OIL DEGRADATION DURING OIL SHALE RETORTING*

J. H. Raley and R. L. Braun

Lawrence Livermore Laboratory, University of California
Livermore, California 94550

INTRODUCTION

The Lawrence Livermore Laboratory is doing retorting research to support the development of modified in situ processes for production of oil from oil shale such as that described by Lewis and Rothman (1). Mathematical modeling studies (2,3) of in situ retorting indicate that the heat-up time for a shale particle can range from hours (combustion retorting) to months (hot gas retorting). A recent study at this Laboratory (4) reported the oil yields from powdered Colorado shale subjected to a wide variety of thermal histories. This study demonstrated that the oil yield from powdered shale is primarily determined by the amount of decomposition of the liberated oil. The present work supplies further data in support of this conclusion. Also, maximum rates for the thermal decomposition of shale oil are estimated and compared with pyrolysis rates for petroleum fractions.

EXPERIMENTAL

Detailed descriptions of the 92 ℓ/tonne (22 gal/ton) shale sample and of the retorting apparatus and method have been given previously (4). In the retorting procedure the temperature of the powdered (<800 μm; ca. 95 g) shale was raised at 12°C/min (Fischer assay schedule) from ambient to the selected level and held constant for a period ranging from 2 to 800 hr (33 days). At the end of the isothermal period the temperature was increased, again at 12°C/min, to 500°C and finally held there for 40 min. The weight fraction of shale converted to oil (condensable at 0°C) by this procedure was compared with the assay value obtained by raising the temperature of an identical sample from ambient to 500°C without interruption, followed by the final 40 min period. This method, then, gives a direct measure of the effect on yield of the isothermal holding period. Isothermal temperatures covered the range from 150 to 450°C. In one set of experiments gas evolution from the retort at 65 to 100 kPa (2/3 to 1 atm) resulted only from that generated by the shale (autogenous atmosphere). In the other set, a flow of nitrogen at 1 atm was passed through the vessel during the entire experiment.

RESULTS

The effect on oil yield of isothermal holding periods of 8, 80, and 800 hr at 150 to 450°C is shown in Figure 1 for the autogenous atmosphere experiments. Yields relative to assay pass through minima of 81 to 92% at 350 to 400°C, depending on the length of the isothermal holding period. In Figure 2 the loss in oil yield is plotted against the amount of oil collected during the isothermal period, expressed as a fraction of the total oil collected over the entire experiment. The direct relationship shown between yield loss and oil produced during the isothermal holding period was observed for holding temperatures of 300 to 375°C. This relationship could not be followed to higher holding temperatures because of difficulty in distinguishing the oil produced isothermally from the large amount formed before the holding temperature was attained.

*This work was performed under the auspices of the U.S. Energy Research and Development Administration under contract No. W-7405-Eng-48.

Addition of nitrogen flow through the retort reduces or eliminates yield loss. Figure 3 illustrates this effect in terms of nitrogen space velocity or sweep rate, i.e., retort vapor volumes per min for the given holding temperatures and periods. The slopes of these curves over the 0 to 5 sweep rate range (Δ yield/Δ sweep rate) are also directly related to the quantities of oil produced during the isothermal periods in the non-sweep experiments (Figure 4).

Both observations support the conclusion that yield loss from powdered shale is due to degradation of oil after its release from the shale and while at high temperature in the retort. Interruption of a rapid rise in shale temperature by an isothermal period reduces the rate of oil and gas formation. Autogenous driving forces to remove oil from the retort — gas evolution and oil vaporization — are reduced correspondingly, residence times lengthened and oil degradation increased. Therefore, a direct relationship between yield loss and amount of oil formed during the isothermal period is the expected result. Similarly, the extent of reduction in yield loss by the sweep gas should be related directly to the quantity of extra-particle oil that otherwise would have a long residence time in the retort for degradation to proceed. As noted earlier (4), this degradation produces mainly a carbonaceous residue ("char") plus some gas.

OIL DEGRADATION RATE

The rates of oil degradation at 350 and 375°C can be estimated from the yields under autogenous atmosphere, the amounts of oil collected during the isothermal holding times, and the volatility of the oil produced from the assay heat-up schedule.

