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## Kinetic Study of the Thermal Decomposition of Low-Ranked Coals of Mongolia and Tuva

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### Abstract

Thermal decomposition of brown coal from the Baganuur deposit in Mongolia and gas coal from the Ulug-Khem deposit in Tuva was studied using thermogravimetry (TG) and differential thermogravimetry (DTG). The stage-by-stage thermal decomposition was revealed under the conditions of programmed heating to 900 °C with different rates in the argon atmosphere. Using the model-free and isoconversion methods of Ozawa-Flynn-Wall (OFU) and Kissinger-Akahira-Sunohara (KAS), the dependence of the activation energy on the degree of coal decomposition was established, and the kinetic parameters of pyrolysis were determined. Within the range of coal conversion degrees from 0.1 to 0.9, the average values of pyrolysis activation energies for brown coal and gas coal were 186 and 239 kJ/mol (OFU method), 182 and 238 kJ/mol (KAS method), respectively. The kinetic compensation effect during coal pyrolysis was observed. This may be due to the multicomponent and multifunctional composition of coals.

**Keywords:** coal, thermal decomposition, differential thermogravimetry, kinetics, activation energy, compensation effect

### INTRODUCTION

The production of carbon materials and composites based on them is to a substantial extent based on the use of aromatic compounds and their mixtures. The need for the derivatives of monocyclic aromatic structures is provided mainly by petrochemical products (by 90 %), and the need for di- and polycyclic compounds is provided mainly (by 95 %) by the components of coke-chemical resin, which is a by-product of the production of metallurgical coke. Modern high-tech carbon materials and composites are obtained mainly using polycondensed aromatic hydrocarbons which are present in the non-volatile residue of coal tar oil – coal tar pitch.

During recent years, a stable trend to decrease the production of coal tar oil and pitch is observed in the majority of countries (except China) because of a decrease in the consumption of ex-

pensive metallurgical coke in the blast-furnace production of cast iron and steel [1]. In the future, an increase in the number of blast furnaces with the injection of dust-like coal, natural gas and oil fractions into the hearth (as reducing agents for partial replacement of coke), as well as large-scale development of competing non-furnace processes of metal obtaining through the direct reducing fusion involving hydrogen and natural gas and melting in electroarc furnaces will promote a further substantial decrease in the need for coke and therefore the production of coal tar oil may be decreased substantially [1].

At the same time, the demand for coal tar oil and pitch as the sources of polycondensed aromatic hydrocarbons, requirements to their quality are continuously increasing in various branches of industry for obtaining high-tech carbon materials for various purposes. This defines the imperative need for the development of alterna-

tive methods of obtaining substituted for coke chemical raw materials including pitch, avoiding the process of coking.

For this purpose, such processes as semi-coking and thermal dissolution are promising. The organic mass of coal contains monomeric, oligomeric and multimeric aromatic and heterocyclic molecules associated through various interbond links and intermolecular interactions to form a polymer-like solid with heterogeneous composition and irregular spatial structure. Due to the complicated composition, detailed data on the kinetics of decomposition of their organic mass under the action of temperature are important for developing efficient and selective processing methods.

Investigation of the kinetics of pyrolysis of organic materials broadly involves thermogravimetric analysis (TGA), both in the isothermal regime and in the dynamic mode [2–5]. The express method of dynamic thermogravimetry is widely used. The proposed methods of the determination of kinetic parameters of non-isothermal pyrolysis may be separated into model-fitting and model-free, or isoconversional ones [6]. When using the model-fitting method, it is sufficient to carry out one thermoanalytical measurement (methods proposed by Freeman–Carroll [7], Coats–Redfern [8]). In the general case, the problem of determination of the constants is reduced to choosing and fitting the mathematical model for the reaction rate to the experimental kinetic curve or its separate regions [9]. At the same time, kinetic analysis involving non-isoconversional methods does not allow evaluating the dynamics of coal pyrolysis at different stages because the obtained total value of the apparent activation energy is a complicated function of reactions proceeding at different stages. Model-free methods of the calculation of kinetic parameters (methods proposed by Kissinger [10], Kissinger–Akahira–Sunos [11], Ozawa–Flynn–Wall [12, 13]) require kinetic curves for different heating rates. Their doubtless advantage is the possibility to determine kinetic characteristics for each value of conversion degree, that is, for different stages of decomposition.

