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FLUIDIZED-BED PYROLYSIS OF OIL SHALE:
OIL YIELD, COMPOSITION, AND KINETICS

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Abstract

A quartz isothermal fluidized-bed reactor has been used to measure kinetics and oil properties relevant to surface processing of oil shale. The rate of oil formation has been described with two sequential first-order rate equations characterized by two rate constants, $k_1 = 2.18 \times 10^{10} \exp(-41.6 \text{ kcal/RT}) \text{ s}^{-1}$ and $k_2 = 4.4 \times 10^6 \exp(-29.7 \text{ kcal/RT}) \text{ s}^{-1}$. These rate constants together with an expression for the appropriate weighting coefficients describe approximately 97⁺ percent of the total oil produced. A description is given of the results of different attempts to mathematically describe the data in a manner suitable for modeling applications. Preliminary results are also presented for species-selective kinetics of methane, ethene, ethane and hydrogen, where the latter is clearly distinguished as the product of a distinct intermediate. Oil yields from Western oil shale are approximately 100 percent Fischer assay. Oil composition is as expected based on previous work and the higher heating rates (temperatures) inherent in fluidized-bed pyrolysis. Neither the oil yield, composition nor the kinetics varied with particle size between 0.2 and 2.0 mm within experimental error. The qualitatively expected change in oil composition due to cracking was observed over the temperature range studied (460–540°C). Eastern shale exhibited significantly faster kinetics and higher oil yields than did Western shale.

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Introduction

There is considerable commercial interest in above-ground oil shale retorting using fluidized-bed processing techniques (Tamm et al., 1981). Such techniques are characterized by rapid heating of the oil shale followed by essentially isothermal retorting with the subsequent rapid removal of the pyrolysis products. A recent kinetic study using one type of Western shale has been reported which is applicable to fluidized-bed processing techniques (Wallman et al., 1981). This study indicated a particle size dependence for both the oil yield and the pyrolysis kinetics, where the particle size was varied between 0.4 and 3 mm. These results were interpreted with the aid of a two-step model for kerogen decomposition with each step following first-order kinetics. The initial kerogen decomposition rate constant varied from 1 to 10 min^{-1} over a temperature range of 480–540°C; the rate constant for the second step varied from 0.1 to 1 min^{-1} over the same temperature range. This second rate constant was associated with the decomposition of a heavy oil intermediate, which, along with a predominantly lighter hydrocarbon fraction, was the result of the initial Kerogen decomposition step.

This paper presents our results for the oil yield, composition and kinetics of the fluidized-bed pyrolysis of oil shale; preliminary accounts of portions of these results have appeared previously (Richardson and Huss, 1982; Richardson et al., 1982). In general, there is good agreement between our kinetic results and those obtained previously by Wallman et al. (1981) for the initial decomposition step; however, we have not found such a definite dependence of the second decomposition step on particle size. The

lack of a dependence on particle size was also observed in the oil yields and oil composition. In general, the oil yield for fluidized-bed pyrolysis of Western oil shale was ca. 100 percent Fischer assay; however, significantly higher yields were obtained for Eastern shale.

Species-selective kinetic data were obtained for methane, ethene, ethane, and hydrogen. Ethene and ethane are indistinguishable; hydrogen clearly evolves, at least in part, from an intermediate in the pyrolysis.

Experimental

Materials. Three Western shales and two Eastern shales were used in this study. The Western shales are from the Piceance Basin, Colorado (RB432, RB560, and Anvil Points) and the Eastern shales are from Lewis County, Kentucky (Sunbury Shale SUN-002 and the Cleveland member of the Ohio shale, CLE-002). The pertinent assay parameters are in Table I. Fischer assays were done both at LLNL using the procedure of Stout et al. (1978) and by outside laboratories. The grade determined by the correlation of Singleton et al. (1982) is very close to the average of the grade determined by the two previously published correlations of Cook (1974) and Heistand and Humphries (1976). The analyses for RB432 and RB560 are nominal values, taken from crushed raw shale (-0.25 inch) prior to further grinding. The other shales, however, were ground, sieved, spun and riffled before selecting samples for analysis. All of the oil yield and oil composition work was done with the more thoroughly characterized shale.

Matheson primary standards were used in calibrating the sensitivity and response time of both the flame-ionization detector (FID) and mass spectrometer.

Equipment. Figure 1 is a schematic of the experimental apparatus. The fluid-bed reactor and condenser are quartz, connected with stainless steel unions and graphite ferrules. The distribution is a seven-hole plate. The bed itself consists of 100 g of sand (Baker), ground, sieved and washed ($-0.25 + 0.125$ mm). Helium is used as the fluidizing medium. Typical flow rates are 60-80 cc/s (NTP) corresponding to a superficial velocity in the fluid bed of about 13 cm/s at 500°C. This value is approximately a factor of ten above the minimum fluidization velocity calculated using either the methods of Zenz and Othmer (1960) or Kunii and Levenspiel (1977). The situation corresponds to smooth fluidization as described by Kunii and Levenspiel (1977).

The heat source is a Lindberg three-zone furnace. Typically the temperature in the sand is isothermal to $\pm 1^\circ\text{C}$. For the oil collection experiments, the temperature profile inside the quartz reactor prior to adding raw oil shale is isothermal to $\pm 2^\circ\text{C}$ throughout the region heated by the furnace; outside the furnace, the temperature is maintained between 300-350°C with heating tape. Consequently, from the standpoint of gas-phase oil cracking losses, the mean residence time in the hotter fluid bed is approximately two seconds. For the kinetic experiments, the temperature refers only to that of the sand; the rest of the quartz fluid bed is cooler (e.g., when the sand was 560°C, the temperature profile inside monotonically decreased to 450°C at the furnace exit).

The amount of oil shale added during the FID kinetic experiments was so small (~50 mg) as to preclude any change in temperature in the sand. However, larger quantities (~4 g) were used in the mass spectrometer

kinetic experiments and the oil yield experiments. In this case, a considerable temperature drop was observed in the sand ($\sim 26^{\circ}\text{C}$). The initial temperature drop and subsequent return in time to the initially-set temperature was independent of the initial temperature (~ 5.8 minutes for 0-90 percent ΔT). Consequently, the temperature reported in these experiments is the temperature at the $1/e$ lifetime (determined from the FID kinetic experiments); the error reflects the temperature range between $t = 0$ (initial drop) and $t = (1/e)^2$ lifetime. Consequently, the lower temperatures with the slower kinetics have the largest temperature uncertainty but also a reported temperature more closely approximating the initial temperature.

