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THE KINETICS OF THE THERMAL DECOMPOSITION OF GREEN RIVER OIL SHALE KEROGEN BY NON-ISOTHERMAL THERMOGRAVIMETRY

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ABSTRACT

The kinetics of the thermal decomposition of Green River oil shale kerogen have been studied by non-isothermal thermogravimetry. Kerogen decomposes to a bitumen intermediate with an activation energy of 62.10 kJ mole^{-1} and a frequency factor given by ~10^6 min^{-1}. The pyrolytic bitumen decomposes into oil, gas and carbonaceous residue with an activation energy of 152.16 kJ mole^{-1} and a frequency factor of ~10^{14} min^{-1}. The weight loss data were analyzed by the direct Arrhenius, Coats—Redfern and Freeman—Carroll techniques. The kinetic parameters derived from the three methods are discussed in the light of previous work on the thermal decomposition kinetics of oil shale kerogen. Factors influencing kinetic data such as sample holder geometry, heating rate and atmosphere are critically reviewed. The concept of kinetic order is examined in the light of existing theory for solid-state decomposition reactions and it is shown that first-order kinetics are adequate in explaining the overall trends in the thermal behavior of Green River oil shales.

INTRODUCTION

Much attention has been focused in recent years on the kinetics of the thermal decomposition of oil shale kerogen (for a review of previous work in this topic, see ref. 1). The majority of these studies have utilized isothermal conditions for heating the shale samples. One difficulty with isothermal techniques is that the time required for the test samples to attain the reaction temperature introduces a significant error in the kinetic data, especially at elevated temperatures when the heat-up time becomes a significant fraction of the total reaction period [1]. As Braun and Rothman [2] have pointed out, a correction factor may be introduced in the isothermal data in favorable cases. The use of large sample sizes in most of the earlier kinetic studies coupled with the rather low thermal conductivity of oil shales, however, results in non-trivial errors even at low temperatures (300—400°C) where the rate of decomposition is low. Non-isothermal kinetic measurements [3] offer a ready means of eliminating this difficulty. A further advantage of the application of non-isothermal techniques to studies on oil shales is that the thermal history perhaps approximates more closely the conditions obtaining in an active oil shale retort. In spite of these attractive features, it appears that the use of non-isothermal techniques in the study of oil shale decomposition kinetics has received only scant attention. Campbell et al. [4] employ nonlinear least-squares fit of non-isothermal thermogravimetry (TG) data to derive kinetic parameters for a Colorado oil shale sample. Herrell and Arnold [5] report the use of non-isothermal TG for the study of Chattanooga shales. In both these studies the kinetic data have been interpreted in terms of a single-step decomposition mechanism. Such an interpretation, however, seems to be contradictory to the conclusions reached in most of the early studies [1] which indicate that the thermal decomposition of oil shale kerogen proceeds in two consecutive steps via a soluble bitumen intermediate, i.e.

$$\text{Oil shale kerogen} \rightarrow \text{pyrolitic bitumen} \rightarrow \text{oil} + \text{gas} + \text{semi-coke residue} \qquad (1)$$

In view of this apparent contradiction, it was decided to re-examine the kinetics of the thermal decomposition of oil shale kerogen. Samples of kerogen concentrate from the Green River formation (from which the mineral matter was largely removed by acid extraction [6]) were employed in this study. The use of small sample sizes and efficient atmosphere control for precluding the deleterious effects of self-generated atmospheres and diffusion limitations [1], was particularly relevant to the objectives of the present study.

EXPERIMENTAL

Samples of Green River oil shale kerogen were obtained from Laramie Energy Technology Center, Laramie, WY. The results of chemical analyses

TABLE 1

Chemical analysis of Green River oil shale kerogen samples employed in the present study

Carbon content (wt.%)	63.36
	63.47
Hydrogen content (wt.%)	8.46
	8.41
Nitrogen content (wt.%)	2.15
	2.01
Oxygen content (wt.%)	9.46
	9.50
Sulfur content (wt.%)	3.16
	3.10
Ash content (wt.%)	14.73
	14.55
Mineral CO_2 content (wt.%)	<0.02
Moisture content (wt.%)	1.22
	1.20

on representative batches are assembled in Table 1. The elemental composition of the present samples shows good agreement with values determined in previous work [6] although the ash content of the present samples is somewhat higher. On the other hand, the sulfur content of the present samples is slightly lower than previous values [6].

