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Research on kinetics of the thermal processing of brown coals of various oxidative ageing degree using the non-isothermal methods

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Abstract

Methods for the complex thermoanalysis of these solid fuels are discussed. The following processes were studied: moisture evaporation, emission of volatile products (separate evaluations of pitch and gas emission), reaction of non-volatile fuel residue with the oxygen in air. The data bank on the reactivity of Beresovsky deposit brown coal oxidatively aged to different extents was gathered. The results of the work can be used in mathematical simulation of processes for the coal processing using the power technology. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Up to now the problem of the rational use of the Kansk-Achinsk basin coals has not been solved. It is caused by a significant share of non-combustibles and by unfavorable chemical properties of their mineral fraction. Moreover, the solution of this problem is essentially complicated by the annual tendency of the coal quality deterioration and increasingly growing environmental requirements for the cleanliness of operation of the fuel operated plants. All this makes scientific bodies and experts develop new methods of processing, combustion and gasifying of solid fuel and ways of their realization.

The most efficient way of accomplishing the abovementioned tasks is mathematical simulation of the studied processes with quantitative characteristics of fuel reactivity as an obligatory condition. Moreover, the economic costs of such a development are essentially reduced, as there is no need to invest in new expensive experimental plants. However, a significant spread in the experimental values of the kinetic parameters, which determine the coal reactivity, and a lack of summarizing methodical studies on getting these parameters predetermined the direction of the researches and their basic results are set forth in this article.

It is known that the global stages of the thermal processing are drying, thermal decomposition and burning-out of the non-volatile residue [1]. As a rule the processes in real technological plants have the character of overlapping stages that creates certain difficulties in evaluation of the kinetic characteristics. The analysis of the existing research studies on the problem has shown that it is purposeful to use the complex thermoanalysis (CTA) developed [2].

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Table 1
The characteristics of the Beresovsky coals of a different oxidative ageing degree

Ageing degree (%)	Proximate analysis				Elemental analysis (wt.%), dry and ash-free				
	Moisture (wt.%), wet basis	Ash (wt.%), dry	VM[a] (wt.%), dry	Heating value (kJ kg^{-1})	C	H	N	O[b]	S
>80	18.9	14.5	53.1	11766	65.8	3.8	1.1	28.6	0.7
40–80	16.0	6.4	48.5	13031	69.3	4.2	0.7	25.1	0.7
<40	12.1	4.6	46.0	15580	72.0	4.6	0.6	22.5	0.3

[a] Volatile matter yield.
[b] Obtained by difference.

2. Experimental

The CTA scheme incorporates thermogravimetry, differential thermoanalysis and gas chromatography within a framework of a single plant. The first two methods are implemented in the MOM derivatograph (type Q-1500D). To analyze the gaseous products of thermolysis the chromatographic gas analyzer "Soyuz 3101" was used. The continuous analysis of a coal sample being heated from 20 to 1600°C in various environments (an inert, oxidative and reductive atmosphere) allows to record not only total process characteristics (the weight loss, rate of the weight loss, temperature variation) but also dynamic change of parameters of the gas products generation (CO, CO_2, H_2, CH_4) under non-isothermal conditions. The operation parameters of the derivatograph were set in such a way that the certain local ranges of the thermal processing of the fuel investigated could be distinguished for the complex evaluation of the kinetic characteristics of the stages investigated. The weight of the coal sample for the experiments in the inert environment (N_2) was 500 mg, that in oxidative environment (N_2+O_2) was 20 mg. The crucible was made of ceramic inert material Al_2O_3, average heating rate was 5°C min^{-1}, gas flow was 200 cm^3 min^{-1}, particle size: polyfraction (R_{90}=45%, R_{200}=30%, R_{1000}<1%). Reading sensitivity (mV): TG-500, DTA-500, DTG-1.

Because many characteristics of the coals from individual deposits in the Kansk-Achinsk basin are similar among themselves, the coals with the best prospects from the point of view of their mining development level and accumulated practical experience in the power use of Berezovsky deposit were investigated. The coal samples were divided into three groups according to their degree of ageing: the run-of-mine coals, oxidatively aged coals and coals with the lowest degree of oxidative ageing. The degree of the coal ageing was determined by a petrographic method. The characteristics of the coals investigated are shown in Table 1.

