A LABORATORY STUDY OF GREEN RIVER OIL SHALE RETORTING UNDER PRESSURE IN A NITROGEN ATMOSPHERE

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INTRODUCTION

In situ retorting of oil shale is being considered as a possible means of energy recovery. Currently proposed in situ processes would involve creation of adequate permeability in the shale beds followed by combustion or gas injection at high temperature. Pressure will increase with depth of the shale for these operations. Retorting data to provide information relative to in situ processes is meagre for the effects of pressure and retorting atmosphere on shale oil production and quality.

In a previous study, Bae (1) investigated effects of retorting atmosphere (N_2, CO_2, H_2O, NH_3, and H_2), pressure and sweep gas rate on oil shale retorting. The retort was vertical, with upward gas flow, and there was no mechanism for removal of produced oil except with the exit gas. Bae (1) found little effect of interchanging the sweep gas or the sweep gas rate. However, there was a large reduction in oil yield with increased pressure, accompanied by greater gas production and coke deposits. Oil yields dropped dramatically with increased pressure, even when hydrogen was used as the sweep gas, in contradiction to typical oil hydrotreating results.

Some proposed in situ recovery methods would allow segregation of produced oil by drainage from the regions where it originated by pyrolysis. Thus it was decided to study the effects of sweep gas identity, sweep gas rate, gas pressure and heating rate on the retorting process in a downflow vertical oil shale retort. This paper summarizes the important results with nitrogen as the sweep gas. In addition, the results now available with hydrogen as sweep gas are included and discussed. This portion of the study is still in progress.

EXPERIMENTAL WORK

Retorting System and Procedure

A flow diagram of the pressure retorting system is shown in Figure 1. Sweep gas was taken from high pressure cylinders and regulated to a desired system inlet pressure. The nitrogen and hydrogen sweep gases were used as obtained commercially. No detectable impurities were found in either gas by chromatographic analysis. For atmospheric pressure experiments, the cylinder gas was regulated to about 50 psig, and flow rate was controlled with a metering valve, the compressor being bypassed. To obtain the desired flow rate for the higher pressure experiments, the cylinder gas was regulated to appropriate pressure for inlet to the reciprocating diaphragm compressor. The gas pressure in the retort vessel was fixed by a back-pressure regulator for these high pressure experiments. The sweep gas entered the pressure retort at the top, flowed down through the packed shale bed and exited from the retort bottom.

The pressure retort was a stainless steel commercial high-pressure cylindrical reaction vessel of 2-9/16-inch-inside diameter by 32-inch-inside depth. Vessel access was at the upper end with an outside cap-type compression closure on a flat copper gasket. The top plug was provided with three holes: a sweep gas inlet port, a pressure measurement port and a port for a thermocouple well. The inside bottom of the vessel was hemispherical in shape and was provided with an exit line for gas and oil. A stainless steel screen conforming to the vessel bottom was used to support the shale charge.

The retort vessel below the upper head was surrounded by a cylindrical electrical heater composed of five elements along the length of the retort. A thermocouple was placed between each element and the outside retort wall. Current to each element was proportionally controlled to maintain the corresponding thermocouple reading in line with the desired heat-up rate. The actual heat-up rate of the vessel contents would be somewhat different from the desired rate and was monitored by four internal bed thermocouples spaced vertically in a 1/4-inch thermocouple well.

Shale for all runs came from the Anvil Points Facility of ERDA near Rifle, Colorado. It was crushed and screened (minus 3/4-inch and plus 1/4-inch) and mixed to form a single uniform batch from which portions were taken for each run. The shale analyzed 31.1 gallons of oil per ton by modified Fischer assay. Analysis of the raw shale is shown in Table 1.

The retort vessel was loaded with 2240 grams of crushed raw oil shale for each run. Sweep gas flow and retort pressure were adjusted to the desired values and then the heating initiated. The heat-up was continued until a predetermined final bed temperature was indicated on the external controller thermocouples, after which the heaters were controlled to keep the retort temperature at this fixed value for a period of several hours. At the termination of a run the heaters were turned off and the sweep gas allowed to flow until the bed returned to near ambient temperature.

Oil and gas exiting from the retort bottom entered an oil collection system. This collection system consisted of two knock-out traps in series. Oil collected in the first of these traps could be monitored with time. A differential-pressure cell continuously measured the hydrostatic pressure of the oil in this trap. Since most of the produced oil was collected at this point, a good estimate could be made of total oil produced with time. Total oil produced was determined by draining the various collection points and weighing.