Thermogravimetric analyses were performed on a Dupont 990 Thermal Analysis System fitted with the 951 TG accessory *. The kerogen samples were spread in a thin layer on the platinum sample boat. All experiments were carried out in a flowing atmosphere of pre-purified N_2 gas. The small sample mass (10—20 mg), the shallow sample holder and adequate exposure of the test samples to the ambient inert gas stream ensured the absence of self-generated atmospheres and thermal gradients within the sample. Particular care was exercised in this regard since the use of a sample holder geometry, whereby the escape of product gases from the decomposing sample is inhibited, results in artifacts introduced by diffusion-limited kinetics and concomitantly spurious values for the kinetic parameters (cf. ref. 1).

Measurements were carried out in the temperature range 25—800° C. A small weight loss (0.05—1%) occurred in the temperature range 25—200° C. This initial weight loss is attributed to the loss of moisture from oil shale kerogen (cf. Table 1). Kinetic analyses were restricted to temperatures above this temperature range. The fractional weight loss data above 200° C were therefore normalized with respect to the initial weight loss associated with the loss of moisture and therefore refer solely to the thermal decomposition of oil shale kerogen (vide infra).

All TG measurements were replicated and the weight loss data below pertain to those averaged from duplicate runs.

KINETIC EXPRESSIONS

The kinetics of solid-state decomposition reactions may be represented by an expression of the form [7]

$$d\alpha/dt = k\mathrm{f}(\alpha) \tag{2}$$

where α is the fraction reacted in time t, k is the rate constant, and the function $\mathrm{f}(\alpha)$ depends on the particular decomposition mechanism. The rate constant k is related to the absolute temperature T by the Arrhenius expression

$$k = A\exp(-E/RT) \tag{3}$$

A is the frequency factor, E is the activation energy and R is the gas constant. Substituting eqn. (3) in eqn. (2), we get

$$d\alpha/dt = A\mathrm{f}(\alpha)\exp(-E/RT) \tag{4}$$

For a non-isothermal kinetic experiment with linear heating rate, β ($=dT/dt$),

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* Reference to a brand name or product does not imply endorsement by the author or by the U.S. Department of Energy.

the above expression becomes

$$d\alpha/dT = A/\beta\ f(\alpha)\ \exp(-E/RT) \tag{5}$$

For a reaction which may be represented functionally as $f(\alpha) = (1-\alpha)^n$, where n is the reaction order, the above expression reduces to

$$d\alpha/dT = A/\beta\ \exp(-E/RT)\ (1-\alpha)^n \tag{6}$$

According to eqn. (6), a plot of $\ln[(d\alpha/dT)/(1-\alpha)^n]$ vs. $1/T$ yields a straight line from which the kinetic parameters A and E can be extracted from the intercept and slope, respectively. It is noted here that the concept of reaction order and frequency factor in solid-state kinetics assumes a different significance from that adopted in homogeneous reaction kinetics (cf. ref. 8). Topochemical considerations restrict values of n to 0, 1/2, 2/3 and 1 in solid-state kinetics [9]. This point seems to have been overlooked in previous work on oil shale decomposition kinetics (vide infra).

A second equation of relevance to this work is the integral method developed by Coats and Redfern [9] which takes the form

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\frac{AR}{\beta E}\left[1-\frac{2RT}{E}\right] - \frac{E}{RT} \tag{7}$$

for all values of n except 1 in which case the following equation applies

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E}\left[1-\frac{2RT}{E}\right] - \frac{E}{RT} \tag{8}$$

Thus a plot of either $\ln[\{1-(1-\alpha)^{1-n}\}/\{T^2(1-n)\}]$ against $1/T$ or, where $n = 1$, $\ln[-\{\ln(1-\alpha)\}/T^2]$ against $1/T$ should result in a straight line of slope E/R for the correct value of n (it has been shown [9] that the first term in eqns. (7) and (8) remains sensibly constant for most values of E).

