOSS RATE TEMPERATURES FOR
NEW ALBANY (HK-1) SHALE (Location 64)

Run	Maximum Weight Loss Rate, T (°F)	$k_0 \times 10^{-7}$	Conversion C $\rightarrow$ Liq, %
S-80-20	812	10.51	28.6
S-80-21	930	2.02	37.1
S-80-24	862	5.06	66.5
S-80-25	901	2.78	60.9
S-80-26	917	2.72	49.3
S-80-27	922	2.54	44.7
S-80-27	832	6.97	55.8
S-80-30	870	4.98	46.2
S-80-31	898	3.57	42.4
S-80-32	912	2.46	39.6
S-80-33	820	9.04	48.2
S-80-34	847	7.04	43.4
S-80-35	864	5.22	39.4

As was reported in 1979, the value of W_0^0 was found to be linear with liquid yield and independent of heat-up rate in the NA-2b pure hydrogen series. Figure 17 presents this calculation based on the most recent kinetics. Extrapolation of the best-fit line to zero liquid yield results in a positive value of W_0^0 , which shows that liquid is not the only material contributing to the main weight loss peak. For the HK-1 series W_0^0 was also found to be related to the conversion of carbon to liquid (Figure 18) but involves a dependence on gas composition (Figure 16). The interaction effect of heat-up rate and gas composition is still being studied. The values of W_0^0 found in the current analysis of the NA-2b and HK-1 shales indicate that the relationships of W_0^0 to liquid yield for the two shales in H_2 are parallel, but differ by a constant 2.0% of the feed weight corresponding to the greater conversion of carbon to LHC shown by the NA-2b compared with the HK-1 shale.

Future Work

The kinetics of CH_4 formation and carbon oxides production for the HK-1 shale will be studied with the use of the age distribution function. The runs of HK-1 shale made at various heating rates in H_2 and N_2 will be

Figure 17. RELATION OF CALCULATED WEIGHT LOSS IN THE MAIN PEAK TO LIQUID CONVERSION OF NEW ALBANY NA-2b (Location 89) IN PURE HYDROGEN

Figure 18. RELATION OF CALCULATED MAIN PEAK WEIGHT LOSS TO LIQUID YIELD
NEW ALBANY HK-1 (Location 64) IN HYDROGEN

analyzed and used to extend the kinetic description of the shale reactivity. Larger single particle samples of shale from the same source as HK-1 are being gathered to allow estimation of the effect of particle size on the kinetics and product distributions.

Subtask 1.2. Laboratory-Scale Reactor Tests

Objective

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

Discussion

A small test unit having a shale feeding capacity of a few hundred grams per hour has been designed and all major equipment and instrumentation have now been received (See Figures 19 and 20). An existing laboratory space was provided with the necessary utilities and lighting for the unit. The equipment is now being installed in this laboratory.

Future Work

Installation and assembly of the test unit will be completed. Tests will be conducted on selected samples of Eastern and Western shales.

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 DuPont Model 990 differential scanning calorimeter (DSC) was chosen for these studies. Upon receipt of the instrument in the middle of the second quarter of this program, a gas feed system to allow controlled purging of the DSC cell at high pressures was designed, 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

Figure 19. LABORATORY-SCALE REACTOR UNIT

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Figure 20. INSTRUMENT PANEL FOR LABORATORY-SCALE REACTOR

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.

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 whereupon too much of the heat input was lost to the surroundings to allow programmed heat-up. Attempts to reduce the heat loss by extensive insulation made some improvement. Power supply modification to assure the maximum allowed by the manufacturer brought the upper operation limit to 600°C in 500 psig hydrogen.

If the gas is diluted with nitrogen, the upper limit of operation is extended beyond the material limitation. Thus in atmospheres of $2/3 \text{ H}_2 - 1/3 \text{ N}_2$, operation at 500 psig offers no difficulties although pure hydrogen at the same partial pressure is almost as bad as H_2 at 500 psig. At present, with the limit of 600°C, studies of various shales are being made even in 500 psig H_2 .

In the preliminary tests to establish the required operating conditions, it was demonstrated that careful purging of the cell is necessary since extremely small amounts of air can be very significant. Also the external shell temperature must be within 2° or 3°C of the sample temperature at the start of the run.

The results obtained so far can be considered only as preliminary. While qualitative characteristics such as occurrence of reaction or phase change endo- or exotherms appear reproducible, the quantitative aspects are not. Whether this is the result of the instrument, the operation, or the sample variation has not yet been established.

Future Work

The precision of the determinations will be established. The thermal characteristics of the shales previously studied in a survey of Eastern oil shales will be determined.

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 diameter, electrically heated reactor, sufficient oil shale is processed that complete material and elemental (carbon, hydrogen, and oxygen) balances can be performed, and sufficient oil is produced that its many properties may be determined and it can be used for further testing.

Discussion

Experimental Procedure

A flow diagram of the bench-scale unit (BSU) is shown in Figure 21. The unit essentially consists of a hydrogasification reactor with associated equipment for feeding and measuring the flow rates of shale and hydrogen and for collecting and/or measuring the flow rates of residue shale, liquid product, and product gas. Simple controls are used to maintain reactor temperatures at the desired values, to maintain feed rates at constant values, to maintain constant reactor pressures, and to collect representative samples of the feed and product gases.

Shale is fed by a screw feeder from a pressurized hopper that, before testing, is filled with sufficient shale for the entire run. The cold shale enters the top of the reactor and is preheated by countercurrent contact with the hot product gas. The residue shale is discharged from the bottom of the reactor into a pressurized residue receiver by a second screw feeder. The residue shale is cooled by countercurrent contact with cold feed hydrogen.

The feed gas enters the bottom of the reactor above the discharge screw through a dip tube. (See Figure 22). The exit gas leaves through a dip tube extending down into the top of the reactor. This latter dip tube contains a sintered metal bayonet filter that is positioned at the bottom of heating zone 2. The feed shale drops down through a third, large diameter, dip tube, which serves to keep heavy liquids in the exit gas from condensing on the feed shale at the feed screw outlet and plugging the reactor tube. The

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Figure 21. FLOW AND INSTRUMENTATION DIAGRAM FOR HIGH-TEMPERATURE, BALANCED-PRESSURE PILOT UNIT

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Figure 22. SOLIDS DISCHARGE SYSTEM DETAILS

pressures in both hoppers and in the reactor are maintained essentially equal by connecting them directly with small-diameter tubing. A small purge flow of feed gas is continuously passed into the top of the reactor during tests to make up for the volume of shale lost from the feed hopper as shale is fed and to keep exit gas containing liquid products from entering the feed hopper. The purge gas rate is typically about 10% of the feed gas rate.

The reactor (Figure 23) consists of a cold pressure shell, 24 inches in ID and about 23 feet in length, containing an internal reactor tube (Incoloy 800, 4 inches ips, Schedule 40), which is heated by a seven-zoned Kanthal electric heater. Each heater is 31 inches long and has an ID of about 7 inches. The temperature of each zone is controlled individually by a multipoint controller. The space between the reactor outer wall and the electric heater is packed with refractory-fiber-type insulation. The pressure outside the tube is controlled by a pressure-balancing system to keep the pressures inside and outside the heated reactor tube nearly equal (to keep it from rupturing when hot). This system either bleeds nitrogen into or out of the insulated space, as required, to equalize these pressures. The reactor pressure and bed pressure drop are recorded continuously as are all the reactor-tube temperatures. A total of 32 thermocouples are attached to the outer tube wall along with six internal thermocouples. The internal thermocouples are enclosed in a 3/8-inch OD thermowell and measure temperatures in the bed below the heated zones. Refractory fiber insulation is wrapped around the reactor so that the thermocouples do not "see" the heaters, thus eliminating thermocouple radiation errors. These temperatures are recorded continuously along with temperatures on other major pieces of equipment.

The flow rates of the hydrogen feed gas and the purge gas are both metered by orifice meters and recorded continuously. These meters are calibrated against the exit gas meter before each test. Both screw feeders are calibrated. The shale is fed at the desired rate by setting the shale feed screw speed of rotation at the desired value. The rate of shale discharge then is set manually as required to give a constant shale-bed level. The shale-bed level is indicated by a nuclear-type level indicator and is continuously recorded. The bed level can be controlled to within a few inches. The full-scale range of the indicator corresponds to a bed-level variation of about 3 inches. The differential pressure across the reactor bed is measured using a d-p cell and is recorded continuously. This also provides a check

Figure 23. HIGH-TEMPERATURE, BALANCED-PRESSURE REACTOR DETAILS

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on the bed height. The weight of shale fed is measured accurately for the entire run by weighing the shale initially charged to the feed hopper and that present at the end of the run. The residue shale is weighed after the run. Feed and residue shale rates are calculated by dividing these weights by the measured shale feeding time.

The exit gas volume is measured by a conventional iron-case-type direct-reading meter. An "aliquot" sample of the exit gas is taken by feeding a portion of it at a constant rate into a 10-ft³ water-sealed holder during the steady-state portion of each run. "Spot" samples are also taken throughout each steady-state test period. The exit-gas specific gravity is monitored continuously by a recording gravitometer. An internal, 1 1/2-foot-long, sintered stainless-steel bayonet-filter was installed prior to these tests to prevent solids elutriation. The filter has a mean pore size of 165 microns. Even though the exit gas is filtered, some fine dust is carried out of the reactor. Although the exit gas usually is quite hot, some heavy condensed liquids, as well as some fine dust, may be carried with the gas from the reactor. The exit gas is cooled in a single-stage condenser. The condensed liquids are then collected in a knockout pot. The pot is drained, and the liquid weighed at approximately 20-minute intervals during the steady-state portion of each run to obtain product rates. We define steady-state as a condition wherein the temperature profile in the shale bed is uniform; feed gas, purge gas, and exit gas flow rates are constant; reactor pressure is stable; and the shale feed rate and bed height are essentially constant. Approximately 1 to 2 cc of an anti-oxidant (N, N' Di-secondary butyl para phenylenediamine) is added to the liquids before they are sealed in cans prior to analysis.

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

The feed and residue shale as well as the fine silica sand used in these tests were weighed on a large trip beam scale with an arm balance. The scale has 0.1 pound as the smallest division. Liquid products from the runs are weighed on a small trip beam balance scale having 0.01 pound as the smallest division.

The product gases are analyzed by IGT's mass spectrometer and the liquids by ASTM standard methods. The feed and residue shales are analyzed by methods described in Appendix B of IGT Research Bulletin No. 36.²

Test Results

A total of 9 tests on three different shale types has been performed during the past year in the bench-scale unit. Modifications of the BSU to improve operability and reliability were also finished during this period. The completion of three runs, 80BSU-11 (Kentucky Sunbury shale run), 80BSU-12 (Kentucky New Albany shale run), and 80BSU-13 (Cleveland shale run), during the last quarter of this year, concludes our scheduled BSU tests on these three Eastern shales under both oil- and gas-producing conditions. The results of Runs 80BSU-12 and 80BSU-13 will be reported in the next quarterly report when analytical data become available. The results of the other tests are presented in this report.

A series of runs was made in the BSU under oil-producing conditions for three Eastern shales — Kentucky New Albany (79BSU-2), Kentucky Sunbury (80BSU-11), and a Cleveland member of the Ohio shale (80BSU-2 and 80BSU-3). Summaries of the test results and operating conditions for these four runs are presented in Tables 12 through 15. All four runs were made at shale feed rates of approximately 80 lb/hr, reactor pressures of 500 psig, and shale bed heights of 9.0 feet. The Kentucky New Albany and the Kentucky Sunbury shale runs converted 71.0% and 72.5%, respectively, of the organic carbon in the feed shale to gaseous and liquid products (based on a carbon balance by ash analysis). The two Cleveland shale runs, 80BSU-2 and 80BSU-3, converted 56.1% and 49.0%, respectively, of the organic carbon in the feed shale to gaseous and liquid products. The lower conversion achieved with the Cleveland shale (Run 80BSU-3) may be a result of the lower maximum bed temperature. Based on the results of our oil-producing runs to date in the BSU, it appears that the Cleveland shale tested is substantially less reactive than either the Sunbury or the New Albany shales tested. The Cleveland shale has a high moisture content in comparison with that of the Sunbury or New Albany shales. The Cleveland shale not only has at least double the surface moisture of the Sunbury or New Albany shales tested, but it also contains significantly more high-temperature water (based on total water yields).

Table 12. BENCH-SCALE (79BSU-2) TEST RESULTS — COUNTERCURRENT MOVING BED OPERATION WITH NEW ALBANY SHALE

Operating Conditions and Test Results

Oil Shale Location (State)	64 (Kentucky)
Oil Shale Particle Size (U.S. Sieve)	-20+40
Test Duration, hr	4.50
Steady-State Operating Period, hr	2.00
Bed Height, ft	9.0
Pressure, psig	527
Average Bed Temperature, °F	1197
Maximum Bed Temperature, °F	1259
Oil Shale Feed Rate, lb/hr	79.0
Oil Shale Space Velocity, lb/ft ³ -hr	99
Oil Shale Mass Rate, lb/ft ² -hr	898
Feed Gas*/Shale Ratio, SCF/lb	17.80
Feed Gas* Superficial Velocity, ft/s	0.40
Product Gas Yield, SCF/lb Shale Fed [†]	15.03
Residue Shale Yield, lb/lb Shale Fed	
By Direct Weight Measurement	0.741
By Ash Balance Calculation**	0.806
Liquid Hydrocarbon Yield, lb/lb Shale Fed	0.0606
Water Yield, lb/lb Shale Fed	0.0850
Material Balance, % ^{††}	101.1
Organic Carbon Distribution in Products, %	
Gaseous Hydrocarbons	23.7
Liquid Hydrocarbons	40.4
Residue Shale ^{††}	29.1

Feed and Product Compositions

Oil Shale			Shale Oil	
Sample	Feed	Residue	Lab No.	42222
Lab No.	42258	42259	C/H Weight Ratio	10.71
Moisture, Wt %	1.5	0.10	Sulfur, Wt %	2.17
Ultimate Analysis, Wt % (Dry Basis)			Nitrogen, Wt %	2.21
			Viscosity, SSU at 100°F	66.4
			Specific Gravity, (60/60°F)	1.036
			Distillation, °F	
			IBP	172
			50%	556
			EP	690
			Pour Point, °F	-60
Organic Carbon	13.06	4.68		
Mineral Carbon	1.05	0.48		
Hydrogen	1.51	0.28		
Nitrogen	0.46	0.16		
Oxygen (by difference)	4.45	0.00		
Sulfur	4.94	3.21		
Ash	74.53	91.98		
Total	100.00	100.79		

Gas Composition, Mol %	Feed	Product
Hydrogen Sulfide		0.04
Nitrogen		1.58
Carbon Monoxide		1.14
Carbon Dioxide		0.32
Hydrogen	100.00	93.51
Methane		2.16
Ethane +		0.96
Ethylene +		0.27
Benzene		0.02
Total	100.00	100.00

* Hydrogen.

** Number reported in the second quarterly report was by weight measurement.

† Purge free.

†† By ash balance.

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Table 13. BENCH-SCALE (80BSU-2) TEST RESULTS — COUNTERCURRENT
MOVING BED OPERATION WITH CLEVELAND SHALE

Operating Conditions and Test Results

Oil Shale Location (State)	139 (Kentucky)
Oil Shale Particle Size (U.S. Sieve)	-10+30
Test Duration, hr	2.75
Steady-State Operating Period, hr	1.50
Bed Height, ft	9.0
Pressure, psig	498
Average Bed Temperature, °F	1077
Maximum Bed Temperature, °F	1266
Oil Shale Feed Rate, lb/hr	76.0
Oil Shale Space Velocity, lb/ft ³ -hr	95
Oil Shale Mass Rate, lb/ft ² -hr	860
Feed Gas*/Shale Ratio, SCF/lb	7.36
Feed Gas* Superficial Velocity, ft/s	0.17
Product Gas Yield, SCF/lb Shale Fed†	0.18
Residue Shale Yield, lb/lb Shale Fed	
By Direct Weight Measurement	0.601
By Ash Balance Calculation**	0.850
Liquid Hydrocarbon Yield, lb/lb Shale Fed	0.0421
Water Yield, lb/lb Shale Fed	0.1690
Material Balance, % ††	110.5
Organic Carbon Distribution in Products, %	
Gaseous Hydrocarbons	19.8
Liquid Hydrocarbons	37.4
Residue Shale ††	43.9

Feed and Product Compositions

Oil Shale			Shale Oil	
Sample	Feed	Residue	Lab No.	
Lab No.	119473	119474	C/H Weight Ratio	9.56
Moisture, Wt %	3.1	0.0	Sulfur, Wt %	1.42
Ultimate Analysis, Wt %			Nitrogen, Wt %	2.08
(Dry Basis)			Viscosity, SSU at 100°F	44.8
Organic Carbon	10.08	5.05	Specific Gravity, (60/60°F)	0.985
Mineral Carbon	0.00	0.00	Distillation, °F	
Hydrogen	1.15	0.23	IBP	163
Nitrogen	0.47	0.14	50%	511
Oxygen (by difference)	4.81	0.00	EP	117
Sulfur	0.91	0.74	Pour Point, °F	-45
Ash	82.58	94.16		
Total	100.00	100.32		

Gas Composition, Mol %	Feed	Product
Hydrogen Sulfide		2.00
Nitrogen		0.37
Carbon Monoxide		0.70
Carbon Dioxide	100.00	92.44
Hydrogen		2.93
Methane		1.23
Ethane +		0.32
Ethylene +		0.01
Benzene		
Total	100.00	100.00

* Hydrogen.