Downstream of the oil collection system and backpressure regulator, the exit gases were filtered, and a small portion bled off to a gas chromatograph for analysis. Analysis was accomplished with a three-column system using a thermal conductivity detector.

Experiments and Calculations

Using nitrogen as the sweep gas, the raw shale was retorted at pressures of 0, 750, and 1500 psig (barometric pressure approximately 11 psia). Uniform heating rates of 14, 25, 75, and 125° F per hour were employed at each pressure. At fixed pressure and heat-up rate, a number of sweep gas space velocities were studied, with a maximum of about 120 SCF per hour per square foot of bed cross section.

Hydrogen sweep gas experiments have been performed in the same ranges of pressure, heat-up rate, and space velocity. These experiments are not yet complete.

Actual heat-up rates were determined from the steady-state portion of average bed temperature versus time plots. Actual nitrogen space velocities were calculated from the measured exit gas flow rates and nitrogen content. Hydrogen feed rates were measured with the wet-test meter prior to the heat-up period.

Material balances for each run were made on total mass, ash, carbon and hydrogen. On some of the early nitrogen runs at atmospheric pressure the oil collection system then in use did not trap all of the oil produced. The collection system was subsequently modified to minimize this loss. On these early nitrogen runs the carbon

Table 1. Analyses of raw and retorted shales

		Raw shale	Retorted shales: Atmospheric pressure run[1]	Retorted shales: 1500 psig run[2]
Total weight	g	2240	1861	1911
Organic carbon	wt-pct	13.7	4.4	5.5
Hydrogen	do	2.01	0.22	0.40
Nitrogen	do	0.46	0.29	0.30
Sulfur	do	0.77	0.67	0.61
Water	do	1.2	0.2	0.1
Mineral CO_2	do	16.4	19.0	18.0
Ash	do	66.9	77.6	75.8

[1] Run number 9 of table 2 in Reference (2).
[2] Run number 52 of table 2 in Reference (2).

Table 2. Pressure retort results for two example runs

		Atmospheric pressure run	1500 psig run
Heat-up rate	° F/hr	34.4	21.6
Space velocity	$SCF/hr\text{-}ft^2$	117	116
Max bed temp,	° F	951	921
Organic carbon distribution			
Retorted shale	wt-pct	26.4	33.8
Oil (C_4+)	wt-pct	66.1	56.5
Gas (C_3-)	wt-pct	5.1	9.5
CO_2-free gas (C_3-)	g	29.8	40.8
Oil yield	vol-pct	84.6	77.2
Oil yield (C_4+)	vol-pct	88.7	82.9

Table 3. Oil properties for example runs

	Atmospheric pressure run	1500 psig run
Specific gravity	0.920	0.873
Analysis, weight-percent:		
H_2	11.7	12.1
N_2	2.0	1.9
S	0.8	0.5
C	84.7	84.3
Distillation fractions, weight-percent:		
72-400° F	7	14
400-600	25	34
600-800	34	29
800 +	34	23
Pour point, ° F	86	15
Viscosity, cp:		
at 100° F	24	4
at 130° F	13	3

balances were not good. It was assumed that any initial carbon unaccounted for in the products was due to lost oil. The oil yield figures were adjusted for lost oil. No such corrections have been made for any of the hydrogen experiments.

Two types of oil yields as volume percent recovery of the raw shale modified Fischer assay were calculated. One oil yield was based on liquid product only and the other on liquid product plus all C_4 and heavier hydrocarbons analyzed in the exit gases.

The final distributions of the organic carbon in the raw shale were also calculated. Organic carbon in the raw shale, retorted shale, oil and gas were all independently determined. For presentation, the carbon in the C_4+ gases was added to the carbon in the oil. Any carbon as CO_2 in the exit gases was assumed to have come from mineral decomposition and was not included as organic carbon.

RESULTS

Nitrogen Sweep Gas Experiments

For the nitrogen runs, there was a definite decrease of oil yield with increase of pressure. The average oil yield (including C_4+ gases) for 22 atmospheric pressure runs was 93%, with a standard deviation of 5%. At 750 psig, the average C_4+ oil yield for 21 runs dropped to 82%, with a standard deviation of 8%. At 1500 psig, the average C_4+ oil yield for 18 runs was only 78%, with a standard deviation of 6%. Within the scatter in the data, no dependence of the oil yield on either heat-up rate or sweep gas space velocity could be detected.