Almost all methods of the calculation of kinetic parameters according to TGA data under isothermal conditions are based on the application of the equation for reaction rate

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (1)$$

Here  $\alpha$  is the relative degree of conversion;  $T$  is absolute temperature;  $A$  is preexponential factor;

$E_a$  is activation energy;  $R$  is the universal gas constant;  $t$  is time;  $f(\alpha)$  is the mathematical model of a dimensionless kinetic function [14].

Under non-isothermal conditions, at the constant heating rate, factor ( $\beta$ ) characterizing heating rate is introduced:

$$\beta = \frac{dT}{dt} \quad (2)$$

The expression for dynamic heating:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \frac{dt}{dT} = \frac{1}{\beta} \frac{d\alpha}{dt} \quad (3)$$

Substituting (3) into (1), we determine the process rate under non-isothermal conditions:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (4)$$

Mathematical models used to determine the kinetic characteristics of polymers cause definite difficulties in application to coal pyrolysis because of the complicated structure of coal, diversity of the types of chemical bonds and reactions proceeding simultaneously [2–4, 15]. Because of this, the elaboration of recommendations for choosing and developing an adequate kinetic model of pyrolysis and the formation of a unified database of kinetic coefficients is an essential research problem.

The goal of the present work was to study the kinetics of thermal decomposition of two samples of low-ranked coal using model-free methods proposed by Ozawa–Flynn–Wall (OFW) and Kissinger–Akahira–Sunos (KAS).

## EXPERIMENTAL

Brown coal samples from the Baganuur coal open-pit mine (B) and black gas coal from the Ulug-Khem deposit of Tuva (G) were chosen for investigation. The collected samples relate to vitrinite type and are usually considered as the preferable reactive raw material for pyrolysis and thermochemical processing. Black gas coal possesses the ability to sinter, the thickness of the plastic layer is 10 mm. Brown coal does not get sintered. Samples for experiments were ground (particle size <0.2 mm) and dried in a vacuum box.

The contents of moisture, ash and volatile substances in the samples under investigation were determined using standard procedures. Elemental analysis was carried out with a Flash EA 1112 analyzer (Thermo Finnigan, USA). The parameters of the special supramolecular structure of the organic mass of coal were calculated relying on diffraction patterns recorded with an

X'Pert PRO instrument (PANalytical, the Netherlands) in  $\text{CuK}_\alpha$  radiation within  $2\theta$  angle range from 7 to  $52^\circ$ . Interpretation of diffraction patterns and calculation of the structural parameters were carried out according to the procedure described in [16].

Thermogravimetric investigation was carried out with the STA 449 F1 Jupiter instrument (Netzsch, Germany) in corundum crucibles within temperature range 298–1173 K in argon flow (the flow rates of protective and purging gas was 20 and 50 mL/min, respectively). Measurement results were processed with the help of Netzsch Proteus Thermal Analysis. 5.1.0 software delivered with the instrument. Kinetic characteristics were determined on the basis of TG data obtained at three different heating rates: 5, 10 and 20  $^\circ\text{C}/\text{min}$ . Calculations were carried out with the help of Excel 2007 and OriginPro 8.

The kinetic treatment of the results of TG/DTG analysis was carried out using model-free OFW and KAS methods.

