

INFLUENCE OF PRE-OXIDATION ON KEROGEN CONCENTRATE (KC) PYROLYSIS

A thermal method for kerogen type identification

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In this study, the rate of pyrolysis and oxidation of 8 different samples of oil shale kerogen concentrate (KC) were investigated using TG/DTG technique. The rate of pyrolysis after preoxidation step performed at low temperature (below 230°C), was also studied. The determined pyrolysis activation energy increases with increasing paraffinic structure in the KC: an opposite effect was determined in the case of oxidation. Comparison of the reaction rate constants of the pyrolysis as well as the oxidation of untreated and pre-oxidized KC samples indicated the basis of the proposed thermal method for kerogen type determination.

Keywords: oil shale kerogen, oxidation and pyrolysis

Introduction

The influence of pre-oxidation on the composition of different type of oil shale kerogen and on the yield of oil and gas from the pyrolysis process are not well known. In this study, the rate of pyrolysis and oxidation of eight different samples of oil shale kerogen concentrate (KC) were investigated using the TG/DTG technique. The rate of pyrolysis after a pre-oxidation step performed at low temperature (below 230°) was also studied. The meaning of activation energy is quite different to that corresponding to the activation energy of certain chemical reactions in homogeneous phase. In the case of solid substances pyrol-

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ysis i.e. thermal degradation of kerogen concentrate it means more a parameter which indicates the influence of temperature on the degradation processes.

Recent investigations indicate significant structural differences between kerogens of various origin, as well as the inadequacy of their classification only on the basis of elemental composition (Van Krevelen's diagram of H/C and O/C atomic ratios). Various methods (microscopic, pyrolytic, chemical and physical) have been applied in the structural studies of kerogen. Due to the complete insolubility of kerogen, degradation methods have been applied, either at higher temperatures (for example pyrolysis, hydrogenolysis, hydrolysis) 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]. Various types of kerogen have been investigated under different reaction conditions. 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 types 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 shapes of the TG curves. 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 H₂O, CO₂, SO₂ and H₂S. 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, at smaller extent, H₂O, CO₂, SO₂ and H₂S.

Data from the literature indicate that it is possible to classify kerogen according to type, i.e. structure, on the basis of information on the pyrolysis activation energy, commonly determined by TG [2]. However, many published results on the pyrolysis activation energy depend on several factors such as sample preparation and age, TG conditions, carrier gas flow rate, etc., so one may speak only of 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.

The samples of kerogen concentrate used in this study were classified in previous investigations on the basis of the assumed structures into type I, I-II, II and III. The classification was performed on the basis on the products of the stepwise oxidative degradation of kerogen in alkaline KMnO₄ solution [3-6]. The sample classification is shown in Table 1. The samples that mostly evolve aliphatic acids upon oxidation by KMnO₄ 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 one major type of acid upon oxidation.

The recently published study of Khan [7] indicates the influence of pre-oxidation and ageing on the pyrolysis of oil shales and coals. It has been established that low-temperature oxidation leads to reduction of the H/C atomic ratio, a decrease in the hydrocarbon yield, and also to an increase in the yield of H₂O and CO₂, which is explained by the formation of oxygen bonds and bridges and/or by the reduction of aliphatic hydrogen in oil shale.

Table 1

Ref.	Type	Kerogen concentrate sample	Quality and nature of oxidation products		
			Aliphatic acids / %	Alkane-Polycarboxylic and cycloalcanic acids / %	Aromatic acids / %
3; 4		1. GREEN RIVER	87.69	9.44	2.87
3	I	2. ALEKSINAC	75.25	16.82	7.93
3		3. IRATI	83.61	5.26	11.13
5	I-II	4. TIMAHDIT	50.20	6.60	43.20
5		5. S. PYONGAN	79.58	2.59	17.83
3; 6	II	6. MESSEL	53.43	25.40	21.25
6		7. XIN-YANG	44.80	15.10	40.10
4	III	8. 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. The average sample size was 4 mg, while both the argon flow in the case of pyrolysis and the air flow in the case of oxidation were 25 cm³/min. The heating rates were 2, 5, 10 and 20 deg/min in the interval from room temperature to 600°C.

The same instrument was used to follow the pyrolysis after low-temperature oxidation. The samples were first subjected to oxidation in air up to about 230°C followed by isothermal oxidation for 15 minutes. During this pre-oxidation the samples lost 5 to 10% of their initial mass depending on sample type. Consequently, the largest mass loss in that period was registered in the samples with a distinct aliphatic structure (GREEN RIVER – type I). After pre-oxidation the samples were cooled to room temperature and then subjected to pyrolysis in argon up to 600°C.

Calculation of kinetic parameters

The activation energy and frequency factor of pyrolysis, oxidation and pyrolysis after low-temperature pre-oxidation were calculated using the integral method proposed by Gorbachev [8]. The activation energy was determined from the slope and the frequency factor from the intercept of the:

$$-\ln(-\ln(1-x)/T^2) \text{ vs. } 1/T \text{ plot;}$$

where x , the degree of conversion of the organic part of the kerogen concentrate, of the pyrolysis process after low-temperature pre-oxidation was calculated using the mass of the sample after pre-oxidation as the initial value.