The evaluation of the kinetics of the processes studied is based on analyses of the experimental data obtained with help of CTA of two experiments: thermal decomposition (an inert environment) and burning of the non-volatile residue (an oxidative environment) [3]. The reactivity of the fuel was evaluated taking into consideration the rate of moisture evaporation, the rate of emission of volatile products and the rate of reaction of the non-volatile residue. Activation energy (E) and pre-exponent multiplier (k_0) describing the coal thermal processing without diffusion complications were assumed to characterize the fuel reactivity.

3. Results and discussion

The results of the experimental researches on kinetics of moisture evaporation from the coal particles were processed using the equation

$$\frac{dU}{dt} = k_u(U_0 - U), \qquad (1)$$

where U_0 is the starting fuel moisture content, U the value of the fuel moisture content measured during the process of thermoanalysis, k_u the constant of the drying rate, and t the time.

The CTA of the Berezovsky coal has shown that moisture evaporation from the coal goes through two stages differing in intensity of the weight loss of the fuel sample on curve TG (Fig. 2a). It is determined that the sorbed moisture of the fuel is removed in the

Table 2
The average statistic kinetic parameters of the evaporation processes of the sorbed and chemically bound moisture of Beresovsky coal of the different degree of the oxidative ageing

Ageing degree (%)	Sorbed moisture						Chemically bound moisture					
	W^{a} (wt.%), db	Initial temperature (°C)	Maximum temperature (°C)	Final temperature (°C)	E (kJ mol^{-1})	k_0 (s^{-1})	W^{b} (wt.%), db	Initial temperature (°C)	Maximum temperature (°C)	Final temperature (°C)	E (kJ mol^{-1})	k_0 (s^{-1})
>80	18.8	20	120	160	12.33	1.40	5.8	160	240	280	18.76	1.5×10^{2}
40–80	16.0	20	120	160	11.79	1.05	4.2	160	245	285	22.93	2.1×10^{2}
<40	12.0	20	120	160	14.40	4.02	3.0	160	250	290	28.32	3.5×10^{2}

[a] Sorbed moisture content.

[b] Chemical bound moisture content.

first stage (20–160°C) and chemically bound moisture in the second (160–280°C). The values of the kinetic parameters for the evaporation of the two forms of fuel moisture are shown in Table 2. The results show that the binding energy of the sorbed moisture of Berezovsky coal does not practically depend on the coal ageing degree while the binding energy of the chemically bound moisture increases from 18.76 kJ mol^{-1} for the coal with the lowest degree of ageing to 28.32 kJ mol^{-1} for the run-of-mine coal. It is necessary to note that the determination of the amount of the chemically bound fuel moisture has not been standardized yet and, therefore, there is no mechanism for its inclusion in the technological calculations although according to CTA that of Berezovsky coal reaches 5.8% and it could probably lead to additional errors in the calculation of the dynamic change of parameters of coal drying.

The kinetic analysis and the evaluation of the complex experimental curves describing the dynamic changes in the emission of the volatile products from thermal decomposition of Berezovsky coal were carried out assuming that this process is described by a system of irreversible overlapping reactions of the first order and there is no cross-interaction between destruction products. The total kinetic equation is

$$\frac{\mathrm{d}C}{\mathrm{d}t}=\sum_{i=1}^{n}\sum_{j=1}^{m}C_{0ij}\left(1-\frac{C_{ij}}{C_{0ij}}\right)k_{0ij}\exp\left(-\frac{E_{ij}}{RT}\right), \tag{2}$$

where i=1,. . .,N is an amount of the gas vapor components taken into consideration, j=1,. . .,M is a number of individual stages responsible for the emission of the ith component, C_{0ij}, C_{ij} are the starting concentra-