Kinetics. The kinetics of total volatile hydrocarbon generation were measured using a Varian FID with Wilkens gas chromatograph electrometer. A quartz capillary sampled the pyrolysis products at a distance approximately eight inches above the sand bed and nearly on the vertical axis through the fluid bed (i.e., near the maximum of the velocity profile). Preliminary experiments demonstrated the need for a back pressure regulator at the system exit to ensure that the detector response was attributable solely to changes in hydrocarbon concentration and not pressure fluctuations. The water-adjusted regulator used (Moore Products) reduced the pressure fluctuations from up to 0.5 psi to less than 0.01 psi and also reduced the duration of the pressure fluctuations to less than a couple of seconds at the very onset of pyrolysis.

The FID response is calibrated with primary standards of methane in helium. The maximum detector response at 560°C to a typical 50 mg oil shale

sample is comparable to that obtained with a one percent methane/helium mixture. The temporal response of the detection system was less than three seconds (10-90 percent, both fall and rise times), measured both by switching between the one percent methane/helium standard and helium as well as by introducing solid naphthalene samples into the bed.

The difference in transit delay times between introduction of standards and introduction of oil shale samples was used to estimate the heating rate. While admittedly very crude, the samples in these experiments were heated at approximately 5000°C/min; this is in contrast to slower heating rates used in simulated MIS (modified in-situ) experiments (0.1 to 10°C/min).

The output of the FID and the exit pressure transducer is recorded on a two-pen Hewlett-Packard recorder. The resulting traces were digitized by manual tracing on an HP 9864A digitizer. The digitizer data were then analyzed using an HP 1000 computer.

Species-selective kinetics were obtained using a quadrapole mass spectrometer (Analog Technology Corporation, prototype model 2001). The flow was split prior to the back pressure regulator but after the trap (-78°C). Methane, ethane, ethene, hydrogen and carbon dioxide were analyzed as a function of time; digitized output was stored on tape for subsequent manipulation using the HP 1000 computer. The temporal response of this detection system was ~11 seconds (10-90 percent, both fall and rise times), also measured by switching between the one percent methane/helium standard and helium. The slower response time of this detector is attributed to the wider distribution of velocities being sampled.

Oil Yield and Composition. The oil is collected in a condenser similar in design to that used by Wallman et al. (1981). The optimal rod temperature was $\sim 300^{\circ}\text{C}$; glass wool was packed into the exit. Fines are excluded from the condenser by quartz wool and a quartz frit. Preliminary experiments were done with an ice bath at 0°C ($\pm 2^{\circ}\text{C}$). However, only about 90 percent of the oil (Fischer assay) was collected at 0°C ; capillary gc analysis showed the light ends to be missing ($\text{C}_6\text{--C}_{11}$). Consequently, all oil yield experiments were done using dry ice/isopropanol (-78°C) or liquid nitrogen/methyl ethyl ketone (-82°C). Only relatively small amounts of C_5 's escaped the trap; C_6^+ was retained.

Typical experiments involved ~ 4 g of raw shale, yielding ~ 400 mg of oil. Prior to removing the condenser, the system was backflushed with dry air to eliminate helium buoyancy effects. Oil yield was determined by weight and corrected for the experimentally determined water. A minimum of carbon disulfide (2 ml) was used to remove oil samples for subsequent chromatographic analysis. Different oil samples were prepared for water or chromatographic analysis. The water was extracted from the oil by washing the condenser with methanol (Burdick and Jackson).

Analysis. Water analysis was done by the Karl Fischer technique using the Photovolt Aquatest-IV. C, H, and N analysis was determined using the Perkin-Elmer Elemental Analyzer Model 240; sulfur was done by the Fisher Sulfur Analyzer Model 475. The light hydrocarbon gases ($\text{C}_1\text{--C}_4$) were collected and analyzed both by mass spectrometry and gas chromatography. All chromatography of the oil was done with a HP 5880A gas chromatograph with data acquisition and subsequent data reduction using an HP 1000 computer system; the procedures have been described by Burnham et al. (1982).

Results and Discussion

FID Kinetics. The FID essentially measures total organic carbon (Jones, 1970) and cannot distinguish oils from gases; consequently, for the purposes of this experiment, the pyrolysis of the organic material (kerogen plus bitumen) in the oil shale can be simply described:

where the term oil is used to include all volatile compounds containing organic carbon. Assuming for the moment first-order global kinetics (vide infra), the rate of oil production, $R(t)$ can be empirically described by a single rate constant, k_1 , and a simple exponential,

$$R(t) = R_0 e^{-k_1 t} \quad (2)$$

where R_0 is the initial rate (i.e., the maximum FID response). The amount of oil produced at any time t , $AOP(t)$, is simply the integral of $R(t)$ from 0 to t ; the total oil produced, TOP , is the integral of $R(t)$ over the total time for the experiment. Consequently, the integral form of Eq (2) is also a simple exponential,

$$1 - \frac{AOP(t)}{TOP} = 1 - FOP(t) = e^{-k_1 t} \quad (3)$$

where $FOP(t)$ is the fraction of oil produced at time t .

The FID kinetic data obtained in the fluidized-bed pyrolysis of oil shale was analyzed by using Eqs (2) and (3). The FID output is directly

proportional to $R(t)$ if the flow is held constant (i.e., if there are no pressure fluctuations), so the rate constant k_1 was determined from semilog plots of the data using Eqs. (2) and (3). In general, the data was reproducible to better than ± 10 percent over a decay of nearly two orders of magnitude in the normalized FID signal; Figure 2 represents typical FID output obtained in this experiment.

Non-linear semilog plots of either the FID data or the integral of the FID data imply either non-first-order kinetics or a non-unimolecular decomposition model, or both. In general, our data was described using two straight line segments with rate constants k_1 and k_2 ; the range over which each segment was a good description of the data was determined by inspection. This empirical description of the data using two single exponents is similar to that used previously by Wallman et al. (1981). It is consistent with models which include an intermediate in the production of oil and gas (e.g., Wallman et al., 1980; Braun and Rothman, 1975; Campbell et al., 1980). However, there is currently insufficient data to completely determine the nature of the intermediate and its decomposition products (e.g., heavy oil vs gas).

Figure 3 illustrates a typical data reduction for a Western oil shale from Anvil Points, with one average particle size, but at several different temperatures and using either Eq. (2) (Figure 3A) or Eq. (3) (Figure 3B). It is apparent from Figure 3 that integrating the FID data results in smoother curves; this is reflected in better correlation coefficients using the integrated data. In general, the square of the correlation coefficient for k_1 determined with the integrated data

ranged from 0.95 to 0.99 versus 0.93 to 0.98 when the FID data was used directly. For k_2 , the square of the correlation coefficient ranged from 0.96 to 0.99 using the integrated data versus 0.87 to 0.98 using the FID data directly.

