Kerogen Decomposition at Subpyrolysis Temperatures

The thermal decomposition of Colorado oil shale was studied at subpyrolysis temperatures, 533 to 611 K, as part of an investigation of rates of supercritical extraction. Thermal degradation followed by solution in the solvent is a possible, partial explanation for the enhanced solubility at supercritical conditions for a complex mixture such as kerogen.

In the region of the critical temperature of toluene, up to 26% of the kerogen in the original shale was converted by thermal reactions to gases and soluble (in toluene at 298 K and 101 kPa) products. The kinetics of the decomposition of the insoluble organics in shale could be explained by a combination of series and parallel reactions.

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The role of the solvent in supercritical extraction is not well understood. For polymeric substances such as rubber it has been suggested (Funazukuri et al., 1985) that the molecules swell and straighten out in the solvent, and are then more readily cleaved into soluble products. Estevez (1983) found that an extraction process alone could not explain observed effects of particle size on rates of supercritical extraction. For systems of complex mixtures of molecules, such as kerogen in oil shale and with solvents of relatively high critical temperature, it is possible that thermal degradation into smaller molecules partially explains the high solubility at supercritical conditions. Such an explanation would appear less likely for solvents, such as carbon dioxide, that have low critical temperatures. To investigate this possibility, rates of thermal decomposition of a Colorado oil shale were measured in nitrogen (no solvent) at subpyrolysis temperatures (533 to 611 K). The products of decomposition were divided into two groups: gases at the reaction temperature and 101 kPa, and material (termed bitumen) that was soluble in toluene at 298 K and 101 kPa.

A packed-bed reactor with nitrogen flow was employed to measure the quantities of gases and bitumen produced as a function of time. From these data reaction rates were determined and a reaction scheme proposed.

CONCLUSIONS AND SIGNIFICANCE

For the shale used (Anvil Points Mine, Colorado, Occidental Petroleum Corp., 15 wt. % organics), 10.2 wt. % of the original organic content was found to be bitumen, that is, material soluble in toluene at 298 K, 101 kPa, and the remainder insoluble kerogen. After decomposition at the maximum temperature studied, 611 K, about 10% of the originally insoluble kerogen was decomposed at a reaction time of 1.8 ks and 26% at 18 ks reaction time. The product distribution, which could include bitumen from the original sample, was 9.5 wt. % bitumen, 24.1% gases, and 66.4% residual kerogen.

The kinetics studies showed that some kerogen was directly converted to gaseous products while other kerogen was converted to bitumen, followed by reaction of some bitumen to additional gaseous material. Analysis of the data in terms of first-order reactions suggested that, as an approximation, kerogen could be

divided into two groups of components, heavy and light. The light components were rapidly converted to gaseous products according to an activation energy E_3 of 46 kJ/mol, while the heavy components reacted to bitumen more slowly according to an activation energy E_1 of 100 kJ/mol. Visual examination of the reacted shale particles showed no evidence of coke, probably due to the low reaction temperatures. Since the samples contained only 15% active material, the measurements involve small quantities. Hence, the accuracy of some of the kinetics results is not high. This is particularly so for the rate of gas production (obtained by difference).

These results indicate that kerogen degradation reactions occur at supercritical, but subpyrolysis, temperatures. Also, the extent of such reactions is sufficient to explain in part the enhanced solubility at supercritical conditions. This finding supplements the conclusion of Estevez (1983) that extraction alone could not explain rates of supercritical extraction.

Introduction

One advantage of supercritical extraction over pyrolysis for the production of fuels is that the temperature is lower. Pyrolysis of Colorado shales does not occur at a rapid rate below about 648 K, while for toluene the critical temperature is 591 K and for other solvents the critical temperature is considerably less. Little knowledge is available on the mechanism of supercritical extraction. From information on extraction of oils from rubber tire samples, Funazukuri et al. (1985) proposed that the solvent (nitrogen, toluene, or *n*-pentane) swells the rubber and loosens the polymer molecules which then are more easily decomposed into smaller species. It seems clear that reaction as well as the physical process of solution occurs during supercritical extraction (Martin and Williams, 1977; McKay et al., 1983; Estevez, 1983). However, the role of the solvent is not understood in the case of complex solids such as kerogen, particularly when the extraction is carried out at near-pyrolysis temperatures. It is possible that thermal reactions at subpyrolysis temperatures result in soluble products that are removed by the solvent.

The objective of this research was to determine the extent and kinetics of such thermal reactions. Uncertainty about the chemical structure and composition of the organic material in shale has been a hindrance to understanding shale pyrolysis and supercritical extraction. Recent studies of structure reported by McKay (1984) suggest that rather than a polymeric material, kerogen is a complex mixture of organic compounds containing heteroatoms (S, N, O, etc.) and with an average molecular weight of 600 to 800. Others (Vitorovic et al., 1974; Yen, 1974; Schmidt-Collerus and Prien, 1974) have suggested that kerogen in Western shale consists of polymeric-type organic macromolecules.

In analyzing our data, the organic material in shale is divided into two main parts, kerogen and bitumen. Kerogen refers to the material that is insoluble in toluene at 298 K and 101 kPa, and bitumen refers to the soluble part. As a result of thermal decomposition, kerogen is partially converted into bitumen and gaseous products. The original shale samples contain bitumen as well as kerogen, presumably because some thermal decomposition has occurred over the years in the shale formation.

