PYROLYSIS KINETICS FOR WESTERN AND EASTERN OIL SHALE

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INTRODUCTION

Experiments over the past several years at Lawrence Livermore National Laboratory (LLNL) and the Kentucky Institute of Metals and Mining Research (IMMR) have fairly well defined the organic pyrolysis reactions expected during processing of both Western and Eastern oil shales. Information has been obtained on both the rates of product formation and the yields expected over a range of processing conditions. This paper consists of a brief review of these results, a comparison of the behavior of Eastern and Western oil shale, and discussion of the implications for process design and selection.

METHODS FOR KINETIC EXPERIMENTS

Before discussing the oil shale pyrolysis results, it is appropriate to review a few results from elementary kinetics. There are two situations where kinetic parameters can be conveniently derived: (1) isothermal reactions, and (2) reactions during linear heating (constant heating rate). The equations for product formation by a single first-order reaction are given in Figure 1 for both cases. For multiple, parallel first-order reactions, the isothermal reaction will be described by a sum of exponentials while the linear heating experiments will result in a sum of reaction peaks. In the isothermal case, the logarithm of product formation vs time will no longer be linear for multiple reactions.

There are several circumstances in which linear-heating experiments are preferable to isothermal experiments. For large samples, it is difficult to do a true isothermal pyrolysis experiment because a significant degree of pyrolysis occurs before the sample reaches constant reaction temperature. In this case, a good kinetic analysis would have to include numerical integration over the time-temperature history. A linear heating experiment avoids this problem unless the sample is so large that the sample surface is significantly hotter than the center. In cases where isothermal experiments are desirable, we have dropped a small, powdered sample into a preheated fluidized bed of sand to avoid these problems. In many oil-shale processing schemes, the pyrolysis occurs during

Figure 1. Equations for kinetic analysis of first-order reactions, where \( V_0 \) is the total quantity of evolved product.
a time-temperature history' closely approximated by linear heating. Kinetics determined from experiments having a similar thermal history would be desirable. Linear-heating experiments can also unravel additional features of a complex composite of reactions. In these experiments, the given reaction occurs over a range of temperatures and the temperature of maximum reaction rate, $T_m$, is often used as a characteristic temperature. The reaction products are not affected by the final temperature as long as it is high enough to complete the reaction and the rate of product removal is fast compared to the heating rate $H_r$.

**KINETICS OF OIL AND GAS GENERATION**

The tradeoffs between time and temperature for oil and gas evolution are described by global kinetics. For heating rates less than 4°C/min, as encountered in in-situ processing, Campbell et al. found that oil evolution is adequately described by the first-order evolution profile shown in Figure 1. His results were later confirmed by Shin and Sohn. As the heating rate is increased from 0.03 to 6°C/min, the temperature of the maximum rate ($T_m$) of oil generation increases from 380 to 455°C. For comparison, the calculated $T_m$ for 12°C/min (Fischer Assay) is about 470°C.

When the heating time to the final temperature is less than 0.1 $k^*$ (e.g., 32 s at 450°C or 0.6 s at 550°C), where $k$ is the first-order rate constant, a negligibly small amount of reaction occurs during heatup. The reaction is then properly characterized as an isothermal reaction at the final temperature. Total hydrocarbon evolution kinetics have been obtained for Green River (Colorado), Sunbury, and Ohio (Cleveland member) shales at temperatures from 468 to 555°C. A comparison of the rate data at 468°C is shown in Figure 2. All three samples show a deviation from first-order (log-linear) behavior. The hydrocarbon generation from the Eastern shales is roughly twice as fast as that for the Colorado shale. A more complete kinetic analysis has been given by Richardson et al. Additional results indicating a faster hydrocarbon generation rate for Eastern shale heated at 20°C/min have been reported by Herrell and Arnold.

A more general kinetic scheme for oil and gas evolution is given in Figure 3. Oil, gases and a carbonaceous residue are formed during the primary pyrolysis of the raw-shale organic material. Upon close examination, it is evident that the primary decomposition reaction is not a simple first-order reaction. For Colorado oil shale heated at 2°C/min, the $T_m$'s for different gas species vary from about 400°C for CO$_2$ to about 465°C for H$_2$. The light hydrocarbon $T_m$ of 455°C is about 20°C higher than $T_m$ for total oil. This corresponds to a rate constant that is approximately three times slower for hydrocarbon gases than oil. For

- Oil generation
  \[(\text{Kerogen} \rightarrow \text{Bitumen}) + \text{CH}_4 + \text{H}_2 + \text{CO}_2 + \text{Char}\]

- Char pyrolysis
  \[\text{Char} \rightarrow \text{Char} + \text{H}_2 + \text{CH}_4\]
  \[\text{Char} \rightarrow \text{Char} + \text{H}_2\]

A determination of gas evolution kinetics during
fluidized-bed pyrolysis is currently in progress.16 Typical preliminary data at 510°C are shown in Figure 4. These data agree with the conclusion from the linear-heating experiments that different gases have different generation rates.

![Figure 4](image)

Figure 4. Preliminary species-selective kinetic data for fluidized-bed pyrolysis of Western oil shale (Anvil Points, Mahogany zone, -0.5 +0.25 mm) at 510°C. The evolution kinetics for CjHg and C2H4 are very close and are indicated by CjH*. Dispersion occurs during the 30-second transit between the fluidized bed and mass spectrometer (i.e., 0-90% falltime is 0.15 seconds), but the faster generation of CO2 and the slower generation of H2 compared to the hydrocarbons is unmistakable.