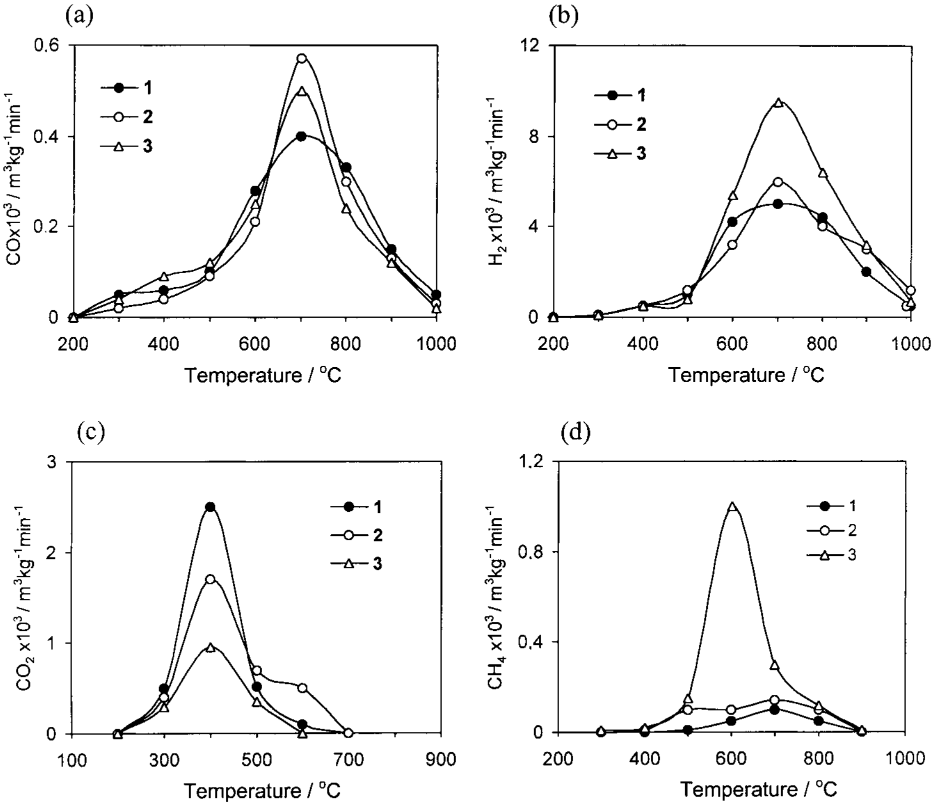

Fig. 1. (a) Dynamics of the carbon monoxide emission, (b) hydrogen, (c) carbon dioxide, and (d) methane under the thermal decomposition of the Beresovsky coal (average heating rate β=5°C min^{-1}; the same is for Fig. 2). Ageing degree coal — 1: >80%, 2: 40–80%, 3: <40%.

tion of the reacted ith component in the jth stage and that measured during the process accordingly, E, k_0 are the activation energy and pre-exponent multiplier, respectively, R the universal gas constant, and T the process temperature.

The components of the volatile products of the thermal decomposition are represented by a set of individual gas components (CO, CO_2, H_2, CH_4) and by the vapors of hydrocarbon compounds (pitches). The initial data on the dynamic changes of the pitch emission were obtained by means of differentiation of the total rate of emission of individual gaseous components (Fig. 1) with respect to DTG curve for the volatile product emissions (Fig. 2a).