In all cases, irrespective of particle size, the two Western shales (RB 432 and Anvil Points) exhibited a similar dependence of k_1 and k_2 on temperature. Qualitatively, the RB 560 shale was also similar although a detailed study of its kinetics was not performed. The Eastern shales had significantly different rates of pyrolysis (Figure 4); only CLE-002 was used in a detailed kinetic study. This result is qualitatively consistent with the results reported previously by Snow et al. (1979) and Herrell and Arnold (1976) using thermogravimetric analysis (TGA) but differs from the TGA results of Wen and Yen (1979).

Figures 5 and 6 are Arrhenius plots of k_1 and k_2 , respectively, comparing our results with those of Wallman et al. (1981). (Our rate constant, K_2 , is equivalent to their rate constant, $K_2 + K_c$). In both figures the integral form of the rate equation was used (i.e., Eq. (3)) in order to permit a more direct comparison. Two major conclusions are apparent: (1) the major difference in retorting rate between these Western and Eastern oil shale is attributable to differences in k_1 and not in k_2 ; and (2) the value of k_2 measured in this work for Western shale differs by approximately a factor of three to five from that measured previously by Wallman et al. (1981) over a similar temperature range. Figures 7 and 8 compare the effect of particle size on k_1 and k_2 , respectively, for both a Western and an Eastern shale. Neither rate

constant exhibits a significant dependence on particle size over the range of particle sizes studies within experimental error.

For comparison, Wallman et al. (1981) would predict a factor of 1.7 difference between the two particle sizes used for the Western shale (based on the average of the distributions). Furthermore, limited data was taken for a smaller particle size, $-0.5 + 0.25$ mm. A comparison of the results for two particle sizes, $-2.36 + 1.0$ mm and $-0.5 + 0.25$ mm, is shown in Figure 9. Both of these curves were obtained using RB432 at 467°C on the same day. In this case, Wallman et al. (1981) would predict a factor in excess of 2.0 difference between the k_2 's (based on the average of the distributions). We simply do not see such a large effect, which would be in excess of the experimental error.

The above conclusion with respect to the dependence of the kinetics on particle size should be qualified in the following respects. First, a discrepancy has been pointed out in our earlier data (Richardson et al., 1981), where it first appears that two sets of data taken on different days with RB432, $-0.5 + 0.25$ mm, are not consistent, particularly at long times. The two data sets in question have been replotted in Figure 10; it is apparent that the k_2 rate constants calculated are similar ($0.64 \pm 0.05 \text{ min}^{-1}$). The apparent discrepancy noted earlier can be attributed to changes in signal intensity, a small baseline drift in one of the runs, and the shape at early times.

Second, the absolute magnitude of our k_2 is considerably larger than that reported by Wallman et al. (1981). In their results the coking reaction (particle size dependent) dominates the heavy oil production; the

sum corresponds to our k_2 (and is what they experimentally measured). A similar dependence of our rate constant, k_2 on particle size in absolute, as opposed to relative magnitude, would not be detected within the experimental error for k_2 (e.g., for 1.0 mm particles its contribution is less than 20 percent).

Third, additional work with other particle sizes would be helpful in making the conclusion about a lack of a particle size dependence more definite. It may be necessary to narrow the range of the particle size distribution.

Table II summarizes the kinetic parameters determined in this work and compares them to values previously reported for fluidized-bed pyrolysis of oil shale (Wallman et al., 1981). Typical errors (± 95 percent confidence limit or three standard deviations) in the empirical activation energies are ~ 3 kcal/mole for k_1 and ~ 5 kcal/mole for k_2 ; typical errors in the A factor are factors of seven and 10^4 for k_1 and k_2 , respectively. The larger uncertainty in k_2 is attributable to both the poorer signal-to-noise ratio and probably more significant deviations from the assumed global first-order kinetics near the conclusion of the pyrolysis reaction.

The activation energy in this work for k_1 with Western shale agrees quite well with that reported previously by Wallman et al. (1981). With respect to k_2 , it is apparent that the preexponential A factor is the major difference between our results and those previously reported by Wallman et al. (1981); the difference in the activation energies is relatively less significant.

The Eastern shale has both a significantly lower activation energy and a lower preexponential A factor for k_1 than that observed with Western shale. The lower preexponential A factor is consistent with the general description of Eastern shale being more "coal-like" than Western shale (i.e., lower H/C ratio). Consequently, the "average transition state" for Eastern shale pyrolysis is expected to be more rigid, compared to the ground state, than is the "average transition state" for Western shale. However, several other factors are also likely to influence the A factor so this observed trend may be merely fortuitous. The activation energy is significantly lower than values previously reported by Snow et al. (1979), Herrell and Arnold (1976), and Wen and Yen (1979) using TGA techniques (~33 vs ≥ 56 kcal/mole), although more recent studies by Coburn (1982) with a non-TGA technique have yielded similar values (~30 kcal/mole).

It is instructive to compare the values of rate constants calculated from expressions derived from different kinetic experiments. Only k_1 will be compared with rate constants calculated using other expressions because k_1 pertains to the majority of oil conversion, and that was the basis of the other expressions. Table III compares these values of k_1 for Eastern shales derived from the following experiments: isothermal fluid bed (this work), nonisothermal gas evolution with a linear heating rate (T. Coburn, 1982), and isothermal thermogravimetric (Snow, et al, 1979). However, it should also be noted that different Eastern shales have different deposition environments and geological histories; consequently, all kinetics of Eastern shale pyrolysis are not necessarily expected to be the same.

Similarly, Table IV compares values of rate constants for pyrolysis of Western oil shale calculated for three temperatures by expressions derived from different kinetic experiments: isothermal fluid bed (this work and Wallman et al., 1981), nonisothermal oil and gas evolution with a linear heating rate (Campbell et al., 1980, Huss and Burnham, 1982; Shih and Sohn), isothermal with a thermal induction time (Braun and Rothman, 1975), isothermal for the initial stage of kerogen decomposition (Johnson et al., 1975), isothermal pyrolysis (Weilkamp and Getberlet, 1970), and isothermal thermogravimetric (Snow et al., 1979).

Tables III and IV clearly illustrate that different kinetics are obtained for different experimental procedures using different shales. The observation that the apparent kinetics vary with experimental technique is a reflection that decomposition of the organic material in oil shale is not truly a first order, unimolecular reaction. Instead, as is well known, decomposition proceeds through a series of both chemical and physical processes with a distribution of activation energies and preexponential A factors. Consequently, Tables III and IV emphasize the need for kinetic studies in the laboratory to approximate as closely as possible the industrial process being modeled (e.g., fluid-bed retorting, MIS) and to use the appropriate raw shale.