The difference-differential method developed by Freeman and Carroll [10] offers the advantage of directly yielding the value of n. Again, starting with eqn. (6) and taking logarithms

$$\ln Z - E/RT = \ln(d\alpha/dT) - n\ln(1-\alpha) \tag{9}$$

where $Z = A/\beta$. Differentiating eqn. (9) with respect to $d\alpha/dT$, α and T, we get

$$E\frac{dT}{RT^2} = d\ln(d\alpha/dT) - nd\ln(1-\alpha) \tag{10}$$

Integration of the above equation yields

$$-E/R\ \Delta(1/T) = \Delta\ln(d\alpha/dT) - n\ \Delta\ln(1-\alpha) \tag{11}$$

Dividing eqn. (11) by $\Delta\ln(1-\alpha)$, we get

$$\frac{-E/R\ \Delta(1/T)}{\Delta\ln(1-\alpha)} = \frac{\Delta\ln(d\alpha/dT)}{\Delta\ln(1-\alpha)} - n \tag{12}$$

A plot of $\Delta(1/T)/\Delta\ln(1-\alpha)$ vs. $[\Delta\ln(d\alpha/dT)]/[\Delta\ln(1-\alpha)]$ should yield a straight line according to eqn. (12) from which values of E and n may be determined from the slope and intercept, respectively.

ANALYSIS OF EXPERIMENTAL DATA

Figure 1 illustrates the fractional weight loss, α, as a function of temperature for Green River oil shale kerogen at three different heating rates. The sigmoid-shaped conversion curves are characteristic of solid-state decomposition reactions [7]. The raw TG data were used to generate α values at each temperature from the following equation

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f} \tag{13}$$

where W_0 = initial mass of sample, W_t = mass of sample at temperature T and W_f = final mass remaining at the end of the reaction. The total weight loss usually amounted to 50—60%, depending on the heating rate.

The derivative of the weight loss as a function of temperature, $d\alpha/dT$, is a more sensitive index of the reaction rate. Figure 2 illustrates typical DTG behavior for the data shown in Fig. 1. The systematic shift in the rate maxima to lower temperatures with increasing heating rate is to be noted. This shift arises because of differences in the rate at which heat is transferred to the test sample as the heating rate is varied.

Figure 3 is a plot of eqn. (6) for Green River oil shale kerogen at three different heating rates. A value of $n = 1$ was initially assumed for these calculations. Two points may be noted in the results shown in Fig. 3: (a) the experimental data are in agreement with a kinetic scheme involving two consecutive reactions as shown by two sets of straight lines with differing slopes at the various heating rates; and (b) variations in heating rate do not result in systematic changes in the gradient of the straight line plots in Fig. 3. The derived kinetic parameters therefore are likely to be insensitive to the efficiency of heat transfer between the sample and the ambient [11] and thus more representative of the chemical process involved. In this regard, heating rate variations are a reliable diagnostic criterion for the efficacy of a particular non-isothermal kinetic analysis method and also a sensitive probe for gleaning information on mechanistic aspects.

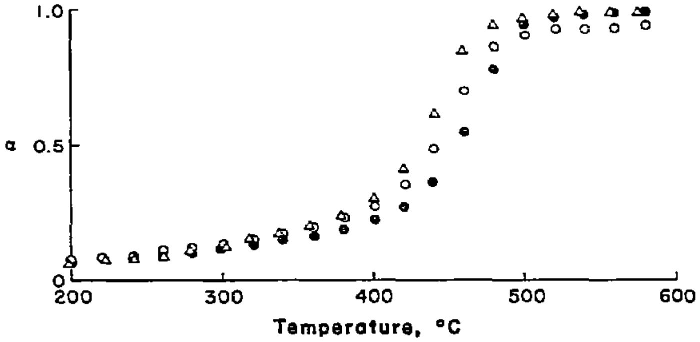
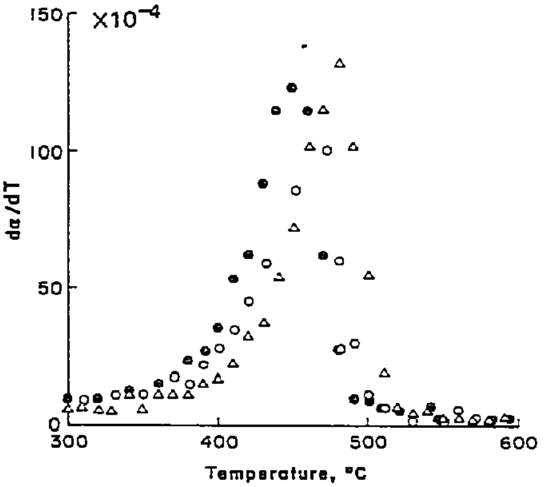


Fig. 1. Fractional weight loss (α) as a function of temperature for Green River oil shale kerogen. Heating rate: △, 5°C min^{-1}, ○, 10°C min^{-1}; ●, 20°C min^{-1}.



