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DETERMINATION OF KEROGEN TYPE BY USING DSC AND TG ANALYSIS

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Abstract

The rate of pyrolysis and oxidation of 8 different samples of oil shale kerogen concentrate (KC) were investigated using DSC analysis. Recently performed thermogravimetric studies (TG and DTG) with the same samples of KC indicated that the activation energy of the pyrolysis of specific KCs increases with increasing paraffinic structure in the KC. An opposite effect, i.e. a decrease of the activation energy with an increase of paraffinic structure was determined in the case of KC oxidation. In this study, using the standard ASTM E-698 method based on the determined temperature at which the maximum heat effect could be observed (exo in the case of oxidation and endo in the case of pyrolysis), an activation energy for the pyrolysis, as well as for the oxidation process was determined and also successfully correlated with the content of paraffinic structure of KC. Thus, the higher content of paraffinic structure in KCs indicates that higher values of the activation energy could be determined either in the case of pyrolysis or oxidation followed by DSC analysis.

Keywords: DSC, kerogen, oxidation, pyrolysis, type determination

Introduction

Recent investigations performed by TG/DTG analysis indicate significant structural differences between kerogens of various origin [1]. Moreover, other methods used for the classification of kerogen type such as those based on elemental composition (van Krevelen's diagram of H/C and O/C atomic ratios) shows the inadequacy of their classification. Various other methods (microscopic, pyrolytic, chemical and physical) have been applied in structural studies of kerogen. Due to the complete insolubility of kerogen, degradation methods have been applied, either at higher temperatures (for example pyrolysis, hydrogenolysis, hydropyrolysis) or at low temperatures (chemical methods such as oxidation, reduction, hydrolysis).

Data on the analysis of kerogen structures by TG are available in the literature [1–3]. Various types of kerogen have been investigated under different reaction con-

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ditions. It has been established that different reaction conditions (sample mass, gas flow rate, type of gas, heating rate) strongly influence the kinetics of pyrolysis and oxidation. Also, it is possible to classify kerogen type I and II as opposed to kerogen type III on the basis of the volatile products that are evolved during pyrolysis and on the basis of the shape of the TG curves and moreover on the basis of the relative ratio of the activation energy of pyrolysis and oxidation using TG and DTG analysis [1]. It has been established that a larger mass loss in the first stage of pyrolysis (up to 350 to 400°C) indicates that the kerogen is rich in oxygen (kerogen type III), the volatile products being only small amounts of H_2O, CO_2, SO_2 and H_2S. A greater mass loss in the second pyrolysis stage indicates that the kerogen is rich in hydrogen (type I), the volatile products being mainly hydrocarbons and, to a smaller extent, H_2O, CO_2, SO_2 and H_2S.

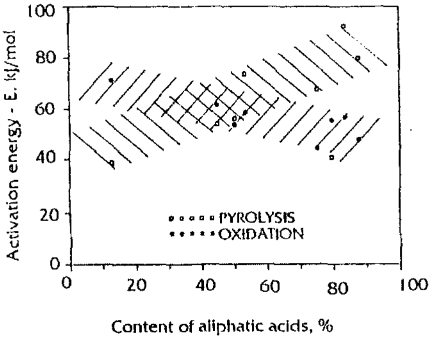

Fig. 1 Dependence of the activation energies (pyrolysis and oxidation) on the content of aliphatic acids in the product of stepwise oxidation of kerogen concentrate [1]

Recently performed analysis obtained using TG and DTG techniques and the investigation of pyrolysis and oxidation, indicated that the activation energy of the pyrolysis of the kerogen concentrate increases with increasing content of aliphatic structures in the kerogen macromolecules, and that an opposite effect appears in the case of the oxidation of the kerogen concentrate [1] (Fig. 1). Furthermore, this investigation showed that in the case of low-temperature preoxidation of the kerogen concentrate (at temperatures below 220°C) a change in the kerogen structure is reflected in such a way that during the pyrolysis of oil shale kerogen concentrate with a mostly aliphatic kerogen structure, the value of the activation energy decreases compared to the activation energy of the unoxidised sample. In the case of kerogen with mostly organic structure, the pyrolysis activation energy increases. In this way it was suggested that on the basis of investigating the processes of oxidation and pyrolysis by the TG and DTG technique and, especially, by applying the preoxidation procedure, one can easily determine the kerogen type of the investigated sample. Other studies also showed the influence of pre-oxidation and aging on the pyrolysis of oil shales and coals [3]. It has been established that low temperature oxidation leads to the reduction of the H/C atomic ratio, a decrease in the hydrocarbon yield, and also to an increase in the yield of H_2O and CO_2, which is explained by the formation of oxygen bonds and bridges and/or by the reduction of aliphatic hydrogen in oil shale [3].

