Reactivity of Coal of Different Stages of Metamorphism in the Processes of Thermooxidative Destruction

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Abstract

Changes of the reactivity of mechanically activated coal from different stages of metamorphism in the processes of thermooxidative destruction were studied by means of thermal analysis. Thermogravimetric curves recorded at different heating rates were processed using the Model Free computer software. It was demonstrated that the intense mechanical treatment of coal at different stages of metamorphism long-flame and lean) causes an increase in the reactivity of coal, which is exhibited as a decrease in the activation energy over the whole temperature range of thermooxidative destruction. It was established that the most reactive coal towards combustion in the air environment among the studied kinds is mechanically activated low-metamorphosed long-flame coal.

Key words: coal, long-flame, lean, thermooxidative destruction, mechanical activation

INTRODUCTION

At the background of the continuous increase in the prices of oil and gas all over the world, interest to coal as alternative source of energy has risen. At present, the major part of mined coal is used for energy purposes.

The value of power station coal of D, DG, G, TS and T grades is determined mainly by its power budget, which is evaluated on the basis of the heat of combustion and the reactivity during combustion. In this situation, the statistical and dynamic (kinetic) characteristics of coal combustion are essentially dependent on the degree of coal metamorphism and petrographic composition. It was demonstrated that for increased stage of metamorphism, the reactivity of coal during combustion decreases, so the specific combustion rate can differ by a factor of 5–7 for the particles of different kinds of coal [1].

In the previous investigations it was established for the B grade coal as example that its reactivity in the processes of thermooxidative destruction depends on the intensity of mechanical action [2–4], which is connected with the transformation of relatively high-molecular components of the organic mass of coal.

The goal of the present work was to study the changes in the reactivity in thermooxidative destruction (TOD) processes for mechanically activated coal of higher stages of metamorphism – long-flame and lean coal.

EXPERIMENTAL

Coal samples from the Kuznetsk coal basin, of T and D grades, with ash value $A^c = 6.46$ and 6.15 % and the yield of volatile components (V^{daf}) equal to 41 and 12.4 %, respectively, were chosen as the objects of investigation. The samples were subjected to activating grinding in the mills with different kinds of mechanical action: in disintegrator for which the shock destruction is typical, and in the centrifugal planetary mill of M-3 type with attrition and crushing kind of action. The ratio of the total mass of milling bodies to the mass of coal was 10 : 1. Using heavy organic liquids, the light fraction of coal was obtained ($d < 1.4$ g/cm^3).

Thermal analysis was carried out using thermobalance TG 209 F1 (Netzsch). Standard corundum crucibles were used as sample holders. To make the gas composition close to the air, we used a mixture of argon and oxygen (flow rate 40 and 10 cm^3/min, respectively). Sample mass varied within the range 5−20 mg.

Thermogravimetric data were processed using the Netzsch Thermokinetics 2 software (version 2004.05). A special software module Model Free allows one to process together several thermoanalytical TG curves recorded at different heating rates, without preliminary information about kinetic topochemical equations. The programs Friedman Analysis and Ozawa−Flinn−Wall Analysis allow one to calculate the energy of activation in each experimental point (within the range of transformation degree values $0.0005 < \alpha < 0.9995$). The Friedman Analysis program is based on the analysis of the dependence between transformation rate and reciprocal temperature, the Ozawa−Flinn−Wall Analysis is based on the analysis of the dependence of heating rate and reciprocal temperature. Then the same set of experimental data is used to search for topochemical equation (a choice among 16 equations of chemical reactions on the interface, nucleation and diffusion). The differential method of linear regression is used for the initial part of calculation.

The calculation program allows one to estimate the contributions from different steps of multistage processes. Evaluation of the correctness of the choice of kinetic equations is performed on the basis of the value of correlation coefficient.

RESULTS AND DISCUSSION

The curves depicting the changes of activation energy of the TOD process of long-flame coal samples, both the initial one and activated in M-3 mill. One can see that in the case of the activated sample activation energy decreases sharply. In this situation, the maximal value of activation energy (120.38 kJ/mol) for initial coal corresponds to 0.20−0.25 transformation degree and the temperature of the maximum of the second exothermal effect (Fig. 2). For activated samples, the maximal value of activation energy (52.3 kJ/mol) is observed for smaller transformation degree ($\alpha = 0.1-0.15$).