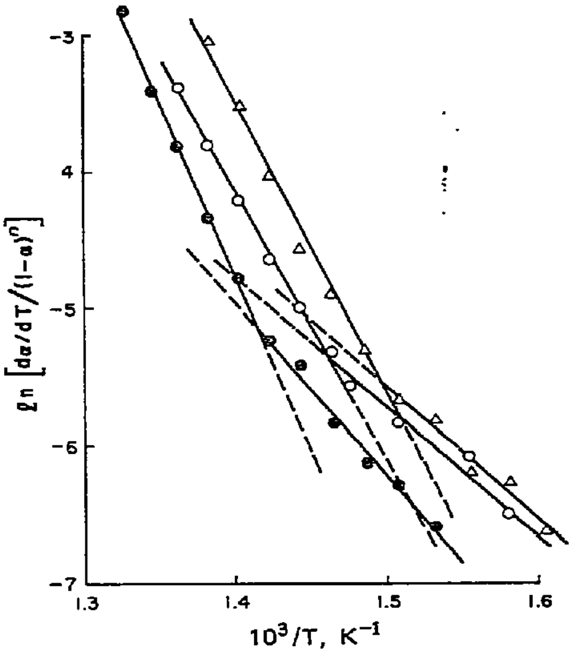
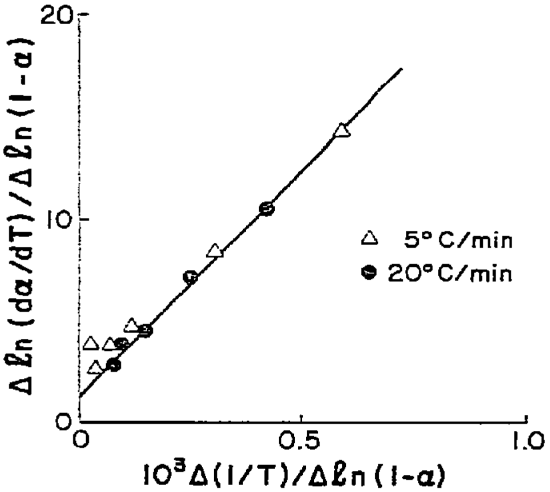


Fig. 2. Derivative thermogravimetric behavior as a function of temperature for the data shown in Fig. 1. Heating rate: △, 5°C min^{-1}; ○, 10°C min^{-1}; ●, 20°C min^{-1}.

Fig. 3. Analysis of the TG data for Green River oil shale kerogen by the direct Arrhenius method [eqn. (6)]. Heating rate: △, 5°C min^{-1}; ○, 10°C min^{-1}; ●, 20°C min^{-1}.



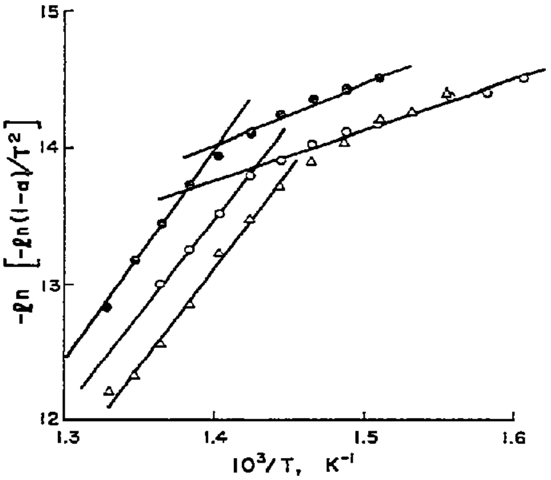


Fig. 4. Analysis of the TG data for Green River oil shale kerogen by the Freeman—Carroll method [eqn. (12)]. The data are shown for the two extreme heating rates employed in the present study. △, 5°C min^{-1}; ●, 20°C min^{-1}.

Fig. 5. Analysis of the TG data for Green River oil shale kerogen by the Coats—Redfern method [eqn. (8)]. Heating rate: △, 5°C min^{-1}; ○, 10°C min^{-1}; ●, 20°C min^{-1}.