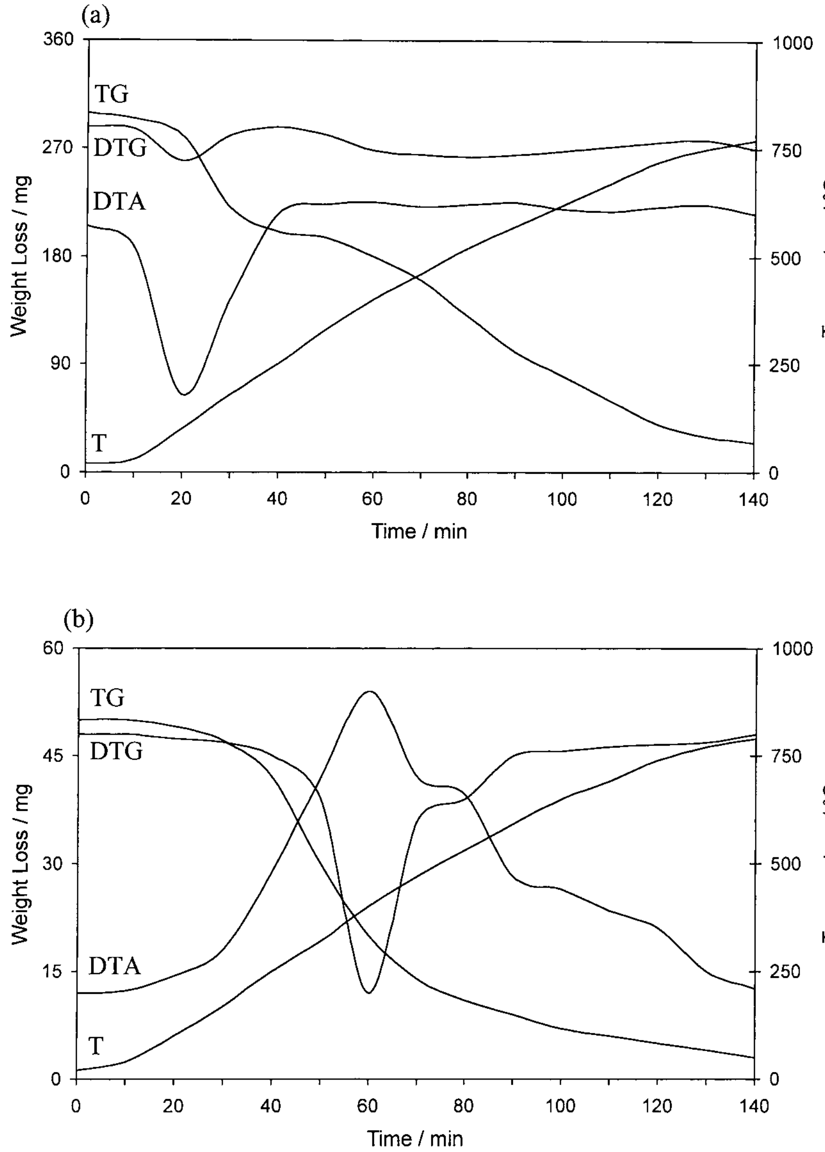

Fig. 2. (a) TG, DTG and DTA curves of the processes of the thermal decomposition, and (b) combustion non-volatile residue of the Beresovsky coal.

The following kinetic equation served as the basic model to develop an algorithm for the determination of the kinetic characteristics and its software realization:

$$\frac{\mathrm{d}\omega_j(t)}{\mathrm{d}t} = \omega_j(t) k_{0j} \exp\left[-\frac{E_j}{RT(t)}\right], \qquad (3)$$

where $\omega_j(t)=(C_j-C_{kj})/(C_{0j}-C_{kj})$ is the transformation degree of the *i*th component in the *j*th stage of the process, and C_{kj} the final concentration of the reacted substance.

To evaluate the kinetic parameters responsible for the pitch and gas emissions the principle of successive calculation and elimination of individual stages was used [4]. Taking into consideration the adopted assumptions the independent analysis of a random *j*th stage of the entire process can be done. The area of the isolated stage on the total kinetic curve was found with the help of the correlation analysis of experimental points. For this purpose the logarithm of the ratio (3) must be taken. The result is

$$\ln\left[\frac{\mathrm{d}\omega_j(t)}{\mathrm{d}t}\frac{1}{\omega_j(t)}\right] = \ln k_{0j} - \frac{E_j}{RT(t)}. \qquad (4)$$

Eq. (4) is the equation of the straight line drawn through the collection of the experimental points referring to the *j*th stage: $y=b_0+b_1x$, where

$$y = \ln\left[\frac{\mathrm{d}\omega_j(t)}{\mathrm{d}t}\frac{1}{\omega_j(t)}\right], \quad x = \frac{1}{T(t)},$$

$$b_0 = \ln k_{0j}, \quad b_1 = -\frac{E_j}{R}.$$

The kinetic parameters sought were determined through factors b_0 and b_1 with help of the method of least squares or linear regression in the temperature range of the *j*th stage: $T(t) \in \left[T_j^{\max}, T_j^{\min}\right]$, where $T_j^{\max}$, $T_j^{\min}$ are the maximum and minimum reaction rates during the *j*th stage. The accuracy of the approximation by the linear dependence of the experimental values y and x is evaluated by the correlation factor. The kinetic parameters obtained allow calculation of the kinetic curve for the *j*th stage using the method of numerical integration of the following equation obtained from the expression (3):

$$\tilde{\omega}_j(t) = \exp\{\ln[\omega_j^{\max} - k_{0j}F_j(t)]\}, \qquad (5)$$

where $\omega_j^{\max}$ is the share of the reacted substance at the maximum temperature of the *j*th stage; $F_j(t) = \int_{t_{\max}}^{t} \exp(-E_j/RT(t))\,\mathrm{d}t$ is the integral exponential function [5].