Isoconversional OFW method is based on the analysis of the temperature dependence of the relative conversion degree  $\alpha$  measured at different heating rates  $\beta$ . According to the OFW theory, activation energy is calculated using equation

$$\ln(\beta_i) = \ln\left(\frac{A_\alpha E_a}{Rg(\alpha)}\right) - 5.331 - 1.052 \frac{E_a}{RT_{\alpha i}} \quad (5)$$

Here  $\alpha = \frac{m_0 - m}{m_0 - m_f}$ , where  $m_0$  is the initial mass

of the sample;  $m$  is the current mass at a temperature of  $T$ ;  $m_f$  is sample mass after completion of thermal destruction;  $g(\alpha)$  is a constant at a given conversion degree. Indices  $i$  and  $\alpha$  denote the used values for the rate of heating and the obtained conversion degree, respectively. Activation energy is determined from the slope of the straight line plotted in the coordinates  $(\ln \beta, (1/T))$ , it is not necessary to know the order of the reaction.

With the KAS method, determination of the activation energy of thermolysis is based on using the equation

$$\ln\left(\frac{\beta_i}{T_{\alpha i}^2}\right) = -\frac{E_a}{RT_{\alpha i}} + \ln\left(\frac{A_\alpha R}{E_a g(\alpha)}\right) \quad (6)$$

The activation energy of thermal decomposition of the sample under investigation is determined by the slope of the straight line plotted in the coordinates  $(\ln(\beta_i/T_{\alpha i}^2), (1/T_{\alpha i}))$  for a set of  $\alpha$  values.

## RESULTS AND DISCUSSION

The parameters determined by means of technical analysis and the elemental composition of coal samples are presented in Table 1. With close values of the content of volatile substances, sulphur and nitrogen, brown coal (B) from the Baganuur deposit contained smaller amount of carbon and larger amount of oxygen, which depicted its lower coalification degree in comparison with black gas coal (G) from the Ulig-Khem deposit.

The diffraction patterns of coal samples contain broad reflections within  $2\theta$  angle range from 7 to  $34^\circ$  and from 34 to  $52^\circ$ , which are due to definite inter- and intramolecular ordering of the fragments in the organic mass, respectively (Fig. 1). Expansion of a broad reflection within the  $2\theta$  range from 7 to  $34^\circ$  into Gaussian components revealed three components. According to [16], these components are related to a comparatively ordered graphite-like component ( $C_{\text{graph}}$  with the maximum at  $2\theta = 25^\circ$ ), which is formed by the packets of flat polyaromatic molecules, and two low-ordered  $\gamma$ -components (with maxima at  $2\theta \approx 17-18$  and  $8-11^\circ$ ), located at the periphery of the packets. The relative contents of the structures were determined from the areas under the peaks of Gaussian functions.

The obtained characteristics of the spatial structure of coal samples are presented in Table 2. The fractions of relatively ordered packets composed of polyaromatic molecules were 29 % for brown coal and 36 % for black gas coal, which is considered [17] as the parameter depicting the degree of aromaticity. The major part of the organic mass of coal (OMC) for both samples is represented by disordered  $\gamma$ -structures (71 % for brown coal and 64 % for gas coal), which according to [16] contain small aromatic fragments, as

TABLE 1

Technical and elemental analysis of the samples of brown and gas coal

Sample	$A^d$ , %	$V^{\text{daf}}$ , %	Elemental composition (per dry ash-free mass), mass %				
			C	H	N	S	$O_{\text{dif}}$
B	5.7	46.0	70.9	5.2	1.0	0.5	22.4
G	10.4	45.2	78.0	6.2	1.2	0.3	14.3

Note. 1.  $A^d$  is ash content in the dry sample,  $V^{\text{daf}}$  is the yield of volatile substances,  $O_{\text{dif}}$  is oxygen by the difference. 2. Here and in Tables 2–6: B is brown coal from the Baganuur deposit in Mongolia, G is black gas coal from the Ulig-Khem deposit in Tuva.