** Number reported in the second quarterly report was by weight measurement.

† Purge free.

†† By ash balance.

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Table 14. BENCH-SCALE (80BSU-3) TEST RESULTS — COUNTERCURRENT MOVING BED OPERATION WITH CLEVELAND SHALE

Operating Conditions and Test Results

Oil Shale Location (State)	139 (Kentucky)
Oil Shale Particle Size (U.S. Sieve)	-10+30
Test Duration, hr	5.25
Steady-State Operating Period, hr	4.00
Bed Height, ft	9.0
Pressure, psig	507
Average Bed Temperature, °F	1020
Maximum Bed Temperature, °F	1158
Oil Shale Feed Rate, lb/hr	85.9
Oil Shale Space Velocity, lb/ft ³ -hr	107
Oil Shale Mass Rate, lb/ft ² -hr	972
Feed Gas*/Shale Ratio, SCF/lb	6.90
Feed Gas* Superficial Velocity, ft/s	0.16
Product Gas Yield, SCF/lb Shale Fed†	7.46
Residue Shale Yield, lb/lb Shale Fed	
By Direct Weight Measurement	0.836
By Ash Balance Calculation	0.847
Liquid Hydrocarbon Yield, lb/lb Shale Fed	0.0168
Water Yield, lb/lb Shale Fed	0.0896
Material Balance, %††	101.0
Organic Carbon Distribution in Products, %	
Gaseous Hydrocarbons	15.6
Liquid Hydrocarbons	15.8
Residue Shale††	51.0

Feed and Product Compositions

Oil Shale			Shale Oil	
Sample	Feed	Residue	Lab No.	42569
Lab No.	119492	119491	C/H Weight Ratio	9.07
Moisture, Wt %	5.8	0.0	Sulfur, Wt %	1.16
Ultimate Analysis, Wt % (Dry Basis)			Nitrogen, Wt %	2.04
			Viscosity, SSU at 100°F	6.19
Organic Carbon	9.85	5.58	Specific Gravity, (60/60°F)	0.973
Mineral Carbon	0.17	0.00	Distillation, °F	
Hydrogen	1.06	0.35		
Nitrogen	0.48	0.27	IBP	168
Oxygen (by HTW)	2.14	1.42	50%	580
Sulfur	0.98	0.88	EP	760
Ash	83.22	92.52	Pour Point, °F	0
Total	97.90	101.02		

Gas Composition, Mol %	Feed	Product
Hydrogen Sulfide		4.50
Nitrogen		0.27
Carbon Monoxide		0.70
Carbon Dioxide		91.29
Hydrogen	100.00	2.09
Methane		0.86
Ethane +		0.28
Ethylene +		0.01
Benzene		
Total	100.00	100.00

* Hydrogen

† Purge free

†† By ash balance

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Table 15. BENCH-SCALE (80BSU-11) TEST RESULTS — COUNTERCURRENT
MOVING BED OPERATION WITH SUNBURY SHALE

Operating Conditions and Test Results

Oil Shale Location (State)	142 (Kentucky)
Oil Shale Particle Size (U.S. Sieve)	-6+30
Test Duration, hr	4.50
Steady-State Operating Period, hr	3.50

Bed Height, ft	9.0
Pressure, psig	498
Average Bed Temperature, °F	1204
Maximum Bed Temperature, °F	1319
Oil Shale Feed Rate, lb/hr	86.0
Oil Shale Space Velocity, lb/ft ³ -hr	108
Oil Shale Mass Rate, lb/ft ² hr	970
Feed Gas [*] /Shale Ratio, DGF/lb	4.77
Feed Gas [*] Superficial Velocity, ft/s	0.12
Product Gas Yield, SCF/lb Shale Fed [†]	3.83
Residue Shale Yield, lb/lb Shale Fed	
By Direct Weight Measurement	0.791
By Ash Balance Calculation	0.811
Liquid Hydrocarbon Yield, lb/lb Shale Fed	0.0755
Water Yield, lb/lb Shale Fed	0.0518
Material Balance, % ^{††}	98.3
Organic Carbon Distribution in Products, %	
Gaseous Hydrocarbons	24.1
Liquid Hydrocarbons	49.6
Residue Shale ^{††}	27.4

Feed and Product Compositions

Oil Shale			Shale Oil	
Sample	Feed	Residue	Lab No.	43549
Lab No.	123527	123529	C/H Weight Ratio	10.02
Moisture, Wt %	1.4	0.0	Sulfur, Wt %	1.89
			Nitrogen, Wt %	2.18
Ultimate Analysis, Wt %			Viscosity, SSU at 100°F	43.9
(Dry Basis)			Specific Gravity, (60/60°F)	0.996
Organic Carbon	13.40	4.52	Distillation, °F	
Mineral Carbon	0.82	0.31	IBP	142
Hydrogen	1.61	0.33	50%	550
Nitrogen	0.42	0.24	EP	730
Oxygen (by HTW)	3.41	0.94	Pour Point, °F	-80
Sulfur	3.02	3.10		
Ash	75.17	92.17		
Total	97.85	101.61		

Gas Composition, Mol %	Feed	Product
Hydrogen Sulfide		3.18
Nitrogen	0.70	1.26
Carbon Monoxide		2.02
Carbon Dioxide		1.12
Hydrogen	99.30	76.81
Methane		9.34
Ethane +		4.67
Ethylene +		1.57
Benzene		0.03
Total	100.00	100.00

* Hydrogen

† Purge free

†† By ash balance

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We attempted to obtain a linear temperature profile in the reactor bed in these "oil-producing" runs by adjusting the temperature controllers for each electric heater. Since heat is supplied electrically for the BSU runs, heat effects due to phase changes and chemical reactions may be masked. The reactor bed-temperature profiles are important because they provide a time-temperature history of the shale as it is hydroretorted. The reactor bed-temperature profiles for Runs 79BSU-2, 80BSU-2, 80BSU-3, and 80BSU-11 are shown in Figures 24, 25, 26, and 27, respectively. The reactor bed temperature profile for Sunbury shale - Run 80BSU-11, Figure 27 - probably best exemplifies the linear temperature profile we hoped to achieve for all of the oil-producing runs. It should be pointed out that the feed shale drops through 3-1/2 heated zones before reaching the top of the bed; the shale is heated rapidly from ambient temperature to approximately 900° to 1000°F. Heat is transferred to the shale rapidly because the shale particle sizes used are relatively small (-6+20 mesh).

The pour points of the oils produced in this series of runs ranged from 0° to -80°F. The product oils can therefore be easily transferred (pumped) for further treatment and upgrading. Oil C/H weight ratios ranged from 8.8 to 12.9. The nitrogen levels of all the shale oils (New Albany, Sunbury, and Cleveland) produced from this series of BSU tests were nearly the same: 2.1% by weight. The sulfur present in the Cleveland shale oils was nearly 1% by weight lower than that for the New Albany or Sunbury oils. The lower sulfur level in the Cleveland product oil is probably due to the lower sulfur present in the Cleveland feed shale (approximately 1% by weight) compared with the sulfur in the Kentucky New Albany (5% by weight) or the Kentucky Sunbury (3% by weight) feed shales.

A second series of runs was made under gas-producing conditions using shales obtained from the same locations as for the oil-producing runs. Summaries of the test results and operating conditions for the three Eastern shale runs - 80BSU-5 (Kentucky New Albany), 80BSU-8 (Cleveland member of the Ohio), and 80BSU-10 (Kentucky Sunbury) - are shown in Tables 16, 17, and 18, respectively. These runs were all made at shale feed rates of approximately 75 lb/hr, reactor pressures of 500 psig, and shale bed heights of 9.0 feet.

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Figure 24. REACTOR BED-TEMPERATURE PROFILE FOR NEW ALBANY SHALE — RUN 79BSU-2

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Figure 25. REACTOR BED-TEMPERATURE PROFILE FOR CLEVELAND SHALE — RUN 80BSU-2

B80123201

Figure 26. REACTOR BED-TEMPERATURE PROFILE FOR CLEVELAND SHALE — RUN 80BSU-3

B80082301

Figure 27. REACTOR BED-TEMPERATURE PROFILE FOR SUNBURY SHALE — RUN 80BSU-11

Table 16. BENCH-SCALE (80BSU-5) TEST RESULTS — COUNTERCURRENT
MOVING BED OPERATION WITH NEW ALBANY SHALE

Operating Conditions and Test Results

Oil Shale Location (State)	64 (Kentucky)
Oil Shale Particle Size (U.S. Sieve)	-6+10
Test Duration, hr	5.50
Steady-State Operating Period, hr	4.00
Bed Height, ft	9.0
Pressure, psig	506
Average Bed Temperature, °F	1443
Maximum Bed Temperature, °F	1517
Oil Shale Feed Rate, lb/hr	69.3
Oil Shale Space Velocity, lb/ft ³ -hr	88
Oil Shale Mass Rate, lb/ft ² -hr	1089
Feed Gas*/Shale Ratio, SCF/lb	7.08
Feed Gas* Superficial Velocity, ft/s	0.17
Product Gas Yield, SCF/lb Shale Fed*	6.49
Residue Shale Yield, lb/lb Shale Fed	
By Direct Weight Measurement	0.767
By Ash Balance Calculation	0.789
Liquid Hydrocarbon Yield, lb/lb Shale Fed	0.0434
Water Yield, lb/lb Shale Fed	0.0649
Material Balance, % ^{††}	99.9
Organic Carbon Distribution in Products, %	
Gaseous Hydrocarbons	44.1
Liquid Hydrocarbons	25.4
Residue Shale ^{††}	16.0

Feed and Product Compositions

Oil Shale			Shale Oil	
Sample	Feed	Residue	Lab No.	42929
Lab No.	120035	120036	C/H Weight Ratio	12.9
Moisture, Wt %	0.7	0.0	Sulfur, Wt %	1.49
			Nitrogen, Wt %	1.29
Ultimate Analysis, Wt %			Viscosity, SSU at 100°F	51.8
(Dry Basis)			Specific Gravity, (60/60°F)	1.071
Organic Carbon	14.90	3.03	Distillation, °F	
Mineral Carbon	0.21	0.02	IBP	168
Hydrogen	1.68	0.11	50%	530
Nitrogen	0.44	0.04	EP	711
Oxygen (by HTW)	2.38	0.41	Four Point, °F	-55
Sulfur	5.71	3.38		
Ash	75.94	96.24		
Total	101.26	103.29		

Gas Composition, Mol %	Feed	Product
Hydrogen Sulfide		2.63
Nitrogen		1.41
Carbon Monoxide		1.04
Carbon Dioxide		0.46
Hydrogen	100.00	69.49
Methane		19.41
Ethane +		5.28
Ethylene +		0.21
Benzene		0.07
Total	100.00	100.00

* Hydrogen

† Purge free.

†† By ash balance.

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Table 17. BENCH-SCALE (80BSU-8) TEST RESULTS — COUNTERCURRENT
MOVING BED OPERATION WITH CLEVELAND SHALE

Operating Conditions and Test Results

Oil Shale Location (State)	139 (Kentucky)
Oil Shale Particle Size (U.S. Sieve)	-6+30
Test Duration, hr	5.00
Steady-State Operating Period, hr	4.00
Bed Height, ft	9.0
Pressure, psig	475
Average Bed Temperature, °F	1261
Maximum Bed Temperature, °F	1416
Oil Shale Feed Rate, lb/hr	80.4
Oil Shale Space Velocity, lb/ft ³ -hr	101
Oil Shale Mass Rate, lb/ft ² -hr	910
Feed Gas ⁺ /Shale Ratio, SCF/lb	6.10
Feed Gas ⁺ Superficial Velocity, ft/s	0.11
Product Gas Yield, SCF/lb Shale Fed ⁺	5.24
Residue Shale Yield, lb/lb Shale Fed	
By Direct Weight Measurement	0.796
By Ash Balance Calculation	0.862
Liquid Hydrocarbon Yield, lb/lb Shale Fed	0.0438
Water Yield, lb/lb Shale Fed	0.1300
Material Balance, % ⁺⁺	107.5
Organic Carbon Distribution in Products, %	
Gaseous Hydrocarbons	27.5
Liquid Hydrocarbons	39.7
Residue Shale ⁺⁺	33.2

Feed and Product Compositions

Oil Shale			Shale Oil	
Sample	Feed	Residue	Lab No.	43253
Lab No.	122068	122070	C/H Weight Ratio	8.81
Moisture, Wt %	6.9	0.0	Sulfur, Wt %	1.30
			Nitrogen, Wt %	1.07
Ultimate Analysis, Wt %			Viscosity, SSU at 100°F	39.7
(Dry Basis)			Specific Gravity, (60/60°F)	0.950
Organic Carbon	10.17	3.92	Distillation, °F	
Mineral Carbon	0.09	0.01	IBP	176
Hydrogen	1.14	0.17	50%	506
Nitrogen	0.38	0.12	EP	730
Oxygen (by HTW)	2.93	0.54	Pour Point, °F	-25
Sulfur	0.94	0.57		
Ash	82.63	95.81		
Total	98.28	101.15		

Gas Composition, Mol %	Feed	Product
Hydrogen Sulfide		0.05
Nitrogen		5.20
Carbon Monoxide		0.42
Carbon Dioxide		0.89
Hydrogen	100.00	81.18
Methane		9.94
Ethane +		1.99
Ethylene +		0.29
Benzene		0.04
Total	100.00	100.00

* Hydrogen

† Purge free

++ By ash balance

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Table 18. BENCH-SCALE (80BSU-10) TEST RESULTS — COUNTERCURRENT
MOVING BED OPERATION WITH SUNBURY SHALE

Operating Conditions and Test Results

Oil Shale Location (State)	142 (Kentucky)
Oil Shale Particle Size (U.S. Sieve)	-6+10
Test Duration, hr	5.17
Steady-State Operating Period, hr	3.67

Bed Height, ft	9.0
Pressure, psig	464
Average Bed Temperature, °F	1304
Maximum Bed Temperature, °F	1457
Oil Shale Feed Rate, lb/hr	74.5
Oil Shale Space Velocity, lb/ft ³ -hr	93
Oil Shale Mass Rate, lb/ft ² -hr	843
Feed Gas [*] /Shale Ratio, SCF/lb	6.56
Feed Gas [*] Superficial Velocity, ft/s	0.17
Product Gas Yield, SCF/lb Shale Fed [†]	6.22
Residue Shale Yield, lb/lb Shale Fed	
By Direct Weight Measurement	0.764
By Ash Balance Calculation	0.790
Liquid Hydrocarbon Yield, lb/lb Shale Fed	0.0829
Water Yield, lb/lb Shale Fed	0.1000
Material Balance, % ^{††}	102.9
Organic Carbon Distribution in Products, %	
Gaseous Hydrocarbons	21.0
Liquid Hydrocarbons	47.5
Residue Shale ^{††}	24.8

Feed and Product Compositions

Oil Shale			Shale Oil	
Sample	Feed	Residue	Lab No.	43424
Lab No.	123048	123049	C/H Weight Ratio	8.97
Moisture, Wt %	3.7	0.4	Sulfur, Wt %	1.34
			Nitrogen, Wt %	2.06
Ultimate Analysis, Wt %			Viscosity, SSU at 100°F	49.8
(Dry Basis)			Specific Gravity, (60/60°F)	0.967
Organic Carbon	15.04	4.56	Distillation, °F	
Mineral Carbon	0.05	0.08	IBP	164
Hydrogen	1.71	0.19	50%	538
Nitrogen	0.55	0.15	EP	699
Oxygen (by HTW)	3.76	0.48	Pour Point, °F	-80
Sulfur	2.70	1.72		
Ash	77.26	94.52		
Total	101.07	101.70		

Gas Composition, Mol %	Feed	Product
Hydrogen Sulfide		0.93
Nitrogen		5.21
Carbon Monoxide		0.45
Carbon Dioxide		0.24
Hydrogen	100.00	82.61
Methane		7.59
Ethane +		2.33
Ethylene +		0.62
Benzene		0.02
Total	100.00	100.00

* Hydrogen
† Purge free
†† By ash balance

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The organic carbon conversion for the Kentucky New Albany shale run (80BSU-5) was 84.0% while the conversions (based on a carbon balance by ash analysis) for the Kentucky Sunbury and Cleveland shales were 75.2% and 66.8%, respectively. However, the Kentucky New Albany shale was hydroretorted at a higher maximum temperature and at a higher hydrogen partial pressure than either the Kentucky Sunbury or the Cleveland shales, which may account for some of the differences in the organic carbon conversions achieved with these shales.