Accompanying the decrease in average oil yield with increasing pressure for the nitrogen experiments, there was an increase in both the average amount of gas produced and the average percentage of the initial organic carbon left on the retorted shale as coke. Other effects of increasing pressure included a decrease in oil specific gravity and viscosity, and an increase in amounts of lighter distillation fractions for the oil.

Detailed results of the nitrogen sweep gas experiments are available in another source (2). Results for only two example runs, one at 0 psig and one at 1500 psig, are included here for illustrative purposes. These are runs 9 and 52 from Table 2 of Reference (2). Retorted shale properties are included in Table 1. Retorting conditions, distribution of organic carbon in the products, gas production and oil yields are given in Table 2. Oil properties are shown in Table 3. Increased coking with increase of pressure is shown by the increase in organic carbon on the retorted shale for the 1500 psig experiment when compared with the 0 psig run (See Tables 1 and 2). This is also confirmed by the increase in gas produced in the high pressure run. The oil properties in Table 3 indicate that the oil from the high pressure run was lighter with lower pour point and viscosity than the oil from the low pressure run. No appreciable differences could be detected in the C/H ratio for oils produced at the various pressures. The increased gas production for the 1500 psig run over the 0 psig run was primarily due to an increase in the light normal alkanes.

Hydrogen Sweep Gas Experiments

The preliminary data for experiments employing hydrogen as sweep gas indicate an increase in oil yield with increase of pressure and also with increase of sweep gas space velocity. Oil yields (including C_4+ gases) of 100 to 125 volume percent of the raw shale modified Fischer assay have been consistantly obtained at pressures of 750 to 1500 psig and hydrogen space velocities in excess of 50 SCF per hour per square foot of bed. The effect of heating rate variations at constant pressure and space velocity does not seem to be pronounced. There appears to be little difference in oil yield between nitrogen and hydrogen sweep gas for runs at atmospheric pressure

Comparison With Previous Work

The present nitrogen results are compared with those of Bae (1) in Figure 2. Oil yields from the present study are in reasonable agreement with the previous work for constant gas residence times in the retort. In no cases did we observe the dramatic reduction in oil yields found in the previous work for constant gas feed rate. In the previous study (1), oil yields were found to decrease with increase of pressure when hydrogen was used as the sweep gas. The present results indicate just the opposite trend, that is, an increase in oil production with increase of hydrogen pressure.

The discrepancies between the present work and the former study are probably due to differences in the way the retorting was conducted. In the previous work the sweep gas entered below the shale bed and exited from near the top of the bed. There was no provision for oil produced at the lower temperatures to be removed from the retort until it was volatilized and carried out with the sweep gas. On the average, the oil was subjected to higher temperatures and a longer retort residence time than in the present work. With increased pressure this effect would be even more pronounced, accounting for the large drops in oil yield noted in the former work.

Mathematical Model

Experimental oil shale pyrolysis data of Hubbard and Robinson (3) were used to develop a simple kinetic model for oil plus gas production versus time. This model will be described in more detail elsewhere (4). Since the Hubbard and Robinson work was with a raw shale of different Fischer assay, the model was adapted to give ultimate amounts of C_4+ oil in line with the average nitrogen sweep gas results of the present study.

The basic model is embodied in the equation

$$\frac{dx}{dt} = K_1 \, x \left(1 - \frac{x}{K_2 F}\right) \qquad 1)$$

where x is the weight percent of the initial available oil in the raw shale (by modified Fischer assay) which has been produced as C_4+ oil and t is the time. The parameters K_1, K_2 and F are given by

$$K_1 = 0 \qquad \text{for } T < 700° \text{ F}$$

$$K_1 = \exp(.03476T - 29.5994) \qquad \text{for } 700° \text{ F} < T < 825° \text{ F} \qquad 2)$$

$$K_1 = \exp(.00645T - 6.0633) \qquad \text{for } T > 825° \text{ F}$$

$$K_2 = 0.0006911T + 0.1766 \qquad 3)$$

$$F = 1 + 0.004647P^{\frac{1}{2}} \qquad 4)$$

where T is the temperature in ° F and P is the pressure in psig. The heating rate (h) is incorporated by letting the temperature at any time be given by

$$T = T_o + ht \qquad 5)$$

where T_o is the initial bed temperature.