The procedure followed for the kinetics experiments was first to heat shale samples in nitrogen over the temperature range 533 to 611 K and determine the extent of gaseous decomposition by weight difference. Subsequently the remaining solid was stirred in toluene at 298 K and 101 kPa and the solution analyzed to establish the conversion of kerogen to bitumen. The analysis required a separate set of calibration experiments at various temperatures and reaction times.

Experimental

Shale samples

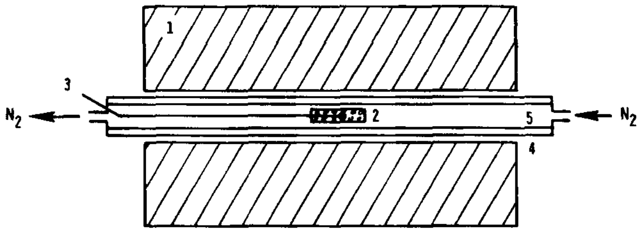
The shale used was from the Anvil Points mine (Colorado) supplied by Occidental Research Corporation. Organic content was 15 wt. % and had the approximate composition (wt. %): carbon 17.3, hydrogen 1.82, nitrogen 0.69, sulfur 0.66, and inorganic carbonates 22.3. The density of the solid is 2,150 kg/m^3 at 295 K.

Randomly chosen pieces of shale were ground and sieved, and samples of 0.147 to 0.208 × 10^{-3}m (average granular size = 0.18 × 10^{-3}m) were used for the reaction experiments.

Apparatus

The shale particles were placed in a small Pyrex tube, 0.01m ID 0.08m long, and held in place with glass wool. This tube was located in a larger Pyrex tube, (*5*) in Figure 1. To obtain more uniform temperature the glass tube was inserted in a copper tube (*4*) and the whole assembly placed in a tubular furnace. Clearances between the small and larger Pyrex tubes and between the large Pyrex and copper tubes were small (~0.0005 m) to ensure nitrogen flow through the bed of particles. The temperature was measured and controlled with an iron-constant thermocouple located in the bed of particles. The thermocouple was enclosed in an insulated Inconel sheath of 1.6 × 10^{-3}m OD.

The bitumen content of the toluene solutions was determined with a Delta Scientific Company, Model 260, colorimeter. The transmittance was measured at a wavelength of 440 nm, in Pyrex cells of volume 60 × 10^{-6} m^3 and path length 2.54 × 10^{-2} m.



1. Tube Furnace
2. Small Glass Tube Holding the Shale Particles
3. Thermocouple
4. Copper Tube
5. Glass Tube

Figure 1. Diagram of apparatus for decomposition in nitrogen.

Table 1. Operating Conditions for Kinetics Experiments

Weight of shale sample	3×10^{-3} to 4.5×10^{-3} kg
Avg. particle dia.	0.18×10^{-3} m
N_2 flow rate (1 atm, 298 K)	0.25×10^{-6} m³/s
Temperature	533, 589, 611 K
Pressure	Atmospheric
Reaction time	0.9 to 18 ks
Critical temp. toluene	591.5 K
Critical press. toluene	4114 kPa
Bitumen determination by solution in toluene	
Stirring time	57.6 ks
Vol. toluene	0.1×10^{-3} m³

SI conversion: kPa = atm × 101.325.

Kinetics Experiments

The operating conditions for determining the extent of decomposition to gaseous products and bitumen are listed in Table 1.

The furnace containing the copper and larger Pyrex tubes was first heated to the desired temperature with a nitrogen flow rate of 1.5×10^{-6} m³/s (298 K, 101 kPa). Then the small Pyrex tube containing the shale particles was located in the center of the furnace. After insertion of the thermocouple, the nitrogen flow rate was reduced to 0.25×10^{-6} m³/s. After holding the sample at the desired temperature for a specified reaction time, the sample was cooled and weighed. The sample was heated rapidly in the hot furnace, reaching the desired temperature in 300 s or less.

Accurate evaluation of the gas and bitumen required several corrections, and preliminary experiments were necessary to ensure that the data measured reflected intrinsic kinetics. These experiments are described in the following paragraphs.

Effect of pressure

An apparatus (Estevez, 1983) was available for measuring the decomposition of kerogen at supercritical pressure. To determine the potential effect of pressure on the decomposition two experiments were carried out at 589 K. In one the weight change was measured for decomposition in N_2 at 101 kPa in the apparatus shown in Figure 1. The second was with N_2 flow at 4,060 kPa (40.1 atm). In the high-pressure experiment more bitumen and fewer gaseous products were obtained, but the conversion of kerogen was the same as that for the low-pressure run. Our kinetics data obtained in subsequent experiments apply for a pressure of 101 kPa.

Water correction

The adsorbed water in the shale samples was determined by weighing the sample before and after drying in nitrogen at 363 K for 18 ks, the maximum reaction time for the kinetics experiments. The weight loss was 0.2%. A second sample was heated for 18 ks at 611 K, which is the maximum temperature. This sample absorbed water on cooling. The weight increase was also about 0.2%. Hence, the kinetics data were corrected for this weight change in calculating the conversion to gaseous products.

