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OIL SHALE PYROLYSIS - A NEW APPROACH TO THE KINETIC INVESTIGATION OF DIFFERENT KEROGEN TYPE SAMPLES

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ABSTRACT

Different thermal methods were used for investigating the kinetics of pyrolysis of oil shale samples characterized by different kerogen type (I, II and III) and particle size (0.65μm-2.6mm).

A first order kinetic law was assumed in the present analysis with the goal to compare the Arrhenius parameter for different oil shales. Large differences between the activation energies were determined in the order $E_I > E_{II} \approx E_{III}$ on the basis of TG data, but in the reverse order using DSC data.

The duration of pyrolysis at a particular temperature influences the total mass loss which depends on the kerogen type. This effect is explained considering the importance of devolatization as the first step in the pyrolysis process, and can be interpreted suitably using the first rate law in which the conversion depends on temperature as well as time.

INTRODUCTION

In the literature data could be found on the differences in the rate of pyrolysis of organic matter in sediments (kerogen) corresponding to their type (I, II,III) [1-3]. In the present work such an analysis was done,for oil shale also characterized by different kerogen type and particle size, using the TG and DSC techniques. The results of these investigations are primarily concerned with samples originating from Yugoslavia (Aleksinac and Knjaževac region); a detailed description of their characteristics is presented in Table 1.

EXPERIMENTAL

The investigations were performed in a standard apparatus (Perkin-Elmer TGS-2 and Du Pont 990 d.s.c. cell), at heating rates of 2.5-20 K/min, in non-isothermal analysis (NI-TG), which took place in the range 30-600^0. Isothermal analysis (I-TG) was performed at temperatures in the range of practical importance for the retorting process (400-521^0). In all cases an inert carrier gas was applied (N_2 or Ar) with a 25 cm^3/min flow rate. The oil shale samples were prepared by grounding in a metallurgical mill, and by subsequent sieving. Three fractions were collected, denoted in Table 1 as 0 (<0.65 μm), 1 (0.5-0.83 mm) and 2 (1.7-2.8 mm).

Non-isothermal (NI-TG) and isothermal (I-TG) data

All the results obtained by NI-TG were analysed using the Doyle-Gorbachev integral method[4]. Applying the statistical procedure the slope and intercept of the linear part of the plot $-\{\ln[-\ln(1-X)/T^2]\}$ versus (1/T) were used for determining

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the activation energy (E) and frequency factor (A). In Table 1 only the determined E values are presented. The conversion of the organic part, X, was calculated on the basis of its total content which was determined using the ash content value, determined by combustion at 700^0 using air as the carrier gas. The calculation procedure resembles the one used in a previously published paper[5].

I-TG was performed adopting the procedure of Pan et al.[6]. Rapid heating from room temperature to the desired isothermal conditions was performed at the maximum heating rate of the thermobalance equipment ($\approx$160^0/min). During the non-isothermal heating period the mass change of the organic part exceeded by about 30% the values obtained in the experiment performed at the highest isothermal temperature (521^0). This effect obviously represents a drawback of isothermal pyrolysis when performed in a standard apparatus. Calculation of the reaction rate constants at different temperatures, using the first order rate law, was the basis for determining the activation energy (Table 1).

Table 1. Determined values of the activation energy, E kJ/mol

Sample	Particle size	Kerogen type	Thermogravimetric Analysis		DSC-max	DTG-max
			NI-TG (average,2-20^0/min)	I-TG (400-521^0)	5-20	2-20^0/min
ALEKSINAC	0	I	114.7 5	141.3	158.6	157.1
ALEKSINAC	1	I	96.4	131.4	203.1	191.5
ALEKSINAC	2	I	89.4	-	154.6	210.1
ALEKSINAC-130	0	II^a	70.2	96.4	208.8	167.0
ALEKSINAC-130	1	II^a	86.5	111.1	228.4	171.9
ALEKSINAC-130	2	II^a	89.6	-	-	185.3
ALEKSINAC-132	0	II^a	90.9	96.4	203.3	198.9
ALEKSINAC-132	1	II^a	92.1	96.4	187.3	188.6
ALEKSINAC-132	2	II^a	112.6	-	252.2	185.2
CREVENEY-France	0	II	77.0	91.1	214.0	170.5
KNJAZEVAC	0	III	77.8	72.5	282.0	-
KNJAZEVAC	1	III	60.0	74.2	162.7	267.9
KNJAZEVAC	2	III	42.9	-	-	189.5

a- as a composite of kerogen type I and III

DSC/DTG analysis

The kinetic parameters of the samples of different oil shales were determined by the ASTM E-698 procedure [7], which is valid for a single first order reaction. The procedure is based on the determination of temperatures at which the maximum rate of heat consumption is registered in experiments at different heating rates (usually 1-50^0/min). In the present work heating rates of 5, 10 and 20^0/min were used. However, the temperatures of the maximum rate of mass change (DTG) were also used. Both parameters are very useful because they indicate the extent of the difference between the heat consumption and sample mass change during pyrolysis [8,9].