Some other data from the literature indicate that it is also possible to classify kerogen according to type, i.e. structure, on the basis of information on the pyrolysis and oxidation activation energy, commonly determined by TG [4, 5]. However, many published results on the pyrolysis activation energy depend on several factors such as sample preparation and age, conditions for TG analysis, carrier gas flow rate, etc., so one may assume only by a certain degree of probability that the pyrolysis activation energy data of kerogen type I will be higher than the activation energies of kerogen types II and III. When DSC analysis was applied to the kinetic investigation of oxidation of different natural substances (bitumen, oil shale), two characteristic temperature ranges were determined: low temperature oxidation below 400°C, and high temperature oxidation above this temperature. TG and DSC curves according to this investigation performed in the temperature range 30–850°C (air or oxygen) indicated at least three peaks as maximum values of the rate of mass change (DTG) or the rate of heat generation (DSC). By using different standard procedure, the activation energies for the oxidation processes were determined, assuming a valid first order reaction rate. For the low temperature range of the oxidation activation energies lie in the range 100–193 kJ mol^{-1} [5].

The samples of kerogen concentrate used in this study were classified in previous investigations on the basis of the assumed structures into types I, I–II, II and III. The classification was performed on the basis of the products of the stepwise oxidative degradation of kerogen in alkaline $KMnO_4$ solution [6–9]. The sample classification is shown in Table 1. The samples that mostly evolve aliphatic acids upon oxidation by $KMnO_4$ were classified as type I and the samples evolving mostly aromatic acids as type III. Type II and the transitional type I–II did not yield any major type of acid upon oxidation.

Table 1 Characterisation of kerogen concentrate of different origin

Ref.	Kerogen type	Kerogen concentrate sample	Quantity and nature of oxidation products/%		
			aliphatic acids	alkanepolycarboxilic and cycloalkanic acids	aromatic acids
6, 7	I	Green River	87.69	9.44	2.87
6	I	Aleksinac	75.25	16.82	7.93
6	I	Irati	83.61	5.26	11.13
8	I–II	Timahdit	50.20	6.60	43.20
8	I–II	S. Pyongan	79.58	2.59	17.83
6, 9	II	Messel	53.43	25.40	21.25
9	II	Xin-Yang	44.80	15.10	40.10
7	III	Mannville	12.91	0.00	87.09

Experimental

The processes of pyrolysis and oxidation were followed using a Stanton-Redcroft-STA 1000 TG/DTG/DTA instrument as well as DuPont 9900 DSC. Some typical diagrams obtained by analyzing the pyrolysis of a kerogen concentrate originating from Green River oil shale are shown in Figs 2 and 3, and those corresponding to the oxidation process in Figs 4 and 5. In all cases the average initial sample mass was about 4 mg, while both the argon flow in the case of pyrolysis and the air flow for oxidation were 25 cm^3 min^{-1}. The heating rates were 5, 10 and 20 K min^{-1} in the interval from 20 to 600°C.