TABLE 2

Kinetic parameters for the non-isothermal decomposition of Green River oil shale kerogen

Method	Heating rate (°C min^{-1})	Kinetic parameters *				
		E_1	E_2	A_1	A_2	n **
Direct Arrhenius [eqn. (6) and Fig. 3]	5	82.96	187.71	5×10^4	5.9×10^{12}	
		(3.44)	(3.23) ***	(1.42)	(1.18)	
	10	74.75	162.57	2.19×10^4	9.7×10^{10}	
		(2.85)	(2.22)	(1.18)	(0.82)	
	20	108.10	209.50	9.78×10^6	2.88×10^{14}	
		(3.06)	(2.98)	(1.18)	(1.06)	
Freeman—Carroll [eqn. (12) and Fig. 4]	5, 20		138.27			1
			(0.42)			
Coats—Redfern [eqn. (8) and Fig. 5]	5	41.9	117.32			
		(0.92)	(2.18)			
	10	27.40	116.48			
		(1.05)	(1.59)			
	20	37.21	133.24			
		(1.76)	(2.31)			

* Units of E and A are in kJ mole^{-1} and min^{-1}, respectively.

** A kinetic order of unity was assumed for the direct Arrhenius and Coats—Redfern methods (see text).

*** Numbers in parentheses represent standard deviation by least-squares analyses.

Figure 4 is a plot of eqn. (12), and shows the data at the two extreme heating rates employed. Again, the effect of heating rate is seen to be negligible and the data for the two heating rates are superimposable. More importantly, the intercept yields a value close to unity, confirming the validity of the above assumption that $n = 1$. Analyses of the TG data in terms of eqn. (12) were restricted to temperatures above ca. 400°C in view of the increasing errors inherent in this method at low fractional conversions (i.e., low temperatures) [12]. The kinetic data in Fig. 4, therefore, refer to the high temperature stage in the thermal decomposition of oil shale kerogen (vide infra).

Having confirmed the validity of describing the decomposition of oil shale kerogen in terms of first-order kinetics, the α vs. T data were analyzed by eqn. (8). Figure 5 illustrates the results, with heating rate shown as the parametric variable. Again, two sets of straight lines with distinctly different slopes are observed (cf. Fig. 3).

Table 2 lists the values of E and A extracted by least-squares analyses of the data shown in Figs. 3—5.

DISCUSSION

The present kinetic data are consistent with a decomposition scheme involving two consecutive reactions

$$\text{Oil shale kerogen} \xrightarrow{k_1} \text{pyrolytic bitumen}$$

$$\xrightarrow{k_2} \text{oil} + \text{gas} + \text{semi-coke residue} \quad (1)$$

The temperature dependence of the rate constants of each of the reactions above may be described by the Arrhenius equation

$$k_1 = A_1 \exp(-E_1/RT) \quad (3b)$$

and

$$k_2 = A_2 \exp(-E_2/RT) \quad (3c)$$

Values of the kinetic parameters A_1, A_2, E_1 and E_2 obtained in the present study are summarized in Table 2. It is seen that $E_1 < E_2$ and $A_1 << A_2$.

We note that in contradiction to the trends observed in the present study, previous studies [4,5] on the decomposition kinetics of oil shales by non-isothermal TG do not seem to resolve the intermediate step associated with the thermal decomposition of kerogen to pyrolytic bitumen. We also conclude, on the basis of the results in the present study, that the ability to resolve multiple processes hinges on the efficacy of the particular kinetic analysis that is employed to extract the reaction parameters and is not an inherent difficulty with non-isothermal TG techniques in general. For example, the direct Arrhenius method and the Coats—Redfern equation clearly indicate the presence of two reactions with distinctly different kinetic parameters (cf. Figs. 3 and 5 and Table 2). The Freeman—Carroll method, on the other hand, is handicapped at low fractional conversions where extraction of difference-differentials from the raw TG data is prone to increasing error [12]. Application of this technique for the analysis of non-isothermal TG data on oil shales would have led, therefore, to incomplete information on the pyrolysis mechanism. Non-linear least-squares curve-fit of TG data (cf. the method employed by previous authors [4] on Green River oil shale) seems to be beset by similar difficulties.