Results

The results of one characteristic heating rate (5 deg/min) are presented.

Figure 1 shows the dependence of the activation energies of pyrolysis and oxidation on the content of aliphatic acids determined by stepwise oxidation in an alkaline solution of KMnO_4 . The activation energy of pyrolysis increases with increasing content of aliphatic structures in the kerogen, so the highest activation energy was found in the case of type I kerogens and the lowest in type III kerogen. In the case of oxidation the opposite effect was registered (Figs 1 and 2). The activation energy decreases with increasing aliphatic structure content.

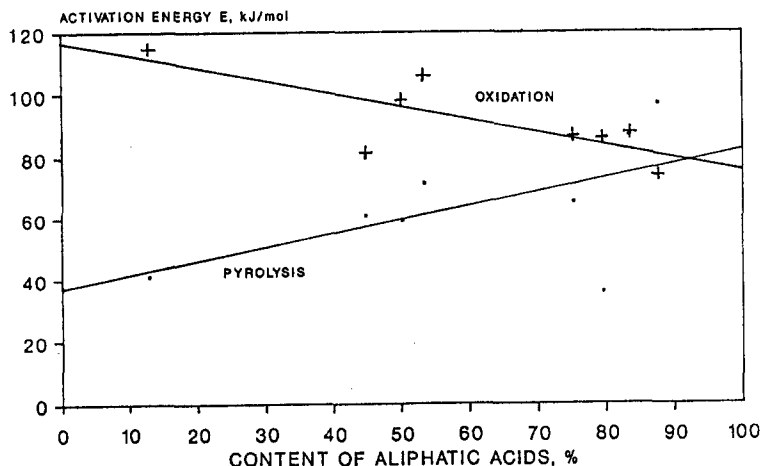


Fig. 1 Activation energy of pyrolysis and oxidation vs. content of aliphatic acids (%) (heating rate 5 deg/min)

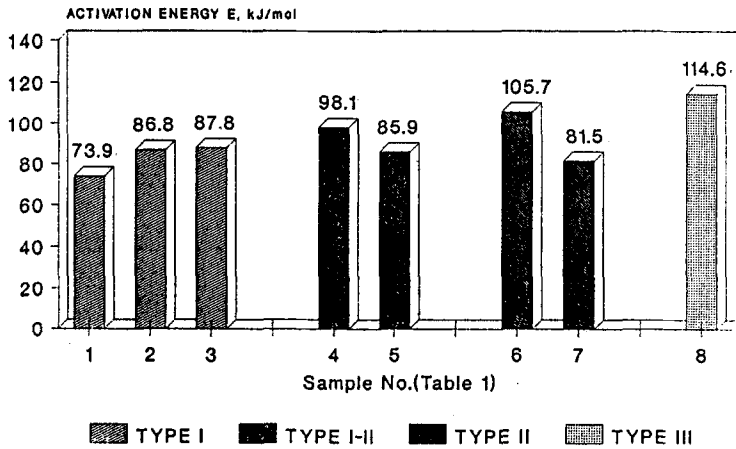


Fig. 2 Activation energy of oxidation process for the different types of kerogen (heating rate 5 deg/min)

Low-temperature pre-oxidation affects the cumulative effects of pyrolysis. A change in the pyrolysis activation energy was found (Fig. 3). A somewhat lower value of the activation energy was determined in the case of kerogens type I, I-II and II. In the case of kerogen type III the pyrolysis activation energy is increased as a consequence of pre-oxidation. These results indicate that the pyrolysis activation energies after pre-oxidation can be related to the structure, i.e. type of kerogen.

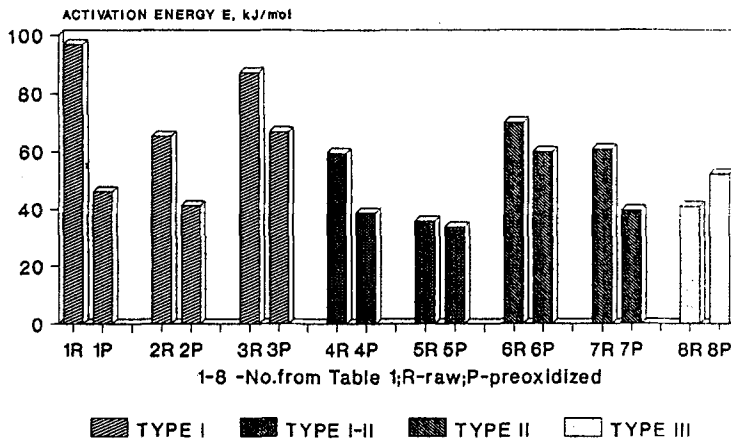


Fig. 3 Influence of low-temperature pre-oxidation on activation energy of pyrolysis (heating rate 5 deg/min)

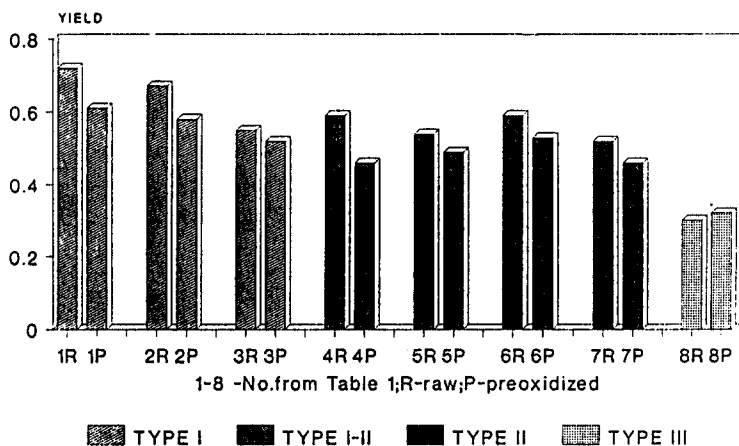


Fig. 4 Influence of low-temperature pre-oxidation on yield of volatilized products of pyrolysis (5 deg/min)

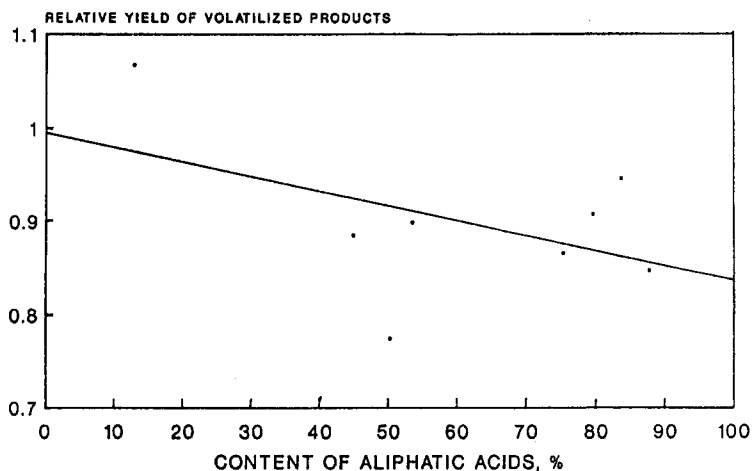


Fig. 5 Relative yield of volatilized products of pyrolysis vs. content of aliphatic acids (heating rate 5 deg/min)

The yield of volatilized products of pyrolysis, calculated in regard to the organic part of the kerogen concentrate (Fig. 4), also changes. In the case of kerogen types I, I-II and II after low-temperature pre-oxidation the pyrolysis yield decreases as compared to the pyrolysis of the corresponding untreated sample. An opposite effect was found in the case of kerogen type III, which is especially clearly illustrated in Fig. 5. The relative yield of volatile pyrolysis products after low-temperature pre-oxidation compared to the yield after pyrolysis of the un-

treated sample is the highest (greater than I) for the kerogen and the lowest content of aliphatic structures (type III), and the lowest for the kerogen with the highest content of aliphatic structures (type I).

Conclusions

1) The pyrolysis activation energy of the kerogen concentrate increases with increasing content of aliphatic structures in the kerogen macromolecule. The opposite effect was found in the case of the oxidation of the kerogen concentrate.

2) The low-temperature pre-oxidation of kerogen indicates that the change in the kerogen structure is reflected in such a way that during the pyrolysis of oil shale kerogen concentrate with 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 aromatic structure, the pyrolysis activation energy increases. In this way it is possible, on the basis of investigating the processes of oxidation and pyrolysis, i.e. the influence of pre-oxidation on pyrolysis, to determine the kerogen type of the investigated sample.

3) The procedure developed in this paper, applied to a large number of kerogen concentrate samples of different origin and type, should yield the final clarification of the applicability of the 'thermal-dry' method for defining the composition and type of kerogen in oil shale.

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Zusammenfassung — Mittels TG/DTG wird die Pyrolyse- und Oxidationsgeschwindigkeit von 8 verschiedenen Ölschieferkerogenkonzentraten (KC) untersucht, ebenso die Pyrolysegeschwindigkeit nach einem Präoxidationsschritt bei niedriger Temperatur (unter 230°C). Die Pyrolyse-Aktivierungsenergie steigt mit zunehmender Paraffinstruktur im KC, ein entgegengesetzter Effekt kann bei der Oxidation beobachtet werden. Ein Vergleich der

Reaktionsgeschwindigkeit von Pyrolyse und Oxidation sowohl bei unbehandelten als auch voroxidierten KC-Proben zeigt auf die Basis der empfohlenen thermischen Methode bei Bestimmungen von kerogenen Substanzen.