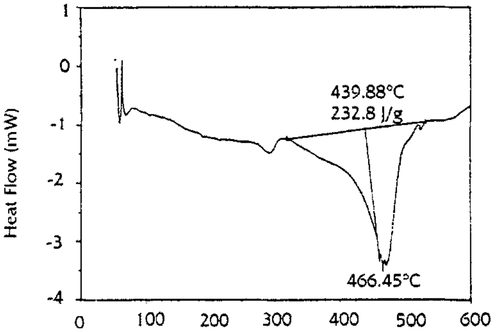

Fig. 2 Analysis of the pyrolysis process. Sample: kerogen concentrate from Green River oil shale; instrument DuPont 9900; heating rate 10 K min^{-1}; argon; 30–600°C

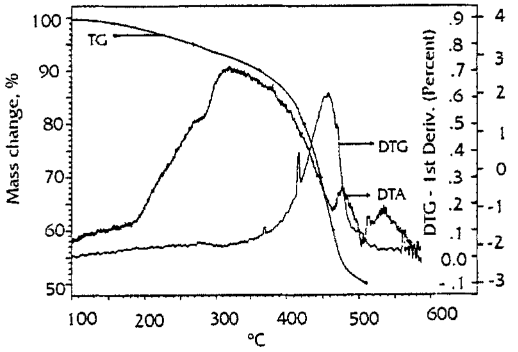

Fig. 3 Analysis of the pyrolysis process. Sample: kerogen concentrate from Green River oil shale; instrument Stanton Redcroft-STA 1000; heating rate 10 K min^{-1}; □ – argon 25 cm^3 min^{-1}; 30–600°C

Results and discussion

Calculation of kinetic parameters

The activation energy and frequency factor of pyrolysis and oxidation were determined using the standard ASTM E-698 procedure. This method requires precise

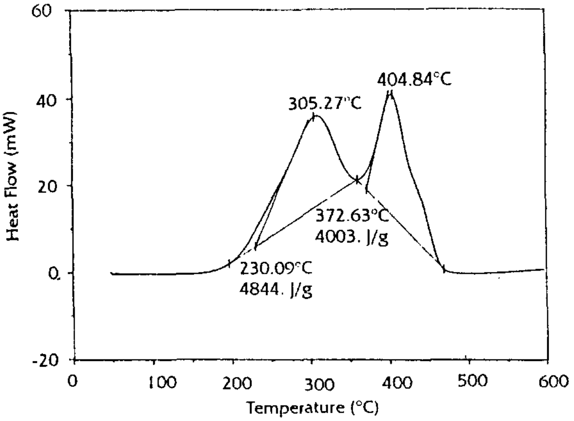

Fig. 4 Analysis of the oxidation process. Sample: kerogen concentrate from Green River oil shale; instrument DuPont 9900; heating rate 10 K min^{-1}; air; 30–600°C

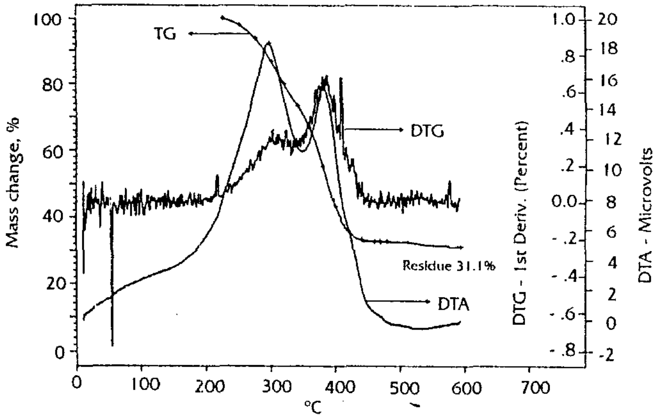

Fig. 5 Analysis of the oxidation process. Sample: kerogen concentrate from Green River oil shale; instrument Stanton Redcroft-STA 1000; heating rate 5 K min^{-1}; argon 25 cm^3 min^{-1}; 30–600°C

determination of the peak temperatures at which the maximum heat absorption or generation are observed (DSC) or where the maximum temperature differences compared to the temperature of the internal standards are recorded (DTA). The analysis of the influence of heating rate (q) on peak temperature (T_{max}), shown in Table 2, enables determination of the activation energy and frequency factor of the first order reaction rate constant of pyrolysis or oxidation. Diagrams obtained by analyzing the oxidation of Green River kerogen concentrate are shown in Figs 6 and 7, corresponding to the first peak (temperature) when the heat generation has a maximum value (Fig. 6) and the second peak (temperature) where heat generation also has a maximum value (DSC analysis).