The rate of isothermal oil formation (R_1) is given by

$$R_1 = k_1 x_o e^{-k_1 t}, \qquad 1)$$

where k_1 is the first order rate constant for oil formation and x_o is the mass of oil formed during the isothermal period, t_f. To calculate the rate of oil degradation (R_2), two regimes can be distinguished conceptually. In the first regime, R_1 is rapid and R_2 will be essentially constant, given by

$$R_2 = k_2 y_o, \qquad 2)$$

where k_2 is the first order rate constant for oil degradation and y_o is the constant mass of oil in the retort. In the second regime, which begins when R_1 has decreased to the value of $k_2 y_o$, R_2 can be approximated by R_1. That is,

$$R_2 = k_1 x_o e^{-k_1 t}. \qquad 3)$$

Let t_e be the time at which $R_1 = k_2 y_o$. Then from Equation 3, t_e can be expressed as

$$t_e = \frac{1}{k_1} \ln\left(\frac{k_1 x_o}{k_2 y_o}\right) . \qquad 4)$$

The fraction of oil degraded during t_f is then given by

$$\alpha = \frac{1}{x_o} \int_o^{t_f} R_2 dt = \int_o^{t_e} \frac{k_2 y_o}{x_o} dt + \int_{t_e}^{t_f} k_1 e^{-k_1 t} dt. \qquad 5)$$

This approximation neglects the small amount of oil in the retort which is degraded after oil formation becomes imperceptible. Integration of Equation 5 gives

$$\alpha = \frac{k_2 y_o t_e}{x_o} + e^{-k_1 t_e} - e^{-k_1 t_f} . \qquad 6)$$

With known values for α, k_1, t_f, x_o, and y_o (derived in the Appendix), Equations 4 and 6 can be solved for t_e and k_2 by a series of approximations. The results are summarized in Table 1. It should be noted that estimation of y_o from simulated distillation analysis involves the assumption that oil exists in the retort only as vapor and spray, not as a discrete liquid phase. This assumption appears justified under conditions of rapid oil and gas generation, as is the case of a Fischer assay heating schedule (to 500°C in 1 hr). Under these conditions, yield from this apparatus that permits downflow escape of liquid oil is identical with that from a Fischer Assay apparatus, which allows only upflow escape (4). If a discrete liquid phase exists and flows from the retort more slowly than the spray, the estimated value of y_o is low and that of k_2 correspondingly high.

Table 1: Values for α, k_1, t_f, t_e, x_o, y_o, and k_2

	350°C		375°C
α	0.180	0.190	0.162
$k_1 (10^{-5} s^{-1})$ (5)	0.72	0.76	4.0
$t_f (10^5 s)$	28.8	28.8	2.88
$t_e (10^5 s)$	4.35	4.03	0.818
x_o (g)	7.5936	8.0426	7.6580
y_o (g)	0.0560	0.0560	0.0532
$k_2 (10^{-5} s^{-1})$	4.3	5.1	22.0

Using the mean value of k_2 at 350°C, the rate constant can be expressed as:

$$k_2 = 1.00 \times 10^{13} \, e^{-49,400/RT} . \qquad 7)$$

As shown in Table 2, the values for k_2 at 350 and 375°C are substantially higher than the rate constants for pyrolysis of kerogen to oil and for thermal cracking of petroleum fractions. As noted above, the method used to estimate k_2 gives maximum values. On the other hand, the high olefin and heteroatom contents of shale oil (8) would be expected to impart thermal instability, especially with respect to condensation or polymerization processes. Such reactions of shale oil have been proposed previously (9) and have been observed in a closed vessel (10).

Table 2: Pyrolysis Rate Constants

	k_2 at 350°C (10^{-5} s^{-1})	k_2 at 375°C (10^{-5} s^{-1})	Activation energy (kcal/mole)
Shale Oil → Gas + Char	4.7	22.0	49.4
Kerogen → Oil (5) + Gas + Char	0.74	4.0	54.0
Asphalt (6)	1.6	7.6	49.7
California Petroleum (7)			
766 $\bar{M}$ a),b)	0.25	1.6	59.2
388 $\bar{M}$ a),c)	0.28	1.7	57.5

a) $\bar{M}$ represents the average molecular weight of the distilled fraction. The value of $\bar{M}$ for assay shale oil in our experiments is about 330 (see Appendix).

b) Conversion to lower boiling products only.

c) Conversion to lower and higher boiling products.