Table 2. Effect of Particle Size and Stirring on Solution of Bitumen From Shale Particles

A. Effect of Particle Size (initial particle size = 2.2×10^{-3} m)

	Heating in N_2		No Stirring		With Stirring	
Exp. No.	Time ks	Temp. K	Extraction Time ks	Transmittance %	Extraction Time ks	Transmittance %
7	0	—	7,970	75.5	238	75.4
14	0	—	1,375	71.5	86	73.5
4	5.4	580	2,671	15.8	15	15.8

B. Effect of Stirring Time (initial particle size = 0.79×10^{-3} m)

Exp. No.	Stirring Time ks	Transmittance %
28	21.6	41.5
26	57.6	36.6
27	86.4	36.5

Effect of particle size and stirring on dissolution of bitumen

To determine the bitumen content of the toluene solution, the residual shale particles were removed by filtration. This process is more accurate the larger the particles. In contrast, solution of all the bitumen becomes more difficult with larger particles. Also, with stirring the particles were observed to disintegrate into smaller sizes. To determine whether or not all the bitumen is dissolved, experiments were carried out on two samples that were not heated in N_2, runs 7 and 14, and one sample heated for 5.4 ks at 579 K, run 4. In all cases the initial particle size was 2.2×10^{-3} m. These samples were first placed in toluene and held without stirring for the times indicated in Table 2A, column 4. The mixtures were then stirred magnetically for the additional time shown in column 6. Transmittance measurements, columns 5 and 7, show little change due to stirring, accompanied by breakup of particles. Hence it is concluded that the 0.18×10^{-3} m particles used for the kinetics experiments were small enough to ensure that all bitumen was dissolved. In fact the results show that stirring is not necessary for particles as large as 2.2×10^{-3}.

The time required to dissolve all the bitumen was determined by heating a shale sample at 589 K for 7.2 ks. The sample was then divided into three parts, each part stirred in toluene for a different time. The initial particle size was 0.79×10^{-3} m. Table 2B shows that there is no significant decrease in transmittance (increase in bitumen concentration) after a stirring time of 57.6 ks for samples as large as 0.79×10^{-3} m. Hence, all samples were stirred for 57.6 ks.

Original bitumen content and reproducibility

The original shale samples contain some toluene-soluble material (bitumen). To determine this amount and also to check reproducibility of the measurements, original shale particles of three sizes were stirred in toluene for 57.6 ks. Table 3 shows the results as the percent bitumen of total organics:

$$\frac{W_B}{W_o} = \frac{\text{(conc. of bitumen in toluene) (vol. of toluene)}}{0.15\, W_s} \qquad (1)$$

Table 3. Bitumen Content of Original Shale

Exp. No.	Particle Size $\times 10^3$ m	W_B/W_o %	Max. Dev. %
7	2.2	7.93	16.2
20	2.2	9.46	—
14	0.79	9.46	7.8
19	0.79	10.2	—
15	0.18	10.2	—
21	0.18	10.1	2.1
85	0.18	10.2	—
107	0.18	10.3	—

Two to four runs were made for each particle size so that the data in Table 3 also show the degree of reproducibility. For the smallest particle size (0.18×10^{-3} m) the maximum deviation is 2.1%. The larger deviations for the larger particles probably are due, primarily, to heterogenity of the particles. Many fewer particles were needed to make the 0.003 kg sample used in all cases. Considering the errors involved in all the measurements, the uncertainty is estimated to be about 15%.

The results for the 0.18×10^{-3} m particles indicate that about 10.2% of the total organics in the original shale is bitumen.

Effect of particle size on observed decomposition in N_2

The data in Table 3 are for original shale samples. To find the possible influence of transport processes on the rate of the thermal reactions, samples were heated at 589 K for 1.8 and 10.8 ks. Results for different particle sizes are shown in Table 4.

The values of W_B/W_o were calculated by Eq. 1. The gaseous products are reported as W_G/W_o and calculated from the weight measurements before and after heating in N_2:

$$\frac{W_G}{W_o} = \frac{\text{change in weight on heating}}{0.15\ W_s} \tag{2}$$

The conversion of x_k of organics in the original sample was determined by subtracting from the weight of kerogen $(W_k)_o$ in the original sample the weight, W_k, of unconverted kerogen.

$$x_k = \frac{(W_k)_o - W_k}{(W_k)_o} = \frac{[0.15\ W_s - (W_B)_o] - W_k}{[0.15\ W_s - (W_B)_o]} \tag{3}$$

where

$$(W_B)_o = 0.10\ (0.15\ W_s) \tag{4}$$

Table 4. Effect of Particle Size on Decomposition in N_2

Exp. No.*	Temp. K	Heating Time ks	Particle Size $m \times 10^3$	W_B/W_o %	W_G/W_o %	Conv. x_k %
16	589	1.8	2.2	5.9	7.2	3.2
17, 18, 35	589	1.8	0.79	6.3	10.9	7.8
37, 47, 49	589	10.8	0.79	8.8	13.6	13.5
46, 48	589	10.8	0.18	7.1	13.5	11.6
38	589	10.8	<0.14	7.0	13.9	11.9

*Where more than one experiment is indicated, results are for the average of the runs.