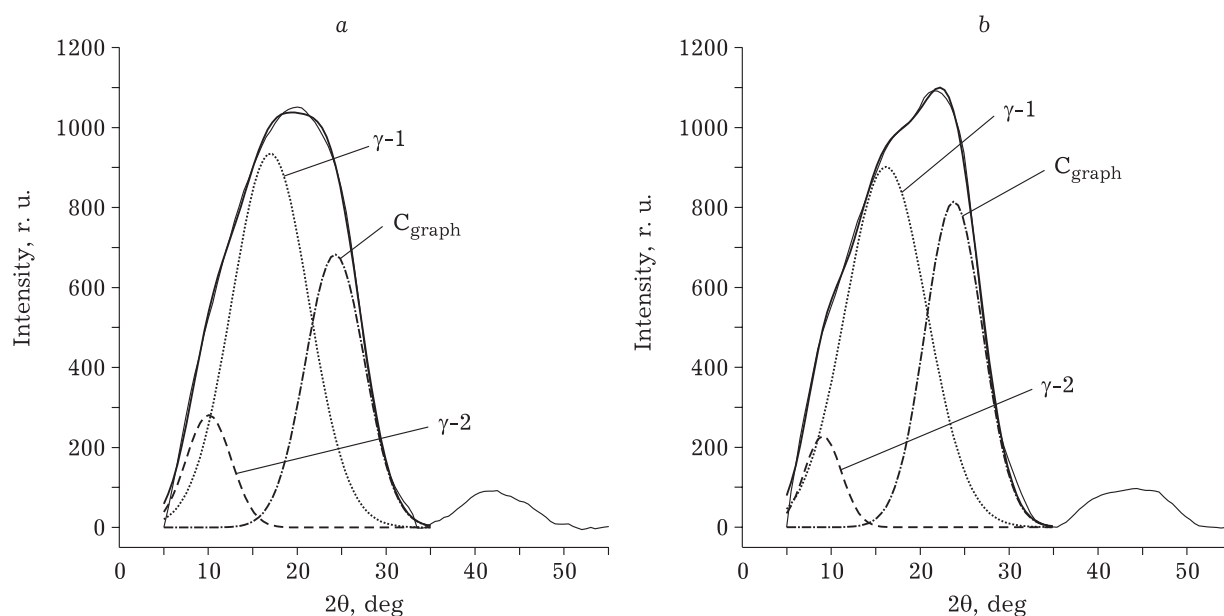


Fig 1. Fragments of diffraction patterns of brown (a) and black gas (b) coal samples obtained by means of expansion into Gaussian components.

well as aliphatic and oxygen-containing groups localized at the periphery of polyaromatic packets. The diameter of the packets and the number of graphene layers in the packets in black gas coal and in brown coal were 18.6 and 15.9 Å, 4.1 and 3.7, respectively.

TG and DTG curves illustrating the dependence of coal mass decrease and the rate of mass loss on temperature are shown in Fig. 2. The profiles of TG and DTG curves depict the multistage nature of thermal decomposition. Preliminarily, we may distinguish three main stages of decomposition proceeding in three different temperature regions (Table 3). At the first stage, within temperature range 30 to 200–300 °C, processes connected with the removal of moisture and occluded volatile substances from coal take place. At the second stage, with further heating to 600–650 °C, the major reactions of the thermal destruction of OMC take place. They are accompanied by the substantial evolution of volatile sub-

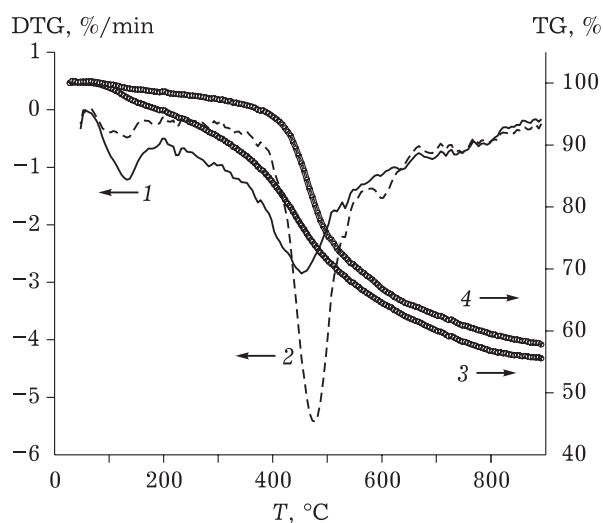


Fig. 2. Thermograms of pyrolysis of the samples of brown (1, 3) and black gas (2, 4) coal samples. Heating rate: 20 °C/min.