CONCLUSIONS

Further evidence is supplied to show that the oil yield from retorting powdered Colorado oil shale is primarily determined by the extent of decomposition of the liberated oil. Yield losses occasioned by interrupting a rapid shale heating schedule with isothermal holding periods are directly related to the amounts of oil produced during the holding periods. These amounts are also related directly to the inert gas flow rates required to raise the yields to the assay value. The estimated maximum first order rate constant for thermal decomposition of the oil to char and gas is given by: $k_2 = 1.00 \times 10^{13} e^{-49,400/RT}$. Oil from Colorado shale apparently is more thermally unstable than virgin petroleum fractions. Additional experimental data are needed on the rate of shale oil thermal degradation.

ACKNOWLEDGMENTS

We are indebted to G. J. Koskinas, R. J. Opila, and N. D. Stout for supplying unpublished retorting data and to J. E. Clarkson for the simulated distillation results. We also thank Shell Development Company for permission to use unpublished data on pyrolysis of California petroleum fractions.

APPENDIX

Values of α, k_1, t_f, x_o and y_o for Table 1

The values of α and t_f, the latter corresponding to 800 or 80 hr, were reported earlier (4).

With the assumption that all oil degradation occurs during the isothermal period, t_f, and since no oil was collected in the receiver after t_f,

$$x_o = x_A - x_i$$

where x_A is the mass of oil obtained by assay and x_i is the mass of oil collected before t_f. Similarly,

$$x_f = x_t - x_i$$

where x_f is the mass of oil collected during t_f and x_t is the mass of oil collected during the entire experiment. The mass of oil degraded, x_d, then is:

$$x_d = x_o - x_f$$

and

$$\alpha = \frac{x_d}{x_o} \quad .$$

The experimental values of these quantities are (4,11) given in Table 3.

Table 3: Values of α and Oil Masses Collected

	350°C		375°C
Raw Shale Charge (g)	91.8983	96.7522	93.1773
Assay Oil (wt%)	8.407	8.407	8.407
x_A (g)	7.7259	8.1340	7.8334
x_i (g)	0.1323	0.0914	0.1754
x_o (g)	7.5936	8.0426	7.6580
x_t (g)	6.3561	6.6100	6.5942
x_f (g)	6.2238	6.5186	6.4188
α	0.180	0.190	0.162

As noted in the text, the mass of free oil in the retort, y_o, is assumed to consist only of vapor and spray. The fraction of oil vaporized can be estimated from the equilibrium flash vaporization (EFV) curve which, in turn, can be related to the molecular weight distribution. The EFV curve was constructed (12) from the gas chromatographic simulated distillation data (13) for oil produced under assay conditions (Figure 5). The molecular weight scale in Figure 5 is based on the relationship between molecular weight and boiling point of n-paraffins corrected

for the lower volatility of unsaturated components. The correction factor was taken from the ratio of the average molecular weight of the 388 $\bar{M}$ fraction of California petroleum to 421, the average molecular weight of the saturates contained therein (7).

The mass of free oil in the retort is

$$y_o = m_v + m_\ell,$$

where m_v is the mass of oil vapor in the retort and m_ℓ is the mass of oil liquid as spray in the retort. The quantities m_v and m_ℓ are calculated by the following relationships. First, the number of moles of oil vapor in the retort is

$$n_v = \frac{m_v}{M_v} ,$$

where M_v is the molecular weight taken from the EFV curve (Figure 5) at the appropriate temperature. Second, the number of moles of co-produced non-condensable gas in the retort is

$$n_g = \frac{0.22(m_v + m_\ell)}{21} .$$

This equation is based on the experimentally determined ratio of the mass production rate of non-condensable gas to that of oil, which is 0.22, and the gas molecular weight of 21 (11). Third, the total number of moles of oil vapor and non-condensable gas in the retort is calculated from the ideal gas law for the measured retort free volume of 35.1 cm^3:

$$n_v + n_g = \frac{35.1}{(22400)\left(\frac{T}{273}\right)} .$$

Finally, the fraction of oil in the vapor state, taken from the EFV curve, is

$$f_v = \frac{m_v}{m_v + m_\ell} .$$

Combining the above equations yields the desired expression for the mass of free oil in the retort:

$$y_o = \frac{(n_v + n_g)}{\left(\frac{f_v}{M_v} + \frac{0.22}{21}\right)} .$$

Values of y_o calculated from these relationships are given in Table 1.