The main difference between the test conditions for the oil-producing runs and the gas-producing runs are the temperature gradients set for each run. In the oil-producing runs a linear temperature profile was imposed while for the gas-producing runs an isothermal profile was set. The temperature profiles for the New Albany gas run (80BSU-5), the Cleveland gas run (80BSU-8), and the Sunbury gas run (80BSU-10) are shown in Figures 28, 29, and 30, respectively. The temperature gradient for the Kentucky New Albany shale run, Figure 28, was more nearly isothermal compared with that for either the Cleveland shale run or the Sunbury shale run. The relatively uniform bed-temperature profile in the New Albany run helped to convert more of the organic carbon to gases (44.1%) than to liquids. Methane and ethane comprised nearly 25 mole percent of the product gas. In the Sunbury and Cleveland runs, methane and ethane comprised only 12 mole percent and 10 mole percent, respectively, of the product gases.

A comparison of some thermobalance runs and bench-scale tests of the same batches of shales is shown in Table 19. There is excellent agreement between the thermobalance runs and the corresponding bench-scale gas runs with the same shale. There is only 2.0% to 3.7% difference in the organic carbon conversions in the BSU versus the corresponding thermobalance tests. The BSU oil runs do not correlate with the thermobalance runs as well as the BSU gas runs do. The difference is probably primarily due to the lower maximum temperatures at which the BSU oil runs were made. In future oil runs, we will still maintain a linear temperature gradient, but we will subject the shale to the same maximum temperature in the oil runs that we use in the gas runs to show whether we can increase the organic carbon conversion without a loss in the oil yield.

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Figure 28. REACTOR BED-TEMPERATURE PROFILE FOR NEW ALBANY SHALE — RUN 80BSU-5

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Figure 29. REACTOR BED-TEMPERATURE PROFILE FOR CLEVELAND SHALE — RUN 80BSU-8

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Figure 30. REACTOR BED-TEMPERATURE PROFILE FOR SUNBURY SHALE — RUN 80BSU-10

Table 19. COMPARISON OF ORGANIC CARBON CONVERSIONS IN THERMOBALANCE AND BENCH-SCALE TESTS

Shale Type	Thermobalance Tests*		Bench Scale Unit Tests							
			Oil Runs				Gas Runs			
	Run Number	Organic Carbon Conversion, %	Run Number	Organic Carbon** Conversion, %	Maximum Temperature, °F	Hydrogen Partial Pressure, psig	Run Number	Organic Carbon** Conversion, %	Maximum Temperature, °F	Hydrogen Partial Pressure, psig
New Albany (Loc. 64)	S-80-24	87.7	79-BSU-2	70.9	1259	489	80-BSU-5	84.0	1517	401
Cleveland (Loc. 139)	S-80-9	68.8	80-BSU-2	56.1	1300	413	80-BSU-8	66.8	1380	367
			80-BSU-3	49.0	1158	443				
Sunbury (Loc. 142)	79-29	78.5	80-BSU-11	72.5	1319	398	80-BSU-10	75.2	1457	319

* Hydrogen partial pressure is approximately 500 psig for all runs at a maximum temperature of 1400°F.

** Ash balance is used to calculate residue shale yield.

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Future Work

Bench-scale tests will be performed on additional Eastern and Western shale samples after thermobalance tests are completed on them.

Subtask 2.2. Hydrogen Production Studies

Objective

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

Discussion

Equipment Description

The equipment used for the oil shale gasification tests, except for minor modifications, is the same as that used earlier in the study of steam-oxygen gasification of bituminous coal chars. These modifications were made to allow simulation of the bottom portion of a moving-bed HYTORT reactor with oxygen and steam injection to gasify residual organic carbon.

A simplified flow diagram of the experimental equipment is shown in Figure 31. Heated nitrogen is fed to the bottom of the reactor to preheat the reactor tube and the bed of oil shale. Unheated oxygen is premixed with superheated steam before being fed to the bottom of the reactor gasification zone. Natural gas and hydrogen are metered separately and premixed, without preheat, before being fed through a separate feed-gas nozzle to the bottom of the reactor heat-transfer zone.

The exit-gas system is designed so that hot gases from the gasifier are cooled quickly (in 1 to 2 seconds) from 1600° to 1000°F to minimize the extent of the carbon monoxide shift and other reactions, which could alter the exit gas composition. A water-jacketed gas cooler is used for indirect cooling of the gases. The gas cooler consists of a 10-foot-long, 1-1/2-inch-diameter, Schedule 160 Type 316 stainless steel pipe. It is jacketed with a 3-inch-diameter Schedule 40 carbon steel pipe and constructed

Figure 31. FLOW DIAGRAM FOR OIL SHALE GASIFICATION TEST UNIT

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so that hot reactor-product gas directly enters the cooler. Gas from the cooler is filtered in a 6-inch-diameter, 6-foot-long filter vessel in which oil shale fines are removed as the gas passes through a sintered-metal bayonet filter. This vessel is operated at 1000°F to avoid condensation until the gas enters the condenser; then, the gas is further cooled to 150°F. Condensate water and liquid hydrocarbons are removed by a float-actuated valve at the bottom of the condenser. This valve discharges all the water and oil from the condenser at 500 psig operating pressure to a collecting tank at atmospheric pressure, where it is weighed periodically during the course of the run. Gas from the condenser passes through a mist filter before entering the exit-gas metering system.

Conventional apparatus and instrumentation are used to control and measure the inlet- and exit-gas flows. The oil shale feed rate to the reactor is maintained at a steady rate by controlling the speed of a screw feeder at the bottom of the unheated, pressurized feed hopper. The feed hopper has an internal volume of 22 ft³ (approximately 1500 lb of oil shale). The bed height of the moving bed of oil shale is controlled by manually adjusting the speed of another screw feeder, which delivers the oil shale residue to a pressurized residue shale receiver (5.4 ft³ capacity). The shale bed height is measured by a radiation-type bed-level gauge and is continuously recorded.

Typical procedures for each test (after the feed hopper is charged with 600 to 800 lb of oil shale) begin with the pressurization of the system with nitrogen to the operating pressure and the preheat of the empty reactor tube with hot nitrogen. Oil shale feed is then started and the reactor is filled to the 6-foot level. The discharge of oil shale residue is started after the bed level is reached. When the oil shale is preheated to the highest level possible (550° to 600°F) with the hot nitrogen, oxygen flow is initiated to raise the bed temperature by combustion of the oil shale carbon. Hydrogen and natural gas feeds are started shortly after the oxygen flow is started. Steam feed is initiated when the reactor bed temperature reaches 1200°F, and the hot nitrogen flow is reduced to a low rate. All gas feed rates are then adjusted to the desired values as the

reactor bed temperature is brought up to the desired gasification level (typically 1600° to 1800°F). The oxygen flow rate is adjusted to maintain the desired temperature while all other gas feed rates, the oil shale feed, and the discharge rates are held constant during the steady-state portion of the test. This condition is maintained for several hours during which time product gas samples are taken at specified times. Sampling of the solids from the reactor, the receiver, and the bayonet filter is done after shutdown, when the system is depressurized.

A cross-sectional view of the reactor used in the test program is shown in Figure 32. A balanced-pressure reactor design is employed so that the reactor tube-wall thickness can be minimized. The space between the outer 24-inch-OD carbon steel shell and the 6-inch Schedule 10 Type 316 stainless-steel reactor tube is filled with insulation and purged with nitrogen. The purge nitrogen helps avoid differential pressure being developed across the reactor wall, as well as steam condensation in the insulation. The reactor tube diameter is 18 inches at the top to reduce the carryover of fines. Sixteen sheathed chromel/alumel 1/16-inch-diameter thermocouples are installed for sensing the tube-wall temperatures. The thermocouples are housed in three longitudinal thermowells that are tack-welded to the outside of the reactor tube. Each thermowell has a 5/16-inch OD and a 20-ga. wall, and is made of Type 304 stainless-steel tubing, capped at the top. The positions of the tube-wall thermocouples along the tube wall and the orientation of the three thermowells around the outside of the tube are shown in Figure 33. Six thermocouples are installed through the top reactor closure to sense oil shale bed temperatures at 13, 25, 41, 58, 73, and 78 inches above the bottom of the reactor tube. This spacing provides for one thermocouple in the 2-foot-high heat transfer zone, one thermocouple at the heat transfer-gasification zone interface, three thermocouples within the gasification zone, and one thermocouple in the reactor freeboard. Also shown in Figure 33 are the relative positions of the bed level radiation gauges and the steam-oxygen and methane-hydrogen feed nozzles. Both feed-gas nozzles are capped at the end and have 12 ports in the upper 1-1/2 inches. The ports are 9/64-inch diameter and are oriented 90 degrees apart at three levels, 1/2 inch apart.

Figure 32. CROSS-SECTIONAL VIEW OF THE 6-INCH-DIAMETER STEAM-OXYGEN GASIFICATION REACTOR

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Figure 33. 6-INCH REACTOR TUBE THERMOCOUPLE, FEED NOZZLE, AND BED LEVEL RADIATION GAUGE LOCATION

Test Results

Three steam-oxygen gasification tests were performed in the 6-inch reactor to study hydrogen production from spent oil shale. Conditions for these tests are based on a process concept in which the organic carbon remaining in spent oil shale is gasified with oxygen and steam to produce additional hydrogen. The spent shale would then be contacted with recycle gas to extract heat from the residual oil shale before removal from the reactor. A 4-foot-high gasification zone was used, with a 2-foot-high heat-transfer zone immediately below. Spent oil shale from PDU tests is fed to the top of the reactor and moves downward as a moving-bed plug flow through the two zones before discharge into the receiver. Steam and oxygen are fed to the bottom of the gasification zone, while 2 feet below this level natural gas and hydrogen (simulating recycle gas) are fed to the bottom of the heat transfer zone.

Feed rates and conditions for these initial tests were selected to be a pressure of 500 psig and a gasification zone temperature of 1600°F. Oil shale feed was set to provide for a residence time of 15 to 20 minutes in the gasification zone, and a flow rate of approximately 900 lb/hr-ft² of reactor cross-sectional area. Steam and oxygen feed ratios are 0.28 lb and 0.52 SCF per pound of oil shale, respectively. The recycle gas (consisting of equal volumes of natural gas and hydrogen) ratio was 5.88 SCF/lb of oil shale. Spent Cleveland oil shale from the PDU Run 80PD-1 was used in the first three tests. This shale was screened to a -6+80 mesh size range.

Preliminary test results for the first test, Run OS-1, are given in Table 20 along with data for Runs OS-2 and OS-3.

Complete operating conditions and results of the above three runs will be presented when analytical results of the oil shale feed, residual oil shale, and oil shale bayonet filter fines are completed.

Table 20. PRELIMINARY TEST CONDITIONS AND PARTIAL RESULTS OF OIL SHALE
GASIFICATION TESTS IN 6-INCH REACTOR
(Spent Cleveland Oil Shale, -6+80 Mesh)

Run No.	OS-1	OS-2	OS-3	
Duration of Test, hr	6 3/4	3 1/4	5	
Operating Conditions				
Reactor Pressure, psia	467	484	485	
Gasification Zone Temperature, °F				
Internal				
Maximum	1675	1540	1760	
Average Maximum	1195	1245	1285	
Tube Wall				
Maximum	1450	1120	1265	
Average Maximum	1095	1065	1050	
Heat Transfer Zone Temperature, °F				
Internal				
Maximum	1060	750	940	
Average Maximum	745	635	570	
Tube Wall				
Maximum	1145	1120	955	
Average Maximum	785	940	550	
Oil Shale Feed Rate lb/hr	119	94	89	
Gasification Zone Feed Gases				
Nitrogen, SCF/hr	680	702	472	
Oxygen, SCF/hr	128	154	122	
Steam, lb/hr	56	52	57	
Heat-Transfer Zone Feed Gases				
Hydrogen, SCF/hr	416	616	629	
Natural Gas, SCF/hr	284	211	337	
Oxygen Concentration in Feed Gas, mole %	6.4	7.9	6.8	
Superficial Feed Gas Velocity, ft/s				
Gasification Zone	0.30	0.30	0.30	
Heat-Transfer Zone	0.048	0.052	0.045	
Operating Results				
Product Gas Rate (Purge-Nitrogen Free), SCF/hr	1591	1616	1650	
	<u>Feed *</u>	<u>Product</u>	<u>Product</u>	<u>Product</u>
Gas Properties (Natural Gas Feed and Product Gas)				
Gas Composition (Product-Gas Purge-Nitrogen Free), mole %				
Nitrogen	3.8	43.5	43.9	29.4
Carbon Monoxide	0.0	0.0	1.4	1.1
Carbon Dioxide	0.57	4.7	3.2	2.1
Oxygen	0.0	0.0	0.0	0.0
Hydrogen	0.0	36.0	40.6	45.4
Argon	0.0	0.01	0.0	0.01
Helium	0.05	0.0	0.0	0.01
Methane	92.4	15.3	10.6	21.3
Ethane	2.3	0.35	0.27	0.59
Propane	0.53	0.08	0.04	0.07
n-Butane	0.10	0.0	0.0	0.02
Isobutane	0.08	0.0	0.0	0.0
Pentane	0.07	0.0	0.0	0.0
Hexane	0.05	0.0	0.0	0.0
Heptane	0.02	0.0	0.0	0.0
Ethylene	0.0	0.05	0.01	0.0
Total	99.97	99.99	100.02	100.0
Heating Value, Btu/SCF	987	276	246	374
Specific Gravity, (Air = 1.00)	0.598	0.610	0.580	0.486

* Same in Runs OS-2 and OS-3.

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Run OS-1 was generally successful in that oil shale feeding was sustained over a period of 6-3/4 hours until the residue receiver was filled, at which time the run was shut down. However, oil shale feeding and discharging rates were not as uniform as in earlier atmospheric pressure feed tests. Both the feed and the discharge screws required frequent rpm adjustments as both screws tended to stall at the set rotation rates. The result was a varying oil shale feed rate that averaged about 119 lb/hr during the data-taking portion of the test. Natural gas feeding was also irregular.

Although temperatures of 1500° to 1675°F were reached at times, the average maximum temperature in the gasification zone was only 1195°F. Eight product gas samples taken over a 2-1/2 hour period of the test showed no oxygen breakthrough. Although not evident during the test, a small ash sinter was found in the reactor after shutdown. The sinter was comparatively small (total weight 1 pound) and was not attached to the reactor walls. The level at which it formed above the oxygen feed nozzle is undetermined, as it was found at the lower end of the reactor tube, having fallen there from an upper region.

Spent oil shale feed for Run OS-2 was the same as used in Run OS-1. Conditions for this test were similar to those of Run OS-1. The objective of the run was to perform a test with more stable conditions than were obtained in Run OS-1, specifically, the oil shale feed and discharge rates, the natural gas feed rate, and the gasification zone temperature profile. The test lasted 3-1/4 hours and was terminated before steady-state operation was reached when oil shale solids plugged the outlet of the feed inlet tube to the reactor. Preliminary operating conditions, flows and partial results of this test are summarized in Table 20. As in Run OS-1, the temperature profile through the gasification zone was irregular, even with the more uniform gas feed rates. The maximum temperature attained in the bed was 1540°F, but the average maximum temperature was only 1245°F. Product gas samples showed no oxygen breakthrough. After shutdown, an ash sinter was found in the reactor. It formed about 11 inches above the oxygen-steam feed nozzle in the center of the reactor, and extended over about 50% of the reactor cross-section.