The weight of unconverted kerogen at any time, W_k, is obtained by subtracting, from the kerogen in the original sample, the sum of the gas product and bitumen (corrected for bitumen in the original sample) produced:

$$W_k = 0.15\ W_s - W_B - W_G \tag{5}$$

The results in Table 4 show a significantly lower conversion for 2.2×10^{-3} m particles. However, the data in the bottom part of the table indicate no change, within the limits of reproducibility, for particles 0.79×10^{-3} m or smaller. The variation in x_k between 0.79×10^{-3} m and smaller particles is a measure of the reproducibility of the data. Reproducibility is poorer for heated particles (data in Table 4 vs. Table 3), probably because two measurements, W_B and W_G, are required for the heated samples. Final kinetics data were obtained with 0.18×10^{-3} m particles as indicated in Table 1.

Calibration Results

The concentration of bitumen in the toluene solutions was determined from calibration experiments with the colorimeter. Weighed samples of shale were introduced into a known volume of toluene and stirred for 57.6 ks. The solution was filtered and the particles dried in air at 343 K for 10 to 28.8 ks to remove the remaining toluene. The drying process was continued until the weight of the particles was constant. The concentration was calculated from the difference in weight and the volume of the solution, and related to the transmittance. Larger particles 0.589 to 0.991×10^{-3} m (average size 0.79×10^{-3} m) were used for the calibration experiments since with a smaller size it was difficult to avoid particle loss during filtration. Larger particles were permissible because for the calibration experiments it was not necessary to extract all the bitumen from the samples, but only to know the mass extracted. It was not convenient to use particles larger than 0.79×10^{-3} m because of the time required to remove the remaining toluene. Figure 2, which is for original shale samples (not heated in nitrogen), is typical of the resultant calibration curves. Table 5 summarizes the calibration conditions and the reaction conditions to which the samples were subjected prior to extraction in toluene. Measurements for extraction times less than 57.6 ks indicated that the time of extraction did not measurably affect the calibration curve.

We have defined bitumen as one component, while it is probably a mixture of numerous hydrocarbons, some of which contain

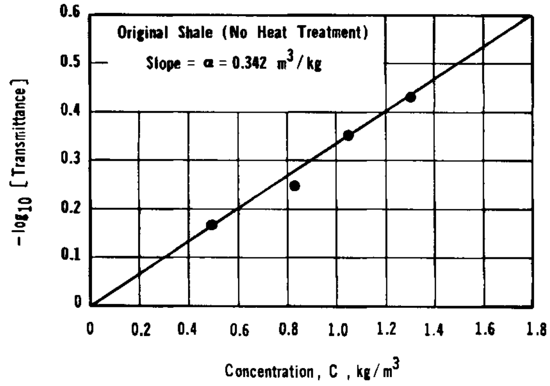


Figure 2. Typical calibration curve.

Table 5. Calibration Conditions

Physical Characteristics	
Weight of shale sample	3×10^{-3} to 7×10^{-3} kg
Shale particle dia.	0.79×10^{-3} m
Reaction Conditions (Decomposition in N_2)	
N_2 flow rate (101 kPa, 298 K)	0.25×10^{-6} m³/s
Temperature	533, 589, 611 K
Pressure	101 kPa
Reaction time	0.0 to 18 ks
Extraction Conditions	
Time of extraction in toluene	57.6 ks
Vol. of extracting toluene	0.1×10^{-3} m³
Temperature	298 K
Pressure	101 kPa
Drying Conditions	
Temperature	343 K
Drying time	18 to 28.8 ks

heteroatoms. Therefore, the composition of the bitumen is expected to depend upon the temperature and heating time of the decomposition in nitrogen. This is the reason for carrying out calibration experiments over the same range of conditions as for the kinetics experiments.

The relation between transmittance τ measured in the colorimeter, considering bitumen as a single component, and the concentration C is given by Lambert-Beer's law:

$$\log_{10}\left(\frac{\tau}{\tau_o}\right) = -apC = -\alpha C \qquad (6)$$

Since the path length p is constant, the product α is a measure of the absorptivity or composition of the bitumin extracted. Values of α calculated from the known concentrations and transmittances in the calibration experiments are shown in Figure 3 as a function of reaction conditions (temperature and heating time).

The increasing value of α with heating time in Figure 3 suggests that lighter molecules (lower absorptivity) are produced first in the decomposition process. However, at the two lower temperatures the asymptotic values of α indicate that the decomposition products do not change with heating time after the initial period. At the highest temperature, 611 K, no asymptote is observed, suggesting that heavier products are produced at increasing reaction times over the entire period. The α values increase with temperature for the same heating time. This means that the transmittances are less for solutions of the same concentration at higher temperatures, and indicates that heavier products are produced by decomposition in N_2 at higher temperatures.