REFERENCES

1. Lewis, A. E. and Rothman, A. J., Rubble In Situ Extraction (RISE): A Proposed Program for Recovery of Oil from Oil Shale, Lawrence Livermore Laboratory, Rept. UCRL-51768 (1975).

2. Braun, R. L. and Rothman, A. J., "Research and Development on Rubble In-Situ Extraction of Oil Shale (RISE) at Lawrence Livermore Laboratory", Colorado School of Mines Quarterly, 70, 159 (1975).

3. Johnson, W. F., Walton, D. K., Keller, H. H., and Couch, E. J., "In-Situ Retorting of Oil Shale Rubble: A Model of Heat Transfer and Product Formation in Oil Shale Particles", Colorado School of Mines Quarterly, 70, 237 (1975).

4. Stout, N. D., Koskinas, G. J., Raley, J. H., Santor, S. D., Opila, R. J., and Rothman, A. J., "Pyrolysis of Oil Shale: The Effects of Thermal History on Oil Yield," Lawrence Livermore Laboratory, Rept. UCRL-77831 (1976); Colorado School of Mines Quarterly (in press).

5. Campbell, J. H., Koskinas, G. H., and Stout, N. D., "The Kinetics of the Decomposition of Colorado Oil Shale, Part I, Oil Generation", Lawrence Livermore Laboratory Rept., in preparation.

6. Nelson, W. L., Petroleum Refinery Engineering, (McGraw-Hill, New York, 1958), 4th ed., p. 651.

7. Data supplied by Shell Development Company from work of R. D. Mullineaux, J.H. Raley and D.H. Rowe.

8. Dinneen, G. U., Ball, J. S., and Thorne, H. M., "Composition of Crude Shale Oils", Ind. Eng. Chem., 44, 2632 (1952).

9. Schnackenberg, W. D., and Prien, C. H., "Effect of Solvent Properties in Thermal Decomposition of Oil Shale Kerogen," Ind. Eng. Chem., 45, 313 (1953).

10. Hill, G. R., Johnson, D. J., Miller, L., and Dougan, J. L., "Direct Production of a Low Pour Point High Gravity Shale Oil", Ind. Eng. Chem. Product. Res. and Dev., 6, 52 (1967).

11. Data supplied by G. J. Koskinas, R. J. Opila, and N. D. Stout at this Laboratory.

12. Ref. 6, p. 113.

13. (a) ASTM D 2887-73, "Boiling Range Distribution of Petroleum Fractions by Gas Chromatography",
    (b) ASTM D-2 Research Division 4, Study Group 2, "Proposed Method of Test for Boiling Range Distribution of Crude Petroleum by Gas Chromatography."

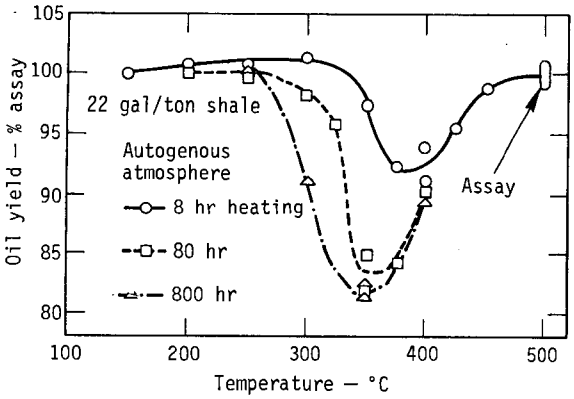

Figure 1. Effect of Isothermal Holding Periods on Oil Yields.

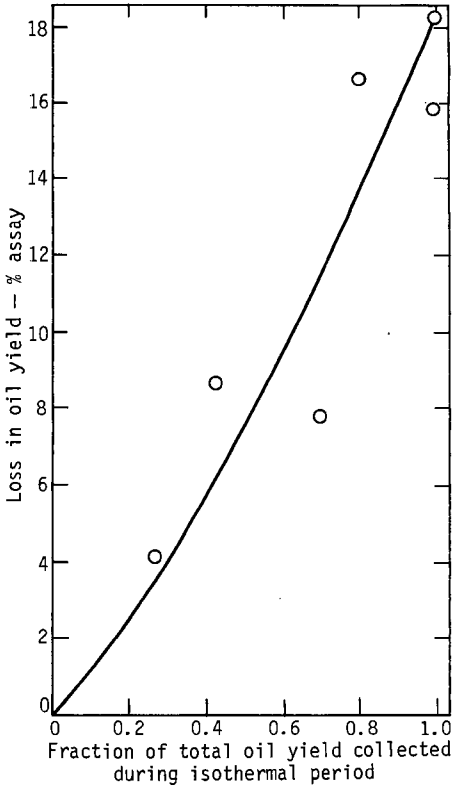

Figure 2. Correlation between Yield Loss and Oil Production During Isothermal Period.