Run OS-3 was also performed with the same spent oil shale as used in Runs OS-1 and OS-2, under conditions similar to those of the first two tests. The test lasted 5 hours during which time oil shale was fed for a period of 3-1/2 hours. An early termination of the test was made when oil shale could not be discharged from the reactor. The basic cause for the solids holdup has not been established. Solids flow through the reactor was not a problem in Runs OS-1 and OS-2. Although an ash sinter was found in the reactor after shutdown, indications are that it formed after the downward flow of the solids stopped, and was, therefore, not responsible for the holdup.

As in the two earlier tests, the temperature profile through the gasification zone was generally irregular during Run OS-3. The maximum temperature attained was 1760°F, while the average maximum temperature was 1285°F. Ash sintering was more extensive in Run OS-3 than in Runs OS-1 and OS-2, probably because of oil shale holdup in the reactor. The ash sinter formation was found at levels of 17 and 23 inches above the oxygen-steam feed nozzle, was 3 to 4 inches thick, and extended over about 75% of the reactor cross-section. Although some portions of the sinter formation extended to the reactor walls, no ash sinter was attached to the walls.

Future Work

In future tests we will try to obtain more uniform and stable temperature profiles in the gasification zone. To do this we will install a modified oxygen-steam feed gas nozzle to improve the feed gas distribution at the entry to the gasification zone. The nozzle will have smaller diameter feed ports (1/32-inch diameter) to increase the inlet gas velocity and obtain a broader lateral gas distribution. The ports will also be extended over a longer length of nozzle for more extended vertical gas distribution. The improved gas distribution should minimize gas channeling through the solids bed, which may be partially responsible for the irregular temperature profiles in the three tests made.

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, 500 to 1000 ppm nitrogen will be the level normally used as a target value.

Discussion

Experimental Procedure

A flow diagram of the bench-scale catalytic hydrotreating unit is shown in Figure 34. The unit essentially consists of a hydrotreating reactor with associated equipment for feeding and measuring the flow rates of raw shale oil and hydrogen and for collecting and/or measuring the flow rates of liquid and gas products.

The hydrogen feed rate is measured by an orifice meter and is recorded continuously. The flow rate is controlled by use of a pneumatic controller and a diaphragm-operated valve. The hydrogen then flows through a preheat coil where it mixes with the preheated shale oil before entering the reactor.

To calibrate the hydrogen feed rate, the entire unit is brought up to operating pressure and the hydrogen flow control system activated. The hydrogen feed rate is measured by the reactor product gas exit meter. Calibrations are made without oil feed both before and after each test run.

Raw shale oil is charged into a feed drum that is placed on a triple-beam balance. The shale oil feed rate is determined by weight difference measured per unit time. The shale oil is fed to a preheat coil by a variable-stroke, positive-displacement pump.

The reactor is a 2-inch, Schedule XX pipe, 108 inches long. The furnace surrounding the reactor consists of four 24-inch heating zones with an ID of 6 inches. The catalyst bed is located within the bottom heating zone and is 14 inches long with a volume of 1000 cc. The bed temperatures are measured by thermocouples located 6 inches above the bed, 4 inches into the bed and 7 inches into the bed inside a thermowell.

Figure 34. BENCH-SCALE CATALYTIC HYDROTREATING UNIT

The initial bed temperatures are maintained below the operating temperature by controllers before the oil is introduced to the reactor. As the exothermic reaction completes heating the catalyst bed, the desired operating temperature is reached and maintained for the steady-state run period.

The oil exits the reactor and passes through a concentric-pipe, water-cooled heat exchanger before collecting in a 4-gallon sample bomb. The entire sample is then submitted for analysis.

The product gas exits through a diaphragm-loaded backpressure regulator and is metered by a dry test meter before venting. During intervals in the steady-state run period, a sample bomb is inserted in the vent line and the gas is collected for analysis by mass spectrometer.

Test Results

During the year, hydrotreating screening runs were conducted with New Albany, Sunbury, and Colorado shale oils. A Shell 324 nickel/moly catalyst (1/16-inch diameter extrusions) was used for all the hydrotreating tests to date. The hydrotreated shale oil was analyzed for sulfur and nitrogen content for each test. The oil was then water-washed (with a 1:1 volume ratio of oil-to-water) and the sulfur and nitrogen content determined. This was followed by an acid wash (of 1:1 volume ratio of oil to 1N HCl) and the sulfur and nitrogen content was determined on the acid-washed material.

At our original operating conditions, the target value of 500 to 1000 ppm nitrogen in the acid-washed, hydrotreated shale oil was not achieved on any of the three shale oils. However, with the New Albany oil the nitrogen content was reduced to 1600 ppm, which would be acceptable in conventional refineries. By increasing the hydrogen feed ratio and decreasing the liquid hourly space velocity, the target values were achieved during the second series of Sunbury shale oil tests.

The results of the New Albany series are summarized in Table 21. The denitrification of the New Albany shale oil as a function of the average catalyst bed temperature is shown in Figure 35. The results of the Sunbury

Table 21. NEW ALBANY SHALE OIL UPGRADING TESTS
 (Catalyst: Shell 324 Ni/Mo; Catalyst Volume: 1000 cc)
 (Feed Oil: Nitrogen - 1.87 wt %, Sulfur - 1.06 wt %)

Run No.	HTNA-1	HTNA-2	HTNA-3	HTNA-4	HTNA-5
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	8.3	9.2	8.6	8.0	6.7
H ₂ /Oil Ratio, SCF/bbl	3180	3130	3270	2950	2910
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 35. DENITRIFICATION OF NEW ALBANY SHALE OIL

series are summarized in Table 22, and the denitrification/average catalyst bed temperature relationship is shown in Figure 36. The Colorado series results summary appears in Table 23, and the denitrification as a function of average catalyst bed temperature is shown in Figure 37.

Future Work

The IGT hydrotreating unit will be upgraded by use of a new reactor and new temperature controllers. The reactor will be a 1-1/2-inch, schedule 160 pipe with a 72-inch heated zone. This will allow the use of a 2000 cc catalyst bed, double the present size, and will allow closer temperature control and monitoring to observe any catalyst deactivation. This should also improve oil flow distribution throughout the bed and enable higher oil throughputs for the extended runs. A nickel/tungsten catalyst may also be tested in some of the future hydrotreating tests.

The next scheduled series of runs will be with Colorado shale oil at the conditions used in Runs HTS-5 and HTS-6. A run will be made with a liquid hourly space velocity of 0.6 to determine if the increased hydrogen feed ratio used in Runs HTS-5 and HTS-6 was the primary reason for the improved denitrification, or if the improved denitrification was primarily the result of the use of a higher H_2 /oil ratio.

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

Possible laboratory test systems for evaluation of techniques of enhancing mist formation were studied. A test system appropriate to hydrotreating conditions was designed. Construction has almost been completed, and testing of major equipment and instrumentation is currently being carried out.

Table 22. SUNBURY SHALE OIL UPGRADING TESTS
 (Catalyst: Shell 324 Ni/Mo; Catalyst Volume: 1000 cc)
 (Feed Oil: Nitrogen - 1.57 wt %, Sulfur - 1.77 wt %)

Run No.	HTS-1	HTS-2	HTS-3	HTS-4	HTS-5	HTS-6
Duration, hr	3	3	3	2.5	4	4
Pressure, psig	2016	2015	1987	2010	2012	2010
Average Catalyst Temperature, °F	801	779	824	802	825	804
Oil Feed Rate, g/hr	603	603	600	602	403	401
H ₂ Feed Rate, SCF/hr	11.3	11.2	11.5	12.0	12.2	12.8
Product Gas Rate, SCF/hr	7.5	7.4	6.7	8.2	7.4	8.4
H ₂ /Oil Ratio, SCF/bbl	2850	2830	2920	3030	4620	4870
Liquid Hourly Space Velocity, hr ⁻¹	0.6	0.6	0.6	0.6	0.4	0.4
Product Oil						
Sulfur, wt %	0.11	0.15	0.11	0.10	0.06	0.06
Nitrogen, wt %	0.57	0.67	0.37	0.75	0.11	0.25
Water-Washed Oil						
Sulfur, wt %	0.09	0.11	0.09	0.10	0.05	0.04
Nitrogen, wt %	0.51	0.44	0.35	0.42	0.12	0.22
Acid-Washed Oil						
Sulfur, wt %	0.09	0.11	0.09	0.10	0.05	0.04
Nitrogen, wt %	0.34	0.38	0.30	0.44	0.08	0.15

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Figure 36. DENITRIFICATION OF SUNBURY SHALE OIL

Table 23. COLORADO SHALE OIL UPGRADING TESTS
 (Catalyst: Shell 324 Ni/Mo; Catalyst Volume: 1000 cc)
 (Feed Oil: Nitrogen - 2.01 wt %, Sulfur - 0.59 wt %)

Run No.	HTC-1	HTC-2	HTC-3	HTC-4
Duration, hr	4	4	4	3.15
Pressure, psig	2006	2007	2015	2004
Average Catalyst Temperature, °F	773	801	828	799
Oil Feed Rate, g/hr	602	625	609	584
H ₂ Feed Rate, SCF/hr	11.2	11.5	11.3	11.9
Product Gas Rate, SCF/hr	7.4	7.8	7.2	9.9
H ₂ /Oil Ratio, SCF/bbl	2680	2650	2680	2940
Liquid Hourly Space Velocity, hr ⁻¹	0.6	0.6	0.6	0.6
Product Oil				
Sulfur, wt %	0.08	0.14	0.07	0.10
Nitrogen, wt %	0.96	0.88	0.78	1.07
Water-Washed Oil				
Sulfur, wt %	0.07	0.08	0.05	0.08
Nitrogen, wt %	0.91	0.89	0.79	0.99
Acid-Washed Oil				
Sulfur, wt %	0.07	0.07	0.05	0.08
Nitrogen, wt %	0.76	0.64	0.70	0.61

Figure 37. DENITRIFICATION OF COLORADO SHALE OIL

Figure 38 shows a schematic diagram of the apparatus. There are two modes of operation for this apparatus. In the first mode of operation, the bed consists of raw shale. The shale is retorted by nitrogen gas heated by an electrically heated furnace to a predetermined temperature before it enters the reactor. Band heaters 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. Furnace temperature is controlled by a temperature controller and is recorded. Temperatures throughout the bed are also measured and recorded. The bottom and middle portions of the reactor, which are exposed to high temperatures, are 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 will 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 may 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 solids (possibly spent shale) 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. As this mode of the operation can be done at a much lower temperature than the shale retort, the middle section of the reactor (which is made of stainless steel) will be replaced by Pyrex glass to make visual observation of the inside of the reactor possible.

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 complete condensation of vapors. The oil-saturated cold nitrogen is then vented.

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 38. SCHEMATIC DIAGRAM OF LABORATORY TEST SYSTEM

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),³ or to ionize a stream of vapor in inert gas for direct vapor injection into the reactor.

Techniques for measuring mist particle size are also 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.

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

Some preliminary plots of temperature profiles generated at some fixed point as a function of time are given in Figure 39 for values of $v_g = 2$ ft/s and $v_g = 1$ ft/s where v_g is the gas velocity at inlet condition. The presumed diameter of the bed is 3 inches and the bed length is 2 feet. Other values used in determining these profiles are 16 Btu/hr-ft²-°F for the gas-film coefficient, 0.25 inch for the equivalent spherical particle diameter, 0.35 Btu/lb-°F for the shale heat capacity, 135 lb/ft³ for the shale density, 7 Btu/lb mole-°F for the gas heat capacity and 0.5 for the void fraction of the bed. If we allow an exit temperature rise of 20% to 30% of the possible values to assure condensation of the vapor, a run would be about 100 minutes in duration.

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

Figure 39. TEMPERATURE HISTORY AT BED EXIT

supply the heat that will be lost at very high temperatures when shale is being retorted, a small amount of air may be added to the inert gas so that combustion may supply some of the energy. For operation with inert solids, lighter oil will be used and heat losses will be significantly less.

The power requirement for this system has been estimated to 1.5 kW, which can be supplied electrically.

Future Work

Future work will involve completion of construction of the apparatus and testing of major equipment. Initial experimental studies will be based on detection of substantial improvement in the yield of oil fog upon introduction of foreign nuclei.

Subtask 2.5. Liquid-Sealed Lockhopper Tests

Objective

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

Discussion

Experimental Procedure

Equipment for the solids feeding device is designed for operation at pressures up to 1000 psig, with a nominal solids feeding capacity of 1 ton/hr. The major equipment components of the feeder device are a solids feed hopper, solids lockhopper, water reservoir, screw feeder housing and screw feeder, and reactor. The capacity of the lockhopper is about 200 pounds of shale in order to study short cycle time operation. A schematic diagram of the test unit, as erected and operated, is shown in Figure 40. Included in the schematic are key dimensions and capacities of the major equipment components. All vessels are carbon steel since special alloy steels are not required.

The two 8-inch ball valves for the top and the bottom of the solids lockhopper are of a spherical body design, and have a design pressure rating of 1440 psi WOG. Pneumatically powered piston operators are used to open and close these valves.

A 10 ton/hr capacity bucket elevator (not shown in Figure 40) is used to convey test solids from ground level to the top of the feed hopper. With on-off operation, a lockhopper charge of solids may be readily transferred to the feed hopper during the lockhopper discharge cycle of the operation.

Operating procedures include the following major steps:

- Pressurizing reactor
- Charging lockhopper with shale
- Pressurizing lockhopper with water
- Feeding solids to reactor
- Depressurizing lockhopper
- Recharging lockhopper with solids and the start of the next operating cycle.

Control functions in the operating sequence consist of —

- Reactor pressure control during feeding period
- Water level control in screw feeder housing during feeding period.
- Solids level control in reactor during feeding period.

Pressures are monitored at critical locations in the solids feeding device by Bourdon-tube pressure gauges. A differential pressure gauge is used to indicate the pressure between the lockhopper and the reactor vessel, because balanced pressure between the two vessels is necessary before the bottom ball valve can be opened. Operation of the lockhopper ball valves is through safety interlocks with pressure switches that do not allow the top ball valve to be opened with pressure in the lockhopper, or the bottom ball valve to be opened with a pressure differential between the lockhopper and the reactor vessel. The solids feed screw and the water pump are controlled by on-off switches at the unit control panel.

Valves and motorized equipment are manually controlled by electrical switches at the control panel. Manual operation was selected over operation with a programmed timer to permit flexibility in operation.

Test Results

A 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 is being used during this program with a few shale types. The program presented in Table 24 shows the two variables (shale feed rate and particle size range) with the operating pressure being held constant at 500 psig. 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 24. INITIAL PROGRAM FOR LIQUID-SEALED LOCKHOPPER UNIT

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

Where X₁ represents the weight percent water carry-over 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 40) were performed during April 1980. 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 major equipment for the solids feeding device operated well with the exception of a few minor problems. In 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. Instrument line plugging forced early termination of Run 80PF-1, therefore no data are reported for this run.

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 25; also included are times for key operating steps used in the other tests performed this year, Runs 80PF-3, 80PF-4, and 80PF-5.

The results of Run 80PF-2, presented in Table 26, show the net water gain of the discharge sample as well as screen analyses of the feed and discharge samples. Test results for Runs 80PF-3, 80PF-4, and 80PF-5 are included for comparison purposes. It shows the net water gain at 2000 lb/hr feed rate was about 6 weight percent with the Cleveland shale. In previous testing with Colorado shale, net water gains were only about 3 weight percent.¹

In Run 80PF-3, a Kentucky New Albany shale with particle size in the range of $-1/2$ inch to +6 mesh was fed to the reactor at 500 psig. The test consisted of 8 feeding cycles with about 220 pounds of oil shale charged to the lockhopper during each cycle. The feed rate to the reactor was 2200 lb/hr. Times required for major operating steps were presented in Table 25.