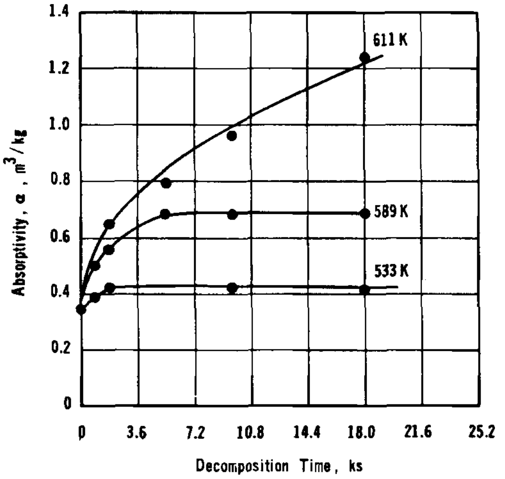


Figure 3. Absorptivity as a function of temperature and decomposition time in nitrogen.

In evaluating the concentration of bitumen in the toluene solution for the reaction experiments, values of α corresponding to reaction conditions were obtained from Figure 3. Then these values of α were employed in Eq. 6 to calculate the concentration from the measured transmittance. Finally, the weight of bitumen in the reacted sample was determined from Eq. 1.

Kinetics of Decomposition

Reaction scheme

Pyrolysis of kerogen at temperatures greater than about 648 K yields about 10% coke as one product. Such pyrolyzed shale particles are black. In our experiments at lower temperatures, the spent particles after reaction in N_2 did not appear black. It is concluded that little coke is produced at temperatures of 611 K or less. Assuming no coke, the measured products of decomposition in nitrogen permit calculation of the unreacted kerogen, and the gaseous product and bitumen produced, as a function of heating time and temperature. The results, shown in Figures 4–6, are referred to the total mass of organics (W_o), kerogen plus bitumen in the original samples.

The results in Figures 4–6, and auxiliary experiments, suggest reaction sequences of the form

$$K \rightarrow B \rightarrow G \qquad (7)$$

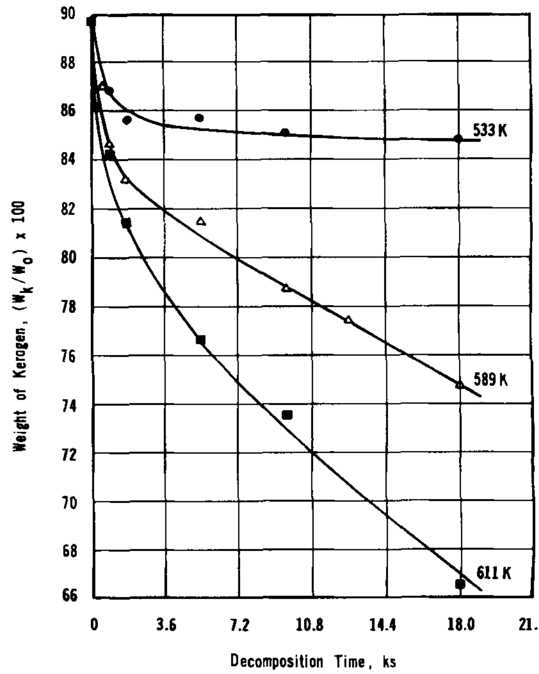


Figure 4. Weight of unconverted kerogen as a function of decomposition time and temperature.

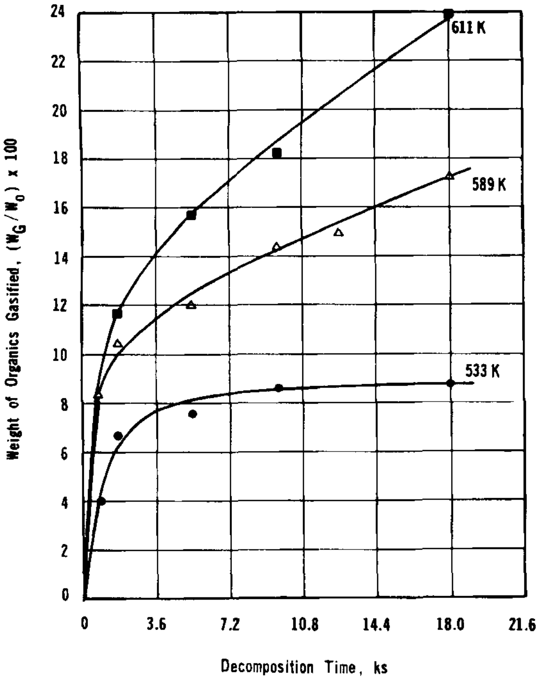


Figure 5. Weight of organics gasified as a function of decomposition time and temperature.

or

$$\begin{tikzcd} K \arrow[r] \arrow[d] & B \arrow[r] & G \\ G & & \end{tikzcd} \tag{8}$$

Parallel reactions of the kerogen and bitumen in the original samples to gaseous products is not likely due to the shape of the bitumem curves in Figure 6. If both kerogen and bitumen had reacted to gas products, the bitumen curves in Figure 6 would have shown a continual decrease with time. Further evidence for the series reaction sequence of Eqs. 7 and 8 was observed from experiments on shale particles from which bitumen had been removed by dissolution in toluene. An original sample of shale containing 10.2% of total organics as bitumen (Table 3) was stirred in toluene. The bitumen content was reduced to 0.55%. The particles were filtered, dried, and then heated in nitrogen for 9.6 ks at 589 K. Stirring the particles in toluene and measuring the transmittance of the filtered solution indicated a bitumen content of 2.3%. The increase of bitumen from 0.55 to 2.3% indicated that at least part of the kerogen is first converted to bitumen.