Table 2 Experimentally determined values of temperatures at wich maximum endo- or exo-heat effects appeared

	Pyrolysis			Oxidation					
	Heating rate/K min^{-1}			Heating rate/K min^{-1} 1. step			Heating rate/K min^{-1} 2. step		
	5	10	20	5	10	20	5	10	20
Green River	731.3	739.6	756.9	565.0	578.4	593.5	663.6	678.0	692.6
Aleksinac	726.8	738.5	750.1	562.3	576.3	588.5	669.5	685.7	702.7
Irati*	703.5	718.4	731.6	579.8	597.3	608.6	703.4	722.7	737.7
	768.2	782.7	796.6						
S. Pyongan	617.8	628.4	646.7	567.5	582.2	–	672.8	688.4	–
	739.9	752.4	764.2						
Messel	724.0	733.4	745.0	569.1	580.2	594.9	662.1	672.8	686.2
Xin Yang*	722.2	728.8	747.9	559.0	569.3	578.0	638.4	649.2	671.8
	764.7	778.2	792.6						
Mannville	737.6	752.0	764.6	572.3	585.7	605.5	711.8	720.9	753.5
Timahdit*	637.5	650.0	659.8	559.9	571.7	590.4	671.8	687.1	705.8
	712.8	721.4	732.2						

*DSC analysis of the pyrolysis indicated the existence of two endothermic peaks. The presented values show temperatures at which these effects were detected (T_{max}).

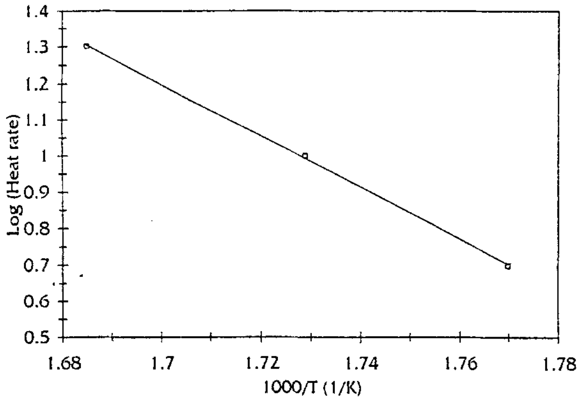

Fig. 6 Kinetic parameter determination of the first step of the oxidation of kerogen concentrate originating from Green River oil shale (ASTM E-698 method)

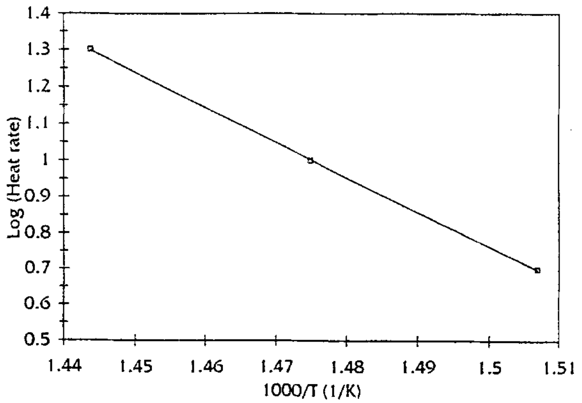

Fig. 7 Kinetic parameter determination of the second step of the oxidation of kerogen concentrate originating from Green River oil shale (ASTM E-698 method)

Pyrolysis study

The pyrolysis activation energies for all 8 kerogen concentrate samples (Table 1) lie in the range of 210 to 330 kJ mol^{-1} (Fig. 8). The kerogen concentrate of the mixed type I–II (Timahdit and S. Pyonyan), as well as those characterised as type II (Messel), indicated the existence of two peaks of endothermic heat absorption. The first is in the temperature range 340–380°C (for kerogen type I–II) and at temperatures slightly higher than 400°C (kerogen type II). The second and actually main endo-heat effect of pyrolysis appears at higher temperatures (>450°C). The existence of two endpeaks for these kerogen types is obviously a consequence of the more complex structure of kerogen macromolecules. In this study only the second heat effect, as a higher one and more important, was used to correlate the activation energy of pyrolysis process and the kerogen concentrate composition. The content