A test (Run 80PF-4) was made to determine net water gain at higher feed rates. In Run 80PF-4, a Michigan Antrim oil shale in the size range $-1/2$ inch to +6 mesh was fed to the reactor at 500 psig. Ten feeding cycles were completed with 200 pounds of oil shale being fed to the reactor in each cycle. The feed rate to the reactor was 2500 lb/hr. Times required for key operating steps in Run 80PF-4 were presented in Table 25.

Table 25. TIMES FOR VARIOUS STEPS IN FEEDING CYCLES

Run No.	80PF-2	80PF-3	80PF-4	80PF-5
Shale Type	Cleveland	New Albany	Antrim	Antrim
Operating Pressure, psig	500	500	500	500
Number of Feed Cycles	7	8	10	4
Feed/Cycles, lb	200	220	200	200
	Time, s			
<u>Operating Step</u>				
1. Open Feed Hopper Slide Valve	8	9	8	9
2. Open Top Lockhopper Ball Valve	4	2	2	2
3. Drop Shale from Feed Hopper Into Lockhopper	35	40	38	39
4. Close Top Lockhopper Ball Valve	2	2	2	2
5. Pressurize Lockhopper With Water	2	3	3	2
6. Open Bottom Lockhopper Ball Valve	2	2	2	2
7. Discharge Oil Shale From Lockhopper With Screw Feeder	300	360	300	360
8. Close Bottom Lockhopper Ball Valve	2	2	2	2
9. Depressurize Lockhopper	4	6	8	8

Table 26. RESULTS OF HIGH-PRESSURE FEEDING TESTS

Run No. Shale Type Feed Size Pressure, psig	80PF-2 Cleveland -1/2 inch +6 mesh 500		80PF-3 New Albany -1/2 inch +6 mesh 500		80PF-4 Antrim -1/2 inch +6 mesh 500		80PF-5 Antrim -1/2 inch +6 mesh 500	
	121686	121687	123158	123154	123155	123156	123346	123347
Lab No.	Feed	Discharged	Feed	Discharged	Feed	Discharged	Feed	Discharged
Material	4.3	10.3	1.4	3.3	4.2	6.5	3.8	--
Moisture, wt %	--	7.0	--	2.0	--	2.6	--	--
Net Water Gain (Dry Basis), wt %								
Screen Analysis (U.S. Sieve), wt %								
+1/2 in.	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
+3/8 in.	4.3	1.5	5.9	1.8	2.8	1.0	1.4	1.3
+1/4 in.	45.6	39.9	50.2	41.2	28.2	35.9	36.8	33.9
+6	45.4	48.2	38.5	50.1	62.1	55.0	53.1	55.2
+8	--	--	4.9	5.7	6.8	8.1	6.8	8.4
+12	3.6	9.6	0.5	1.2	--	--	0.4	0.9
+14	--	0.8	--	--	0.1	--	1.5	0.3
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bulk Density, lb/ft ³	64.5	66.4	67.1	72.8	65.4	73.0	82.4	88.6

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In Run 80PF-5, all the equipment of the unit operated well with the exception of a few minor mechanical problems. In Run 80PF-5, 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 completed with 200 pounds of oil shale charged to the lockhopper during each cycle. The feed rate to the reactor was 2000 lb/hr.

The results of the tests presented previously in Table 26 show the screen analyses of the feed and discharge samples of Run 80PF-5. As only four feeding cycles were completed, the net water gain of the discharge sample is not reported in the table. It appears that the Cleveland shale retains nearly twice as much water as the Antrim or the New Albany shales under similar operating conditions.

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

Discussion

Experimental Procedure

A schematic diagram of the 1 ton/hr (nominal shale feeding capacity) PDU is shown in Figure 41. The shale conversion system consists of a feed hopper, first-stage reactor (preheater/prehydrogenator), second-stage reactor (hydrogasifier/hydrotretort), and residue receiver. Before each test, the feed hopper is charged with sufficient shale for an entire test. Each reactor stage is provided with its own hydrogen feed stream, which is preheated in a split-flow fired heater. Screw feeders are used to transfer shale from stage to stage. The shale feed rate from the feed hopper is set at a constant rate. The speeds of revolution of the Nos. 2 and 3 screws are then controlled automatically at rates sufficient to keep the bed levels in Stages 1 and 2 constant. Nuclear-type gauges are used to sense bed level, and the output signals from these gauges are input signals to the bed-level controllers, which control the screw speeds. Bed levels can be controlled to within a few inches during normal steady-state operation. The weight of shale fed is measured accurately for the entire run by weighing the shale initially charged to the feed hopper and that present at the end of the run. The residue shale is weighed after the run. Feed and residue shale rates are calculated by dividing these weights by the measured shale feeding time. A sampling container for obtaining residue shale samples during steady-state operation is installed inside the residue receiver.

Figure 41. PROCESS DEVELOPMENT UNIT — COUNTERCURRENT OPERATION

Each reactor is 36 inches in diameter and is internally insulated to minimize heat losses and to provide essentially adiabatic conditions. The reaction zone in each reactor is contained within a tapered stainless-steel tube averaging about 12 inches in diameter (the diameter at the bottom is larger). Shale-bed heights up to 10 feet can be used. The two reaction zones are in separate vessels to allow completely individual control of each zone and to provide better measurement and control of shale and gas flows to and from each reaction zone. Each reactor contains "slip-joints" to allow for thermal expansion of the 316 stainless-steel (316 SS) internals. A small purge flow of nitrogen is continuously passed into the reactor shell of Stage 1 and Stage 2 to prevent product liquids from condensing on the cooler Fiberfrax insulation packed between the reactor and the shell.

Reactor temperatures are measured by Type "K" chromel-alumel thermocouples. There are ten thermocouples spaced 12 inches apart in Stage 1, and nine thermocouples spaced 13 inches apart in Stage 2. The thermocouples are protected by a thermowell 3/8-inch ips 316 SS pipe in each reactor. These temperatures are recorded continuously along with temperatures of other major pieces of equipment.

The flow rates of the hydrogen feed gas streams for Stages 1 and 2 are maintained at a constant value by flow recording controllers. The flow rates for both gas streams are metered by orifice meters that are calibrated against the exit gas meters. The hydrogen feed gas stream temperature for Stage 1 is controlled by bypassing a portion of the feed gas around the fired heater and blending the hot gas with cold feed gas.

The raw product gas from each stage first passes through a cyclone separator to remove dust and heavy liquid droplets. These gas streams are cooled by a direct liquid quench. Because the quench liquid is recirculated continuously, it must be cooled. Therefore, each quench liquid stream, containing oils and water, is cooled in two separate water-cooled heat exchangers. Because liquids are formed continuously, the quench liquid is drained as required during operation. Product liquid rates are measured by weighing, and liquids are sampled for analysis after each run. Product gas rates are measured by positive displacement meters. Gas compositions and densities are monitored continuously during tests by a gas chromatograph and a Ranarex density recorder, respectively.

An "aliquot" sample of the exit gas for each stage is taken by feeding a portion of it at a constant rate into a 10-ft³ water-sealed holder during the steady-state portion of each run. "Spot" samples are also taken throughout each steady-state test period.

The reactors are filled with silica sand prior to each run to establish a bed and a stable temperature profile prior to the run. This also avoids rapid heating of the initial shale feed, a varying bed height at the start of a run, and subsequent problems with tar formation, and also subjects all feed shale to a similar time-temperature history.

The product gases are analyzed by a on-line process-type gas chromatograph and IGT's mass spectrometer, and the liquids by ASTM standard methods. The feed and residue shales are analyzed by methods described in Appendix B of IGT Research Bulletin No. 36.²

Test Results

Six PDU runs were made during this year. The first run (79PDU-1) was made with Kentucky Sunbury shale, which was the first large sample of Eastern shale received for this program. This run was made to obtain information on hydroretorting product yields and quality using Kentucky Sunbury shale under oil-making conditions. A Kentucky New Albany shale (Run 80PDU-2) and a Cleveland shale (Run 80PDU-1) were also tested under oil-making conditions.

Summaries of the test results and operating conditions for these three runs are presented in Tables 27 through 29. All three runs were made at shale feed rates of approximately 1000 lb/hr, reactor pressures of 400 psig, and shale bed heights of 10.0 feet. The average hydrogen partial pressures (calculated by numerically averaging the inlet hydrogen partial pressure with the exit hydrogen partial pressure) were all approximately 335 psig. The hydrogen-to-shale ratios for these oil runs were chosen so that the enthalpy of the shale would nearly equal the enthalpy of the feed gas for each respective stage. The Stage 2 feed-hydrogen-to-shale ratio is lower than the ratio for Stage 1 because a small amount of air was added to Stage 2, which increased the total enthalpy of the feed gas. Some of the feed hydrogen was burned (with injected air) to increase the enthalpy of the Stage 2 gas.

Table 27. PDU (79PDU-1) TEST RESULTS — COUNTERCURRENT OPERATION WITH SUNBURY SHALE

Operating Conditions and Test Results

Oil Shale Location (State)	151 (Sunbury)
Oil Shale Particle Size (U.S. Sieve)	-1/2 inch to +6 mesh
Test Duration, hr	8.00
Steady-State Operating Period, hr	6.00

	Stage 1	Stage 2
Bed Height, ft	10.0	10.0
Pressure, psig	403	403
Average Bed Temperature, °F	310	1378
Maximum Bed Temperature, °F	813	1381
Oil Shale Feed Rate, lb/hr	1095	--
Oil Shale Space Velocity, lb/ft ³ -hr	127	126
Oil Shale Mass Rate, lb/ft ² hr	1272	1255
Feed Gas*/Shale Ratio, SCF/lb	30.4	12.8
Feed Gas* Superficial Velocity, ft/s	0.38	0.57
Air/Shale Ratio, SCF/lb	--	0.495
Product Gas Yield, SCF/lb Shale Fed	16.45	15.99
Residue Shale Yield, lb/lb Shale Fed		
By Direct Weight Measurement	--	0.670
By Ash Balance Calculation	--	0.827
Liquid Hydrocarbon Yield, lb/lb Shale Fed	0.007	0.044
Water Yield, lb/lb Shale Fed	0.068	0.068
Material Balance, %		103.0
Organic Carbon Distribution in Products, %		
Gaseous Hydrocarbons	2.2	19.2
Liquid Hydrocarbons	4.2	26.5
Residue Shale		35.0

Feed and Product Compositions

Oil Shale			Shale Oil		
Sample	Feed	Stage 2 Residue	Sample	Stage 1	Stage 2
Lab No.	42465	42494	Lab No.	42466	42467
Moisture, Wt % (Dry Basis)	1.4	0.4	C/H Weight Ratio	7.21	8.83
Ultimate Analysis, Wt %			Sulfur, Wt %	2.29	1.38
Organic Carbon	14.71	6.17	Nitrogen, Wt %	0.78	2.07
Mineral Carbon	.03	.01	Viscosity, SSU at 100°F	NA**	NA**
Hydrogen	1.74	.36	Specific Gravity (60/60°F)	0.875	0.977
Nitrogen	.56	.75	Distillation, °F		
Oxygen (by Difference)	2.66	0.00	IBP	180	163
Sulfur	3.23	1.52	50%	425	616
Ash	77.05	92.26	EP	602	738
Total	100.00	101.07	Pour Point, °F	-80	-5
Gas Composition, Mol %	Feed		Stage 1 Product†		Stage 2 Product†
Hydrogen Sulfide	0.00		0.01		0.01
Nitrogen & Argon	.87		0.00		1.93
Carbon Monoxide	2.60		2.58		1.73
Carbon Dioxide	0.00		0.11		0.11
Hydrogen	95.48		95.88		91.05
Methane	1.05		1.22		4.29
Ethane +	0.00		0.15		0.73
Ethylene +	0.00		0.05		0.14
Benzene	0.00		0.00		0.01
Total	100.00		100.00		100.00

* Hydrogen.

** NA means not available.

† Purge and Stage 2 combustion air-free.

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Table 28. PDU (80PDU-1) TEST RESULTS — COUNTERCURRENT OPERATION WITH CLEVELAND SHALE

Operating Conditions and Test Results					
Oil Shale Location (State)	139 (Cleveland)				
Oil Shale Particle Size (U.S. Sieve)	-1/2 inch to +6 mesh				
Test Duration, hr	8.25				
Steady-State Operating Period, hr	6.00				
	Stage 1	Stage 2			
Bed Height, ft	10.0	10.0			
Pressure, psig	402	402			
Average Bed Temperature, °F	275	1100			
Maximum Bed Temperature, °F	795	1245			
Oil Shale Feed Rate, lb/hr	1021	--			
Oil Shale Space Velocity, lb/ft ³ -hr	119	117			
Oil Shale Mass Rate, lb/ft ² -hr	1127	1170			
Feed Gas*/Shale Ratio, SCF/lb	19.72	12.74			
Feed Gas* Superficial Velocity, ft/s	0.33	0.45			
Air/Shale Ratio, SCF/lb	--	0.504			
Product Gas Yield, SCF/lb Shale Fed	17.36	14.52			
Residue Shale Yield, lb/lb Shale Fed					
By Direct Weight Measurement	--	0.745			
By Ash Balance Calculation	--	0.844			
Liquid Hydrocarbon Yield, lb/lb Shale Fed	0.001	0.029			
Water Yield, lb/lb Shale Fed	0.091	0.066			
Material Balance, %		103.0			
Organic Carbon Distribution in Products, %					
Gaseous Hydrocarbons	1.0	27.2			
Liquid Hydrocarbons	0.6	25.8			
Residue Shale		48.3			
Feed and Product Compositions					
	Oil Shale		Shale Oil		
Sample	Feed	Stage 2 Residue	Sample	Stage 1	Stage 2
Lab No.	119731	119857	Lab No.	42833	42834
Moisture, Wt % (Dry Basis)	5.0	0.0	C/H Weight Ratio	8.27	8.75
Ultimate Analysis, Wt %			Sulfur, Wt %	2.70	1.50
Organic Carbon	10.56	5.74	Nitrogen, Wt %	0.55	1.73
Mineral Carbon	0.11	0.04	Viscosity, SSU at 100°F	113.8	48.4
Hydrogen	1.18	0.32	Specific Gravity (60/60°F)	0.974	0.965
Nitrogen	0.53	0.11	Distillation, °F		
Oxygen (by HTW) ^{AA}	3.36	1.81	IBP	208	190
Sulfur	0.95	0.48	50%	608	550
Ash	82.16	92.47	EP	702	739
Total	98.85	100.97	Pour Point, °F	35	15
Gas Composition, Mol %					
	Feed		Stage 1 Product†	Stage 2 Product†	
Hydrogen Sulfide	0.00		0.00	0.00	
Nitrogen & Argon	0.70		0.00	1.99	
Carbon Monoxide	3.00		2.63	1.49	
Carbon Dioxide	0.00		0.10	0.21	
Hydrogen	94.40		95.08	89.82	
Methane	1.90		2.12	5.75	
Ethane +	0.00		0.04	0.59	
Ethylene +	0.00		0.03	0.11	
Benzene	0.00		0.00	0.04	
Total	100.00		100.00	100.00	

* Hydrogen.

** High-temperature water.

† Purge and Stage 2 combustion air-free.