stances. With the transition from brown coal to black coal, the maxima of TG and DTG curves

TABLE 2

Composition of spatial structures and characteristics of the structure of graphite-like component in coal samples according to the data of X-ray diffraction

Sample	Fraction of structures, %			Parameters of graphite-like components		
	$C_{\text{graph}}$	$\gamma_1$	$\gamma_2$	Interplanar spacing $d_{002}$ , Å	Number of layers in packets, $n$	Diameter of packets, $L_a$ , Å
B	29	59	12	3.67	3.7	15.9
G	36	57	7	3.70	4.1	18.6

TABLE 3

Data of thermogravimetric analysis of coal samples

Sample	Temperature range, °C	$T_{\max}$ , °C	$V_{\max}$ , %/min	Mass loss, %	Coke residue at 900 °C, mass %
B	30–217	130	–0.92	7.4	54.7
	217–650	433.7	–1.45	28.32	
	650–900	–	–	10.25	
G	30–313	109.4	–0.22	2.4	60.8
	313–576	456.9	–2.83	28.38	
	576–900	–	–	8.45	

Note. 1.  $T_{\max}$  is temperature corresponding to the maximal rate of mass loss,  $V_{\max}$  is the maximal rate of mass loss. 2. Dash means that extremums are not observed.

shift to higher temperatures, which depicts an increase in thermal stability. The peak on the DTG curve for brown coal is less intense and broad than the peak for black coal, which may be the evidence of more diverse molecular composition and less ordered structure of brown coal. The third stage of thermolysis is characterized by slow processes of further decomposition and polycondensation of organic substances. Brown coal undergoes deeper destruction than black gas coal does (the percentage of coke residue is 54.7 and 60.8 %, respectively).

TGA data were used to calculate the kinetic parameters of the thermal decomposition of coal. The reactivity of the substance may be characterized by  $E_a$ : high values of this parameter imply low reactivity. Kinetic parameters were determined for the temperature range from 350 to 600 °C, because the major reactions involved in

thermal destruction proceed within this temperature range. Linearization of results obtained within the OFW and KAS methods is presented in Fig. 3, 4, displaying isoconversion lines connecting the points with equal  $\alpha$  obtained at different heating rates.

The integral OFW method allows distinguishing different stages of thermal destruction relying on the slopes of isolines. According to the data obtained (see Fig. 3, 4), within the range of  $\alpha = 0.1$ –0.9 the occurrence of three main stages of decomposition may be assumed for brown coal and two stages for black gas coal. One can see in the results of kinetic analysis by means of OFW shown in Table 4 that  $E_a$  varies within the range from 24 to 362 kJ/mol for brown coal and from 143 to 283 kJ/mol for black gas coal, and the pre-exponential factor ( $\ln A$ ) varies from 5.3 to 39.1 s<sup>-1</sup> and from 16.1 to 41.4 s<sup>-1</sup>, respectively. The analy-

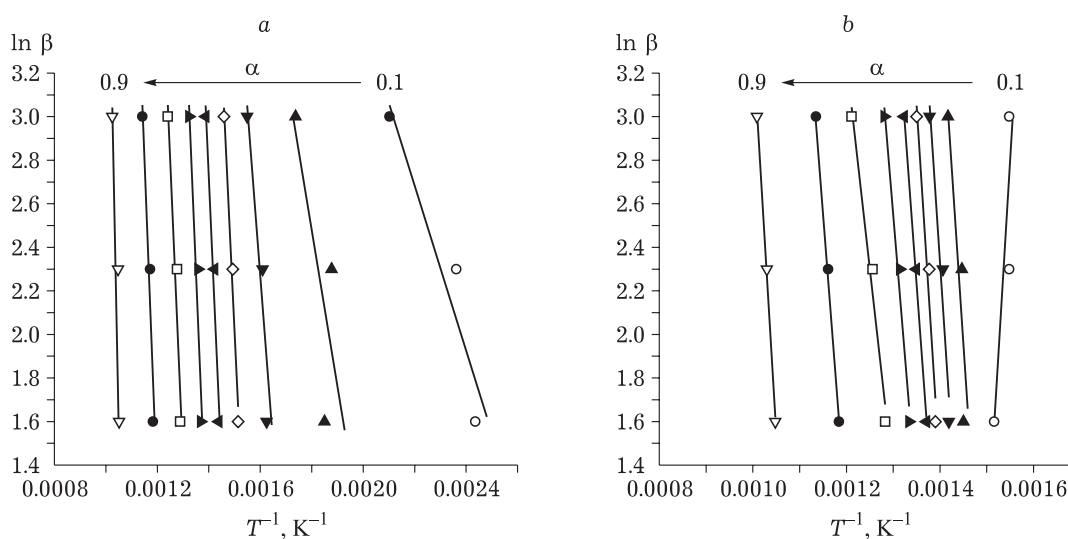


Fig. 3. Kinetic analysis of the thermolysis of the samples of brown (a) and black gas (b) coal by means of OFW.  $\alpha$  is relative conversion degree.

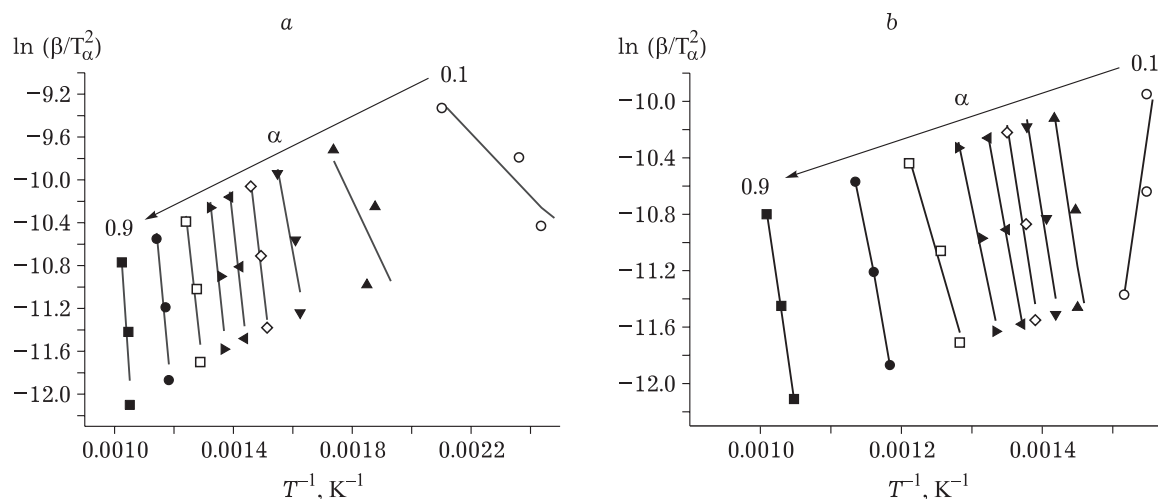


Fig. 4. Kinetic analysis of the thermolysis of the samples of brown (a) and black gas (b) coal by means of KAS.  $\alpha$  is relative conversion degree.

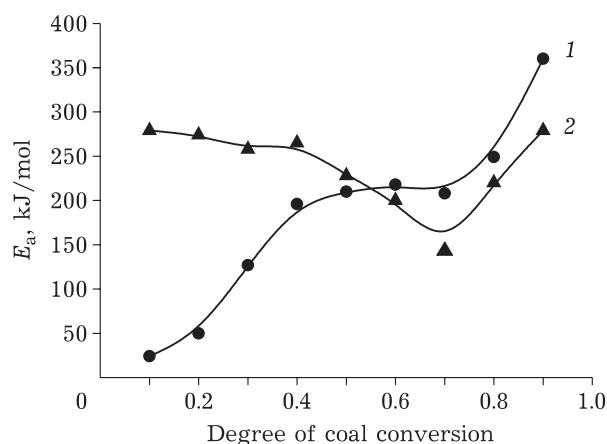


Fig. 5. Dependence of activation energy  $E_a$  on the degree of conversion of brown (1) and black gas (2) coal in thermolysis (OFW method).

sis carried out using KAS method (Table 5) shows that  $E_a$  values vary from 24 to 360 kJ/mol for brown coal and from 143 to 279 kJ/mol for gas coal; the preexponential factor varies from 4.6 to 35.2 s<sup>-1</sup> and from 20.2 to 43.2 s<sup>-1</sup>, respectively. The observed substantial changes in activation energy and preexponential factor during pyrolysis provide evidence that the limiting stages change during the process, which is due to the multicomponent and polyfunctional composition of coal. The best correlation of experimental data is observed within the range  $\alpha = 0.4$ – $0.8$ .

Calculated  $E_a$  values depending on  $\alpha$  during thermal decomposition of coal are presented in Fig. 5. One can see that in the case of brown coal activation energy increases in the course of decomposition, that is, more and more stable molecular structures are involved in thermal destruction with an increase in temperature. Low  $E_a$

TABLE 4

Activation energies of the pyrolysis of B and G coal samples in the atmosphere of argon according to OFW method

Relative conversion degree, $\alpha$	B			G		
	$E_a$ , kJ/mol	$\ln A$ , s <sup>-1</sup>	$R^2$	$E_a$ , kJ/mol	$\ln A$ , s <sup>-1</sup>	$R^2$
0.1	30	5.3	0.906	259	37.9	0.808
0.2	57	6.8	0.879	274	41.4	0.818
0.3	131	19.1	0.900	258	37.9	0.957
0.4	197	29.4	0.982	266	37.9	0.961
0.5	212	29.9	0.959	230	31.3	0.998
0.6	221	29.8	0.917	205	26.0	0.980
0.7	213	26.4	0.923	151	16.1	0.980
0.8	252	29.0	0.933	226	25.2	0.999
0.9	362	39.1	0.883	283	28.7	0.998
Average	186	23.9		239	31.4	

TABLE 5

Activation energies of the pyrolysis of B and G coal samples in the atmosphere of argon according to KAS method

Relative conversion degree, $\alpha$	B			G		
	$E_a$ , kJ/mol	$\ln A$ , s <sup>-1</sup>	$R^2$	$E_a$ , kJ/mol	$\ln A$ , c <sup>-1</sup>	$R^2$
0.1	24	4.6	0.845	279	47.4	0.764
0.2	50	9.2	0.488	274	42.5	0.804
0.3	127	23.0	0.883	258	42.8	0.952
0.4	196	34.4	0.979	265	43.2	0.956
0.5	210	35.2	0.955	228	36.3	0.997
0.6	218	34.5	0.907	200	30.6	0.978
0.7	208	31.0	0.911	143	20.2	0.976
0.8	249	34.0	0.924	220	29.7	0.998
0.9	360	44.4	0.875	279	33.3	0.998
Average	182	27.8		238	36.7	

at the initial stage (24–50 kJ/mol) may be due to the superposition of diffusion stages.

The thermal decomposition of black coal is described by a more complicated kinetic curve. After achieving  $\alpha = 0.4$ , further reactions of OMC decomposition proceed with lower activation energy. This may be connected with the transition of coal into the plastic state, in which the radical polycondensation processes are developing in addition to destruction. It may be assumed that within temperature range 400 to 550 °C ( $\alpha = 0.4$ –0.7) the amount of volatile substances and the rate of their evolution are determined mainly not by the rupture of bonds in initial molecules but by radical polycondensation processes leading to the formation of carbonized structures. Activation energies of polycondensation participated by radicals are usually substantially lower than those for reactions participated by molecules [18, 19].