At temperatures greater than 500°C, H2 and CH4 evolution continues due to pyrolysis of the carbonaceous residue. Campbell et al.5 found it necessary to use a distribution of activation energies to fit both the width of the evolution profile and the dependence of the Tm on heating rate. A comparison of experimental and calculated CH4 and H2 evolution rates is shown in Figure 5. The generality of these kinetics for Colorado shale has been recently demonstrated by Huss and Burnham.17

![Figure 5](image)

Figure 5. Comparison of experimental and calculated rates of H2 and CH4 evolution at a heating rate of 2°C/min. The kinetics of the second and third peaks are described by an equation that is based on a distribution of activation energies and is more complicated than given in Figure 1.

EFFECT OF PYROLYSIS CONDITIONS ON OIL YIELD

It has long been recognized that the fraction of organic carbon converted to oil depends on the H/C ratio of the oil shale or coal. The distribution of organic carbon in Western shale is 72% in oil (C5+), 6% in gas (C4-) and 22% in char.7 The corresponding distribution for Eastern oil shale is about 36% in oil, 57% in char and 7% in gas.18

Some of the first pyrolysis experiments conducted at LLNL were designed to characterize the changes in oil yield expected during the slow heating rates typical of in-situ processing of Green River (Western) oil shale.2 Similar experiments were later conducted at IMMR on Sunbury and Ohio shales from Kentucky. The results of these experiments are summarized in Figure 8. At the slow heating rates characteristic of Occidental modified-in-situ retorts, 15% to 20% of the Fischer assay oil from Western shale is coked (i.e., converted into carbonaceous residue, CH4 and H2).19 In contrast, 30 to 40% of the oil from Eastern (Sunbury and Cleveland) oil shale is coked at the same heating rates.

![Figure 8](image)
The oil coking has been attributed to reactions that occur when the oil has a relatively long liquid-phase residence time prior to its removal from the particle by evaporation (Figure 9). It is, therefore, quite reasonable that a gas sweep or reduced pressure can diminish the oil coking at slow heating rates. Figure 8 also shows that a gas sweep can increase oil yield by about 8% of the assay value at slow heating rates where oil coking would otherwise occur. Moreover, vacuum retorting resulted in 13% more oil than from Fischer assay for the Ohio oil shale. Finally, a steam sweep appears to have a chemical as well as physical effect because it increases oil yield from fine particles by slightly more than a corresponding sweep with argon.

Even greater oil yields can be obtained by combining the effects of gas sweep and rapid heating in a fluidized bed. For 0.21 to 0.43 mm particles of Ohio shale, Richardson obtained an oil yield of 198% of Fischer assay at pyrolysis temperature of 514°C. Similarly, Margolis has obtained a yield of 172% of Fischer assay for a Sunbury shale pyrolyzed at 580°C. These yields are comparable to yields obtained using a hydrogen pressure of 35 atm during pyrolysis. The corresponding effect for Western shale is much smaller, i.e., the increase in oil yield is less than 10% for fluidized-bed pyrolysis.

It should be noted that the additional oil does not have the same composition as the Fischer assay oil. A comparison of gas chromatograms
indicates that much of the additional oil gives a large, unresolved hump in the C20 to C30 range of the chromatogram. This material is probably quite hydrogen deficient and susceptible to coking. However, it would seem to be easier to nd from the oil after formation than to re¬
to the whole rock in high pressure hydrogen.

While it is important to quickly reach pyrolysis temperatures so the oil does not have a long residence time within the particle, it is equally important not to expose the shale oil to too high a temperature. While low temperature pyrolysis enhances liquid-phase reactions that convert oil to coke, high temperatures enhance cracking reactions that convert oil vapor to low-molecular-weight gases. Cracking of oil vapor is probably responsible for a decrease in yield from 172% to 139% of Fischer assay of a Sunbury shale when the fluidized-bed temperature was increased from 530 to 715°C.

The schematic oil degradation mechanism shown in Figure 9 summarizes the principal features of the oil degradation reactions discussed above. At low temperatures, oil lingers in the liquid state after generation and undergoes competing coking and vaporization reactions. Rapid heating rates, inert gas sweeps, or reduced pyrolysis pressures minimize oil coking. However, the generated oil will undergo thermal cracking if it is exposed to excessively high temperatures.

Figure 9. A simplified kinetic scheme for oil degradation during retorting of oil shale. At temperatures lower than optimum, oil yield is decreased by liquid-phase coking reactions. At temperatures higher than optimum, oil yield is decreased due to cracking of oil vapor.

**Summary**

There are numerous differences in the pyrolysis characteristics of Eastern and Western oil shale. The rate of hydrocarbon generation is about twice as fast for Eastern shale. For slow heating rates, the distribution of organic carbon and gas evolution characteristics of Eastern shale is intermediate to that of coal and Western shale. The effect of heating rate on oil yield is much greater for Eastern shale than for Western shale. While slow heating rates typical of in-situ processes would result in about a 40% yield loss due to oil coking, rapid heating rates obtainable in fluidized beds or possibly other solids-mixing devices offer the possibility of yields near 200% of Fischer assay for Eastern shale. Finally, it is important not to expose the generated oil to excessively high temperatures, or oil yield loss will occur due to cracking of oil vapor.

**References**