The mass change in relation to temperature and duration of pyrolysis

Although the non-isothermal pyrolysis of oil shale is usually expressed as a function of temperature only, one can expect the existence of some influence of time or duration of pyrolysis. Such an assumption was already used in the model of the total-thermal history of rocks (Lopatin's model [3]) expressed in a very simple way.

The influence of total pyrolysis time of oil shale containing type I kerogen can be observed in Figure 1a.

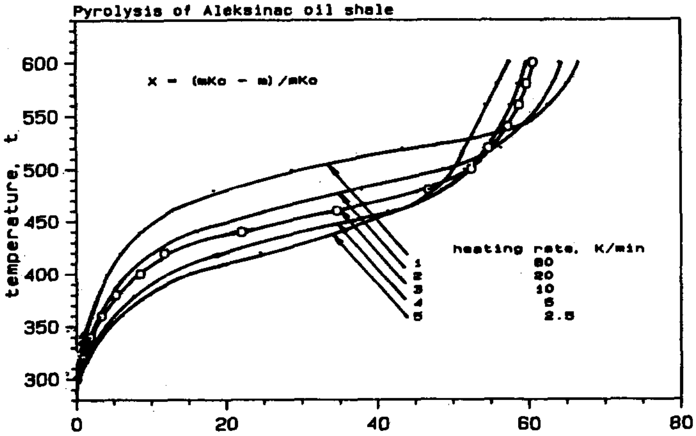

Figure 1a. conversion degree, X

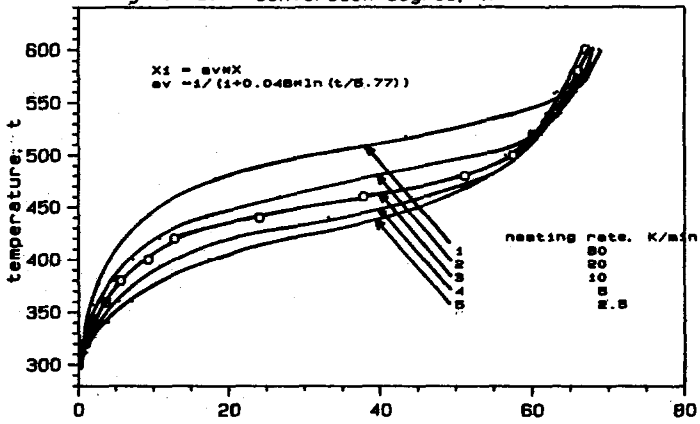

Figure 1b. conversion degree, X

It is noticeable that at higher heating rates, the smaller changes in conversions, registered in the initial period, i. e. in the temperature range 300-400°C, are accompanied by higher values of the final conversion. Considering temperature as the time-dependent varaiable, it appears that shorter exposure of the sample to relatively low temperatures in the range 300-400°C brings about the higher final conversion. This phenomenon could be explained assuming the important role of the presence of still non-volatilized lighter components in the suppression of non-desirable coking at higher temperatures. Thus, the presence of lighter organic material in the sample, resulting from the short exposure time, brings about the higher final conversion.

In order to describe this effect quantitatively, a new parameter a_v, is introduced, which governs the actual yield of volatilized products of pyrolysis, when combined with the kerogen conversion, $\overline{X}$; comprising the formation of all potentially volatilized products:

$$\overline{X} \cdot a_v = X = (m_{Ko} - m_K)/m_{Ko} \qquad (1)$$

Assuming that the maximum production of volatilized products occurs at minimum pyrolysis time, i.e. the maximum heating rate of 100^0/min, parameter a_v can be calculated for each experiment as:

$$a_v = X_{f,actual}/\overline{X}_f = X_{f,actual} / X_{f,100^0/min} \qquad (2)$$

where subscript f, denotes the final conversion values.

The relation between a_v and time was derived using a_v values calculated by eq.(2), as well as corresponding data on the duration of pyrolysis, t, in the form:

$$[a_v/(1-a_v)]^{-1} = k_v\,[\ln(t) - \ln(t_{min})] \qquad (3)$$

where t_{min} corresponds to the pyrolysis at the maximum heating rate.

The coefficient k_v was determined by the least squares method (Fig. 2). The modified conversion values were then calculated using eq.(1); the obtained results are shown in Figure 1b. These values were used for calculating the kinetic parameters by the Doyle-Gorbachev method (Fig.3).

RESULTS AND DISCUSSION

The activation energies determined from NI-TG and I-TG have higher values for oil shale with kerogen type I as compared to the samples with kerogen type II and III. The results also indicate, that the absolute values of the activation energy are greater, as well as the differences between E for kerogen type I and III, when the thermal degradations were performed under isothermal conditions. Generally, the results agree with some other previously reported data [1], especially the results which were obtained by NI-TG.