The derivative of the thermogravimetric curve of the *j*th stage is calculated according to formula (3) after determination of the values $\tilde{\omega}_j(t)$ using ratio (5).

After subtraction of the calculated values $\tilde{\omega}_j(t)$ and $\mathrm{d}\tilde{\omega}_j(t)/\mathrm{d}t$ from the initial curves $\omega_j(t)$ and $\mathrm{d}\omega_j(t)/\mathrm{d}t$, the parameters of the next stage, were searched and determined.

The calculation using the mathematical expressions (3–5) allows successive deduction of the kinetic curves of the stages found from the basic process and, thus, further data processing to the starting point of the gravimetric curve of the initial process of the coal thermal decomposition.

The calculated values of the kinetic parameters of volatile products emission during thermal decomposition of Berezovsky coals of different ageing degree were determined using the above technique and shown in Table 3.

From the presented material it is seen that there is no precise law of changing of the kinetic parameters of volatile products emission depending on the ageing degree of Berezovsky coal. At the same time, with increase of the ageing degree the thermal stability of the coal substance also increases, i.e. the temperatures of maximum carbon oxide and hydrogen emission and pitch emission moves to the higher values. The formation of the temperature stages for the pitch emission as a result of destruction of the oxidatively aged Berezovsky coals and those with the lowest ageing degree probably shows that the activation energy of each process stage must be correlated with sizes of the elementary structure units of the investigated fuels. So, the vitrinit microcomponents of the coals with high ageing degree are characterized by the arrangement of flat networks of aromatized carbon consisting of only four rings with decreased carbon content and average statistic distance of the paramagnetic centers as well as decreased condensation degree of their structure units [6,7].

The non-volatile residues generated as a result of the CTA of Berezovsky coals in the experiments on their thermal decomposition were used to determine the kinetic characteristics of their reactions with oxygen in air.

Table 3
Kinetic characteristic of the individual independent reactions of the emission of the volatile substances under the thermal decomposition of the Beresovsky coal

Gas component	Ageing degree (%)	Stage number j	C_0 (%)	Temperature (°C)			E (kJ mol^{-1})	k_0 (s^{-1})
				Initial	Maximum	Final		
	>80	1	53.4	540	780	900	136.0	84.9
		2	37.0	460	640	740	92.7	1.1×10^5
		3	9.4	380	520	600	159.4	8.4×10^6
H_2	40–80	1	49.1	615	810	900	151.6	1.7×10^5
		2	45.8	525	645	750	110.2	7.6×10^3
		3	5.1	355	505	570	115.7	2.2×10^4
	<40	1	68.0	520	740	900	92.4	45.0
		2	32.0	490	640	715	142.3	4.9×10^6
	>80	1	77.8	485	715	875	84.1	83.2
		2	20.0	465	635	725	116.0	2.5×10^4
		3	2.2	210	395	515	56.1	1.3×10^2
CO	40–80	1	51.4	535	785	900	108.8	56.5
		2	34.2	525	660	720	184.6	6.2×10^5
		3	10.8	350	400	605	67.2	66.0
		4	3.6	180	260	360	41.3	2.4
	<40	1	46.8	590	760	890	90.2	87.9
		2	31.3	490	655	720	140.9	4.5×10^6
		3	16.9	280	410	535	71.5	4.54×10^2
		4	5.0	180	250	340	43.2	0.3
	>80	1	24.0	590	740	825	199.7	2.4×10^7
		2	60.4	370	565	715	74.9	40.9
		3	15.6	300	425	515	102.2	1.2×10^4
CH_4	40–80	1	48.7	415	655	815	58.1	7.2
		2	51.3	290	495	565	69.8	1.0×10^2
	<40	1	89.0	390	600	705	106.9	1.4×10^5
		2	11.0	285	365	465	92.3	5.2×10^5
	>80	1	65.7	350	540	645	79.4	1.6×10^3
		3	34.3	285	385	435	117.0	3.8×10^9
CO_2	40–80	1	54.9	305	465	590	95.4	3.9
		2	45.1	250	345	415	76.4	5.2×10^6
	<40	1	100.0	280	380	470	71.7	1.1×10^3
	>80	1	33.3	420	620	740	54.5	4.6×10^3
		2	28.4	460	520	560	129.5	8.5×10^{15}
		3	15.2	340	420	480	61.8	2.8×10^7
		4	9.2	300	340	380	48.9	2.9×10^6
Pitch	40–80	1	9.2	690	790	840	123.8	3.2×10^{14}
		2	38.6	500	600	660	78.4	2.4×10^7
		3	16.8	360	460	520	52.8	2.8×10^5
		4	35.4	280	320	380	30.9	1.7×10^3
	<80	1	100.0	280	500	780	75.9	2.5×10^2