Wallman et al. (1981) interpreted k_2 in terms of a two step pyrolysis mechanism which included bitumen as an intermediate. Their second step involved heavy oil retorting at >90 percent total oil conversion and was dependent on particle size (3 to 0.4 mm). Our results do not indicate a significant particle-size dependence over the

investigated range of sizes studies (~2.36 to 0.5 mm) and range of total oil conversion (0 to ~95 percent). Furthermore, our values of k_2 are significantly larger. On the one hand, this result does not rule out a particle-size dependence at higher total oil conversion (>95 percent), but on the other hand the appearance of a bend in the Arrhenius plot at relatively lower total oil conversions (>80 percent) eliminates signal-to-noise arguments as a cause for not seeing any particle-size dependence. Thus, possible causes for the discrepancy between these results and those of Wallman et al. (1981) are experimental procedures and possibly the type of shale itself. A particle-size dependence is generally expected in fossil fuel pyrolysis because of the ultimate dependence of product evolution on diffusion related processes (e.g., coking) vs competing chemical processes (e.g., additional decomposition). However, this particle size dependence is not always manifested with varying experimental techniques (Scaroni et al., 1980) and different samples (Anthony and Howard, 1976). The FID cannot distinguish between oil and gas, but further experiments are planned using the fluid-bed reactor in which the product analysis will be species and/or functionality specific. Additional experiments are also planned to determine the influence of variables related to the fluid bed itself (e.g., engineering parameters) on the measured kinetics.

A final point regards the difference in k_1 calculated using Eq. (2) or Eq. (3). This difference is much larger than expected based on the signal-to-noise ratio and the reproducibility from run to run. The two methods would be expected to agree only if the reaction is truly first

order. Although the approximation of global first-order kinetics is reasonably correct and certainly useful for modeling industrial processes, it should not be surprising to find instances where the approximation begins to break down. In this respect, the difference between k_1 calculated using Eq. (2) and (3) is part of the general problem of the differences in k_1 calculated using rate constants derived from different experiments (Tables III and IV). Consequently, a detailed mechanistic model may be better deferred until species-selective and functionality-selective kinetics are obtained.

Species-selective Kinetics. Preliminary species-selective kinetics have been determined for three gases by connecting a mass spectrometer to the fluid-bed experiment. Figure 11 illustrates representative data obtained with this apparatus.

Five species were monitored in these preliminary experiments: CO_2 , H_2 , CH_4 , C_2H_4 and C_2H_6 . Different scale factors were used for each species; at the lowest initial temperature (Figure 9) the maximum intensities were approximately in the ratio 30:2:6:1:1.5 for CO_2 : H_2 : CH_4 : C_2H_4 : C_2H_6 . At the highest initial temperature (530°C), the ratios became more equal, changing to 4:4:3:1:1 for CO_2 : H_2 : CH_4 : C_2H_4 : C_2H_6 .

Evolution of CO_2 was too rapid to be adequately monitored; hydrogen evolution clearly is related to the reaction(s) of an intermediate and is not solely connected to the initial kerogen decomposition step.

Consequently, linear semilog plots were only obtained for CH_4 , C_2H_4 and C_2H_6 (Figure 12). Arrhenius plots for evolutions of these gases are shown in Figures 13 and 14; the larger uncertainties in temperature make the analysis of only qualitative value.

Table V summarizes the kinetic parameters evaluated for evolution of CH_4 , C_2H_4 and C_2H_6 . These values are of qualitative interest; relative errors (± 95 percent confidence level) are 4.7, 9.7 and 9.7 kcal/mole in the activation energies for CH_4 , C_2H_4 and C_2H_6 , respectively. The corresponding errors in A are factors of 2.2, 4.5 and 4.5, respectively. The rate constants calculated for CH_4 or C_2 evolution using the parameters in Table III are consistently higher by factors of two to seven than those calculated using kinetic parameters determined by Campbell et al. (1980) and Huss and Burnham (1982) at slow heating rates (0.1 to $10^\circ\text{C}/\text{min}$). Thus, the species selective kinetics confirm the conclusion made earlier on the basis of FID kinetics; namely, the kinetics measured for oil shale pyrolysis depend to a certain extent on the experimental procedure. This conclusion should not be surprising considering the complex nature of kerogen/bitumen pyrolysis, but does emphasize that any modeling effort should use kinetic parameters which were measured under conditions closely approximating the conditions being modeled.

Another comparison can also be made with the previously reported species-selective kinetics. The rate constant determined for CH_4 and C_2 , over the temperature range $460\text{--}540^\circ\text{C}$ in our fluid bed experiments, are slower than those determined for total hydrocarbon evolution. Qualitatively, this is consistent with the results of Huss and Burnham (1982), who reported slower rates for gas evolution than oil evolution, but contrary to the model of Wallman et al. (1981), which associates the light oil and gas with k_1 and the heavy oil with k_2 . (Based on the kinetics of Burnham and Taylor (1979), there is little potential for cracking as measured by oil loss at the short residence times and low temperatures used in these experiments.)

Kinetics for Modeling. The two empirical sequential rate constants for hydrocarbon production, k_1 and k_2 , do not easily lend themselves to inclusion into a framework for computer modeling. Three approaches were investigated to circumvent this problem using Western shale: 1) weighting coefficients for k_1 and k_2 ; 2) two parallel first order reactions; 3) non-first order kinetics.

The first approach involved normalizing the rate to ~100

$$\frac{R(t)}{R_0} = \alpha \cdot \beta e^{-k_1 t} \quad 0 < t < \tau \quad (4a)$$

and

$$\frac{R(t)}{R_0} = \beta e^{-k_2 t} \quad t > \tau \quad (4b)$$

where R_0 is determined by integration, τ is the empirical break in the semilog plots (i.e., where k_2 dominates k_1) and α and β , the weighing coefficients, are determined independently rather than being forced to yield a product of 100. Several functional forms were tried for α and β , but the following equations gave a satisfactory fit (e.g., Figure 15):

$$\ln \alpha = -9.89 + 0.0224 T (^{\circ}\text{C}) \quad (5a)$$

$$\ln \beta = 14.1 - 0.0216 T (^{\circ}\text{C}) \quad (5b)$$

A representative fit is shown in Figure 16. A sample calculation for 500°C and using 4.0 g of 24.8 gal/ton oil shale (100 percent Fischer assay yield, vida infra) yields the following parameters: $k_1 = 0.0378 \text{ s}^{-1}$,

$k_2 = 0.0177 \text{ s}^{-1}$, $\alpha = 3.706$, $\beta = 27.11$, $\alpha \cdot \beta = 100.47$, $\tau = 65 \text{ s}$, $R_0 = 0.129 \text{ mg oil/s}$. This empirical description of the data is at best difficult to implement in non-isothermal modeling, but does have the salient advantage of only requiring the oil yield (i.e., Fischer assay grade) instead of a mythical kerogen concentration (e.g., kerogen stoichiometry in Eastern oil shales is much less well defined than for Western shales, so the procedure described above may be particularly well suited for modeling Eastern shale pyrolysis). Furthermore, errors introduced in non-isothermal modeling by assuming an average isothermal condition (e.g., ± 15 percent maximum difference in R_0 for using 505°C instead of $500\text{--}510^\circ\text{C}$) must be weighed against errors introduced in simplifying the kinetics to a form tractable for non-isothermal modeling.