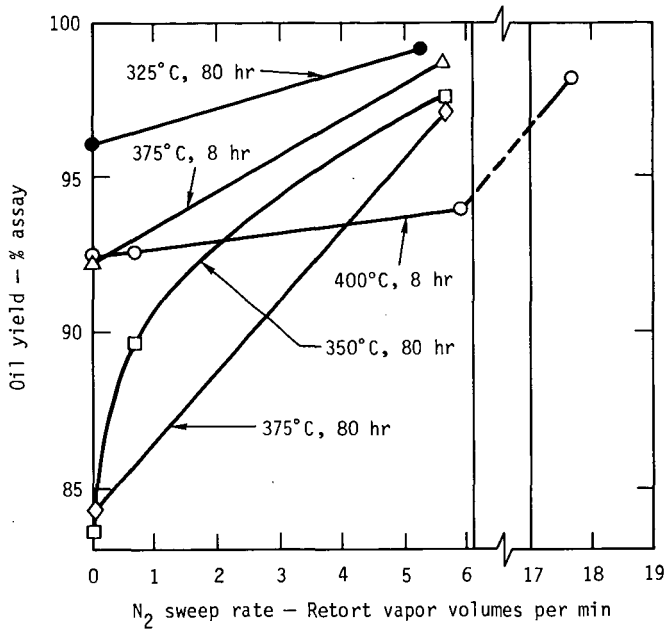

Figure 3. Effect of Nitrogen Sweep Rate on Oil Yield (Note abscissa scale change).

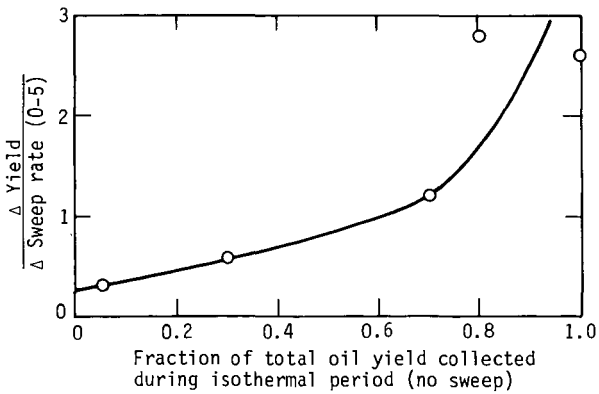

Figure 4. Correlation between Effect of Sweep Rate and Oil Production During Isothermal Period.

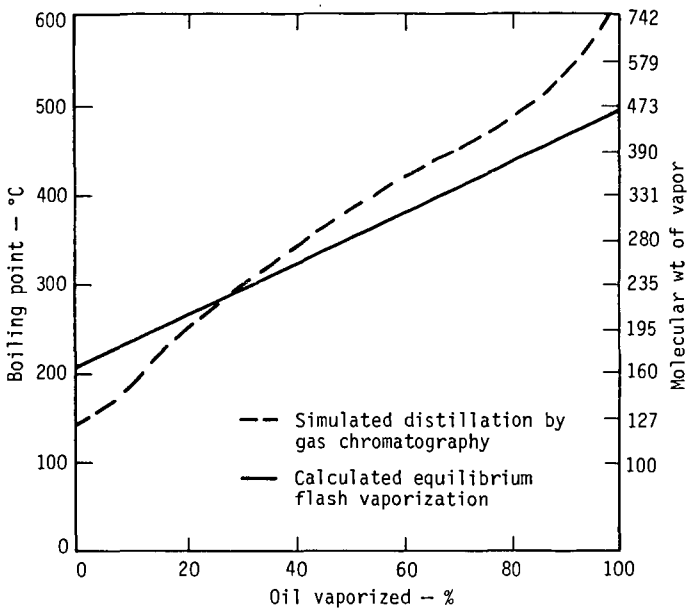

Figure 5. Oil Vaporization.

NOTICE

"This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research & Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights."