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INVESTIGATION OF FAST-HEATING PYROLYSIS OF SAPROPELITIC COALS BY MASS-SPECTROMETRIC THERMAL ANALYSIS

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The products of the fast-heating pyrolysis of two sapropelitic coals, from Taymalyr and Budagovo, in a helium flow were studied by differential mass-spectrometry (in the mass number range from 2 to 110). Equations describing the kinetics of the process under different conditions were produced. The mass-spectra of the sapropelitic coals are similar to those of switch oil evaporation products, which indicates the similarity of their chemical structures. The results obtained allowed the conclusion that the fundamental chemical structure of sapropelitic coals is a polycyclic hydrocarbon matrix of CH_2 and CH groups with joined *n*-alkane chains containing end-capping CH_3 and COOH groups.

Thermodestruction is a traditional method for the study of coal composition and structure. This method is especially suitable for the investigation of sapropelitic coal, which produces considerable amounts of tar on pyrolysis, this consisting mainly of aliphatic compounds [1, 2]. However, since the processes of thermal treatment of coal are accompanied by cyclization and dehydrogenation of the reaction products and appreciable semi-coke formation, conclusions about the coal structure may be drawn only very tentatively. Therefore, the thermodestructive study of sapropelitic coals under conditions where the secondary reactions of the products are excluded is of special interest.

We obtained the boghead sample from Taymalyr, the characteristics of which are given in Table 1. Preliminary DTG analysis of a small portion of

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Table 1 Coal samples characteristics

Sample	Approximate analysis, wt.%			Ultimate analysis, % daf					Petrographic composition, %	
	W^a	A^d	V^d	C	H	N	O	S	alginite	vitrinite
Taymalyr boghead	1.9	3.2	81.4	76.4	9.2	0.6	13.5	0.3	95.0	5.0
Budagovo sapropelitic coal	6.6	46.1	69.6	63.6	6.7	1.7	27.4	0.6	68.0	32.0

the boghead (sample size 42 mg) in a helium flow showed that the weight decrease was about 95% at 480°. For the experiments, coal samples of 10-30 mg were investigated under non-isothermal conditions (at a heating rate of 45-85 deg min^{-1}), by differential mass-spectrometry. During pyrolysis in a helium flow, an on-stream analysis of the reaction products was performed in the automatic mass-spectrometry complex [3] with molecular-beam sampling.The products were evacuated directly from the pyrolysis zone with a quartz probe that minimized further reaction of the products in the gas-phase (the residence time of the products in the pyrolysis zone was < <0.01 sec). The molecular beam was formed and rapidly analysed by mass-spectrometer (analysis time < <0.1 sec). On the whole, this method allowed the observation of the heavy-volatile products.

Table 2 Mass-spectra of pyrolysis products of Taymalyr boghead, Budagovo sapropelitic coal and switch oil

m/e	Relative mass peak intensites*, %		
	boghead	sapropelitic coal	switch oil
2	18	-	-
27	25	28	34
41	82	100	100
42	25	18	26
43	100	98	70
44	63	3	-
53	6	-	-
54	7	-	-
55	66	88	86
56	34	33	28
57	53	82	82
67	2	40	62
69	29	44	82
71	22	43	54
77	-	10	-
79	5	19	26
81	1	33	73
82	-	24	31
83	-	32	65
95	-	24	38
96	3	23	22
97	-	19	36
105	5	-	-

*The most intense peak of the spectrum is taken as 100%

The time-dependences of the mass peak intensities were measured (in the range of mass numbers from 2 to 110) for the mass-spectra of the reaction products (the mass peak intensities being proportional to the rate of release off all volatile matter at the temperature of the éxperiment). The release of all the components except for CO_2 and H_2 proceeded simultaneously (CO_2 was released in a wide temperature range, and H_2 was released at temperatures of about 600° and higher). The mass-spectra of the destruction products are listed in Table 2.

The most intense peaks in the mass-spectrum of Taymalyr boghead are due to the aliphatic structures; peaks typical of aromatic compounds are negligible.

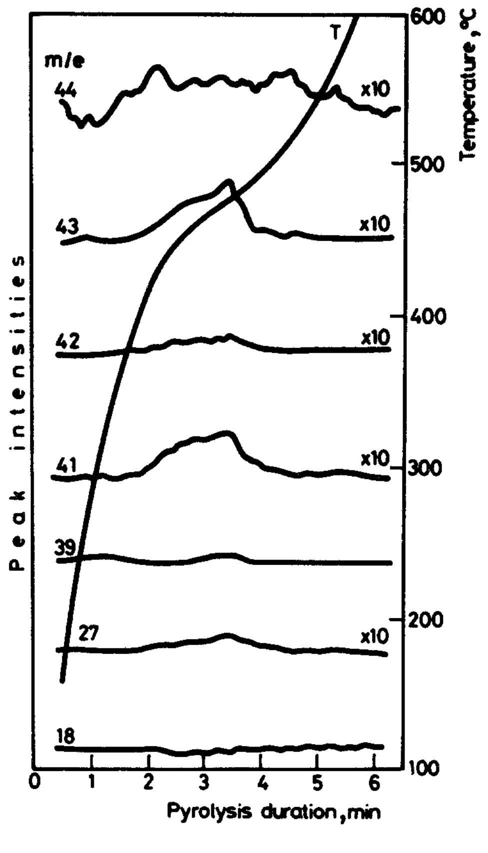

Fig. 1 Temperature and peak intensities as functions of pyrolysis duration. Sample size - 10 mg, heating rate - 45 grad.min^{-1}

For a coal sample of 10 mg at the relatively low heating rate of 45 deg min^{-1}, two stages of pyrolysis were found (Fig. 1). The pyrolysis rate in the first stage is described by the equation:

$$W_1 = 1.59.10^8.(1-x).\exp(-138.0/RT)\,s^{-1}$$

where x is the degree of pyrolysis.

However, only one stage of pyrolysis was observed when a larger sample size (30 mg) was used at a higher heating rate (85 deg min^{-1}), the rate of pyrolysis being described by the equation

$$W_2 = 1.82.10^{14}.(1-x).\exp(-230.0/RT)\,s^{-1}$$

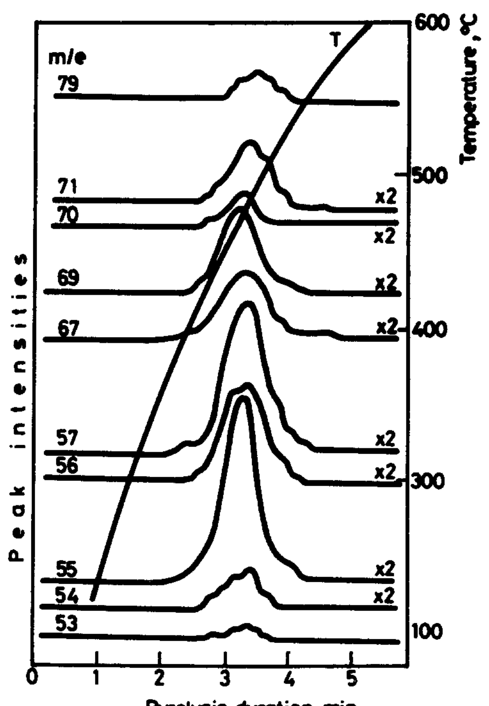

Fig. 2 Temperature and peak intensites as functions of pyrolysis duration. Sample size - 30 mg, heating rate - 85 grad.min^{-1}

The mass-spectrum for the latter case is presented in Fig. 2.

Figure 3 shows the Arrhenius plots for these experiments. In the temperature range 433-453°, the absolute values of the reaction rate constants are close.

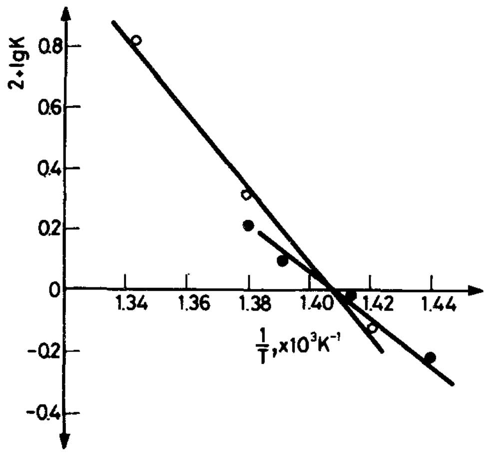

Fig. 3 Arrhenius plots for the process of boghead pyrolysis under different conditions; 1 - sample size - 30 mg heating rate - 85 grad.min^{-1}; 2 - 10 mg, 45 grad.min^{-1}

Similar results were found for Budagovo sapropelitic coal (the characteristics are given in Table 1) under pyrolysis conditions: sample size 10 mg, heating rate 300 deg min^{-1}. The observed mass-spectrum of the destruction products is listed in Table 2. The rate of the process is described by the equation

$$W = 3.98 . 10^{12} . (1-x) . \exp(-213.3/RT)\, s^{-1}$$

A comparison of the data on the above product compositions with the corresponding data on Donetsk Basin coal obtained earlier under similar conditions [4] revealed the predominance of low-molecular products in the latter (carbon monoxide, methane, hydrogen) and of high-molecular products in Taymalyr and Budagovo sapropelitic coals.

It should also be noted that the mass-spectra of the pyrolysis products of the investigated samples are similar to those of the evaporation products of switch oil (Table 2), which consisted mainly of aliphatic hydrocarbons. This indicates the similarity in their chemical compositions. The only difference is that the content of high-molecular components in the mass-spectrum of switch oil is higher than that in the mass-spectrum of the fast-heating pyrolysis products of the samples under study (more prominent peaks are observed at m/e = 67, 69, 81, 83, 95 and 97).

A comparison of the data relating to the mass-spectra of the high-temperature and fast-heating pyrolysis products of the investigated coal samples and the Donetsk Basin coking coal sample [4] (peak intensities in the mass range $>>110$ are small) with the analogous data on the low-temperature pyrolysis products of coking and bituminous coals [5] (intense mass peaks are observed in the mass range 170-300) allows the conclusion that the yield of high-molecular products is lower in the case of high-temperature pyrolysis. This may result either from the decomposition of heavy-volatile pyrolysis products or from the fact that the probability of product formation during the secondary reactions of condensation involving radical recombination decreases.

The results obtained confirm the assumption [1] that the fundamental chemical structure of the sapropelitic coal is a polycyclic hydrocarbon matrix of CH_2 and CH groups, with joined n-alkane chains containing end-capping CH_3 and COOH groups. The decarboxylation reaction is significantly different from any carbon-carbon bond rupture, and thus the behaviour of the mass-peak intensity for m/e = 44 (carbon dioxide) versus heating duration has a particular character (Fig. 1). The presence of the peak (weak intensity) for m/e = 105 in the mass-spectrum of boghead indicates the availability of compounds in its structure whose destruction lead to the formation of dialkyl derivatives of benzene. These compounds are either the result of the cyclization of unsaturated carboxylic acid with subsequent dehydrogenation, or are connected genetically with he humus component of the coal. The presence of the mass-peak for m/e = 77 in the spectrum of Budagovo coal may be explained by the high content of humus matter in this sample.

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Zusammenfassung – Mittels Differential-Massenspektroskopie im Massenzahlbereich von 2 bis 110 wurden die Produkte einer in einem Heliumstrom vollzogenen Schnellheizpyrolyse von Faulschlammkohle aus Taymalyr und Budagovo untersucht. Zur Beschreibung der Kinetik des Prozesses unter verschiedenen Bedingungen wurden Gleichungen entwickelt.Die Massenspektren der Faulschlammkohlen gleichen dennen von Verdampfungsprodukten aus Schalterölen, was auf die Ähnlichkeit ihrer chemischen Struktur hinweist. Die erhaltenen Ergebnisse erlauben den Schluß, daß die grundlegende chemische Struktur der Faulschlammkohlen eine polycyclische Kohlenwasserstoffmatrix aus CH_2- und CH-Gruppen ist, von der *n*-Alkanketten mit endständigen CH_3- und COOH-Gruppen abzweigen.