The second approach, two parallel first order reactions, did not result in kinetic parameters that varied in a physically meaningful way. The third approach involved non-first-order kinetics (Braun and Burnham, 1982),

$$R(t) = \frac{d[K/K_0]}{dt} = k_1 [K/K_0]^n$$

where K is the kerogen concentration, K_0 is the initial kerogen concentration and k_1 is initially calculated from the parameters in Table II. This approach was also found to be a good description of the data when $n \approx 1.4$. In this analysis, the contributions of $C_1\text{--}C_3$ hydrocarbons are subtracted from the FID data using the kinetic parameters of Table V; consequently the result represents oil evolution kinetics, not total

hydrocarbon kinetics. This empirical description of the data is more compatible with the mechanics of modeling non-isothermal processes.

Additional work is being done with this approach and existing experimental data to re-evaluate the kinetics for Western shale. Criteria for determining the effect of particle size and shale origin (grade) will be the variation in the three parameters (A, E, and n) for a given quantitative estimate of the goodness of fit (e.g., percent variance explained for similar data sets) and the variation in this quantitative estimate of the goodness of fit for given kinetic parameters.

Oil Yield. Several steps were taken to maximize the amount of collected oil. Higher rod temperatures (350°C vs 150°C) leading to larger thermophoretic effects aided in oil collection as did increasing the surface area (glass wool instead of glass beads). Larger sample aliquots for a given mass, as opposed to more but smaller aliquots totaling the same mass, also led to larger collection efficiencies. All three of these observations are consistent with maximizing mist collection and minimizing mist formation (Goren, 1981).

Initial experiments were done with an ice bath (0°C). Gas chromatographic analysis showed that the light ends (C₆-C₁₁) were missing, and the observed yields were only ~92 percent of that expected based on Fischer assay. Consequently, the ice bath was replaced with either a dry ice/isopropanol bath (-78°C) or liquid nitrogen/methyl ethyl ketone slush bath (-82°C). All reported results were at these lower bath temperatures and using Anvil Points oil shale (Table I).

Figure 17 illustrates the dependence of yield, as a percent of the correlation Fischer assay, on temperature for Anvil Points oil shale (-1.0 ± 0.5 mm). The error bars reflect the uncertainty in temperature due to the large sample size being dropped (vida supra). Figure 18 illustrates the dependence of yield, once again expressed as percent of the correlation Fischer assay, as a function of particle size for two temperatures. The error bars reflect the particle size distribution.

Within the experimental error there is no obvious trend of yield with either particle size or temperature over the ranges studied. In comparison, Wallman et al. (1981) measured an enhancement of ~10 percent in expected oil yield for particle sizes <0.5 mm vs particles ≥ 1.0 mm. Averaging all the data (14 points) irrespective of temperature or particle size, results in an average yield for fluidized-bed pyrolysis of 101 ± 5 percent of the Fischer assay oil yield for Anvil Points shale, based on the correlation of Fischer assay with organic carbon and corrected for variation of that yield with particle size. The average yield would have been approximately 5 percent higher if it had been defined as condensables divided by the sum of Fischer assay oil plus water (this is how Wallman et al. (1981) defined their yields); experimentally, we always measured higher water contents by the Karl Fischer technique than predicted by Fischer assay.

Only preliminary results were obtained for the oil yield using Eastern shale. Using CLE-002, -0.42 ± 0.21 mm at $489 \pm 2^\circ\text{C}$, resulted in an oil yield of ca. 200 percent Fischer assay when the water was determined by Karl Fischer. There was a large discrepancy between this value and that

calculated as total condensables divided by the sum of Fischer assay oil plus water (ca. 150 percent). However, the significant point is that substantial increases in oil yield from Eastern shale can be achieved using fluidized-bed pyrolysis. A similar result has been previously reported (Margolis, 1981). Gas chromatographic analysis of both Fischer assay and fluid-bed Eastern shale oil indicates that the enhancement in yield is due to a large increase in unresolved organic material between C15 and C30; a similar but much smaller enhancement is observed with Western oil shale.

Mass Balance. Table VI summarizes the elemental analysis (N, S, H and percent raw shale organic carbon) for raw shale, spent shale and oil from fluidized bed vs Fischer assay pyrolysis. Anvil Points shale was used (-1.0 ± 0.5 mm), and the temperature of the fluidized-bed pyrolysis was 497^{+3}_{-1} °C. The spent shale values are the average of two determinations, one involving an analysis of the total bed (sand plus char) following four consecutive aliquots of raw shale (one aliquot proved to be insufficient to determine with satisfactory precision), and one involving analysis of just selected spent shale particles. Only one sample of oil from the fluid bed was analyzed. Two samples of gas were collected, and each analyzed by gc and mass spectrometry. All of the gas analyses were very consistent, and only the average is reported. The gas was collected in an evacuated cylinder equipped with a Baratron pressure gauge; care was taken to keep the He flow nearly constant throughout the pyrolysis (future experiments may use a bag to collect the gas at atmospheric pressure).

A completely satisfactory conclusion cannot be reached on the basis of these experiments. The oil yield used was the average of the results for that temperature and particle size, 102.5 percent Fischer assay (Figures 17 and 18), which does not correspond to the enhancement in raw shale organic carbon recovered in the carbon-balance fluid-bed pyrolysis experiments (106.7 percent). The difference in carbon content of the spent shale could have significant ramifications on evaluating the heating content of the spent shale; this result is qualitatively consistent with that seen for combustion of spent shale (Taylor, 1982). In all experiments considerably more CO_2 and CO was generated than expected, even after correcting for carbonate decomposition (less was collected using the liquid nitrogen/methyl ethyl ketone slush bath). Thus, the inability to achieve complete closure of the organic carbon mass balance precludes any definite conclusions.

Oil Composition. All oil composition analysis was done by capillary gas chromatography. Significant differences were observed between fluid-bed pyrolysis and Fischer assay conditions for both Western (Figure 19) and Eastern (Figure 20) shales.