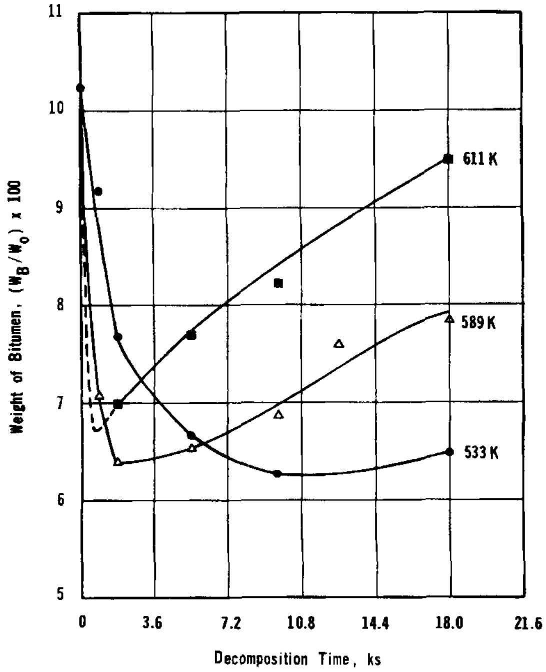


Figure 6. Weight of bitumen produced as a function of decomposition time and temperature.

To discriminate between Eqs. 7 and 8, samples containing about 0.5 and 10 wt. % bitumen (experiments 85 and 60) were both heated in nitrogen for 9.6 ks at 589 K. If the reaction scheme of Eq. 7 were applicable, the gaseous product from experiment 60, with 22 times the bitumen content of experiment 85, would be expected to be large. However, the results in Table 6 show that W_G for experiment 60 is but 1.5 times W_G from experiment 85. Both samples originally contained the same amount of kerogen. Evidently some kerogen is decomposed directly to gaseous products, as indicated by the reaction scheme in Eq. 8.

Plotting the unreacted kerogen data from Figure 4, assuming a first-order decomposition rate according to the expressions,

$$\frac{dW_k}{dt} = -k\,W_k \tag{9}$$

$$\ln\,[W_k/(W_k)_o] = -kt, \tag{10}$$

yields the data points shown in Figure 7. While the data are insufficient to draw a firm conclusion, two different rate constants are indicated, a large one for low times (up to 1.8 ks) and a smaller one at larger times. Since kerogen probably contains compounds of a wide range of molecular weights (McKay, 1984), it is not unexpected that the decomposition rate constant is not a single value. The results in Figure 7 suggest that light components decompose first at a rate which is greater than that at which the heavier components decompose. Further, the break in the curves at 1.8 ks could represent the time at which all of the light components in kerogen have reacted.

As an approximation for kinetic analysis, kerogen is considered to contain two groups of components, designated as light kerogen, K_L, and heavy kerogen, K_H. Furthermore, it is assumed that the light kerogen reacts to gaseous products and the heavy kerogen to bitumen, with the first-order rate constants shown in the following reaction scheme:

$$K_H \xrightarrow{k_1} B \xrightarrow{k_2} G_2 \tag{11}$$

Table 6. Effect of Original Bitumen Content on Gaseous Products of Reaction

Exp. No.	Temp. K	Heating Time ks	$(W_k)_o$ kg × 10^3	$(W_B)_o$ kg × 10^3	W_G kg × 10^3	W_B kg × 10^3	W_k kg × 10^3
85	589	9.6	0.404	0.0021	0.0417	0.0093	0.355
60	589	9.6	0.406	0.046	0.0650	0.0312	0.356

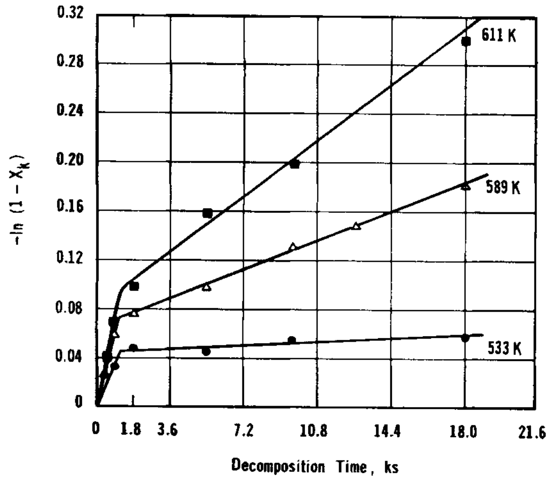


Figure 7. First-order plot for kerogen decomposition; $x_k = [(W_k)_o - W_k]/(W_k)_o$

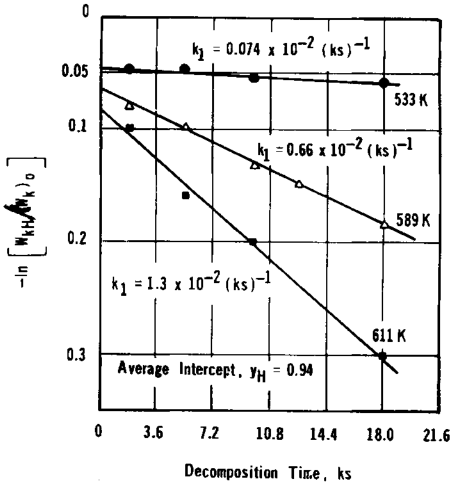


Figure 8. Decomposition of heavy components in kerogen.