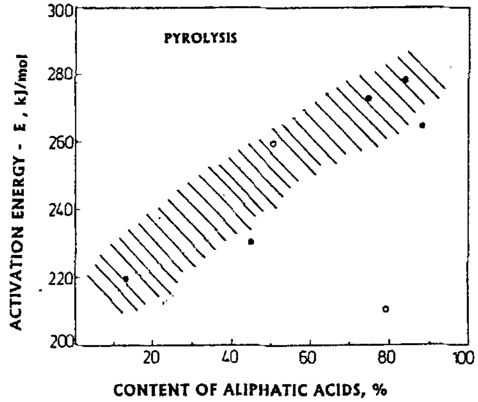

Fig. 8 Relationship between the pyrolysis activation energies and the structure of the kerogen concentrate

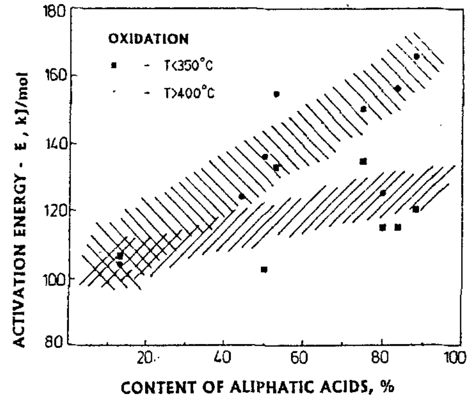

Fig. 9 Relationships between the oxidation activation energies (1^{st} and 2^{nd} step) and the structure of the kerogen concentrate

of aliphatic acids obtained after the stepwise oxidation of the kerogen concentrate was used as a representative parameter defining the structure of kerogen macromolecules.

Oxidation study

The oxidation of all the investigated samples showed two exothermic effects: the first at 300 (1^{st} peak, Fig. 9) and second above 380°C (2^{nd} peak, Fig. 9). Such evidence indicates that the oxidation of kerogen concentrate must be treated as a consecutive process. The activation energies of both steps were determined by applying the same earlier defined procedure. The determined activation energies were correlated on the same diagram (Fig. 9) to the value of the corresponding content of aliphatic acids of specific kerogen concentrates.

Conclusions

By comparing the data presented in Figs 8 and 9, as well as those published earlier which correspond to the same processes followed by the TG and DTG technique, one can conclude the following:

The pyrolysis activation energy of the kerogen concentrate increases with increasing content of aliphatic structures in the kerogen macromolecule in the range from 200 to 280 kJ mol^{-1}. The percentage of aliphatic acids (from 10 to 90) determined by the stepwise oxidation of kerogen concentrate in an alkaline solution of $KMnO_4$ was used as the main parameter for defining the content of paraffinic structures in the kerogen macromolecule. The same result was recently obtained by the TG and DTG analysis of pyrolysis; however, only the range of determined activation energies was different (from 40 to 100 kJ mol^{-1}).

Oxidation of the kerogen concentrate must be treated as a consecutive process with at least two steps and each of them as a first order kinetic equation. The activation energies of both steps depend on the content of paraffinic structures in the kerogen macromolecule. The second effect is more important because the heat generated in this oxidation step is the highest. An increase of the activation energies from 100 to 120 kJ mol^{-1} was determined for the 1st step, and from 100 to 180 kJ mol^{-1} for the 2nd step of oxidation when the content of aliphatic structures in the kerogen macromolecule changed from 10 to 80%.

The procedure of kerogen concentrate analysis (pyrolysis and oxidation) applied in this study using the DSC and DTA techniques, as well as those recently analyzed using the TG and DTG techniques, should yield a final clarification of the applicability of the so-called "thermal-dry" method for defining the composition and type of kerogen in oil shale. The best results could be achieved by the analysis of the pyrolysis and oxidation of kerogen concentrate by both, the thermogravimetric and the calorimetric analysis, and then, the obtained results compared with standard diagrams showing the dependence of the activation energies on the content of paraffinic structures in the kerogen concentrate.

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