There are four major conclusions to be drawn from the gc analysis of the shale oil. The first conclusion has already been alluded to, namely, the enhancement particularly in Eastern shale oil of an unresolved fraction between C15 and C30. This unresolved fraction is probably responsible for the enhanced yield from fluidized-bed pyrolysis of Eastern oil shale.

The second conclusion is the higher 1-alkene/n-alkane ratios observed for fluid-bed pyrolysis as compared to Fischer assay. Figure 21 illustrates this effect for Western shale, and Figure 22 illustrates the effect

for Eastern shale. Figure 21 also compares data taken at a very slow heating rate. The periodicity apparent in Western shale has been well documented (Klesment, 1980; Burnham and Ward, 1981), but is singularly missing in at least this one example of Eastern shale (Figure 22). The explanation for the even-odd trends is not well understood but probably relates to both the structure (origin) of the kerogen and to the pyrolysis conditions (e.g., heating rate). These trends in ratios both even-odd and 1-alkene/n-alkane have potential as process diagnostics (Burnham and Clarkson, 1980).

The third conclusion is an extension of trends previously noted by Burnham et al. (1982). Figures 23-25 illustrate the dependence on heating rate of various ratios derived from the gc analyses; i.e., 1-alkene/n-alkane (Figure 23), isoprenoid alkene/alkane (Figure 24), and isoprenoid/(1-alkene + n-alkane) (Figure 25). These trends are qualitative and empirical; similar plots could be made of some of the ratios vs temperature. The heating rates used in the previous work of Burnham et al. (1982) were 0.03, 0.3, 1, 6 and 12°C/min, which can be related to the temperature of maximum oil evolution rate, 370, 400, 425, 455 and 470°C, respectively, (Burnham, 1982). The fluid bed conditions were 450^{+6}_{-16} °C and approximately 5000°C/min (Anvil Points). However, no correction was made for the effect of gas sweep on the alkene/alkane ratio; it has been previously shown that higher alkene/alkane ratios were obtained with a fast sweep of inert gas, both in comparison to a slow seep and to autogeneous conditions (Burnham and Ward, 1981). In certain cases (e.g., pristene/pristane ratio), the ratios definitely correlate better with heating rate than temperature. Additional

experiments are planned using a pyroprobe/mass spectrometer to access even higher heating rates. Such data will not only extend Figures 23-25 but better resolve the question of temperature vs heating rate as the dominant factor in the chemical character of the evolved shale oil.

Figure 23 essentially contains the same information as Figure 21; much higher 1-alkene/n-alkane ratios are observed in fluid-bed pyrolysis.

Figure 24 illustrates the dependence of the isoprenoid alkene/alkane ratio on heating rate. The most noticeable difference between the fluid bed and Fischer assay chromatograms, the dominance of pristene in the former, is easily interpreted from the trends shown in Figure 24.

Of course, as a process diagnostic there are instances when ratios which are constant with heating rate are desired as well as instances where varying ratios are required. Fortunately, all ratios of gas chromatographic data do not vary with heating rate; Figure 25 illustrates the trends for some ratios which are relatively invariant with heating rate. In Figure 25 the choice of which n-alkane plus alkene was used was dictated by its proximity in the gas chromatogram to the isoprenoid in question.

Trends in shale oil chemical composition as a function of temperature and particle size were partially examined. Little evidence of cracking, at least as measured by oil loss, would be expected at the temperatures and residence times used. There did, however, appear to be a definite redistribution of the chemical composition of the oil. Figure 26 illustrates this trend for a "light" and "heavy" fraction of the oil, as measured by the sum of the normal alkanes plus 1-alkenes for C_9-C_{11}

and C₂₇-C₂₉, respectively. These sums were arbitrarily normalized to the phytane value; phytane appears to be relatively constant with heating rate for a given oil shale (Figure 25), and has no corresponding olefin of major consequence. It is apparent from Figure 26 that the "heavy" fraction appears to decline with an increase in temperature (although there is one anomalous point), while the "light" fraction is somewhat enhanced; this trend was also observed by Wallman, et al. (1981).

Similar qualitative temperature information is shown in Figure 27, where the "light" and "heavy" fractions are plotted as a function of particle size for two temperatures. The data here is probably not good enough for firm conclusions; additional work is needed in both the oil generation and gc analysis (e.g., possibly a simulated distillation instead of summing distinct peak areas). However, qualitatively it appears that the lower temperature favors the "heavy" fraction and the higher temperature enhances the "light" fraction. There does not appear to be a major dependence of either the "light" fraction, or, with one anomalous point, the "heavy" fraction with particle size.

Conclusions

Preliminary results and analysis have been presented for fluidized-bed pyrolysis. One of the major objectives was to confirm the work of Wallman et al. (1981). This we were unable to do in its entirety. We did not see such a pronounced dependence of the kinetics on particle size as they did; within experimental error we can distinguish no effect. A similar conclusion holds true for the dependence of oil yield on particle size.

Finally, a similar tentative conclusion also holds true for the dependence of oil composition; in fact, our preliminary species-selective kinetics suggest that it is light gases, not heavy oil, which are responsible for the tail in the oil evolution kinetics. Unfortunately, additional experimental and theoretical work is required to more precisely determine the dependence of fluidized-bed pyrolysis kinetics, oil yield, and oil composition on particle size and grade, as well as more theoretical work to reduce this dependence accurately into a form tractable for modeling studies. However, the bulk of the oil evolution is particle-size independent, and, in this regard, our results compare quite favorably with those of Wallman, et al (1981). It is significant that both our results differ substantially from those derived using other experimental procedures.

Finally, the exceptionally high yield obtained from Eastern oil shale with fluidized-bed pyrolysis is a major result of this work.

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Table 1. Assay parameters of oil shale used in this work.

Shale	Particle size mm	Elemental Analysis (wt%)			Grade (gal/ton)		
		C _{Tot}	C _{org}	H	FA ₁ ^a	FA ₂ ^b	Correlation ^c
RB431		20.0	15.4	2.13	31.8	--	34.4
RB560		14.1	9.1	1.43	18.7	--	19.9
Anvil Points	-2.4 + 1.0	17.0	12.2	1.78	27.4	26.4	27.2
	-1.0 + 0.5	16.1	11.2	1.63	--	24.8	24.8
	-0.5 + 0.25	16.3	11.5	1.70	--	24.9	25.5
	-0.25 + 0.125	15.7	11.0	1.63	--	--	24.2
CLE-002	-0.42 + 0.21	14.3	14.3	1.67	11.7	--	--
SUN-002	-0.42 + 0.21	13.9	13.9	1.65	--	14.2	--

^aFischer assay done at LLNL.