The high-temperature effect on the DTA curve is connected to a higher extent with the oxidative destruction of the condensed part of "nuclei" in the structure of coal [5]. A distinc-
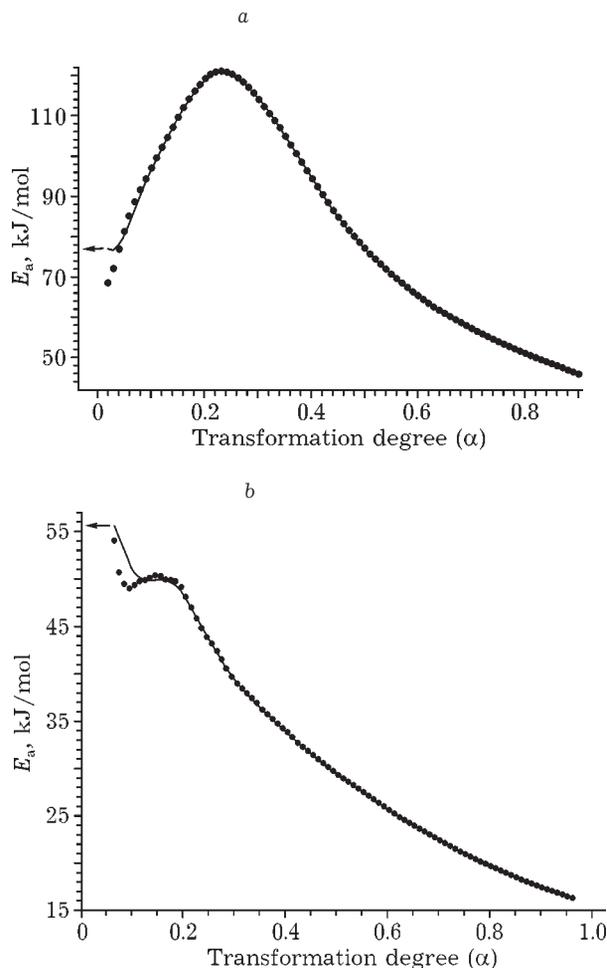
Fig. 1. Changes of activation energy of thermooxidative destruction of the samples of initial (*a*) and activated in M-3 mill (*b*) long-flame coals.
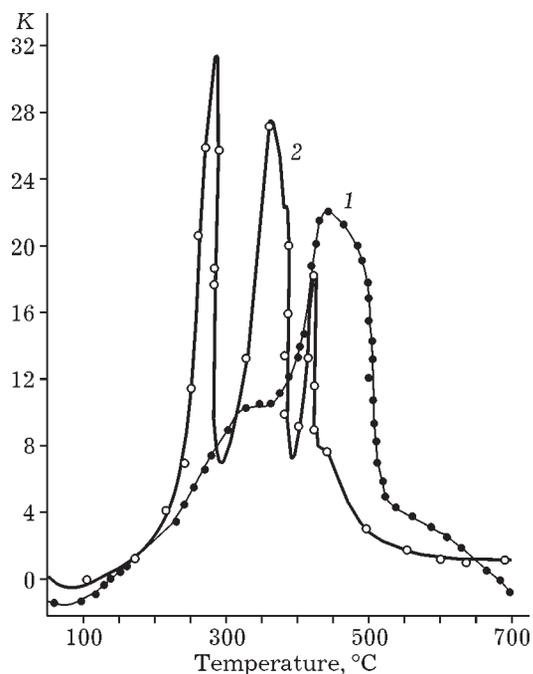
Fig. 2. DTA curves of the samples of initial (*1*) and activated (*2*) long-flame coals.