$$K_L \xrightarrow{k_3} G_3 \tag{12}$$

This simplified reaction scheme for decomposition at subpyrolysis temperatures, and the data, can be used to evaluate the fraction of heavy kerogen in the original shale: that is, $(W_{kH})_o/(W_k)_o$. Suppose that the data in Figure 4 at times beyond 1.8 ks represent the decomposition only of heavy kerogen and that all light kerogen has disappeared. Then first-order kinetics requires that

$$\ln\left\{\frac{W_{kH}}{(W_{kH})_o}\right\} = -k_1 t \tag{13}$$

If y_H represents the fraction heavy components in the kerogen,

$$(W_{kH})_o = y_H\,(W_k)_o \tag{14}$$

Combining Eqs. 13 and 14 yields

$$\ln\frac{W_{kH}}{(W_k)_o} = \ln y_H - k_1 t \tag{15}$$

$(W_k)_o$ is known $[=0.15\ W_s - (W_B)_o]$ and the data in Figure 4 give W_{kH} vs. time. Hence, y_H can be obtained from Eq. 15. Figure 8 shows the results. The intercepts at zero time are equal to y_H and should be the same for all temperatures. The maximum deviation between the intercepts is 3.6% and the average value of $y_H = 0.94$.

Rate constants

The slopes of the lines in Figure 8 determine the values of k_1. These are shown on the Arrhenius plot in Figure 10 and suggest an activation energy of 100 kJ/mol.

Insufficient data are available for accurate evaluation of k_3, for conversion of kerogen to gaseous products, as seen by the few points in Figure 7 at times less than 1.8 ks. However, this rate constant can be approximated, for a first-order reaction, using an equation analogous to that for heavy kerogen:

$$\ln\frac{W_{kL}}{(W_k)_o} = \ln(1 - y_H) - k_3 t \tag{16}$$

First W_{kH} is calculated at times less than 1.8 ks using Eq. 15 with the known values for k_1 and y_H. Then W_{kL} is obtained from the expression

$$W_{kL} = W_k - W_{kH} \tag{17}$$

The total kerogen W_k at any time is available from the experimental value of W_s, W_B, and W_G via Eq. 5. The results plotted according to Eq. 16 are shown in Figure 9. Again, the slopes of

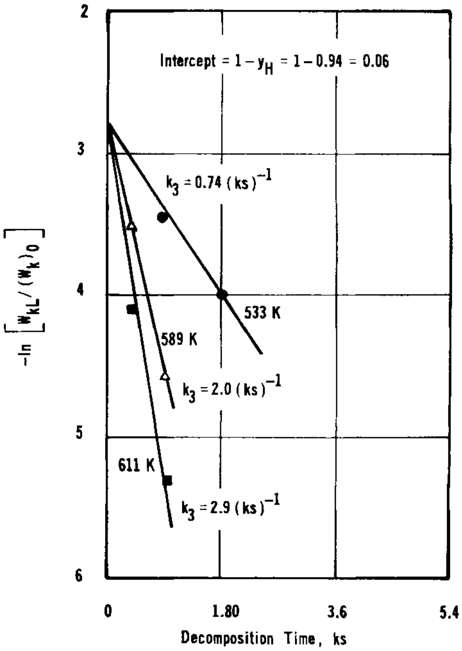


Figure 9. Decomposition of light components in kerogen.

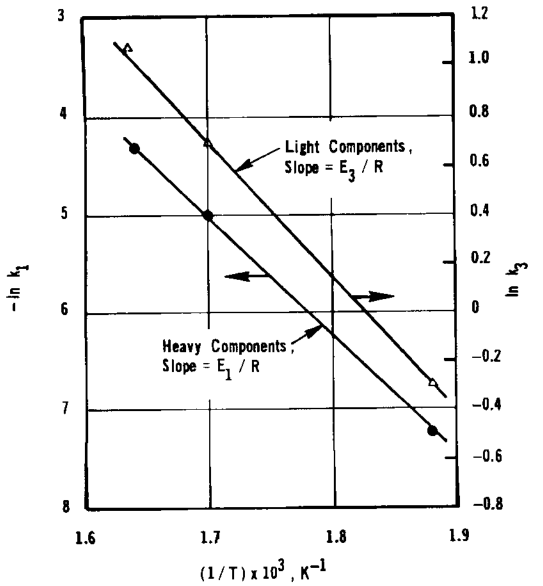


Figure 10. Arrhenius plot for decomposition of heavy and light components in kerogen.