^bFischer assay done at TOSCO (Anvil Points) or at Kentucky Institute for Mining and Minerals Research (SUN-002).

^cGrade (gal/ton) = 2.302 C_{org} - 1.03.

Table II. Comparison of kinetic parameters for 1.0 mm particles derived from integral vs differential analysis.

	k_1			k_2		
	E (kcal/mole)	A (s ⁻¹)	At 500°C (min ⁻¹) ^a	E (kcal/mole)	A (s ⁻¹)	At 500°C (min ⁻¹) ^a
Western shale						
Equation (2) ^b	41.2	1.97×10^{10}	2.76	28.3	1.8×10^6	1.11
Equation (3) ^b	42.6	3.60×10^{10}	2.02	27.7	1.3×10^6	1.11
Composite ^c	41.6	2.18×10^{10}	2.37	29.7	4.4×10^6	1.09
Wallman et al. (1981)	43.6	9.63×10^{10}	2.83	22.6	1.1×10^{4d}	0.27
Eastern shale ^e						
Equation (2)	32.0	8.1×10^7	4.49	25.7	3.6×10^5	1.20
Equation (3)	35.2	4.9×10^8	3.39	31.4	2.0×10^7	1.64
Composite ^c	32.4	9.9×10^7	4.13	28.6	3.0×10^6	1.46

^aRate at 500°C calculated from Arrhenius equation: rate = A exp (-E/RT).

^bIncludes data from RB 432 and Anvil Points.

^cIncludes data from Eq. (2) and Eq. (3).

^dSum of k_2 and k_c for 1.0 mm particles.

^eData from CLE-002.

Table III. Comparison of calculated rate constants (min⁻¹) for Eastern oil shales.

		460°C	500°C	550°C
This work:	k ₁	0.98	4.13	15.2
	k ₂	0.42	1.46	4.70
Coburn (1982)	Propane	0.13	0.46	1.4
	Butane	0.16	0.72	2.7b
Snow et al. (1979)	Oil rate	1.8	13	120

Table IV. Comparison of calculated rate constants (min⁻¹) for Western oil shales.

	Rate constant	460°C	500°C	550°C
This work:	k ₁	0.54	2.37	12.2
	k ₂	0.38	1.09	3.52
Wallman et al. (1981)	k ₁	0.61	2.83	15.9
	k ₂	0.12	0.27	0.67
Campbell et al. (1980)	Oil	0.45	2.89	22.8
Huss and Burnham (1982)	C _{3.0} H _{7.1}	0.087	0.38	1.96
	CH ₄	0.11	0.49	2.51
Shih and Sohn (1980)	Total oil	0.30	1.63	10.8
Johnson et al. (1975)	Initial k	1.01	5.28	33.5
Braun and Rothman (1975)	Oil	0.26	0.84	12.8
Weitkamp and Getberlet (1970)	Oil	0.62	1.10	---
Snow et al. (1979)	Oil	0.03	0.11	0.45

Table V. Kinetic parameters for species-selective kinetics obtained with Anvil Points oil shale, particle size $-2.36 + 1.0$ mm.

	A s^{-1}	E (kcal/mole)
CH_4	7.3×10^5	26.0
C_2H_4	8.8×10^{12}	51.3
C_2H_6	2.0×10^{12}	49.0

Table VI. Elemental analysis for fluid bed vs Fischer assay pyrolysis (Anvil-Points, -1.05 ± 0.5 mm).

	Fluid bed (497^{+3}_{-1} °C) (weight percent)	Fischer assay (weight percent)
N		
Raw shale	0.68 ± 0.19	0.68 ± 0.19
Spent shale	0.48 ± 0.20	0.56 ± 0.13
Oil	2.90 ± 0.59	2.85 ± 0.33
S		
Raw shale	0.60 ± 0.01	0.60 ± 0.01
Spent shale	0.55 ± 0.01	0.49 ± 0.02
Oil	0.77 ± 0.05	0.76 ± 0.05
H		
Raw shale	1.63 ± 0.04	1.63 ± 0.04
Spent shale	0.27 ± 0.01	0.23 ± 0.07
Oil	10.89 ± 0.23	10.97 ± 0.24
C (expressed as weight percent raw shale organic carbon)		
Oil	71.8	67.3
Spent shale	16.2	23.0
C ₁ -C ₄	4.7	5.0
C ₅ -C ₉ (in gas)	<u>0.6*</u>	<u>1.7</u>
TOTAL	92.3	97.0
CO + CO ₂ **	--	1.7

*C₅ only.

**Corrected for mineral carbon.

Table VII. Isoprenoid compounds ratioed in empirical correlation with heating rate.

C ₁₃	2,6-dimethylundecane
C ₁₄	2,6,10-trimethylundecane
C ₁₅	farnesane
C ₁₆	2,6,10-trimethyltridecane
C ₁₉	pristane
C ₂₀	phytane

Figure Captions

- Figure 1 Schematic of the experimental apparatus for fluidized-bed pyrolysis of oil shale (TC: thermocouple).
- Figure 2 Typical untreated FID output for Anvil Points shale, $-1.0 + .5$ mm, at 468°C . Four separate runs are illustrated.
- Figure 3 Typical kinetic results used to generate Arrhenius plots using shale from Anvil Points, $-1.0 + 0.5$ mm: (A) Eq. (2), normalized FID response; (B) Eq. (3), percent of unretorted oil ($1-\text{FOP}(t)$). In each case the straight line segments, either solid (A) or dotted (B), indicate the linear fits.
- Figure 4 Comparison of normalized FID response for Western (RB432, $-0.5 + 0.25$ mm) versus Eastern (CLE-002 and SUN-002, both $-0.42 + 0.21$ mm) oil shales at 468°C .
- Figure 5 Arrhenius plot of k_1 using the integral expression (Eq. (3)) and one particle size: (●) Wallman et al. (1981), 1.0 mm; (Δ) Anvil Points, $-1.0 + 0.5$ mm; (○) RB432, $-1.0 + 0.5$ mm; (□) CLE-002, 1.0 ± 0.1 mm.
- Figure 6 Arrhenius plot of k_2 using the integral expression (Eq. (3)) and one particle size: (●) Wallman et al. (1981), 1.0 mm; (Δ) Anvil Points, $-1.0 + 0.5$ mm; (○) RB432, $-1.0 + 0.5$ mm; (□) CLE-002, 1.0 ± 0.1 mm.
- Figure 7 Arrhenius plot of k_1 using the integral expression (Eq. (3)) and two particle sizes: (Δ) RB432, $-2.36 + 1.0$ mm; (▲) RB432, $-1.0 + 0.5$ mm; (○) CLE-002, 1.0 ± 0.1 mm; (X) CLE-002, $-0.42 + 0.21$ mm.