The main differences can be observed in the absolute values of E determined by NI-TG and I-TG. This could be explained by the fact that the E obtained by NI-TG and I-TG give quite different information: the first is mainly related to the rate of the non-isothermal process and the second is related to the actual energy necessary for the cleavage of the strongest C-C bond (with a large probability of occurrence in kerogen type I) or cleavage of the weaker C-N, C-S and C-O bonds (which are present in greater amounts in kerogen type II and III)[3].

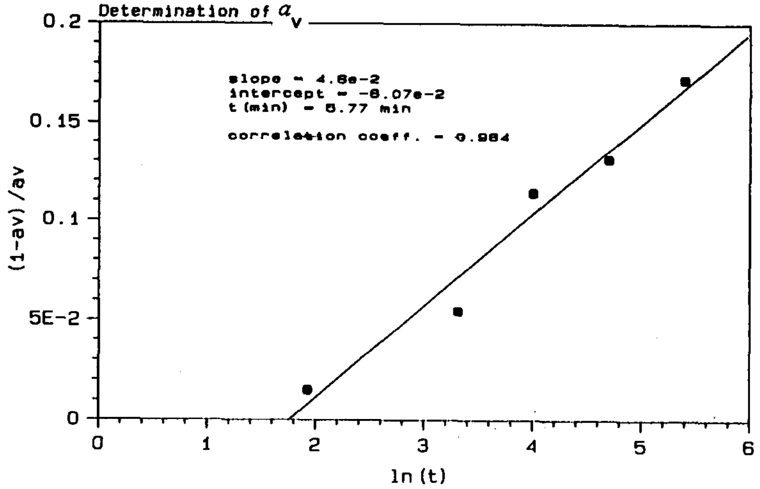

Figure 2.

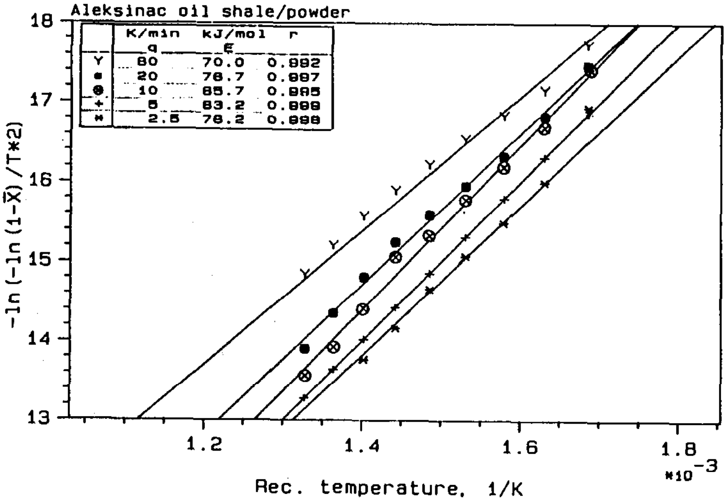

Figure 3.

The conclusions on the influence of particle size are similar to those reported earlier 2 , and with the same trends regardless of whether NI-TG or I-TG were used. The total conversion of the organic part increases with increasing particle size, which has a direct influence on the determined activation energy values.

DSC analysis

The largest disproportionality between energy consumption and total mass change could be expected in the case of oil shale with kerogen type II and III, which was confirmed by DSC-max and DTG-max analysis (Table 1.).

Increase of the sample size was followed by an increase in the activation energy, but only for samples with kerogen I. Practically the same values were obtained for powder, as well as larger particles when the samples with kerogen type II and III were analysed (note that this conclusion is derived only using DTG-max data). DSC-max data and the ASTM E-698 calculation procedure gave larger scattering in the results, probably as a consequence of the heat transfer effects inside the d.s.c. cell, when large particles were pyrolysed.

Influence of time on oil shale pyrolysis

The relation derived in the present work takes into account the time-dependent production of volatalized pyrolysis products, which have been used for the recalculation of kerogen conversion. Better agreement between the calculated activation energies was observed in the investigated heating rate regime (2.5-80^{0}/min), when such a correction was applied.

List of symbols

a_v - driving force for evaporation
DSC-max - maximum rate of heat absorption , J/min
DTG-max-maximum rate of mass change, g/min
k - reaction rate constant, min^{-1}
E - activation energy, kJ/mol
k_v- constant in eq.(3)
m_K- mass of kerogen at time t and temperature T, g
m_{Ko}- initial mass of kerogen, g
t - time, min
t_{min}- duration of NI-TG pyrolysis for 100^{o}/min, (5.5 min)
T - temperature, K
X - conversion degree of kerogen
$\bar{X}$ - corrected values of X, eq.(2)
X_f- actaually observed change in X in the range 50-600^{o}C
X_{max}- maximal value of X for the optimal way of heating

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