Fig. 3. Dependence of activation energy on transformation degree for coal samples of D grade: *1* − initial, *2* − light fraction ($d < 1.4$ g/cm^3), *3* − the same, activated in M-3 mill.

tive feature of thermooxidative destruction is the joint (parallel) course of low-temperature oxidation of the carbon basis of fuel and removal of the peripheral compounds of the main structural units of the organic mass. It may be assumed in this connection that the combustion of volatile components and subsequent initialization of the combustion of the nonvolatile coke basis for activated samples are characterized by a lower energy barrier and hence by a higher reactivity of the coal matter with respect to oxygen. This is also evidenced by a decrease in temperature parameters of the TOD process (the final temperature of burnout, and

temperature corresponding to the maximal rate of mass loss), and narrowing of the temperature range of combustion (Table 1).

The experimental data (Fig. 3) also provide evidence of the substantial difference in the kinetics of the TOD process of the enriched light fraction of coal ($d < 1.4$ g/cm^3) and its activated part. This is confirmed by a decrease in the activation energy: the $E = f(\alpha)$ curves are shifted to smaller values. In both cases no pronounced maxima connected with the transformations of the coal mater are observed.

A decrease in the activation energy of the light fraction in comparison with the initial coal

TABLE 1

Parameters of thermal decomposition of initial and activated coal of grade D

Samples	Temperature range of maximal decomposition, °C	Final burnout temperature, °C	Temperature of the maximum of major burnout, °C	Δm^*, %
Long-flame initial	200	635	484	37
Activated in M-3 for 5 min	240	600	475	50
The same, for 20 min	220	590	469	54
Treated in disintegrator	235	600	484	43

*Mass loss for the sample, corresponding to the maximal decomposition rate.

is due to the changes of the maceral and mineral composition that are observed as a result of the separation of long-flame coal on the basis of density during enrichment. The component that gets concentrated in the heavy fractions is inertinite I which has increased density, while the light products are enriched with vitrinite Vt and macerals of L group for the case of the noticeable content of liptinite in the initial coal. The highest chemical activity during combustion is characteristic of liptinite group, the organic matter of which contains a large amount of hydrogen. Vitrinite occupies an intermediate position in reactivity among macerals. This is explained by the fact that its organic mass has a more aromatic structure than liptinite but less condensed in comparison with the structure of the organic matter of inertinite. Taking this fact into account, we may arrange the major groups of maceral minerals according to their reactivity in coal combustion: L > Vt > I. Along this sequence, the temperature characteristics of the process rise while heat technological parameters worsen [5].

A decrease in the activation energy of TOD along the entire process is the evidence of an increase in the reactivity of light coal fractions, which is connected with different contributions from the major maceral groups of the organic mass and a decrease in the content of the mineral components of coal during combustion. The quantitative ratio between the fractions is of special interest for the use of coal in power engineering, which is connected with different reactivity of microcomponents during combustion and the higher heat of combustion.

Even higher reactivity in combustion process is exhibited by the light coal fraction activated in the centrifugal mill. This fact is due to the processes of mechanical destruction of coal matter under the conditions of intense mechanical action.

For coal sample subjected to treatment in disintegrator where the major kind of mechanical action is free shock (collision), changes of activation energy are not so substantial as in the case of treatment with centrifugal mill but close to the data for enriched non-activated light coal fraction (Fig. 4).

Thermooxidative destruction of highly metamorphosed coal of T grade is characterized by high activation energy in comparison with the
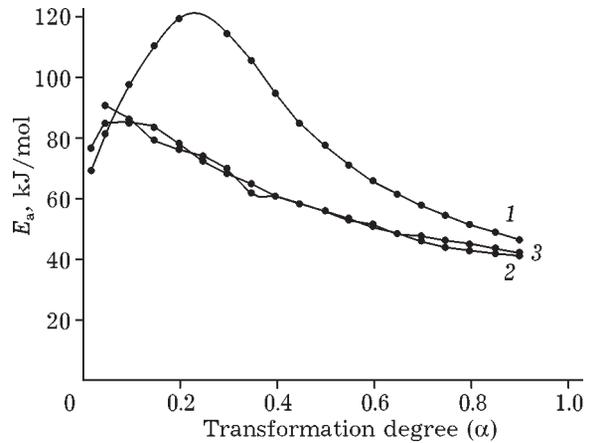
Fig. 4. Changes of activation energy of thermooxidative destruction for long-flame coal samples: *1* − initial, *2* − treated in disintegrator, *3* − light fraction ($d < 1.4$ g/cm^3).