In a kinetic expression of the form of Equation 1, some mechanism is necessary to initiate a non-zero rate. In this work, this was achieved by setting x = 0.125 at T = 700° F.

The above model has been utilized to predict C_4+ oil yield as a function of time for the nitrogen sweep gas experiments. Good agreement was found between model and experimental oil yield - time curves.

REFERENCES

1. Bae, J. H., "Some Effects of Pressure on Oil-Shale Retorting," Soc. Petrol. Eng. J., September 1969, pp. 287-292.

2. Wise, R. L., Miller, R. C., and George, J. H., "A Laboratory Study of Green River Oil Shale Retorting Under Pressure in a Nitrogen Atmosphere," BuMines LERC TPR 76/1, 1976, 23 pp.

3. Hubbard, A. B., and Robinson, W. E., "A Thermal Decomposition Study of Colorado Oil Shale," BuMines RI 4744, 1950, 24 pp.

4. George, J. H., and Finucane, D., "A Simplified Model for Oil Shale Kinetics," In preparation.

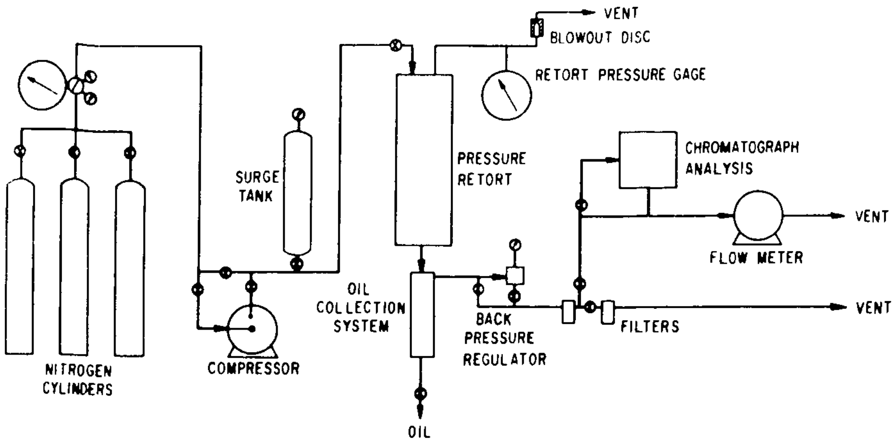

FIGURE 1.- SCHEMATIC DIAGRAM OF PRESSURE RETORT SYSTEM.

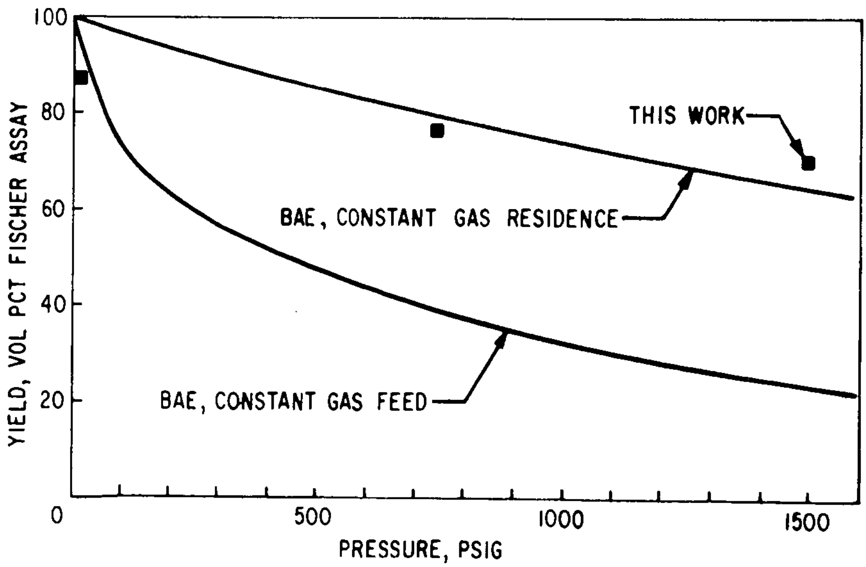

FIGURE 2.-OIL YIELD VERSUS PRESSURE NITROGEN SWEEP GAS.