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Table 29. PDU (80PDU-2) TEST RESULTS — COUNTERCURRENT OPERATION WITH
NEW ALBANY SHALE

Operating Conditions and Test Results

Oil Shale Location (State)	64 (New Albany)	
Oil Shale Particle Size (U.S. Sieve)	-1/2 inch to +6 mesh	
Test Duration, hr	8.00	
Steady-State Operating Period, hr	6.50	
	<u>Stage 1</u>	<u>Stage 2</u>
Bed Height, ft	10.0	10.0
Pressure, psig	406	406
Average Bed Temperature, °F	572	1289
Maximum Bed Temperature, °F	810	1355
Oil Shale Feed Rate, lb/hr	1059	--
Oil Shale Space Velocity, lb/ft ³ -hr	123	121
Oil Shale Mass Rate, lb/ft ² -hr	1231	1214
Feed Gas*/Shale Ratio, SCF/lb	19.0	13.18
Feed Gas* Superficial Velocity, ft/s	0.45	0.53
Air/Shale Ratio, SCF/lb	--	0.636
Product Gas Yield, SCF/lb Shale Fed	17.22	14.73
Residue Shale Yield, lb/lb Shale Fed		
By Direct Weight Measurement	--	0.790
By Ash Balance Calculation	--	0.809
Liquid Hydrocarbon Yield, lb/lb Shale Fed	0.007	0.057
Water Yield, lb/lb Shale Fed	0.035	0.050
Material Balance, %	99.5	
Organic Carbon Distribution in Products, %		
Gaseous Hydrocarbons	3.4	20.0
Liquid Hydrocarbons	4.4	37.5
Residue Shale	24.6	

Feed and Product Compositions

Oil Shale			Shale Oil		
Sample	Feed	Stage 2 Residue	Sample	Stage 1	Stage 2
Lab No.	121005	121035	Lab No.	43055	43056
Moisture, Wt % (Dry Basis)	1.9	0.0	C/H Weight Ratio	6.97	8.66
Ultimate Analysis, Wt %			Sulfur, Wt %	1.63	1.11
Organic Carbon	14.17	4.22	Nitrogen, Wt %	0.73	1.00
Mineral Carbon	0.27	0.08	Viscosity, SSU at 100°F	31.3	75.9
Hydrogen	1.57	0.21	Specific Gravity (60/60°F)	0.863	0.970
Nitrogen	0.54	0.18	Distillation, °F		
Oxygen (by HTW)**	1.93	0.71	IBP	268	182
Sulfur	5.19	3.56	50%	426	650
Ash	77.22	93.59	EP	625	724
Total	100.89	102.55	Pour Point, °F	-75	-15
Gas Composition, Mol %	Feed		Stage 1 Product†		Stage 2 Product†
Hydrogen Sulfide	0.00		0.30		0.28
Nitrogen & Argon	0.70		0.00		1.27
Carbon Monoxide	2.50		2.13		1.50
Carbon Dioxide	0.10		0.10		0.32
Hydrogen	95.10		95.23		90.47
Methane	1.60		2.09		5.26
Ethane +	0.00		0.11		0.74
Ethylene +	0.00		0.04		0.15
Benzene	0.00		0.00		0.01
Total	100.00		100.00		100.00

* Hydrogen.

** High-temperature water.

† Purge and Stage 2 combustion air-free.

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With the Kentucky New Albany (Run 80PDU-2) and Kentucky Sunbury (Run 79PDU-1) shales organic carbon conversions were 75.4% and 65%, respectively, by use of ash balance to calculate the yield of spent shale. In the Cleveland shale run, 80PDU-1, 51.7% of the organic carbon in the feed shale was converted to gaseous and liquid products. The lower conversion of the Cleveland shale compared with the other two shale runs may be attributed partially to a lower maximum bed temperature (1245°F) than the target value of 1400°F . This shale was also found to be less reactive than the other two Kentucky shales tested in thermobalance and bench-scale tests.

The reactor bed-temperature profiles of Stage 1 and Stage 2 for Runs 79PDU-1, 80PDU-1 and 80PDU-2 are shown in Figures 42 through 47. The temperature profiles of Stage 1 for Runs 79PDU-1 and 80PDU-1 indicate that the Stage 1 gas/shale ratio was probably too low. The temperatures in Stage 1 for Runs 79PDU-1 and 80PDU-1 remained constant at a value of approximately 300°F for more than half the bed. The slow shale heat-up at the top of the bed is probably due to the surface water and bound water present in the raw shale, which are driven off in the initial heating stage. It may not be possible to obtain a linear profile for the entire shale bed in Stage 1 for some high-moisture-content shales because of the large amount of water that must be vaporized. The reactor temperature profile for the New Albany shale test (Run 80PDU-2), Figure 46, probably best exemplifies the linear temperature profile we hoped to achieve for all of the oil-producing runs.

The reactor bed-temperature profiles obtained in Stage 2 during Runs 80PDU-1 and 80PDU-2 are representative of the linear temperature profiles we hoped to achieve for all of the oil-producing runs. The bed temperature profile of Stage 2 for Run 79PDU-1 indicates that the gas/shale ratio was probably somewhat high.

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 driven off the shale by passing nitrogen over the sample at 900°C . Condensable oils are removed from the effluent 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

Figure 42. STAGE 1 BED-TEMPERATURE PROFILE FOR RUN 79PDU-1

Figure 43. STAGE 2 BED-TEMPERATURE PROFILE FOR RUN 79PDU-1.

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Figure 44. STAGE 1 AVERAGE STEADY-STATE TEMPERATURES FOR RUN 80PDU-1

A80071740

Figure 45. STAGE 2 AVERAGE STEADY-STATE TEMPERATURES FOR RUN 80PDU-1

B80071739

Figure 46. STAGE 1 BED-TEMPERATURE PROFILE FOR RUN 80PDU-2

A80071742

Figure 47. STAGE 2 BED-TEMPERATURE PROFILE FOR RUN 80PDU-2

determined by weighing the magnesium perchlorate. The total HTW is then determined by subtracting the initial shale surface moisture from the total 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.

Elemental oxygen balances have greatly improved but are still high, 118% for Run 80PDU-2 and 155% for Run 80PDU-1. 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. The greatest source of the oxygen in the products is water. We will continue searching for a more accurate method of determining the oxygen in the feed and spent Eastern shales.

A series of runs was also made under gas-producing conditions. Summaries of the test results and operating conditions for two Eastern shale runs, 80PDU-3 (Cleveland member of the Ohio) and 80PDU-4 (Kentucky New Albany) are shown in Tables 30 and 31, respectively. Kentucky Sunbury shale (Run 80PDU-5) was tested under gas-producing conditions. The results of Run 80PDU-5 will be reported in the next quarterly report when analytical data become available. These three runs were all made at shale feed rates of 1000 lb/hr, reactor pressures of 400 psig, and shale bed heights of 10.0 feet.

The organic carbon conversion for the Kentucky New Albany shale run (80PDU-4) was 78.2%, while the conversion for the Cleveland shale was 60.2%. For Run 80PDU-3, the feed-hydrogen-to-shale ratios in Stage 1 and Stage 2 were 18.8 SCF/lb and 16.3 SCF/lb, respectively, while in Run 80PDU-4, hydrogen-to-shale ratios were 20.2 SCF/lb and 15.7 SCF/lb in Stage 1 and Stage 2, respectively.

Table 30. PDU (80PDU-3) TEST RESULTS — COUNTERCURRENT OPERATION WITH CLEVELAND SHALE

Operating Conditions and Test Results

Oil Shale Location (State) 139 (Cleveland)
 Oil Shale Particle Size (U.S. Sieve) -1/2 inch to +6 mesh
 Test Duration, hr 8.00
 Steady-State Operating Period, hr 5.75

	Stage 1	Stage 2
Bed Height, ft	10.0	10.0
Pressure, psig	402	402
Average Bed Temperature, °F	271	1493
Maximum Bed Temperature, °F	794	1520
Oil Shale Feed Rate, lb/hr	1035	--
Oil Shale Space Velocity, lb/ft ³ -hr	120	119
Oil Shale Mass Rate, lb/ft ² -hr	1203	1187
Feed Gas*/Shale Ratio, SCF/lb	18.8	16.3
Feed Gas* Superficial Velocity, ft/s	0.315	0.73
Air/Shale Ratio, SCF/lb	--	0.555
Product Gas Yield, SCF/lb Shale Fed	15.13	17.47
Residue Shale Yield, lb/lb Shale Fed		
By Direct Weight Measurement	--	0.787
By Ash Balance Calculation	--	0.824
Liquid Hydrocarbon Yield, lb/lb Shale Fed	0.003	0.027
Water Yield, lb/lb Shale Fed	0.068	0.088
Material Balance, %	105.0	
Organic Carbon Distribution in Products, %		
Gaseous Hydrocarbons	1.7	31.5
Liquid Hydrocarbons	2.7	31.6
Residue Shale	39.8	

Feed and Product Compositions

Oil Shale			Shale Oil		
Sample	Feed	Stage 2 Residue	Sample	Stage 1	Stage 2
Lab No.	121531	122733	Lab No.	43221	43222
Moisture, Wt % (Dry Basis)	5.7	0.1	C/H Weight Ratio	7.65	8.94
Ultimate Analysis, Wt %			Sulfur, Wt %	3.43	1.32
Organic Carbon	10.08	4.59	Nitrogen, Wt %	0.72	1.58
Mineral Carbon	1.10	.01	Viscosity, SSU at 100°F	41.3	67.9
Hydrogen	1.17	.18	Specific Gravity (60/60°F)	0.926	0.983
Nitrogen	.43	.05	Distillation, °F		
Oxygen (by HTW)**	2.87	.56	IBP	170	230
Sulfur	.82	.49	50%	506	600
Ash	83.03	93.11	FP	660	742
Total	98.50	100.99	Pour Point, °F	-15	10
Gas Composition, Mol %	Feed		Stage 1 Product †		Stage 2 Product †
Hydrogen Sulfide	0.00		0.00		0.00
Nitrogen & Argon	0.75		0.00		1.70
Carbon Monoxide	2.50		2.44		1.60
Carbon Dioxide	0.00		0.20		0.32
Hydrogen	95.85		96.06		90.65
Methane	0.90		1.24		5.22
Ethane +	0.00		0.02		0.36
Ethylene +	0.00		0.04		0.14
Benzene	0.00		0.00		0.01
Total	100.00		100.00		100.00

* Hydrogen.

** High-temperature water.

† Purge and Stage 2 combustion air-free.

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Table 31. PDU (80PDU-4) TEST RESULTS — COUNTERCURRENT OPERATION WITH NEW ALBANY SHALE

Operating Conditions and Test Results

Oil Shale Location (State):	64 (New Albany)
Oil Shale Particle Size (U.S. Sieve)	-1/2 inch to +6 mesh
Test Duration, hr	8.50
Steady-State Operating Period, hr	6.00

	Stage 1	Stage 2
Bed Height, ft	10.0	10.0
Pressure, psig	408	408
Average Bed Temperature, °F	517	1485
Maximum Bed Temperature, °F	803	1493
Oil Shale Feed Rate, lb/hr	1032	--
Oil Shale Space Velocity, lb/ft ³ -hr	120	118
Oil Shale Mass Rate, lb/ft ² -hr	1200	1184
Feed Gas*/Shale Ratio, SCF/lb	20.19	15.67
Feed Gas* Superficial Velocity, ft/s	0.45	0.69
Air/Shale Ratio, SCF/lb	--	0.773
Product Gas Yield, SCF/lb Shale Fed	16.24	18.36
Residue Shale Yield, lb/lb Shale Fed		
By Direct Weight Measurement	--	0.800
By Ash Balance Calculation	--	0.784
Liquid Hydrocarbon Yield, lb/lb Shale Fed	0.010	0.055
Water Yield, lb/lb Shale Fed	0.028	0.056
Material Balance, %		98.9
Organic Carbon Distribution in Products, %		
Gaseous Hydrocarbons	5.0	26.6
Liquid Hydrocarbons	5.9	34.6
Residue Shale		21.8

Feed and Product Compositions

Oil Shale			Shale Oil		
Sample	Feed	Stage 2 Residue	Sample	Stage 1	Stage 2
Lab No.	122922	122923	Lab No.	43405	43406
Moisture, Wt % (Dry Basis)	1.5	0.1	C/H Weight Ratio	7.07	8.68
Ultimate Analysis, Wt %			Sulfur, Wt %	1.68	1.15
Organic Carbon	14.05	3.85	Nitrogen, Wt %	0.95	1.92
Mineral Carbon	0.33	0.01	Viscosity, SSU at 100°F	36.6	91.9
Hydrogen	1.64	0.14	Specific Gravity (60/60°F)	0.876	0.975
Nitrogen	0.46	0.06	Distillation, °F		
Oxygen (by HTW) **	2.24	0.29	IBP	282	230
Sulfur	5.39	3.31	50%	418	648
Ash	76.84	95.33	EP	589	760
Total	100.95	102.99	Pour Point, °F	-85	-25
Gas Composition, Mol %	Feed		Stage 1 Product†		Stage 2 Product†
Hydrogen Sulfide	0.00		0.27		0.00
Nitrogen & Argon	0.56		0.01		0.55
Carbon Monoxide	2.47		2.30		1.82
Carbon Dioxide	0.00		0.08		0.11
Hydrogen	96.68		96.35		92.07
Methane	0.29		0.72		4.70
Ethane +	0.00		0.23		0.59
Ethylene +	0.00		0.04		0.14
Benzene	0.00		0.00		0.02
Total	100.00		100.00		100.00

* Hydrogen.

** High-temperature water.

† Purge and Stage 2 combustion air-free.

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The bed-temperature profiles of Stage 1 and Stage 2 for Runs 80PDU-3 and 80PDU-4 are shown in Figures 48 through 51. The temperature for Stage 1 in 80PDU-3 is nearly constant at 275°F for about the top half of the shale bed and gave us a nearly isothermal profile for Run 80PDU-3, while the bed-temperature profile for Stage 1 in Run 80PDU-4 is nearly linear throughout the entire bed. Less sensible heat was required to drive off the shale surface moisture and bound water (HTW) in Stage 1 for Kentucky New Albany shale (Run 80PDU-4) than for Cleveland shale (Run 80PDU-3). Thus, the temperature profile of Stage 1 for Run 80PDU-4 is not initially flat like Run 80PDU-3. The bed-temperature profiles of Stage 2 for Runs 80PDU-3 and 80PDU-4 are nearly linear for the top half of the shale bed. The temperature of the Stage 2 beds for both runs rises gradually from 1300° to 1500°F.

A comparison of some thermobalance runs and PDU runs of the same batches of shales is shown in Table 32. There is a fairly good agreement between the thermobalance runs and PDU runs. The PDU gas runs were made at conditions (hydrogen partial pressure and maximum temperature) more comparable to thermobalance runs than the PDU oil runs. There is, therefore, better agreement between the PDU gas runs and thermobalance tests than with PDU oil runs and thermobalance tests.

A comparison of bench-scale tests and PDU runs of the same batches of shales has been made. Runs 79PDU-1 and 80BSU-11 were both made with the same batch of Kentucky Sunbury shale. In Run 79PDU-1 the average hydrogen partial pressure was 336 psig at a maximum bed temperature of 1319°F. The carbon conversion for Run 79PDU-1 is 65% and for Run 80BSU-11 is 72.5%. Thus, results of the two runs are in good agreement.

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 psig greater in the BSU run than 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 predict PDU test results from BSU test results.

Figure 48. STAGE 1 BED-TEMPERATURE PROFILE FOR RUN 80PDU-3

Figure 49. STAGE 2 BED-TEMPERATURE PROFILE FOR RUN 80PDU-3

Figure 50. STAGE 1 BED-TEMPERATURE PROFILE FOR RUN 80PDU-4

Figure 51. STAGE 2 BED-TEMPERATURE PROFILE FOR RUN 80PDU-4

Table 32. COMPARISON OF THERMOBALANCE AND PDU RUNS

Shale Type	Thermobalance Tests ^a		Process Development Unit Tests							
			Oil Runs				Gas Runs			
	Run Number	Organic Carbon Conversion, %	Run Number	Organic ^b Carbon Conversion, %	Maximum ^c Temperature, °F	Hydrogen ^d Partial Pressure, psig	Run Number	Organic ^b Carbon Conversion, %	Maximum ^c Temperature, °F	Hydrogen ^d Partial Pressure psig
New Albany (Loc. 64)	S-80-24	87.7	80PDU-2	75.4	1355	339	80PDU-4	78.2	1493	344
Cleveland (Loc. 139)	S-80-9	68.8	80PDU-1	51.7	1245	331	80PDU-3	60.2	1520	333
Sunbury (Loc. 142)	79-29	78.5	79PDU-1	65.0	1381	336	80PDU-5 ^e	N/A	1510	N/A

^a Maximum temperature 1400°F and H₂ partial pressure 500 psig.

^b By use of ash balance to calculate residue shale yield.

^c Stage 2.

^d Average partial pressure.

^e Complete analytical data for 80PDU-5 are not available.

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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.

Runs 80PDU-3 and 80BSU-8 were both made with a Cleveland member of the Ohio shale under gas-making conditions. Run 80PDU-3 had an average hydrogen partial pressure of 333 psig, an average bed temperature of 1493°F, a maximum bed temperature of 1520°F and a total organic carbon conversion of 60%. Run 80BSU-8 had an average hydrogen partial pressure of 367 psig, an average bed temperature of 1261°F, a maximum bed temperature of 1380°F, and a total organic carbon conversion of 66.8%. Considering the differences in the maximum bed temperatures and the partial hydrogen pressures, there is excellent agreement between the two runs in organic carbon conversion.