long-flame coal samples, which is the evidence of its lower activity in oxidation processes (Fig. 5). It is known that the low-metamorphosed coal samples (vitrinite reflection measure $R_0 < 0.8$ %) exhibit the highest reactivity towards oxygen. At the same time, starting from the stage of medium volatile coal, the rate of interaction with oxygen decreases substantially. This is due to structural and chemical transformations during coalification resulting in an increase in the fraction of aromatic carbon, density and the strength of structure [6]. Activation energy for the combustion of the light frac-
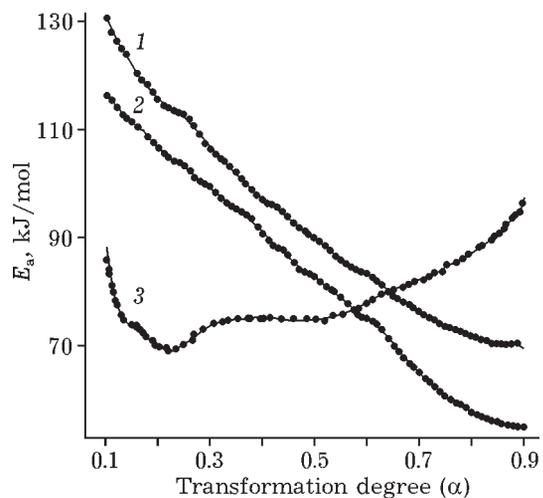
Fig. 5. Changes of the activation energy of thermooxidative destruction of T grade coal samples: *1* − initial, *2* − treated in disintegrator, *3* − activated in centrifugal mill.

TABLE 2

Results of kinetic analysis of combustion of long-flame and lean coal samples

Coal samples	Best versions of multistage processes	Equations corresponding to these processes	E_a, kJ/mol
Initial, D grade	$A \rightarrow B$	$f_{AB}(\alpha) = (1 - \alpha)[-\ln(1 - \alpha)^{0.61}]$ (Avrami–Erofeev equation)	43.2±0.7
	$C \rightarrow D$	$f_{CD}(\alpha) = (1 - \alpha)^{1.0}$ (order equation Fn)	95±5
	$E \rightarrow F$	$f_{EF}(\alpha) = (1 - \alpha)^{2.0}$ (order equation Fn)	150±2
	Parallel processes	Correlation coefficient = 0.99997	
D grade coal activated in M-3 mill	$A \rightarrow B$	$f_{AB}(\alpha) = (1 - \alpha)^{0.66}/[1 - (1 - \alpha)^{0.33}]$ (equation of three-dimensional diffusion according to Jander D3)	56±5
	$C \rightarrow D$	$f_{CD}(\alpha) = (1 - \alpha)^{0.66}/[1 - (1 - \alpha)^{0.33}]$ (equation of three-dimensional diffusion according to Jander D3)	67±6
	Parallel processes	Correlation coefficient = 0.99986	
Fraction with $d < 1.4$ g/cm³ (D grade)	$A \rightarrow B$	$f_{AB}(\alpha) = (1 - \alpha)[-\ln(1 - \alpha)^{0.61}]$ (Avrami–Erofeev equation)	140±6
	$C \rightarrow D$	$f_{CD}(\alpha) = (1 - \alpha)^{0.69}$ (order equation Fn)	49±1
		Correlation coefficient = 0.99995	
D grade coal treated in disintegrator	$A \rightarrow B$	$f_{AB}(\alpha) = (1 - \alpha)^{0.70}$ (order equation Fn)	56±2
	$C \rightarrow D$	$f_{CD}(\alpha) = (1 - \alpha)^{0.54}$ (order equation Fn)	79±3
Initial, T grade	$A \rightarrow B$	$f_{AB}(\alpha) = (1 - \alpha)^{0.72}\alpha^{0.001}$	127±7
	$B \rightarrow C$	$f_{BC}(\alpha) = (1 - \alpha)^{0.68}$ (Prout–Tompkins equation Bna and order equation Fn)	48±2
Activated in M-3 mill (grade T)	$A \rightarrow B$	$f_{AB}(\alpha) = (1 - \alpha)^{1.2}\alpha^{0.2}$	82±2
		Correlation coefficient = 0.9999	

tion of this coal sample ($d < 1.4$ g/cm³) decreases insignificantly (within 10 kJ/mol).