The rate constant of the burning-out of non-volatile residues was calculated using DTG curve on the derivatogram (Fig. 2b) taking into consideration a correction with respect to the total surface area of the particles in the mass unit of the fuel sample and the volumetric coke density according to the following equation [2]:

$$k = \frac{W}{x_0 - x}\frac{1}{S\rho}, \tag{6}$$

Table 4
The kinetic parameters of the process of the burning of the non-volatile residue of the Beresovsky coal

Ageing degree (%)	Share of the reacted substance C_0 (%)	Maximum temperature (°C)	E (kJ mol^{-1})	k_0 (m s^{-1})
>80	64.0	645	132.8	2.8×10^8
40–80	69.1	640	151.2	4.2×10^9
<40	73.0	630	147.0	8.54×10^8

where W is the weight loss rate, x_0, x are the starting weight of the sample and that measured during the process (from the TG-curve) accordingly, S the total surface area of the non-volatile residue particles, and ρ the volumetric density of the non-volatile residue.

The kinetic parameters sought were determined as a result of computer processing of the equation $\lg K = f((1/T)10^3)$ [3]. The results of the determination of the kinetic constants of the burning of the Berezovsky coal non-volatile residues are shown in Table 4.

It is necessary to note that some distortions of the temperature dependence of the burning-out rate at the final stage of the process (80–85% weight loss) were observed at the time of processing the experimental derivatographic curves. Here, an additional slowdown of the oxygen penetration into the particles bulk from the ash shell formed in burning began to result. Therefore, this upper temperature range was not taken into consideration during the data processing.

The data of Table 4 show that the influence of the ageing degree of Berezovsky coals in case of combustion of their non-volatile residues is of no significance value. Changing of the kinetic parameters of that process as a function of ageing degree can be represented by a common dependence for all the Berezovsky coals:

$$E = -4206 + 1.4118 \times 10^3 \frac{\mathrm{H}}{\mathrm{C}} - 1.1432 \times 10^6 \left(\frac{\mathrm{H}}{\mathrm{C}}\right)^2, \quad (7)$$

$$\lg k_0 = \frac{1}{0.2121 - 0.0007E}, \quad (8)$$

where H, C are the hydrogen and carbon contents in the fuel accordingly.

To check adequacy of the adopted kinetic models of the studied processes of the coal thermal processing to the real conditions the measurement results of the chemical and mechanical incompleteness of combustion obtained from the heat losses tests of steam boilers E-320-140, E-420-140, E-500-140 were compared to the calculated values. From the measured mass losses the values of the rate constants for the main combustion stages of the Berezovsky coal were determined. The calculation was made for various ranges of the operation parameters of the furnaces. The flame temperature was taken from the averaged data of direct measurements taking into consideration the arrangement of the experimental of the fuel drying process it was established that their relative error was 2–3% with the 95% confidence interval of the Student's t statistical test and the relative error of the parameters describing the processes of volatile products emission and burning-out of fuel non-volatile residue is 5–7%.

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