- Figure 8 Arrhenius plot of k_2 using the integral expression (Eq. (3)) and two particle sizes: (Δ) RB432, -2.36 ± 1.0 mm; ($\blacktriangle$) RB432, -1.0 ± 0.5 mm; ($\circ$) CLE-002, 1.0 ± 0.1 mm; ($\times$) CLE-002, -0.42 ± 0.21 mm.
- Figure 9 Example of data taken at two different particle sizes for RB432 at 467°C : (—) -2.36 ± 1.0 mm and ($\cdots$) -0.50 ± 0.25 mm.
- Figure 10 Comparison of data previously published for RB432, -0.50 ± 0.25 mm: ($\bullet$) 467°C , 8/28/82 (also shown in Figure 9); ($\circ$) 468°C , 10/1/82 (also shown in Figure 4). The measured values for k_2 are similar.
- Figure 11 Typical mass spectrometer data used for species-selective kinetics. The particle size was -2.36 ± 1.0 mm; different scale factors were used for each species.
- Figure 12 Typical kinetic results used to generate Arrhenius plots. Only a single first order expression was fitted to the data for CH_4 , C_2H_4 and C_2H_6 because of the generally qualitative nature of the data.
- Figure 13 Arrhenius plot for CH_4 (Anvil Points, oil, hole, -2.36 ± 1.0 mm). The uncertainty in rate constant is the standard deviation from multiple runs; the uncertainty in temperature is due to the large sample size.
- Figure 14 Arrhenius plots for C_2H_4 ($\bullet$) and C_2H_6 ($\circ$), Anvil Points oil shale, -2.36 ± 1.0 mm.

- Figure 15 Natural logarithm (α) vs temperature ($^{\circ}\text{C}$). Data derived from Anvil Points (-1.0 ± 0.5 mm) and RB432 (-2.36 ± 1.0 mm and -1.0 ± 0.5 mm).
- Figure 16. Comparison of experimental data ($\square$) to fit using weighting coefficients ($—$). The experimental data was from Anvil Points, -1.0 ± 0.5 mm. (A) normalized FID response vs time; (B) semilog plot of normalized FID response vs time.
- Figure 17 Dependence of oil yield (percent correlation Fischer assay which in this case equalled the measured value) on temperatures for Anvil Points oil shale, -1.0 ± 0.5 mm, 24.8 gal/ton.
- Figure 18 Dependence of oil yield (percent correlation Fischer assay calculated from organic carbon content) on particle size for Anvil Points oil shale at two temperatures, nominally 448°C ($\bullet$) and 497°C ($\circ$). The error bars represent the range in particle size about the arithmetic mean.
- Figure 19 Capillary gc chromatograms of Western shale, Anvil Points, -1.0 ± 0.5 mm, Fischer assay (A) and fluid-bed pyrolysis at 502°C (initial), or $481 \pm 5^{\circ}\text{C}$ (B).
- Figure 20 Capillary gc chromatograms of Eastern shale, CLE-002, -0.42 ± 0.21 mm, Fischer assay (A) and fluid-bed pyrolysis at 514°C (initial), or $491^{+4}_{-3}^{\circ}\text{C}$ (B).
- Figure 21 1-alkene/n-alkane ratio for Western shale (Anvil Points) generated under different conditions: ($\circ$) fluid bed, 514°C ; ($\bullet$) fluid bed, 450°C ; (Δ) Fischer assay ($\blacktriangle$) simulated modified in situ (MIS) experiment, $0.1^{\circ}\text{C}/\text{min}$.

- Figure 22 1-alkene/n-alkane ratio for Eastern shale oil (CLE-002) generated by fluid-bed pyrolysis at 491°C (—) and Fischer assay (---).
- Figure 23 Dependence of the 1-alkene/n-alkane ratio on heating rate.
- Figure 24 Dependence of the isoprenoid alkene/alkane ratio on heating rate. See Table VII for a list of the specific isoprenoids (e.g., C_{19} = pristene/pristane). C_{14}' refers to trimethylundec-1-ene/trimethylundecane, and C_{14}'' refers to trimethylundec-2-ene/trimethylundecane.
- Figure 25 Dependence on heating rate of the ratio of the isoprenoids (alkane plus alkene) to the normal alkane plus alkene nearest to the isoprenoids in the chromatogram (e.g., C_{19}/C_{17} is (pristene plus pristane)/(n-heptadecane plus n-heptadec-1-ene). The C_{14} ratio includes both the 1- and 2-alkenes.
- Figure 26 Dependence on pyrolysis temperature of the chemical composition of shale oil (Anvil Points, -1.0 ± 0.5 mm); (●) sum of normal alkanes plus 1-alkenes for C_{27} - C_{29} divided by phytane; (○) sum of normal alkanes plus 1-alkenes for C_9 - C_{11} divided by phytane.
- Figure 27 Dependence on particle size of the chemical composition of shale oil (Anvil Points) using the same phytane-normalized sum of normal alkanes plus 1-alkenes for C_9 - C_{11} and C_{27} - C_{29} :
 (○) C_{27} - C_{29} /phytane, 450^{+6}_{-16} °C; (□) $(C_{27}-C_{29})$ /phytane, 495^{+3}_{-1} °C;
 (●) (C_9-C_{11}) /phytane, 450^{+6}_{-16} °C; (■) $(C_{27}-C_{29})$ /phytane, 495^{+3}_{-1} °C.
 The particle sizes were -2.36 ± 1.0 mm, -1.0 ± 0.5 mm, -0.5 ± 0.25 mm and -0.25 ± 0.125 mm; the average value of the distribution is plotted.

Figure 1

Figure 2

ANVIL POINTS -1.0 ± 0.5

Figure 3A

Figure 3B

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

ANVIL POINTS 469 C

Figure 11

ANVIL POINTS 469 C

Figure 12

Figure 13

Figure 14

ALPHA COEFFICIENT

Figure 15

ANVIL POINTS 491 C

Figure 16A

ANVIL POINTS 491 C

Figure 16B

ANVIL POINTS (24.8 GAL/TON)

Figure 17

ANVIL POINTS

Figure 18

Figure 19A

Figure 19B

Figure 20A

Figure 20B

ANVIL POINTS (24.8 gal/ton)

Figure 21

CLEVELAND/OHIO 11.7 GAL/TON

Figure 22

Figure 23

Figure 24

Figure 25

ANVIL POINTS (24.8 gal/ton)

Figure 26

Figure 27

DISCLAIMER

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