While two consecutive reaction steps have been clearly identified by the present data, it is pertinent to note that additional processes may be readily incorporated into the overall scheme [eqn. (1)] without affecting its general applicability. For example, physical transformations such as the volatilization of shale oil (cf. ref. 13) and softening of the initial kerogen to an insoluble intermediate prior to formation of bitumen (cf. ref. 14) have been invoked as distinct steps in rather elaborate schemes proposed by previous authors. These processes, however, are not expected to alter the overall kinetics in a marked manner *as long as the sample holder geometry is such that diffusion limitations do not become rate determining.*

An examination of Table 2 reveals that the Coats—Redfern method yields somewhat lower values for the activation energy relative to the other analysis techniques employed in the present study. The average of six values for

E_1, seven values for E_2, and three values for A_1 and A_2 in Table 2 respectively yield the following kinetic equations for the thermal decomposition of oil shale kerogen

$$k_1 = 3.3 \times 10^6 \exp(-7445/T)(\text{min}^{-1}) \tag{14}$$

and

$$k_2 = 9.8 \times 10^{13} \exp(-18\,175/T)(\text{min}^{-1}) \tag{15}$$

Table 3 compares the present values of E_1, E_2, A_1 and A_2 with those reported by previous authors for the thermal decomposition of Green River oil shales. The discrepancy in the kinetic parameters reported in the literature on oil shales has been critically reviewed elsewhere [1]. We note, however, that the present data are in fair agreement with those of Braun and Rothman [2] who modified the earlier kinetic data of Hubbard and Robinson by the inclusion of an induction period. The significantly better correlation of the kinetic parameters obtained in the present study with those in ref. 2 than with the corresponding results of Hubbard and Robinson [15] (compare Tables 2 and 3) underlines the difficulty with isothermal techniques mentioned in the introductory paragraphs.

Finally, analysis of the present kinetic data by the Freeman—Carroll method clearly establishes the validity of representing oil shale decomposition by first-order kinetics (cf. Fig. 4). In this regard, it may be noted that "second-order effects" invoked by previous authors [16,17] appear to have limited validity. As mentioned before, the concept of kinetic order in solid-state decompositions assumes a significance which is completely different from that adopted conventionally in homogeneous reaction kinetics [7,8].

TABLE 3

Comparison of present kinetic data with literature values for Green River oil shale *

Activation energy (kJ mole^{-1})	Frequency factor (min^{-1})	Ref.
56.86 (>435°C) **	10^{20}	15
23.26 (<437°C)	10^9	15
169.70 (>500°C)		13
108.31 (500—730°C)		13
56.82 (<730°C)		13
44.62	10^{14}	2
178.70 (400—525°C)	10^2	2
217.88 (350—425°C)	10^{13}	4
239.25 (250—600°C)		5
62.10 (>395°C)	3.3×10^6	Present work ***
152.16 (<395°C)	9.8×10^{13}	Present work ***

* Earlier studies pertain to Green River oil shale of varying organic content and not to kerogen concentrate. However, this difference is not expected to affect the validity of the comparison for the present purposes.

** The temperature range for the kinetic parameters is shown in parentheses.

*** Values averaged from experiments at different heating rates (cf. Table 2).

The kinetic order in solid-state decomposition reactions merely describes topochemical effects at the reactant/product interface rather than a "concentration" dependence of the rate constant [18]. Detailed considerations show that only values of n equal to 0, 1/2, 2/3 or 1 have theoretical justification [7,9].

SUMMARY AND CONCLUSIONS

The kinetics of the thermal decomposition of Green River oil shale kerogen have been studied by non-isothermal thermogravimetry. Kerogen decomposes to a bitumen intermediate with an activation energy of 62.10 kJ mole^{-1} and a frequency factor given by $\sim 10^6$ min^{-1}. The pyrolytic bitumen decomposes into the final products with an activation energy of 152.16 kJ mole^{-1} and a frequency factor of $\sim 10^{14}$ min^{-1}.

The kinetic parameters do not show a systematic dependence on heating rate. This is compelling proof that the derived parameters refer to distinct chemical processes rather than to processes such as product diffusion from the shale matrix. A key feature of the present study is also choice of sample holder geometry and sample mass which facilitates good atmosphere control and easy escape of product gases. Kinetic data from some of the earlier studies in the literature are clouded by the above effects (cf. ref. 1).

The direct Arrhenius method and the Coats—Redfern method are found to be convenient for the analysis of the present data. The Freeman—Carroll method is rather more tedious and moreover is of little use in analyzing the early stages of the decomposition.

Analysis of the kinetic data by the Freeman—Carroll method is shown to confirm the validity of assuming first-order kinetics for the thermal decomposition of Green River oil shale. More importantly, second-order effects invoked by previous authors [16,17] are shown to be of questionable validity.

The multi-step nature of kerogen pyrolysis is clearly seen in the present data, unlike in earlier non-isothermal TG studies. The scheme of two consecutive reactions adopted in the present study and in previous work [13,15] is shown to have general applicability.

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