Runs 80PDU-4 and 80BSU-5 were made with a Kentucky New Albany shale. Run 80PDU-4 had an average hydrogen partial pressure of 344 psig (Stage 2), a maximum bed temperature of 1493°F, and a total organic carbon conversion of 78.2%. Run 80BSU-5 had an average hydrogen partial pressure of 401 psig, a maximum bed temperature of 1517°F, and a total organic carbon conversion of 84.0%. The beneficial effect of a higher hydrogen partial pressure and higher temperature in the bench-scale run than in the PDU run resulted in an additional organic carbon recovery.

PDU Corrosion Testing

Ultrasonic wall-thickness measurements were made in the piping and vessels of the liquid-filled portions of the exit gas quench system to check for corrosion. These measurements are being performed annually and will provide estimates of corrosion rates for the carbon steels being used for the piping and vessels, as well as providing data needed for material selection in future plant designs. The results obtained thus far are given in Table 33. As can be seen, there was no definite indication of progressive corrosion.

Future Work

PDU tests will be performed on other Eastern and Western shale samples after bench-scale tests are completed and results are available for them.

Table 33. WALL THICKNESS MEASUREMENTS ON PDU QUENCH SYSTEM COMPONENTS

Location	Wall Thickness, in. ^a			
	Original (per drawing)	Measured 7-6-77 ^b	Measured 7-21-78 ^c	Measured 7-29-80 ^d
B-Deck Stage 1 Quench Tower				
Point A	0.562	0.571	0.578	0.560
Point B	0.562	0.562	0.566	0.550
Stage 2 Quench Tower				
Point A	0.562	0.568	0.568	0.550
Point B	0.562	0.568	0.569	0.550
Stage 2 Exit Piping				
Point A	0.154	0.170	0.165	0.140
Point B	0.154	0.170	0.165	0.140
Stage 1 Exit Piping				
Point A	0.145	0.165	0.130	0.135
Point B	0.145	0.140	0.150	0.135
Quench Water Coolers				
Stage 1	0.500	0.495	0.495	0.490
Stage 2	0.500	0.505	0.505	0.485
D-Deck Stage 1 Quench Tower	0.562	0.530	0.535	0.520
Stage 2 Quench Tower	0.562	0.570	0.575	0.565
E-Deck Stage 1 Quench Pot				
Point A	0.875	0.890	0.905	0.870
Point B	0.875	0.890	0.910	0.870
Stage 2 Quench Pot				
Point A	0.875	1.030	1.005	1.015
Point B	0.875	1.025	1.000	1.015
Stage 2 Exit Piping				
Point C	0.154	0.170	0.155	N.A.
Stage 1 Exit Piping				
Point C	0.145	0.145	0.140	N.A.

^a Accuracy of measurement is ± 0.005 inch.

^b After approximately 1 year of operation.

^c After approximately 2 years of operation.

^d After approximately 4 years of operation.

Task 4. Process Environmental Assessment

Objective

The objective of environmental assessment in PDU experiments is to establish a data base to answer process-specific questions about the environmental characterization of HYTORT process water, spent shales, and product gases for scale-up to a commercial-scale HYTORT plant. Environmental data for the HYTORT process must be developed concurrently with process data to enable proper and economical design of wastewater, spent shale, and air-pollution control systems, plus the determination of process environmental impacts for specific sites. The Pace Company from the Jacobs Engineering Group, Inc., has been retained as a subcontractor to assist IGT in the compilation and interpretation of the data base.

Discussion

A draft Phase I report has been completed by Pace. In this report, the HYTORT process concept is reviewed for use on both Eastern and Western shales and questions about major environmental effects are formulated for commercial HYTORT plant operations. A review of the IGT experimental test plant for completeness, cost-effectiveness, and feasibility is also included. Priorities are now being established to rank the more important possible pollutants.

A gas chromatograph for specific analysis of sulfur- or nitrogen-containing compounds in both liquid and gas samples has been placed in service. This instrument uses electrolytic conductivity detection for selective analysis of priority pollutants: for example, thiozenes, and other nitrogen compounds. The chromatograph has been used initially for analyses of sulfur compounds to check the efficiency of process sampling systems. This instrument is located close enough to the PDU to allow timely analysis of process samples and minimize the effects of sample degradation prior to analysis.

A sampling probe has been placed into the second stage of the PDU upstream of the cyclone and quench tower to collect samples for accurate characterization of the HYTORT process gases for possible pollutants. This system provides filtration and bulk solids removal at the operating temperature and pressure of the reactor prior to any pressure reduction for sampling. After pressure reduction, sampled reactor gases are then introduced into a sampling train as shown in Figure 52. The hot sample gas is cooled in a condenser and is then directed through a series of sample bombs, each containing scrubants to recover particular species. To promote high sampling efficiencies, two or three sampling vessels containing the same preservative solution are used in series. Major environmental species are captured in these bombs, and the liquid samples are preserved for laboratory analysis. The exit-gas flow rate is measured to provide a means of calculating the actual environmental species loadings in the gas stream. Basic scrubbing solutions (6N NaOH) are used to trap $S^{=}$, SCN^{-} , and CN^{-} ; acidic solutions (3N HCl) for phenols, NH_3 , and TOC; and organic liquids (methylene chloride, benzyl alcohol) for organic compounds.

The on-line sampling train for the second-stage freeboard gases provides immediate capture and stabilization of reactive and volatile species, eliminates process unit lag times, avoids quench tower inefficiencies for many species, and allows rapid monitoring of differences in pollutant production with changing process conditions.

The environmental sampling train for the second-stage product gases was initially used for Run 80PDU-4. In this run, a Kentucky New Albany oil shale was processed under gas-making conditions. The sampling train was also used for Run 80PDU-5 in which a Kentucky Sunbury oil shale was processed under gas-making conditions.

Three complete sets of environmental samples were taken during the 6 hours of steady-state operation for Run 80PDU-4. Each set consisted of 1 raw condensate, a 2-bomb acid scrub, a 2-bomb base scrub, a 3-bomb organic scrub, and their 4 respective exit gas samples. The analyses of these samples are shown in Tables 34 through 37. Oil yields obtained during sampling were substantially lower than material balance yields. Although the sampling train seemed to be operating properly, the inlet line

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Figure 52. OIL SHALE ENVIRONMENTAL SAMPLING TRAIN

Table 34. RUN 80PDU-4 ANALYTICAL RESULTS OF ACID AND BASE SCRUBS FOR
HYTORT ENVIRONMENTAL ASSESSMENT

	Sample Set 1			Sample Set 2			Sample Set 3			Averaged Total	1b/ton* Wet Shale	1b/ton Dry Shale
	Bomb A	Bomb B	Total	Bomb A	Bomb B	Total	Bomb A	Bomb B	Total			
10 ⁻⁶ lb/SCF, Dry												
<u>Acid Scrub Analyses</u>												
Total Organic Carbon	50.5	11.5	62.0	39.2	19.1	58.3	43.5	13.4	56.9	59.1	2.17	2.2
Ammonia-Nitrogen	90.7	20.5	111.2	34.5	65.2	99.7	49.2	62.4	111.6	108	3.97	4.0
Phenols	15.0	0.49	15.5	7.3	7.7	15.0	7.4	0.39	7.8	12.8	0.47	0.48
<u>Base Scrub Analyses</u>												
Cyanides	0.032	0.0012	0.033	0.097	0.0012	0.098	0.00039	0.00027	0.00066	0.044	0.0016	0.0016
Thiocyanates	1.0	2.7	3.7	0.56	3.4	3.96	0.89	0.43	1.32	3.0	0.110	0.11
Sulfides	4.7	327	332	1.5	345	347	481	94.7	576	418	15.3	15.4
Total Sulfur	29.7	24.7	54.4	2.7	53.8	56.5	20.7	12.9	33.5	48.2	1.77	1.8
Residual Sulfur	0.47	1.5	1.97	0.97	6.6	7.6	12.2	1.4	13.5	7.7	0.28	0.29

* Shale contains 1.5% moisture.

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Table 35. RUN 80PDU-4 ANALYTICAL RESULTS OF ORGANIC SCRUB (Water Phase)
FOR HYTORT ENVIRONMENTAL ASSESSMENT

	Methylene Chloride Scrub "II" ^c			Methylene Chloride Scrubb III ^d	Raw Condensate I & II Combined	Raw Condensate III	Averaged Results	lb/ton ^e Wet Shale	lb/ton Dry Shale
	Bomb A	Bomb B	Total	Bombs A&B					
	10 ⁻⁶ lb/SCF, Dry								
Toluene	--	0.167	0.167	0.071	--	0.019	0.093	0.0034	0.0035
Acetaldehyde	0.272	--	0.272	--	--	--	0.272	0.010	0.010
Acetone	0.019	0.048	0.067	0.133	0.115	0.131	0.104	0.0038	0.0039
Phenols ^a	0.064	0.038	0.102	0.299	2.35	2.87	1.77	0.065	0.066
Acetic Acid	0.075	0.158	0.233	0.536	0.233	0.33	0.27	0.0097	0.0099
Benzyl Alcohol ^b	0.013	4.05	4.06	0.449	3.56	2.83	3.48	0.13	0.13
Acetonitrile	0.079	0.028	0.107	0.062	0.158	0.41	0.23	0.0083	0.0084
Pyridines	0.013	--	0.013	--	0.91	0.27	0.40	0.015	0.015
Acetamide	0.023	0.016	0.039	--	--	--	0.039	0.0014	0.0015
C ₆ H ₇ NO	0.040	0.052	0.092	0.167	0.196	--	0.144	0.0053	0.0054
C ₇ H ₉ NO	0.072	0.076	0.148	0.378	0.610	--	0.38	0.014	0.014
C ₈ H ₁₁ NO	--	--	--	--	0.305	--	0.305	0.011	0.011
C ₉ H ₁₃ NO	--	--	--	--	0.079	--	0.079	0.0029	0.0029
Benzaldehyde	--	0.123	0.123	0.140	0.109	0.195	0.142	0.005	0.005
Naphthalene ^a	--	0.003	0.003	--	--	--	0.003	0.0001	0.00011
Benzothiophene ^a	--	0.005	0.005	--	--	--	0.005	0.0002	0.0002
Benzonitrile	--	--	--	0.193	0.125	0.152	0.139	0.0051	0.0052
Methyl Benzonitrile	--	--	--	--	0.085	--	0.085	0.0031	0.0032
Pentanone	--	--	--	--	0.038	0.015	0.027	0.0010	0.0010
Carboxylic Acid	--	--	--	--	--	0.188	0.19	0.0070	0.0071
Pyrrole ^a	--	--	--	--	0.143	0.169	0.156	0.0057	0.0058
Quinoline ^a	--	--	--	--	0.052	0.114	0.083	0.0030	0.0031
2-Butanone	--	--	--	--	0.044	--	0.044	0.0016	0.0016
Methyl Indole ^a	--	--	--	--	0.040	--	0.040	0.0015	0.0015
Anilines	--	--	--	--	0.674	1.38	1.03	0.038	0.038
Indoles ^a	--	--	--	--	0.162	0.094	0.128	0.0047	0.0048
Unknowns	0.195	0.22	0.415	2.11	0.271	0.664	0.45	0.017	0.017
Total Water Phase Organics	0.864	5.01	5.87	4.46	10.3	9.82	8.66	0.32	0.32

^a These compounds are also found in the organic phase at much higher levels.

^b Benzyl alcohol may be due to residue left from cleansing rinse and/or contamination from Bomb C.

^c Analysis of benzyl alcohol in Bomb C showed no water phase and no organics.

^d This methylene chloride scrub is based on a small gas volume sample and is not considered representative. It is, therefore, not included in averages.

^e Shale contains 1.5% moisture.

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Table 36. RUN 80PDU-4 ANALYTICAL RESULTS OF ORGANIC SCRUB (Oil Phase) FOR HYTORT ENVIRONMENTAL ASSESSMENT

	Methylene Chloride Scrub "II" ^b			Methylene Chloride Scrub III ^c	Raw Condensate ^d I & II Combined	Raw Condensate ^d III	Averaged Results	lb/ton ^e Wet Shale	lb/ton Dry Shale
	Bomb A	Bomb B	Total	Bombs A&B					
	10 ⁻⁶ lb/SCF, Dry								
n-Alkane	51	23	75	190	30	17	41	1.49	1.52
Iso-Alkane	19	10	29	60	7.1	4.5	13.5	0.50	0.50
Cyclo-Alkanes	13	5.0	18	36	6.1	5.3	9.8	0.36	0.37
1-n-Alkane	3.5	3.1	7.6	28	1.6	0.82	3.3	0.12	0.13
Alkadienes	2.3	1.5	3.8	4.2	0.58	0.31	1.56	0.057	0.058
Benzenes (BTX)	76	38	114	234	24	13	50	1.85	1.88
Indanes	19	2.8	22	133	16	9.3	15.8	0.58	0.59
Naphthalenes	23	2.2	25	153	19	14	19.3	0.71	0.72
Biphenyls	2.6	0.22	2.8	27	2.5	2.2	2.5	0.092	0.093
Acenaphthene	0.61	0.087	0.70	7.7	0.48	0.42	0.53	0.020	0.020
Fluorene	0.55	0.083	0.64	6.1	0.41	0.42	0.49	0.018	0.018
Phenanthrene	0.10	0.083	0.18	0.63	0.054	0.031	0.088	0.0032	0.0033
Anthracenes	--	--	--	--	0.030	0.016	0.023	0.00084	0.00086
Indenes	2.5	0.42	2.9	16	1.6	1.0	1.83	0.067	0.068
Quinolines	0.66	0.023	0.68	10	0.71	0.47	0.62	0.023	0.023
Indoles	2.7	0.23	2.9	30	2.0	0.92	1.94	0.071	0.072
Carbazoles	0.15	0.052	0.20	--	0.032	0.11	0.11	0.0042	0.0043
Pyrroles	--	--	--	0.55	--	--	--	--	--
Phenols	8.2	0.50	8.7	48	6.0	1.2	5.3	0.195	0.20
Dibenzofuran	0.30	0.03	0.33	3.9	0.28	0.39	0.33	0.012	0.012
Thiophenes	--	--	--	0.68	0.17	--	0.17	0.0062	0.0063
Benzothiophenes	1.5	0.16	1.7	12.7	1.8	1.4	1.63	0.060	0.061
Dibenzothiophenes	--	--	--	--	0.030	0.021	0.026	0.00094	0.00095
Unidentified	276	69	345	840	97	100	181	6.63	6.74
Total Organic Compounds in Oil Phase	504	155	659	1840	217	174	350	12.9	13.0
Total Oil Yield ^a			673	1860	220	176	356	13.1	13.3
Total Water Yield			1730	8810	1990	2420	2047	75.2	76.3

^a Total oil includes both oil and water phase organics.

^b Analysis of benzyl alcohol in Bomb C shows no organics.

^c This methylene chloride scrub set is based on too small a gas volume to be representative. It is, therefore, not included in the averages.

^d Oil phase samples from raw condensates are quite small and are subject, therefore, to errors in total quantity.

^e Feed shale contains 1.5% moisture.