TABLE 6

Experimental constants in the equation of compensation effect for coal thermolysis

Sample	Constants of compensation effect		Correlation coefficient, $R^2$
	$a$	$b$	
B	0.1081	3.747	0.935
G	0.2005	15.319	0.943

The occurrence of these processes during the pyrolysis of the organic mass of gas black coal may be a reason for a decrease in  $E_a$  within temperature range 400–550 °C. The anomalous effect detected for gas coal requires more detailed consideration, confirmation by the example of other samples of gas coal involving other methods of physicochemical analysis, which is planned for further investigations.

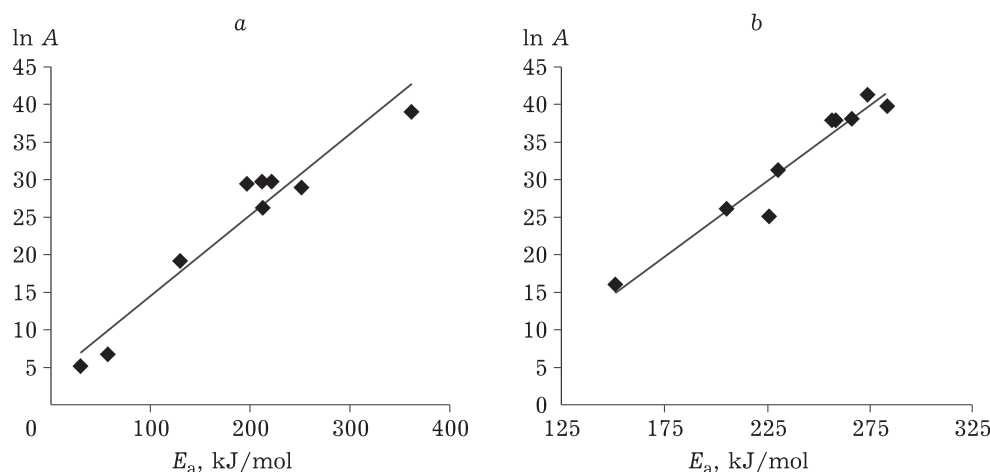


Fig. 6. Dependence of preexponential factor  $\ln A$  on activation energy  $E_a$  of thermolysis for brown (a) and black gas (b) coal (OFW method).

According to the data shown in Tables 4, 5, a correlation was revealed between the activation energy  $E_a$  and preexponential factor  $\ln A$ . One can see in the data shown in Fig. 6 that for both types of coal this dependence is described by the equation of linear regression of the type of  $\ln A = a + bE_a$ , where  $a$  and  $b$  are experimental constants. The numerical values of constants  $a$  and  $b$ , determined through data treatment by means of the least squares, and the corresponding correlation coefficients are presented in Table 6. The deduced relations depict the manifestation of the kinetic compensation effect with high correlation coefficients. This compensation effect may be connected with the fact that OMC contains molecular groups in different concentrations and with different reactivities, that is, decomposing with different activation energies.

## CONCLUSION

The data on the composition, spatial structure and thermal properties of the samples of brown coal from the Baganuur deposit in Mongolia and gas black coal from the Ulug-Khem deposit in Tuva were obtained. The dynamics of thermal decomposition of the organic mass was studied by means of thermal analysis in the dynamic mode with different heating rates.

Activation energies of the reactions involved in the thermal decomposition of coal for the degree of conversion within the range  $\alpha = 0.1-0.9$  were determined with the help of isoconversion methods proposed by Ozawa-Flynn-Wall (OFW) and Kissinger-Akahira-Sunoo (KAS). It was shown that with an increase in temperature, the activation energies of reactions proceeding at different stages of the decomposition of organic mass vary within a broad range and depends on conversion degree.

The average values of the energies of brown coal decomposition are equal to 186 (OFW method) and 182 (KAS method) kJ/mol, 239 and 238 kJ/mol for black gas coal, respectively. Activation energies determined with the help of two methods of kinetic analysis are in good agreement with each other, which is the evidence of their suitability for characterization of so complicated processes as the pyrolysis of solid fuel.

In the course of coal pyrolysis, the kinetic compensation effect was established, the

equations of the linear regression of activation energy and preexponential factor were deduced, and kinetic constants were calculated.

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