More substantial differences in combustion kinetics were detected for T grade coal activated in M-3 mill (see Fig. 5). The process runs not only with lower activation energy but also the behaviour of the $E = f(\alpha)$ curve changes. This may be connected with the features of mechanical activation of lean coal affecting to some extent the aromatic systems of the organic matter in view of comparatively small amount of non-aromatic fragments in coal structure.

So, activation energy for combustion in the air is not a constant value, it depends on the degree of coal burnout, that is, it changes during the process, which confirms the multistage character of coal oxidation process. The serial-parallel course of processes does not allow their sufficiently exact differentiation. It is necessary to stress that the activation energy should be considered in this case as an effective parameter of formal kinetics characterizing the multistage gross process of the interaction between the oxidizer and the carbon basis.

In the studies of coal combustion, the appearance of unresolved (non-separated) steps on the mass loss curves is likely to be connected with the presence of several grain fractions in the sample; each of them is oxidized according to its own kinetic law within a definite temperature range. These combustion processes with several fractions should be not serial but serial-parallel reactions. Such an approach has been used in subsequent kinetic analysis with the search for a kinetic equation.

In solving this task, we used several versions of multistage processes, in particular $(A \rightarrow B \rightarrow C)$, $(A \rightarrow B \rightarrow C \rightarrow D)$ with different kinetic equations. Analysis by means of the least regression allowed us to choose the best versions (Table 2).

So, the kinetic analysis with search for kinetic equation gave the information about topochemical equations. The obtained "order" equations $\{f(\alpha) = (1 - \alpha)^n\}$ as a rule, correspond to the chemical reaction of combustion at the interface ($n = 0.50$, 0.66). The first-order equation $\{f(\alpha) = (1 - \alpha)\}$ and Avrami−Erofeev equation $\{f(\alpha) = (1 - \alpha)[-\ln(1 - \alpha)^n]\}$ describe nucleation processes.

Prout–Tompkins equation
$\{f(\alpha) = (1 - \alpha)^n \alpha^m\}$
should describe the autocatalytic process in which the presence of reaction product accelerates decomposition. However, formally it sometimes describes decomposition processes that are accompanied by the change of sample volume during heating. In addition, the description of combustion process by means of a set of parallel reactions additionally points to the presence of several grained fractions with different ability to combustion in the samples (both before and after mechanical activation).

Taking into account the fact that coal is a mixture of macerals, it is natural to suppose that these fractions are macerals of coal matter differing by the rate of interaction with oxygen. During coal combustion, the organic substances of vitrinite group burn out more intensively than the macerals of inertinite group, and the residues are enriched with unburnt inertinite. In addition, the kinetics of combustion is strongly affected by the specific surface area of coal samples with is increased several times after activation.

CONCLUSION

It is shown that mechanical activation of coal samples at different stages of metamorphism, of D and T grades, leads to a decrease in the temperature parameters of thermooxidative destruction (the final burnout temperature, temperature corresponding to the maximal mass loss rate), narrowing of the temperature range of combustion, which is the evidence of an increase in the reactivity and intensification of fuel burning out.

The degree of coal metamorphism has a substantial effect on an increase in the reactivity, exhibited as a decrease in activation energy within the entire temperature range of thermooxidative destruction. The degree to which this parameter decreases for low-metamorphosed long-flame coal is much higher.

It was established that for combustion in the air the maximal reactivity is demonstrated by low-metamorphosed long-flame coal treated in M-3 mill. The most substantial decrease in activation energy is characteristic of this coal sample, which is explained by mechanical destruction of the macromolecules of coal matter.

It was established in the analysis of combustion process that the samples of the light fraction of long-flame coal and coal treated in disintegrator are close to each other in oxidation kinetics. Due to the lower activation energy of thermooxidative destruction than that of initial coal, these samples can be considered as a potential high-quality raw material doe use in power engineering.

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