Table 7. Rate Constant for the Decomposition of Bitumen

Temp. K	Reaction Time in N_2 ks	k_2 ks^{-1}
	0.9	0.13
	1.8	0.16
533	5.4	0.086
	9.6	0.058
	18.0	0.032
	0.45	0.45
	9.0	0.47
	1.8	0.33
589	5.4	0.15
	9.6	0.11
	12.6	0.09
	18.0	0.07
	0.9	0.65
	0.45	0.60
611	1.8	0.34
	5.4	0.17
	9.6	0.17
	18.0	0.10

the lines establish the rate constant, and these are also shown on the Arrhenius plot, Figure 10. The activation energy for this relatively fast reaction is 46 kJ/mol. The lines in Figure 10 are represented by the equations

$$k_1(ks)^{-1} = 6.0 \times 10^6 \exp\left(-\frac{100}{RT}\right) \tag{18}$$

$$k_3(ks)^{-1} = 2.6 \times 10^4 \exp\left(-\frac{46}{RT}\right) \tag{19}$$

According to Eq. 11 the rate of production of bitumen is

$$\frac{dW_B}{dt} = k_1 W_{kH} - k_2 W_B \tag{20}$$

with initial condition

$$W_B = (W_B)_o = 0.10\ (0.15\ W_s) \text{ at } t = 0 \tag{21}$$

Using Eq. 15 for W_{kH}, integration of Eq. 20 yields

$$W_B = (W_B)_o e^{-k_2 t} + (W_{kH})_o k_1 \left[\frac{e^{-k_1 t}}{k_2 - k_1} + \frac{e^{-k_2 t}}{k_1 - k_2}\right] \tag{22}$$

In Eq. 22, k_1 and y_H are known from the prior analysis. Then $(W_{kH})_o$ is given by Eq. 14 and $(W_B)_o$ is 0.10 (0.15 W_s). Hence, the data in Figure 6 for W_B vs. time can be used with Eq. 22 to calculate k_2. The results are shown in Table 7 where a separate k_2 is estimated for each decomposition time.

The values in Table 7 are approximate since they depend upon the prior calculations (k_1). However, the results appear to be of two types: a high value at low times and lower values at $t >$ 1.8 ks. This suggests that bitumen, like kerogen, is a mixture of components that can be characterized approximately as light and heavy bitumens. Assuming that the same type of reaction occurred over the years in the shale formation as in our decomposition experiments, the bitumen in the original samples also consists of light and heavy components. In this view, the reaction scheme of Eqs. 11 and 12 can be enlarged to the following scheme:

$$\begin{tikzcd} K_H \arrow[r, "k_1"] & B_H \arrow[d, "k_4"] & + & B_L \arrow[d, "k_5"] \\ & G_4 & & G_5 \end{tikzcd} \tag{23}$$

$$K_L \xrightarrow{k_3} G_3 \tag{24}$$

where $k_3 > k_1$; k_5 or $k_4 > k_1$

Wallman et al. (1981) in studies of pyrolysis at higher temperatures (755–810 K) also found that some kerogen was directly converted to light products as suggested by Eq. 24. The experimental kerogen decomposition curves of Wallman et al. (1981) were similar to those in Figure 4 in that two different kinetic regimes were indicated. Also, the pyrolysis data of Johnson et al. (1975) were best correlated by including a reaction for producing gases directly from kerogen.

Individual values for k_4 and k_5 cannot be established since the relative amounts of B_H and B_L in neither the original samples nor after decomposition are known. The initial rapid decrease in W_B shown in Figure 6 is due to the gasification of rapidly reacting, toluene-soluble components (bitumen) in the original samples by the reactions shown in Eq. 23. After all components have been converted to gaseous products, the slower conversion of heavy kerogen to bitumen results in an increasing bitumen level as shown in Figure 6 at long times. According to Eq. 23, the bitumen level would ultimately decrease, although such long times were not investigated in our work.

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Notation

a = absorptivity of toluene solution, m^2/kg
B = bitumen
B_H = heavy components of bitumen
B_L = light components of bitumen
C = concentration of bitumen in toluene solution, kg/m^3
E = activation energy, kJ/mol
G = gaseous products of decomposition
G_3 = gaseous products of decomposition from kerogen
G_2, G_4, G_5 = gaseous products of decomposition from bitumen
K = kerogen
K_H = heavy components of kerogen
K_L = light components of kerogen
k = first-order rate constant for decomposition of total kerogen, ks^{-1}
k_1 = first-order rate constant for decomposition of heavy kerogen components to bitumen, ks^{-1}
k_2 = first-order rate constant for decomposition of bitumen to gaseous products, ks^{-1}
k_3 = first-order rate constant for decomposition of light components of kerogen to gaseous products, ks^{-1}
k_4 = first-order rate constant for decomposition of heavy components of bitumen to gaseous products, ks^{-1}
k_5 = first-order rate constant for decomposition of light components of bitumen to gaseous products, ks^{-1}
p = path length in colorimeter, m
R = gas constant, 8.3×10^{-3} kJ/mol · K
T = temperature, K
t = decomposition time, ks
W = weight, kg
W_B = weight of bitumen, kg
W_G = total weight of gaseous products, kg
W_k = total weight of kerogen, kg
W_{kH} = weight of heavy components of kerogen, kg
W_{kL} = weight of light components of kerogen, kg
W_o = total weight of organics in original sample, kg
W_s = total weight of samples, kg
y_H = fraction of heavy components in kerogen in original sample
$1 - y_H$ = fraction of light components in kerogen in original sample

Greek letters

α = absorptivity × path length, m^3/kg
τ = transmittance of toluene solution, %
τ_o = refers to pure toluene

Subscript

o = value in original sample

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