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Table 37. RUN 80PDU-4 GAS PHASE ANALYSES FOR HYTORT ENVIRONMENTAL ASSESSMENT

	Organic Scrub			Raw Condensate			Acid Scrub			Base Scrub			Average	Averaged Results	lb/ton	lb/ton
	I	II	III	I	II	III	I	II	III	I	II	III		10 ⁻⁶ lb/SCF, Dry	Wet Shale (1.5% Moisture)	Dry Shale
CH ₂ Cl ₂ *	8.6	9.9	10.8	0.03	0.03	0.02	0.02	0.09	0.11	1.3	0.19	0.02	0.17*	436*	N.A.*	N.A.*
H ₂ S	0.3	0.4	—	0.5	0.4	—	—	0.4	0.4	—	—	—	0.40	359	13.2	13.4
N ₂	7.0	6.6	8.9	6.9	7.8	7.1	11.2	6.0	6.9	6.8	6.7	7.4	7.1	5250	193	196
CO	1.6	1.7	2.1	1.7	1.7	1.9	1.7	1.4	1.7	1.6	1.8	1.9	1.7	1260	46	47
CO ₂	0.3	0.2	0.3	0.3	0.3	0.3	0.4	0.3	0.3	0.2	0.2	0.1	0.3	350	13	13
H ₂	85.6	86.2	82.8	84.5	84.0	85.1	81.2	86.1	84.8	86.2	85.4	84.5	84.7	4480	164	167
CH ₄	4.4	4.3	5.2	5.3	5.1	4.8	4.5	5.0	5.1	4.4	5.0	5.4	4.9	2070	76	77
C ₂ H ₆	0.45	0.45	0.44	0.42	0.34	0.37	0.48	0.43	0.42	0.40	0.39	0.42	0.42	330	12	12.3
C ₃ H ₈	0.09	0.08	0.08	0.08	0.08	0.09	0.10	0.09	0.09	0.09	0.11	0.07	0.88	1000	36.7	37.3
n-C ₄ H ₁₀	0.03	0.02	0.02	0.04	0.03	0.03	0.05	0.03	0.03	0.04	0.05	0.02	0.03	46	1.7	1.7
i-C ₄ H ₁₀	0.02	—	—	0.01	0.01	0.01	0.01	0.02	0.01	—	0.01	0.01	0.01	15	0.55	0.56
C ₅ H ₁₂	—	—	—	0.02	0.01	0.03	0.03	0.02	0.02	0.02	0.03	0.02	0.02	38	1.4	1.4
C ₆ H ₁₄	—	—	—	—	—	—	—	—	0.02	—	0.02	—	—	—	—	—
C ₇ H ₁₆	—	—	—	—	—	—	—	—	—	—	0.01	—	—	—	—	—
C ₂ H ₄	0.02	0.01	0.03	0.06	0.05	0.06	0.02	—	0.06	0.08	0.12	—	0.05	34	1.4	1.4
C ₃ H ₆	0.07	0.05	0.02	0.04	0.05	0.04	0.04	0.03	—	0.04	—	0.05	0.04	44	1.6	1.6
C ₄ H ₈	0.04	0.03	0.02	0.06	0.06	0.05	0.08	0.07	0.03	0.06	—	0.04	0.05	74	2.8	2.8
C ₅ H ₁₀	—	—	—	—	0.02	0.02	0.03	0.02	0.03	0.02	0.03	0.02	0.02	37	1.4	1.4
C ₆ H ₁₂	—	—	—	—	—	—	0.01	—	0.01	—	0.03	—	—	—	—	—
C ₄ H ₆	—	—	—	—	—	—	—	—	—	—	0.01	—	—	—	—	—
C ₅ H ₈	—	—	—	—	—	—	—	—	—	—	0.01	—	—	—	—	—
C ₅ H ₆	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
C ₂ H ₂	—	—	—	—	—	—	—	0.01	—	—	—	—	—	—	—	—
C ₃ H ₄	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Benzene	—	—	—	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.06	0.01	0.02	41	1.5	1.5
Toluene	—	—	—	—	—	0.01	—	—	—	—	0.01	0.01	0.004	9.7	0.35	0.36
Xylene	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ethyl Benzene	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Total														15440	567	576

* Results from solvent use.

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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 was moved down one deck from its previous location so that the inlet line could slope steeply from the reactor probe position to the top of the condenser on the sampling train.

Three complete sets of samples were taken during PDU Run 80PDU-5, which continued for 6 hours of steady-state operation. Each set consisted of a 3-bomb raw condensate, a 3-bomb acid scrub, a 3-bomb base scrub, a 3-bomb organic scrub, and corresponding exit gas samples. To improve trapping efficiencies, the sampling train was modified so that water-ice could be used to cool the traps. Samples from Run 80PDU-5 are now being analyzed.

Future Work

The immediate objective is to complete an environmental test plan that remains within both budget and time restraints, and yet addresses the major environmental questions concerning larger HYTORT process plants. This test plan is being completed through the combined efforts of IGT and Pace engineers.

Although the sampling train operated without apparent problems during Run 80PDU-5 (one deck lower than previously and line temperatures over 200°F), oil yields obtained with the sampling train were substantially lower than process material balance yields. Examination of the packed sample probe showed substantial amounts of oil trapped in the packing. Consequently, several changes are being made to collect and sample all the oil produced for representative characterization. These changes include 1) removal of the steel wool packing leaving an open sample probe in Stage 2, 2) installation of an electrostatic precipitator after the probe to collect liquid phase oil droplets (mist) and prevent line deposition, 3) addition of heating tapes on sample lines and components to maintain a sufficiently high temperature and prevent any vapor condensation, and 4) installation of a solvent wash prior to the sample train condenser to wash out oils that may deposit on the tubing walls.

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

An estimate was prepared of the cost of synthetic oil produced from Western Eocene (Colorado) oil shale by the HYTORT process. The process description and cost estimate are presented below. The oil produced in the HYTORT reactor is hydrotreated to remove sulfur and nitrogen. During the process the oil is upgraded to 44°API 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 that 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 53 is a flow diagram for the process. Table 38 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.

Table 38. COMPOSITIONS AND FLOW RATES FOR PROCESS STREAMS IN FIGURE 53

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	24.59
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	45,949	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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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°F 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 H_2S and CO_2 that are dissolved in the water streams are recovered via the Chevron process.

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 H_2S and 32% of the CO_2 . 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.⁴ 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 39.

Table 39. 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
bb1/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 40 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 40. 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 41 summarizes steam requirements. These are relatively small, but boiler fuel is 13.7% of hydrotreated product.

Table 41. 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 42. The 75,000 gpm is supplied by a cooling tower operating in the range of 85° to 115°F.

Table 42. 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	5,000
Total Process Cooling Water	73,360
Total Cooling Tower Capacity; Sized for	75,000

Table 43 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 43. 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	877.6 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	177.2
	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 44) 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 45) 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.

Table 44. 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	
<u>Return on Investment During Construction</u>				
(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	48.6	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 45. 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			
	0/100	25/75	50/50	0/100
Debt/Equity Ratio		12		15
Discounted Cash Flow Rate of Return, %		9	9	--
Interest on Debt, %	--			
Raw Shale Ccst, \$/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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Two published estimates of the cost of mining Western oil shale were used.^{5,6} 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 46.

Table 46. 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 47.

Table 47. 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.⁷ 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 44) 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 45, the following basic equation was used:

$$\text{Revenue} = N + 20 \text{ yr-average depreciation} + X + (48/52) X + S/20 \quad (11)$$

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 11 and solving for the net income, Equations 12 through 15 are obtained for calculating net annual income:

Case 1

(12% DCF, 100% Equity)

$$X = 0.52 (\text{REV} - N) - 0.0319I - 0.026S \quad (12)$$

Case 2

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

$$X = 0.52 (\text{REV} - N) - 0.0315I - 0.026S \quad (13)$$

Case 3

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

$$X = 0.52 (\text{REV} - N) - 0.0311I - 0.026S \quad (14)$$

Case 4

(15% DCF, 100% Equity)

$$X = 0.52 (\text{REV} - N) - 0.0333I - 0.026S \quad (15)$$

The 20-year average syncrude price (Table 45) 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 48 gives the equations used in calculating prices for the four different financial cases given in Table 45.

Sensitivities to Changes in Shale Cost and Plant Investment

Figure 54 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 55. 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 48. SUMMARY OF EQUATIONS USED TO CALCULATE SYNCRUDE PRICES
USING DCF METHOD

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

$$P = \frac{N + 0.2317I + 0.1339S + 0.2305W}{G} = \frac{\text{Revenue}}{G} \quad (16)$$

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

$$P = \frac{N + 0.1992I + 0.1339S + 0.2128W}{G} = \frac{\text{Revenue}}{G} \quad (17)$$

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

$$P = \frac{N + 0.1674I + 0.1339S + 0.1949W}{G} = \frac{\text{Revenue}}{G} \quad (18)$$

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

$$P = \frac{N + 0.3006I + 0.1598S + 0.2885W}{G} = \frac{\text{Revenue}}{G} \quad (19)$$

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 45.

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Figure 54. 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 55. 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

A one-dimensional mathematical model to describe moving-bed retorts has been developed. The key assumptions in this development are as follows:

- The system is a counter-current steady-state one-dimensional process.
- Solid shale particles are fed from the top of the bed while hot gas is supplied from the bottom of the bed.
- Four different phases are considered. They are gas phase, solid phase, mist phase, and liquid phase on the solid surface.
- Mist-phase velocity is the same as gas-phase velocity.
- Liquid-phase velocity and temperature are the same as solid-phase velocity and temperature.
- The mist and gas phases may be at different temperatures.
- The system is adiabatic.
- The solid particle volume is constant.
- An average solid particle diameter can represent all shale particles.
- The densities of liquid and mist phases are equal and constant throughout the bed.
- The gas phase obeys the ideal gas law.
- The system pressure variation is negligible compared with the total pressure. No hydrodynamic equations are considered.
- Ash is inert and remains with the particle. Ash is used as a tracer in formulating solid-phase continuity equations.
- The shale particle consists of p species. The gas phase consists of m species. Liquid and mist phases consist of n species.
- The rates of formation of mist and liquid film are mass-transfer limited.
- The rate of mist deposition on the liquid film is first order.
- Multicomponent vapor-liquid equilibrium relationships are known.
- Each solid particle can be described in terms of its average temperature. An effective solid-gas heat transfer coefficient could be made to take into account the heat transfer resistance inside the particles. The Final Report for Hydrogasification of Oil Shale¹ showed that the average solid temperature profile along the bed for 1/2-inch-diameter particles does depend upon the heat transfer resistance inside the particle under the conditions of interest. However, a similar average temperature profile can be obtained by modifying the mathematical heat transfer analysis and applying an effective heat transfer coefficient ($\bar{h} = 15.92$ compared with 20 Btu/hr-ft²-°F) and the isothermal particle assumption.
- The heat of solid-gas phase reaction affects solid temperature only. The condensation and vaporization of liquid oil occurs at the liquid-vapor interface. Mist formation occurs at mist-vapor interface.

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 8 species (Table 49). 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 56 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 thermobalance runs.

In addition to the mass and energy balance equations, the model also includes the rate of mist deposition on the liquid film.

The rate of mist deposition on the liquid film is assumed to be first order and is expressed as follows:

$$\dot{m}_{\text{dep}} = a_l K_d \rho_m \epsilon_m \quad (20)$$

Where a_l is the contact area between the liquid film and the gas phase per unit volume of the bed, K_d is the deposition rate constant resembling a mass transfer coefficient, and ρ_m and ϵ_m are the density and volume fractions of the mist. The deposition rate assumes that mist particles may diffuse into the existing liquid film or be intercepted by the solid shale particles.

The deposition rate constant K_d could be calculated by an effective Sherwood Number ($\text{Sh}_{\text{eff}} = \frac{K_d D_p}{D}$), which combines the diffusional and interceptional deposition of the mist particles.

$$\text{Sh}_{\text{eff}} = \text{Sh}_D + \text{Sh}_R \quad (21)$$

Tardos's correlation for diffusional deposition efficiency⁸ and Lee and Gleseke's correlation for interceptional deposition efficiency⁹ for the filtration or aerosol particles are applied in this model.

Table 49. SOLID, GAS, LIQUID, AND MIST SPECIES USED IN THE
PRELIMINARY KINETIC MODEL

Solid Species

Ash

Gas Species

Inert

Liquid Species

Mist Species

Figure 56. PRELIMINARY SHALE HYDRORETORTING SCHEME

$$Sh_D = 0.997 g (\epsilon_g) Pe^{1/3} \quad (22)$$

$$Sh_R = \frac{Pe}{4} \left[\frac{3}{2} g^3 (\epsilon_g) \frac{r^2}{(1+r)^m} \right] \quad (23)$$

Where $Pe (= \frac{V_D}{D_1})$ is the Peclet number, $g (\epsilon_g)$ is a correction factor that is function of gas volume fraction only, r is the ratio of mist particle diameter and solid shale particle diameter (D_p), m is another interception parameter, and D_1 is a diffusivity parameter.

We are currently assuming the change of mist particle size is only dependent on the rate of mist formation and the change of mist particle number flux is only dependent on the rate of mist deposition.

An empirical correlation for the Nusselt Number (Nu) for flow through a bed of particles¹⁰ is -

$$Nu = 2.0 + 0.6 (Pr^{1/3})(Re^{1/2}) \quad (24)$$

Equation 24 is valid when no mass exchange takes place between particle and gas. Particles producing large mass flows of gas (S_g) tend to reduce this heat transfer coefficient. Smoot and Smith's suggestion is used to calculate the modified Nusselt Number (Nu')¹¹ -

$$\frac{Nu'}{Nu} = \frac{\phi_b}{\exp(\phi_b) - 1} \quad (25)$$

Where blowing parameter ϕ_b is defined as -

$$\phi_b = \frac{C_p D_p^2 S_g}{(12) k_g \epsilon_s} \quad (26)$$

An empirical correlation for the Sherwood Number (Sh) for flow through a bed of particles¹⁰ is used to calculate the mass transfer coefficient.

$$Sh = 2.0 + 0.6 (Sc^{1/3})(Re^{1/2}) \quad (27)$$

Smoot and Smith also suggested a correction factor for the Sherwood Number similar to the Nu Number correlation.

$$\frac{Sh'}{Sh} = \frac{\phi_m}{\exp(\phi_m) - 1} \quad (28)$$

and the blowing parameter for mass transfer, ϕ_m , is defined as -

$$\phi_m = \frac{12D_v \rho_g \epsilon_s S}{D_p^2} \quad (29)$$

In summary, the mathematical model consists of a set of simultaneous nonlinear first-order differential equations that serve to describe the -

- Flow of each species in liquid, solid, gas, and mist phases
- Temperature of each phase
- volume fraction and velocity of each phase.

Currently, the moving-bed retort is described by 42 simultaneous nonlinear first-order differential equations. The 42 variables are summarized in Table 50.

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 42nd-order two-point boundary value problem that must be solved iteratively to match the boundary conditions. The following solution procedure is being used. To begin the solution, the exit gas and mist fluxes, compositions, and temperature are estimated; and, with the known composition and temperature for the inlet solid and liquid stream, the 42 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.¹² If the calculated inlet gas and mist 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 gradient-type procedure which is derived from Stillman's studies.¹³

A preliminary computer program for the model using this solution procedure has been developed and is being tested by applying the preliminary kinetic model and operating conditions. The integration method and the iteration scheme for matching the boundary conditions appear adequate and achieved convergence in a reasonable number of iterations.

Table 50. 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	ρ_g	Gas density
9	ρ_s	Solid density
10	ρ_m	Mist density
11	ρ_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_t	Gas phase mass flux
22	S_t	Solid phase mass flux
23	F_t	Mist phase mass flux
24	L_t	Liquid phase mass flux

Table 50, Cont. SUMMARY OF THE VARIABLES

<u>No.</u>	<u>Variable</u>	<u>Description</u>
25	N_m	Number flux of mist particles
26	G_{H_2}	Mass flux of H_2 in gas phase
27	G_{H_2O}	Mass flux of H_2O in gas phase
28	G_{CO}	Mass flux of CO in gas phase
29	G_{CO_2}	Mass flux of CO_2 in gas phase
30	G_{CH_4}	Mass flux of CH_4 in gas phase
31	G_{CH_2}	Mass flux of CH_2 in gas phase
32	G_{CH_M}	Mass flux of CH_M in gas phase
33	G_{Inert}	Mass flux of inert gas in gas phase
34	F_{CH_M}	Mass flux of CH_M in mist phase
35	L_{CH_M}	Mass flux of CH_M in liquid phase
36	$\xi_{(H_2O)_M}$	Fraction of solid moisture H_2O converted
37	$\xi_{(H_2O)_H}$	Fraction of solid high-temperature H_2O converted
38	ξ_{CO_2}	Fraction of solid CO_2 converted
39	ξ_{CH_x}	Fraction of solid CH_x converted
40	ξ_{CH_M}	Fraction of solid CH_M converted
41	ξ_{CH_y}	Fraction of solid CH_y converted
42	ξ_{Ash}	Fraction of solid ash converted

The preliminary calculations also show the following results:

- Because of very small mist particle size, the heat transfer between the gas and the mist phases is high enough to assume that the mist phase has the same temperature as the gas phase.
- With a preliminary vapor pressure curve for the shale oil of interest, the rate of mist generation was calculated. The calculations showed that the mist phase achieves equilibrium with the oil vapor in the gas phase in less than 0.03 seconds. This result implies that equilibrium conditions between mist and gas phases could be used in the model.

Future Work

Further modifications on the above new assumptions of the preliminary program will be made. Further studies on the liquid formation will also be made. The efficiency and accuracy of the revised program will be tested. Updated kinetic model and operating conditions will be applied in the model.

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